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BUTYL ACRYLATE/VINYL ACETATE EMULSION-BASED PRESSURE SENSITIVE ADHESIVES

by
Renata Jovanović

A thesis submitted to the Faculty of Graduate and Postdoctoral Studies
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Statements of Contribution of Collaborators

I hereby declare that I am the sole author of this thesis. I performed polymerization experiments, polymer characterization, pressure-sensitive adhesives testing, and data analysis. The acquisition of ^{1}H-NMR data was contracted out to the Department of Chemistry at the University of Ottawa. DSC measurements presented in Chapters 3 and 5 were performed by myself at the Institute for Research in Construction, National Research Council, Ottawa, Canada. Particle size analyses presented in Chapter 3 were performed by myself at AVESTIN Inc., Ottawa, Canada.

The scientific guidance throughout the project and editorial comments for the written work were provided by my thesis supervisor Dr. Marc A. Dubé.

A part of this project, presented in Chapter 4 was performed in collaboration with the **L**aboratorie de **C**himie et **P**rocédés de **P**olymérisation – LCPP, **É**cole **S**upérieure de **C**himie **P**hysique **É**lectronique - ESCPE, Lyon, France. The scientific guidance and editorial comments on this chapter were provided by Dr. M.A. Dubé of the Department of Chemical Engineering, University of Ottawa and Dr. T.F. McKenna of the LCPP/ESCPE, Lyon.

Renata Jovanović Date: October 22, 2004

Abstract

Pressure-sensitive adhesives (PSAs) are adhesives that bond upon application of light pressure. With applications ranging from everyday home and office supplies to bioelectrodes and spaces shuttle parts, PSAs are among the fastest growing adhesive markets.

Emulsion polymerization is increasingly used for the production of PSAs due to its higher environmental compliance as well as other advantages (e.g. lower energy consumption, lower capital costs...) compared to other technologies. However, there is a considerable lack of the integration of different areas of knowledge required for the production of PSAs using this technology. Process conditions (e.g. feed composition, temperature, solids content...) are only one area of interest. These conditions will result in inherent polymer properties (e.g. composition, molecular weight distribution, particle size distribution, gel content...), which govern final product properties (e.g. loop tack, peel and shear strength). Better understanding of each area separately (e.g. process parameters, inherent polymer properties, final product properties) and finally, their integration will lead to the improvement of existing and development of new emulsion-based products and processes.

In this work, the above-mentioned three areas of PSA production were investigated for butyl acrylate/vinyl acetate emulsion-based polymers. The objectives were to investigate different variables affecting polymerization process, polymer and adhesive properties. The ultimate objective was to develop empirical models that will

incorporate these variables to enable better prediction of the PSA properties. The knowledge gained during building of empirical models could later be used for development of mechanistic ones.

In this work a screening design was used first to manipulate eight different process variables in order to generate a wide range of inherent polymer properties and final PSA properties. The properties obtained ranged from good, to moderate and to less desirable. However, the major obstacle in this step was the presence of different modes of failure for the same type of adhesive tests. Under these conditions, modeling was not possible due to the lack of a uniform failure mode in all PSA tests. However, as a result of the screening design, two different experimental regions were further explored. In one region, polyvinyl alcohol (PVOH) was used as stabilizer. A three-component mixture design was used to investigate the influence of three monomers (BA, VAc, and acrylic acid, AA) on final PSA properties while keeping all other variables constant. Although, not one model was found to fit all responses, the most significant factor affecting final PSA properties under the investigated conditions was AA.

In a subsequent study, the combined knowledge from the screening and PVOH studies was used as a starting point. Thus, three variables were investigated: acrylic acid, which was found to be the most influential among three monomers in the PVOH study, concentration of sodium dodecyl sulphate, SDS, and concentration of chain transfer agent (in the screening design there were indication that these two were important variables).

For each final adhesive property (i.e. loop tack, shear and peel strength), different models were found to fit the data. However, in most cases, the amount of chain transfer agent, CTA added was the most significant among the three factors investigated. It was interesting to note that similar models were valid for the same substrate when different adhesive thicknesses were used. The only property for which all parameters were similar regardless of the nature of the substrate was the shear strength.

In addition, in this work the potential for using miniemulsion polymerization for the production of PSAs was investigated. Compartmentalization in miniemulsion (i.e. the absence of mass transfer between particles) is one of the issues that could potentially be valuable to the production of PSAs. For example, under the assumption that compartmentalization is valid, each particle can be regarded as an independent, nano-

scale reactor. Thus, one can use these nano-scale reactors to obtain polymers and final products using some "tailoring" of properties at the nano-level. In this study, BA/VAc miniemulsions were prepared using two different procedures so that the evidence of compartmentalization can be investigated using Attenuated Total Reflectance Fourier Transform (ATR-FTIR) spectroscopy. High similarity between the ATR-FTIR spectra led to the conclusion that for the case of BA/VAc miniemulsion polymerizations, monomer transfer from droplets to particles takes place. The high water solubility of the VAc monomer could be a possible culprit for this behaviour despite the presence of a hydrophobe. Thus, though compelling, the idea of particles as independent property carriers is not applicable for this system under the conditions studied.

In conclusion, this work is a first systematic study of the influence of different variables on the final performance properties of butyl acrylate/vinyl acetate emulsion-based PSAs. Among the most significant are the amount of AA as well as the amount of CTA used in the recipe. Empirical models were developed for prediction of the final properties of the obtained PSAs. In the future, different monomers could be investigated as a basis for PSAs as well as to obtain more data for the development of more universally applicable mechanistic models for PSA production.

Résumé

Les adhésifs sensibles à la pression (ASPs) sont des adhésifs qui nécessitent une légère pression pour coller à une surface. Avec des applications diversifiées comme les fournitures de bureau, les fournitures de maison, les bioélectrodes et les pièces de la navette spatiale, les ASPs font partis d'un marché croissant très rapidement.

La polymérisation en émulsion est de plus en plus employée pour la production de ASPs grâce à sa conformité environnementale plus élevée ainsi qu'à d'autres avantages comme une consommation d'énergie et des frais financiers inférieure. Cependant, il y a un manque considérable dans l'intégration des différents domaines requis pour la production de ASPs en utilisant cette technologie. Les conditions du processus comme la composition en alimentation, la température et le contenu en solide sont seulement un centre d'intérêt. Ces conditions vont affecter les propriétés inhérentes du polymère comme la composition, la distribution de poids moléculaire, la distribution de dimension particulaire et le contenu de gel. Ces propriétés inhérentes du polymère régissent les propriétés finales du produit comme l'habileté à coller, la résistance au décollement et la résistance au cisaillement. Une meilleure compréhension de chaque secteur séparément (par exemple, les paramètres du processus, les propriétés inhérentes du polymère, les propriétés finales du produit) et leur intégration mènera à l'amélioration et au développement de nouveaux produits basés sur les émulsions ainsi qu'à de nouveaux processus.

Dans ce travail, les trois secteurs mentionnés ci-dessus pour la production d'un ASP ont été étudiés pour un system en émulsion comprenant de l'acrylate butylique (BA)

et de l'acétate de vinyle (VAc). Les objectifs étaient d'étudier différentes variables affectant les propriétés du procédé, du polymère et de l'adhésif. L'objectif final était de développer les modèles empiriques qui incorporeront ces variables pour permettre une meilleure prévision des propriétés de cet ASP. Les connaissances acquises pendant la construction de ces modèles empiriques vont pouvoir être employée pour le développement de modèles mécanistiques.

Dans ce travail une conception de ciblage a d'abord été employée pour manipuler huit variables de processus différentes afin de produire un éventail de propriétés inhérentes de polymère et de propriétés finales d'ASP. Les propriétés obtenues ont variées entre bon, modérer et moins souhaitable. Cependant, l'obstacle principal dans cette étape était la présence de différents modes d'échec pour le même type d'essais adhésifs. Dans ces conditions, modeler n'était pas possible dû au manque d'uniformité du mode de défaillance dans tous les essais d'ASP. Cependant, grâce à la conception de ciblage, deux régions expérimentales différentes ont été explorées avec plus d'intérêt. Dans une région, l'alcool polyvinylique (PVOH) a été employé comme stabilisateur. Une conception de mélange de trois-composant a été employée pour étudier l'influence de trois monomères (BA, VAc, et acide acrylique, AA) sur les propriétés finales de l'ASP tout en maintenant toutes les autres variables constantes. Bien qu'aucun modèle ne se soit avéré adapter pour toutes les réponses, le facteur le plus significatif affectant les propriétés finales de l'ASP dans les conditions étudiées était AA.

Dans une autre étude, les connaissances combinées du ciblage et des études de PVOH ont été employées comme un point de départ. Ainsi, trois variables ont été étudiées : acide acrylique qui s'est avéré le plus influent des trois monomères utiliser dans l'étude de PVOH, concentration de SDS, et concentration de l'agent de transferts des chaînes ou CTA (dans la conception de ciblage il y avait indication que ces deux variables étaient importantes).

Pour chaque propriété adhésive finale (c.-à-d. l'habileté à coller, la résistance au décollement et la résistance au cisaillement), différents modèles se sont avérés adapter pour les données. Cependant, dans la plupart des cas, la quantité de CTA supplémentaire était la plus significative parmi les trois facteurs étudiés. Il était intéressant de noter que les modèles semblables étaient valides pour le même substrat quand différentes

épaisseurs adhésives ont été employées. La seule propriété pour laquelle tous les paramètres étaient semblables indépendamment de la nature du substrat était la résistance au cisaillement.

De plus, dans ce travail le potentiel des mini-émulsions pour la production d'ASP a été étudié. La compartementalization dans les mini-émulsions (c.-à-d. l'absence du transfert de masse entre les particules) est l'une des caractéristique qui pourraient potentiellement être très valable pour la production d'ASP. Par exemple, avec la prétention que cette compartementalization est valide, chaque particule peut être considérée comme un nano-réacteur indépendant. Ainsi, on peut employer ces nano-réacteurs pour modifier, au niveau nano-moléculaire, les propriétés des polymères et des produits finaux. Dans cette étude, des mini-émulsions de BA/VAc ont été préparés en utilisant deux procédures différentes de tel sorte que l'évidence de la compartementalization puisse être étudiée en utilisant la spectroscopie totalement atténuée avec transformation de Fourier (ATR-FTIR). La similitude élevée entre les spectres d'ATR-FTIR a mené à la conclusion suivante ; pour le cas des polymérisations de mini-émulsion de BA/VAc, le transfert de monomère à partir des gouttelettes d'huile aux particules a lieu. La solubilité élevée dans l'eau du monomère de VAc a pu être une cause possible pour ce comportement en dépit de la présence d'un hydrophobe. Ainsi, l'idée des particules en tant que porteurs indépendants de propriété n'est pas applicable pour ce système dans les conditions étudiées.

En conclusion, ce travail est une première étude systématique de l'influence de différentes variables sur les propriétés finales pour un system en émulsion comprenant de l'acrylate butylique et de l'acétate de vinyle. Parmi le plus significatif, ont retrouve la quantité de AA aussi bien que la quantité de CTA utilisé dans la recette. Des modèles empiriques ont été développés pour la prévision des propriétés finales de l'ASP obtenu. À l'avenir, différents monomères ont pu être étudiés comme base pour l'ASP aussi bien que pour obtenir plus de données pour le développement des modèles mécanistiques plus universellement applicables pour la production d'ASP.

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Very, very special thanks go to my family. To my Biggy Z: The winner of the best husband award for unconditional love "since clocks kept time". Without you, I would have never dared to explore the world beyond my cocoon and have never grown into the person I am today. To my dad, physicist, who taught me to experiment and my mum, biologist, who taught me to persist: Thank you both, for a wonderful gift of wonder and exploration.

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For the financial support during this project, I am grateful to the Ontario Ministry of Training, Colleges and Universities for the three consecutive Ontario Graduate Scholarships, as well as the University of Ottawa for one Admission and three Excellence Scholarships.

Life is a sheet
of paper white
Whereon each one
of us may write
His word or two.
And then comes night.

Greatly begin!
Tho thou have time
But for a line,
Be that sublime;
Not failure,
But low aim is crime.

James Russell Lowell

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Nomenclature

Symbols

G' = storage modulus

G'' = loss modulus

E(y) = expected value of the response

f = initiator efficiency

$\overline{F}_i$ = weight fraction of monomer i bound into polymer

I = initiator

K = Mark-Houwink pre-exponential parameter

k_d = initiator decomposition rate constant

k_p = propagation rate constant

k_{plj} = propagation rate for the addition of monomer j to an initiator fragment

k_{pij} = rate constant of addition of monomer j to the radical ending with monomer unit i

k_t = termination rate constant

k_{tc} = termination by combination rate constant

k_{td} = termination by disproportionation rate constant

$M^{\bullet}$ = total concentration of all chain radicals

M_j = monomer j

m_i = mass of monomer i

M_n = instantaneous number average molecular weight

$[M]_p$ = monomer concentration inside a particle

M_w = instantaneous weight average molecular weight

MW_m = molecular weight of the repeat unit

N = number of latex particles

$\bar{n}$ = average number of radicals per particle

N_a = Avogadro's number

n_i = mole of monomer *i*

P = polymer

$R^\bullet$ = primary radical

R_I = rate of initiation

$R_m^\bullet$ = growing polymer chains size of *m*

$R_n^\bullet$ = growing polymer chains size of *n*

$R_{r,j}^\bullet$ = radical of chain length *r* ending in monomer unit *j*

$R_{r+1,j}^\bullet$ = radical of chain length *r* + *1* ending with monomer unit *j*

R_p = rate of polymerization

r_i = reactivity ratio of monomer *i*

R_t = rate of termination

t = time

T_g = glass transition temperature

X = overall conversion

x_i = conversion of monomer *I*

Greek Leters

α = Mark-Houwink exponential parameter

β = molecular weight contribution due to termination by combination

γ = shear rate

η = viscosity

τ = molecular weight contribution due to termination by disproportionation and transfer to small molecules

Θ = angle of incidence

List of Abbreviations

AA = Acrylic Acid

AFERA = Association ds Fabricants Européens de Rubans Auto-Adhésifs

AFM = Atomic Force Microscopy

AIBN = 2,2'-Azobis (Isobutyronitrile)

ALMA = Allyl Methacrylate

ASTM = American Society for Testing and Materials

BA = Butyl Acrylate

CTA = Chain Transfer Agent

DMA = Dynamic Mechanical Analysis

DSC = Differential Scanning Calorimetry

EVA = Ethylene-Vinyl Acetate

FINAT = Fédération Internationale des Fabricants et Transformateurs d'Adhésifs et Thermocollants sur Papiers et autres Supports)

GPC = Gel Permeation Chromatography

IBMA = Isobutoxy Methyl Acrylamide

MAA = Methacrylic Acid

MFFT = Minimum Film Forming Temperature

PBA = Poly(butyl acrylate)

PEHMA = Poly(ethylhexyl methacrylate)

PMMA =Poly(methyl methacrylate)

PVAc = Poly(vinyl acetate)

PVOH = Poly(vinyl alcohol)

PSA = Pressure-Sensitive Adhesives

PSP = Pressure-Sensitive Products

PSTC = Pressure-Sensitive Tape Council

SAFT = Shear Adhesion Failure Temperature

SDS = Sodium Dodecyl Sulphate

SEM = Scanning Electron Micrography

T_g = Glass Transition Temperature

TG = Thermogravimetry

TLMI = Tag and Label Manufacturer's Institute

VAc = Vinyl Acetate

^{1}H-NMR = Proton Nuclear Magnetic Resonance

2-EHA = 2-EthylHexyl Acrylate

Chapter 1

Introduction

The pressure-sensitive adhesive (PSA) industry is one of the fastest growing among the adhesives markets. These adhesives, which bond under application of slight pressure, are parts of a variety of products used anywhere from home and office supplies to bioelectrodes and space shuttle parts. The competition to develop new processes for PSA production and to increase the understanding of existing ones as well as finding new products and applications is intense.

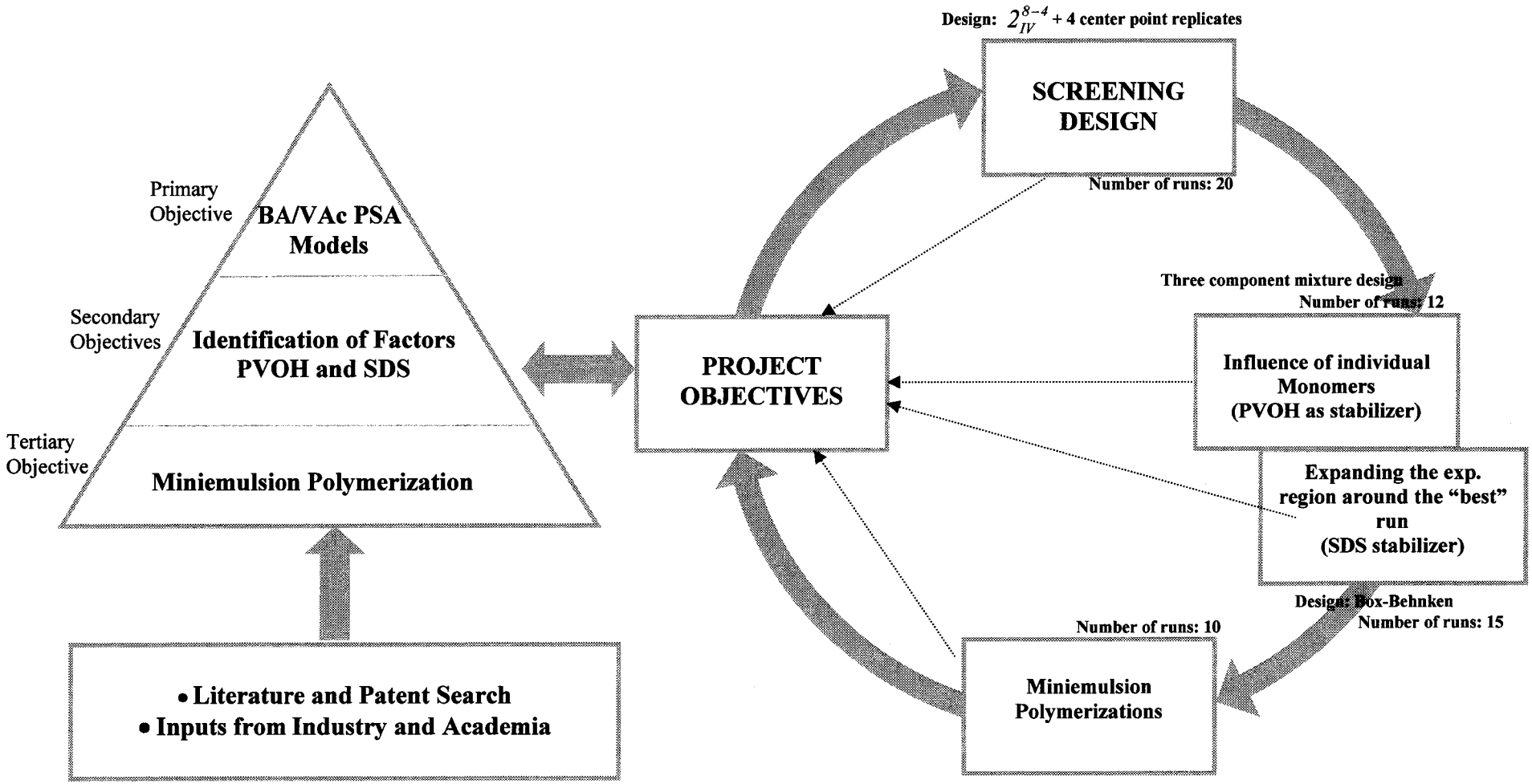
PSAs can be obtained by different technologies: hot melt, irradiation, solution, and emulsion polymerization. Recently, stricter environmental laws and public pressure are favouring the utilization of more environmentally-friendly technologies.

Emulsion-based polymerization for the production of PSAs offers better environmental compliance compared to solution polymerization, higher energy efficiency compared to hot melt technology, and lower capital costs compared to irradiation technologies. However, until recently it was believed that the balanced properties of solvent-based PSA products are unsurpassable. Today, the gap between solvent- and emulsion-based PSAs is narrowing and emulsion-based PSA products are occupying more than 40% of the PSA market.

On the other hand, there is a considerable lack of integration of three areas of knowledge relevant to emulsion-based PSAs: the emulsion polymerization process, inherent polymer properties and final product properties. Thus, in this study, specific objectives were set to investigate and integrate these three areas. The chosen system for the study was butyl acrylate/vinyl acetate (BA/VAc) copolymer due to its suitability as a PSA despite the relatively low number of such studies reported in the open literature.

1.1 Objectives and Scope of the Study

The selection of objectives that are unbiased, specific, measurable and of practical consequence is one of the cornerstones of a systematic approach to a research problem. With this in mind, as well as the relevant knowledge about BA/VAc emulsion polymerization kinetics, the properties of the obtained polymers as well as the physical and chemical requirements for a PSA, a series of objectives were devised for this study. The accomplishment of the objectives at lower levels led toward the accomplishment of the ultimate objective (primary level). The hierarchy of the objectives devised for this study is schematically represented in Figure 1.



a) Project objectives

b) Experimental design sequences

Figure 1 Project objectives hierarchy and experimental design sequences

The primary objective of this study was the development of a model that will incorporate process parameters, inherent copolymer properties and PSA properties. The existence of such models will deepen the knowledge and understanding of BA/VAc emulsion-based PSAs and offer a framework for the development of similar models for other emulsion-based PSAs. It could also be used for parameter estimation, sensitivity analysis and process optimization. Existing models, described in the literature, are mostly oriented toward modeling of emulsion polymerization kinetics and inherent polymer properties (i.e. copolymer composition, molecular weight distribution, particle size distribution) with no inference to the final PSAs properties (i.e. peel and shear strength, tack). The models that incorporate PSA properties are mostly developed for hot melt or solution-based PSAs.

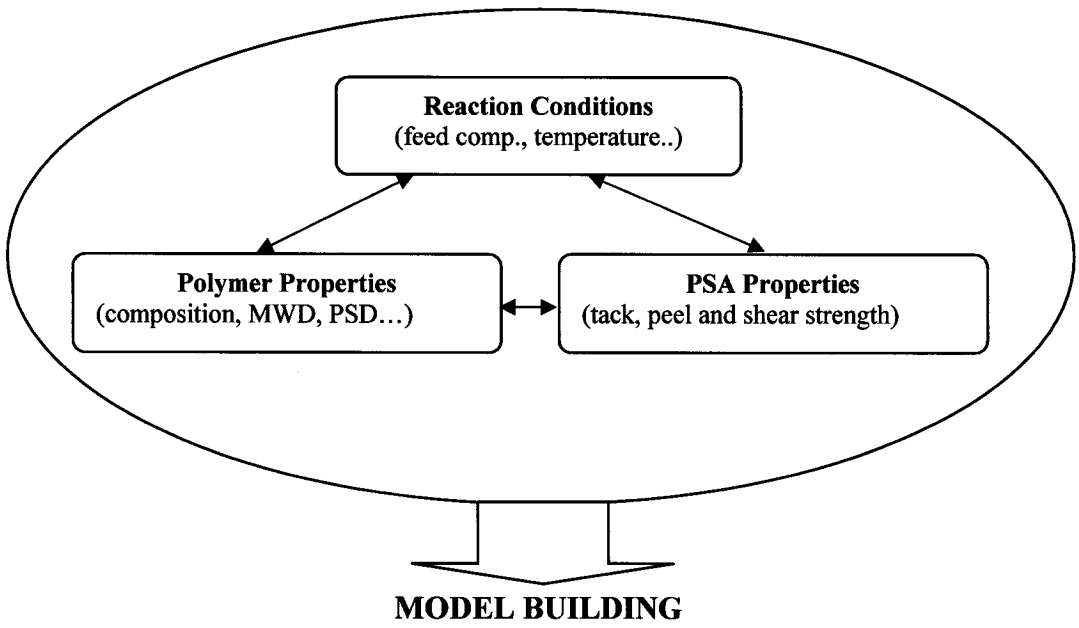


Figure 2 Model building approach

There is a need for a study that will systematically investigate and integrate all three areas of knowledge: reaction conditions, polymer properties and PSA final properties as presented in Figure 2. The focus in this study was on the modeling of the three most commonly determined properties of PSAs: the peel strength measured using a

180^{o} peel test, the tack level measured using a loop tack test, and the static shear strength measured using a static shear test for BA/VAc emulsion-based polymers. These tests were compliant with the standards proposed by the PSTC. Because PSAs are polymers, inherent polymer properties such as polymer composition, molecular weight distribution, and particle size distribution will affect the PSA properties. Ultimately, through the inherent properties of the polymer, final PSA properties will be the result of reaction conditions such as temperature, pressure, and feed composition.

One of the secondary objectives of this study was the determination of the important factors affecting the properties of BA/VAc emulsion-based PSAs. It is known that factors such as monomer feed composition, type and concentration of initiator and stabilizer, polymerization temperature, and pH can affect the emulsion polymerization process and final polymer properties. These have been investigated to a certain extent for BA/VAc emulsion copolymerizations but rarely in light of BA/VAc emulsion-based PSA production. On the other hand, some of these factors have been investigated for other emulsion-based systems. The comprehensive systematic investigation of these factors and their influence on the properties of BA/VAc emulsion-based PSAs is therefore the essence of this project. A systematic experimental approach is needed to assess the overall potential of BA/VAc copolymers as PSAs.

Another secondary objective was the utilization of anionic and polymeric stabilizers in the recipes to determine their influence on final PSA properties. In this study, two stabilizers, sodium dodecyl sulphate (SDS) and polyvinyl alcohol (PVOH), were employed to understand the consequences when anionic or polymeric stabilizers are used in the recipe. In a screening design, the type of stabilizer was used as a variable. It is known that SDS, being a small molecule, can migrate to the interfaces during drying and cause changes in the film and adhesive properties. On the other hand, PVOH, a polymeric stabilizer, will be less likely to migrate to the interfaces but can lower the T_g of the polymer and influence the adhesive properties. Throughout the study these two stabilizers were used in various experimental sequences.

At a tertiary level, the objective of the study was to explore other environmentally-friendly processes to obtain PSAs. There is a variety of processes that can be used for the production of PSAs. Miniemulsion polymerization is an interesting alternative process that offers better control over certain key parameters affecting latex properties and polymer end-use characteristics (e.g. particle size distribution) compared to emulsion polymerization. Because particles in miniemulsion polymerization are considered nano-reactors, it is not hard to imagine that at certain conditions they can be used as "property carriers". For example, one population of particles can "carry" higher molecular weights that will improve shear while others can "carry" low molecular weights that will increase tack in the final product. This is valid if the particles retain their originality from sonication to the end of polymerization i.e. there is no monomer transfer between them. In order to use BA and VAc in such a concept, a study was designed to test compartmentalization in BA/VAc miniemulsion polymerizations using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy.

1.2 Outline of Approach

In order to reach the objectives of the study, four sequences of experiments were performed (Figure 1b). The first series of experiment was a screening design where eight different variables were investigated. These were the BA/VAc ratio, concentration of acrylic acid (AA), type and concentration of stabilizer, concentration of initiator, concentration of chain transfer agent (CTA), temperature, and solids content. Broad ranges were used for all concentrations in order to generate a wide range of final properties. This was followed by two experimental sequences: one utilizing {PVOH) and another utilizing SDS as stabilizer. In the first, a three-component mixture design was used to investigate the influence of the three monomers in the PSA recipe on the polymer and final PSA properties, while in the other, a Box-Behnken design was used to investigate the effect of the most influential monomer found in the previous study and two additional variables: the concentration of CTA and SDS. In all these experimental

sequences, a general experimental procedure was used as far as it was technically possible. Latex synthesis was followed by characterization (e.g. polymer composition, gel content, molecular weight distribution or molecular weight distribution of soluble fraction after separation of gel fraction, particle size distribution, glass transition temperature, etc.), this was followed by film casting onto a polyethylene terephthalate carrier, drying and conditioning at 23 ± 2°C and 50 ± 2% RH. PSA final properties: loop tack, peel and shear strength were tested on two different substrates: stainless steel and high density polyethylene. The thicknesses of the adhesive films were 30 and/or 70 μm.

1.3 Organization of Thesis and Significance of the Contributions

This thesis consists of seven chapters that can be read separately. Each chapter is an independent scientific publication submitted to a refereed scientific journal. Due to this structure, the repetition of some common ideas and elements (e.g. experimental procedures) was inevitable. Chapter I (Introduction) and Chapter VII (Conclusions and Recommendations) relate to all chapters.

CHAPTER II - *Jovanović, R. and M.A. Dubé. Emulsion-Based Pressure Sensitive Adhesives: A Review. Journal of Macromolecular Science – Part C – Polymer Reviews 2004, 44(1): 1-57.*

This chapter is a result of a patent and open literature search relevant to the objectives of the thesis. There was a need to integrate contemporary findings prior to the beginning of the project. The paper summarizes contemporary and significant findings relevant to the production of PSAs starting from emulsion polymerization ingredients and characteristic features, drying and film properties to final PSA properties. Although, there are literature reviews on these subjects individually, none of them have offered an integrated approach for emulsion-based PSAs. Requests for scientific cooperation as well as prizes from academia and industry we have received based on this paper are the best measure that this integrated approach was long overdue.

CHAPTER III - ***Jovanović, R. and M.A. Dubé. Screening Experiments for Butyl Acrylate/Vinyl Acetate Pressure-Sensitive Adhesives*** **(to be submitted to J. Appl. Polym. Sci)**

In this study, the influence of eight emulsion polymerization variables on the final PSA properties of butyl acrylate/vinyl acetate (BA/VAc) emulsion-based PSAs was investigated (i.e. BA/VAc ratio, acrylic acid content, type and concentration of stabilizer, concentration of initiator, concentration of CTA, temperature, solids content). A wide range of properties was generated ranging from very good to poor PSA performance. The screening design fulfilled its purpose in that it was used to generate a wide range of final properties. However, the development of empirical models to relate the process conditions to the final product properties was not possible. The chain transfer agent, which regulated the gel content of the emulsion latexes and the molecular weight of the soluble polymer fraction, as well as the monomer feed composition, were suspected to be among the most influential factors affecting the final PSA performance. In addition, it was possible to obtain balanced final properties using either sodium dodecyl sulphate or poly(vinyl alcohol) as surfactant but at different concentrations.

CHAPTER IV - ***Jovanović, R., T.F. McKenna, and M.A. Dubé. A Statistical Approach to Modeling of BA/VAc/AA-Based Pressure Sensitive Adhesives.*** **Macromol. Mater. Eng. 2004, 289: 467-474.**

In this study, a three-component mixture design was used to investigate the influence of three monomers: BA, VAc and AA on the polymer and final PSA properties. PVOH was used as stabilizer, while all other components were kept constant in the recipe. Empirical model building was used to build models for glass transition temperature, peel and shear strength and loop tack. At the end, contour lines were overlapped to obtain the optimal conditions for the production of PSA. This modeling approach can be used for the development of tailor-made PSAs. The three-component mixture design enables easy selection of monmer ratios for the desired application.

CHAPTER V - ***Jovanović, R. and M.A. Dubé. Modeling of BA/VAc Emulsion-Based Pressure Sensitive Adhesives.*** **(to be submitted to Macromol. Mater. Eng.)**

The influence of the amounts of acrylic acid, chain transfer agent and anionic stabilizer on polymer microstructural properties and final adhesive performance on stainless steel and high density polyethylene substrates was investigated using a Box-Behnken experimental design. For each final adhesive property (i.e. loop tack, shear and peel strength), different models were found to fit the data. In all models, CTA was present either as a linear, quadratic or second-order interaction with mostly AA. This study is among the rare ones that systematically investigated the influence of several factors on adhesive performance. In addition, these performances were tested on two different substrates and two different adhesive thicknesses. The significance of the results lays not only in this systematic investigative approach but also in the modeling of adhesive properties that has not been attempted before for most emulsion-based systems.

CHAPTER VI - ***Jovanović, R. and M.A. Dubé. Butyl acrylate and Vinyl Acetate Miniemulsion Polymerization: A Study on Compartmentalization. Macromol. Chem. Phys. 2004, 205: 258-265.***

This study was designed to answer the tertiary objective of the overall project. Here, the potential of miniemulsion process for production of BA/VAc PSAs was investigated. The idea of independent nanoreactors was tested. Compartmentalization or lack of it in the BA/VAc miniemulsions was tested as a pre-requisite for the concept of particles as "carriers of designated properties". In that concept, one particle population for example can contain lower molecular weight polymers that could improve tack while another population can contain higher molecular weight polymers that could improve peel strength. Using this concept one can tailor properties of the final product – PSA during the synthesis period without less favorable post-synthesis latex mixing.

Chapter 2

Theoretical Background

Jovanović R., Dubé M.A.
Emulsion-Based Pressure-Sensitive Adhesives: A Review
Journal of Macromolecular Science, Part C: Polymer Reviews
2004, 44(1), 1-57

2.1 INTRODUCTION

Defined as substances capable of holding at least two surfaces together, adhesives are used in many different applications. One class of adhesives is referred to as pressure-sensitive adhesives or PSAs. These are characterized by instantaneous adhesion upon application of light pressure.(1) The most common products that utilize PSAs are tapes, labels and protective films. The PSA sector is among the fastest growing in the adhesive market, making the search for new pressure-sensitive products (PSP) and applications highly competitive. Although PSPs can be obtained by different polymerization processes (i.e. emulsion, solution, hot melt or radiation curing), much attention has recently been devoted to the utilization of more environmentally friendly processes such as emulsion polymerization. Emulsion polymerization offers not only better environmental compliance, but also advantages such as a wide selection of raw materials, better control of final product properties, and a low possibility of "runaway reactions" due to the utilization of water as the dispersion medium.

Given the variety of applications of the final emulsion polymerization latex, there is considerable interest in the development of links between three general areas of knowledge: emulsion polymerization process conditions, latex and dry film properties and final product performance. Reaction components and process conditions will affect latex properties such as copolymer composition, molecular weight distribution and particle size distribution. In turn, these can affect rheological properties of the latex and the film formation process. Furthermore, latex rheology and the film formation process can affect final product performance properties. These links between emulsion polymerization process conditions, latex and dry film properties and final product performance exist for all emulsion-based products. For each of these three general areas, one can identify control and response variables and restrictions relevant to a particular application. The development of new, application-specific products and improvements to existing processes and products are the driving forces to seeking a fundamental understanding of these variables and their interrelations.

In this review, various factors related to the three areas of knowledge, which are relevant to PSA production are identified and discussed. First, the emulsion polymerization components and process conditions of interest to PSA performance are reviewed. Next, latex rheology and the film formation process are examined. Finally, PSA performance (i.e. tack, peel strength and shear strength) and attempts to model it are discussed.

2.2 ADHESIVES

Humankind has been using adhesives since the very beginning of civilization. Carvings in Thebes (circa 3300 BC) show a glue pot and brush to bond veneer to a plank of sycamore. According to historical records, the first commercial glue plant was founded in Holland in 1690 and the first U.S. patent (No. 183,024) for a glue was issued in 1876.(2) Today, from home and office to the space shuttle, many products that we take for granted could never exist if it were not for adhesives. An adhesive is defined as a substance capable of holding at least two surfaces together in a strong and permanent manner.(3) Adhesive bonding has advantages and disadvantages when compared to other types of bonding. Among the advantages is the possibility to join any combination of similar or dissimilar materials regardless of their shapes and thicknesses. Also, an adhesive bond has a large stress bearing area and excellent fatigue strength combined with minimal corrosion. Furthermore, adhesive bonding is often faster and less expensive than mechanical fastening. Some disadvantages include the need for careful surface preparation, possible long curing times, and limited performance depending on environmental conditions.(3)

2.2.1 Classification of Adhesives

There are several classification methods for adhesives. One of the broadest classifications discerns structural and non-structural adhesives. Structural adhesives are expected to provide a useful service life that is equivalent to that of the product in which

the adhesive joint is a part. Usually, the shear strength of these adhesives is greater than 6900 kPa (1000 psi) and their properties do not change significantly with moderate aging. Non-structural adhesives find application as pressure sensitive tapes, hot melts, or packaging adhesives. Their shear strength is less than 6900 kPa (1000 psi) and their durability requires a sheltered or relatively mild environment.(3) Some ambiguity with such a broad classification is expected. The chemical composition of typical structural adhesives involves epoxy and epoxy hybrids, polyurethanes, acrylates, modified acrylates, resorcinol-, phenol-, melamine- and urea formaldehydes, phenolics and modified phenolics, and polyaromatic high temperature resins (e.g. polyimides). On the other hand, the chemical composition of non-structural adhesives involves natural, butyl and styrene-butadiene rubbers, silicones, polyvinyl acetal, polyvinyl acetate, ethylene-vinyl acetate copolymers, cellulosic resins, polyesters, polyolefins, acrylics, and naturally occurring adhesives (e.g. naturally occurring resins, and cements).

One can also classify adhesives according to their chemical/physical nature. Adhesives can be thermoplastic, thermosetting, elastomeric or hybrids. Thermoplastic adhesives are not cross-linked and revert to a fluid state when heated. Thermosetting adhesives are cross-linked structures that do not soften with heat or solvents. Elastomeric adhesives, formulated from natural or synthetic rubbers, have high elongation and usually low tensile strength. Hybrid adhesives are compounded from a mixture of polymers for specific property adjustment.

Another approach to adhesive classification takes the method of application and subsequent curing or setting into consideration. There are several steps in the adhesion process: application (the adhesive is applied in liquid form), wetting (the adhesive has to wet the surface) and setting (in most cases, it is the transition from fluid to solid form). Setting can be accomplished in several ways: by cooling (typical of thermoplastic adhesives), by releasing solvent or carrier (e.g. solution or water-based adhesives), by an in-situ polymerization reaction (e.g. aerobic, anaerobic, and radiation curable adhesives), and by application of light pressure (e.g. PSAs).(4)

2.2.2 Pressure Sensitive Adhesives

2.2.2.1 Definition and properties.

Unlike other classes of adhesives, PSAs retain their fluid state after the bond is built.(1) They remain in a permanently tacky state. Such material will adhere instantaneously to most solid surfaces with the application of light pressure and can be debonded without leaving a residue of adhesive on the substrate.(5) Even though the word tack can be used to describe various phenomena, in the context of PSA technology, it defines the ability of the adhesive to form a bond with the surface of another material upon brief contact under light pressure.(6) Tack, peel strength and shear strength are the three general adhesive properties that determine PSA performance. Peel strength is measured as a force required to remove a standard PSA strip from a specified test surface under a standard test angle (e.g. 90 or 180°) under standard conditions. Shear strength is the internal or cohesive strength of the adhesive mass. Usually, it is determined as the length of time it takes for a standard strip of PSA to fall from a test panel after application of a load. A PSA is the result of a fine balance between these three major, interrelated properties. The balance is usually tailored according to the end use of the PSA.(7)

Because PSAs are polymeric materials, tack, peel and shear strength are influenced by the properties of the polymer. Inherent properties such as copolymer composition and microstructure, molecular weight and distribution are among the most influential factors affecting PSA properties directly as well as indirectly through their influence on physical properties (e.g. the glass transition temperature, T_g) and thus, rheological properties of the polymer (e.g. viscoelastic regions, moduli). By careful selection of the chemical components, the physical and rheological properties, and thus PSA properties can be influenced. Thus, PSAs can be tailored to suit the needs of a particular application.

2.2.2.2 PSA—based products and technologies

PSAs form an integral part of three major categories of pressure sensitive products (PSP): labels, tapes, and protective films. Each category is further divided into main and specialty categories (7). PSAs can be a part of other products ranging from the simple, such as self-adhesive envelopes, self-adhesive postage stamps and Post-It Notes®, to the highly sophisticated, such as bioelectrodes.(8) In general, a PSP consists of a component that provides adhesivity, i.e. the PSA, and the carrier, i.e. a component that provides desired mechanical properties.(7) Some products can be carrier-less (e.g. carrier-less protective films for roofing insulation and carrier-less transfer tapes used in specialty and experimental products). The general structure and characteristics of the three major types of PSPs are given in Table 1. For most applications, more complex structures are used.(7)

Table 3 General Structure of the Three Major Classes of PSP (7)

PSP	General PSP Structure	Characteristics
Tapes		Self-adhesive materials usually produced by coating an adhesive onto a carrier and used as a continuous web.
Labels		Self-adhesive laminated carrier materials. The self-adhesive layer is protected with a supplemental material (release liner).
Protective films		Carrier material possesses built-in or built-on self-adhesive properties.

 = adhesive;  =carrier;  = release liner;  = adhesive carrier material.

The first U.S. patent for a PSA was issued in 1846.(1) There are approximately 3000 U.S. patents related to composition, process improvement and the application of PSAs for the period 1976-2003. The latest trends in the label and tape markets, given by Schwartz, indicate that the search for novel products and applications is more intense than ever. Today, the PSA market is one of the fastest growing adhesive markets with an estimated global growth of 5-6% for the 2000-2005 period.(9,10) According to Market Tracking International, seven major companies, Henkel, Dexter Adhesives, 3M, Avery Dennison, National Starch, and HB Fuller, control almost half of the global PSA market.(11) In today's market, there are four major classes of PSAs according to process technology: solvent-based, emulsion (water)-based, hot melt and radiation-cured PSAs. The chemical basis for each class is shown in Table 2.

Table 4 Chemical Composition of Four Major Classes of PSAs

PSA process	Chemical composition
Solvent—based	Rubber/resin, acrylics, silicones
Hot—melt	Block copolymers, acrylics
Emulsion (water)—based	Acrylics, natural and synthetic rubber, ethylene—vinyl acetate copolymer
Radiation—cured	Acrylics, rubber

While solvent-based adhesives have been in use since the 19th century and hot melt adhesives since the 1940s, emulsion-based and radiation-cured PSAs only started to be used widely since the 1970s. This was largely due to the need to replace solvent-based formulations with other high-performance alternatives as a result of increased health and environmental concerns. In the beginning, it was considered that the realm of solvent-based PSA performance was out of reach of emulsion-based PSAs. However novel, flexible and versatile high performance emulsion-based PSAs are having an impact on today's market.(12-17)

Currently, it is estimated that with sales of over US$ 9 bn/year more than 40% of the global market belongs to water-borne adhesives.(11) In Table 3, different

performance criteria of PSA technologies are compared.(12) Emulsion- and solvent-based PSA production (compounding) is less expensive compared to hot melt and radiation-cured PSA production. The former two require a stirred tank while the latter two require more expensive and complex equipment (e.g. an electron beam accelerator for radiation-cured PSAs).

Table 5 Comparison of Pressure-Sensitive Adhesives Technologies (12)

	Solution: Acrylic	**Hot Melt: SIS***	**Emulsion: Acrylics**
PS Performance	Excellent	Excellent	Very good
Ease of Compounding	Moderate	Difficult	Easy
Formulation Flexibility	Limited	Excellent	Moderate
Coating Method Flexibility	Limited	Poor	Excellent
Ease of Changeover	Limited	Poor	Excellent
PSA Reproducibility	Excellent	Limited	Excellent
Aging Properties	Excellent	Poor	Excellent
Clarity/Colour	Excellent	Poor	Excellent
Safety/Toxicity	Poor	Poor	Excellent
Raw Material Costs	High	Low	Medium
Coating/Compounding Costs	High	Medium	Low

*SIS-styrene-isobutylene-styrene

Coating costs are lower for emulsion-based systems compared to the other two systems. Health and environmental compliance and improved process safety are other advantages of emulsion-based PSAs: there is no need for organic solvents, as in the production of solvent-based PSAs, nor the utilization of large amounts of heat energy as in the production of hot melt PSAs. Although the ease of compounding is different and favours the use of emulsion-based PSAs, the additives for adhesive system improvement are similar for hot melt, solution- and emulsion-based PSAs. These include tackifiers, antioxidants, cross-linking agents or peel modifiers. Specific to emulsion-based PSAs are additives for improvement of the emulsion system (e.g. wetting agents, stabilizing agents, defoamers, rheology modifiers).(1) The reduced viscosity, absence of molecular weight limitations and the ability to build in cross-linking during the reaction are among the greatest advantages of emulsion polymerization. Even though the performance gap between emulsion- and solvent-based PSAs is closing, there are still areas for

improvement. In particular, the balance of tack, peel and shear strength, low water and humidity resistance, and coatability remain important issues for emulsion-based PSAs. These improvements are governed not only by health and environmental compliance but also by cost. Howard states that along with replacement of solvent-based systems with water-borne or solvent-less adhesives, the future will bring the development of hybrid adhesive systems, recyclable (especially packaging) adhesives and custom-designed products.(18)

2.3 EMULSION POLYMERIZATION FOR PSA PRODUCTION

2.3.1 Emulsion Polymerization

In the large scope of polymer chemistry, emulsion polymerization is classified as a heterogeneous free-radical chain growth polymerization. In emulsion polymerization, a monomer (or mixture of monomers) is polymerized in an aqueous medium. The reaction is typically initiated using water-soluble initiator(s) and the stability of the reaction mixture is usually ensured by the utilization of stabilizer(s). Other ingredients such as buffers and chain transfer agents can also be present. Latex can be used "as is" or with the addition of post-polymerization additives (e.g. surface-active agents, antioxidants, fungicides etc.). For some applications, the obtained polymer must be isolated from the latex. The standard free-radical polymerization reactions, i.e. initiation, propagation, termination and chain transfer all occur in emulsion polymerization, but its heterogeneous nature contributes to its distinctive reaction kinetics and mechanism.

Free-radical copolymerization is presented here assuming the validity of the terminal model (i.e. the reactivity of propagating radicals is dependent only on the last unit in the chain). This model is not valid for some systems. More details about alternative models, such as the penultimate model, can be found among others in the work of Coote and Davis.(19,20) The kinetics of homo- and multi-component polymerization can be easily deduced from this general copolymerization case.

Initiation:

$$I \xrightarrow{k_d} 2R^{\bullet} \quad (1)$$

$$R^{\bullet} + M_1 \xrightarrow{kp_{11}} R^{\bullet}_{1,1}$$

$$R^{\bullet} + M_2 \xrightarrow{kp_{12}} R^{\bullet}_{1,2} \quad (2)$$

Propagation:

$$R^{\bullet}_{r,1} + M_1 \xrightarrow{kp11} R^{\bullet}_{r+1,1}$$
$$R^{\bullet}_{r,1} + M_2 \xrightarrow{kp12} R^{\bullet}_{r+1,2}$$
$$R^{\bullet}_{r,2} + M_1 \xrightarrow{kp21} R^{\bullet}_{r+2,1}$$
$$R^{\bullet}_{r,2} + M_2 \xrightarrow{kp22} R^{\bullet}_{r+2,2} \quad (3)$$

Termination:

$$R^{\bullet}_m + R^{\bullet}_n \xrightarrow{k_{tc}} P_{m+n} \quad \text{(by combination)} \quad (4)$$

$$R^{\bullet}_m + R^{\bullet}_n \xrightarrow{k_{td}} P_m + P_n \quad \text{(by disproportionation)} \quad (5)$$

Chain transfer:

$$R^{\bullet}_n + X \xrightarrow{k_{tr,x}} P_n + X^{\bullet} \quad (6)$$

$$X^{\bullet} + M_i \xrightarrow{k^1_p} R^{\bullet}_{1,i} \quad (7)$$

Free radical copolymerizations begin with initiation, the homolytic decomposition of an initiator, I, into the primary radicals, $R^{\bullet}$, (Eq.(1)) which can add monomer 1 or 2 (M_1 or M_2), Eq.(2). $R^{\bullet}_{r,j}$ denotes a radical of chain length r ending in monomer unit j. Temperature dependent rate constants for these reactions are denoted as k_d and k_{plj}. The rate of initiation, R_I, is given as $R_I = 2fk_d[I]$ where f is an initiator efficiency factor.

In the propagation reactions, the polymer chain continues to grow by the addition of M_1 or M_2. All four possible reactions are presented (Eq. (3)) where k_{pij} denotes the rate constant of addition of monomer j to the radical ending with monomer unit i. $R^{\bullet}_{r+1,j}$ denotes a radical of chain length $r + 1$ ending in monomer unit j. It is assumed that the reactivity of the radical centre is dependent only upon the last monomer unit bound in the polymer chain (i.e. terminal model kinetics). The rate of polymerization, R_p, is given as

$$R_p = k_p[R^{\bullet}][M] \quad (8)$$

where k_p is the propagation rate constant, $[R^\bullet]$ is the total concentration of all chain radicals and $[M]$ is the monomer concentration. One characteristic of the propagation step for multicomponent polymerizations is the difference in the tendency of monomers to enter the polymer chain. The reactivity ratios are used to represent the reactivity of radicals ending in monomer unit 1 toward monomer 1 or monomer 2 in the reaction mixture (Eq. 9). If r_i>1 then homopropagation is preferred. On the other hand, heteropropagation is preferred when r_i<1.

$$r_1 = \frac{k_{p11}}{k_{p12}} \qquad r_2 = \frac{k_{p22}}{k_{p21}} \tag{9}$$

The greater the difference in the reactivity ratios, the greater the possibility of composition drift. Composition drift is the change in chemical composition of the polymer formed throughout the reaction.

Termination can occur via combination where two unpaired free radicals form a paired electron bond, (Eq. (4)), and disproportionation by atom (usually hydrogen) abstraction, (Eq. (5)). In both cases, the reaction starts with two growing polymer chains $R_m^\bullet$ and $R_n^\bullet$, of size m and n, respectively. If combination takes place, only one dead polymer chain, P_{m+n} of length $m+n$ is formed. If disproportionation takes place, two dead polymer chains, P_m and P_n, one of which is terminally unsaturated, are formed. This terminal unsaturation is a potential reactive site. Termination rate constants are given as k_{tc} in Eq. (4) and k_{td} in Eq (5). From the reaction kinetics point of view, the important event is the disappearance of free radicals. Thus, these two can be simply added, and calculations performed with the overall termination constant $k_t = k_{tc} + k_{td}$. For the molecular weight development, it is important to discriminate between the two termination reactions because the molecular weight distribution of the products is different.

During free-radical polymerization, radicals can be involved in the atom transfer or atom abstraction reaction, Eq.(7) with subsequent propagation of a newly formed species, Eq. (8). These are called chain transfer reactions and they involve transfer to initiator, monomer, polymer, solvent (if present) or a chain transfer agent (a deliberately

added substance to induce chain transfer in order to control molecular weight). Traditionally, it is considered that these reactions do not affect the rate of polymerization but only the molecular weight development. However, in heterogeneous polymerizations (e.g. emulsion polymerization) the presence of chain transfer can influence the termination rate and the interphase migration of species, and thus influence the rate of polymerization.

The rate of polymerization (Eq. 8) can be transformed into the experimentally useful expression (Eq. 10) by incorporation of two assumptions: 1. the long-chain assumption, where the reactivity of the propagating radicals is chain length independent when the size of the radical is greater than three; 2. the steady-state assumption, where the rate of radical formation is equal to the rate of radical termination (this steady-state is reached almost instantaneously):

$$R_p = \frac{k_p}{k_t^{1/2}}[M](2 f k_d[I])^{1/2} \qquad (10)$$

In the absence of branching and cross-linking reactions, the number average degree of polymerization, $\overline{X}_n$, can be expressed as:[21]

$$\frac{1}{\overline{X}_n} = \frac{k_t R_p}{k_p^2[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{k_t R_p^2}{k_p^2 f k_d[M]^3} + C_{CTA} \qquad (11)$$

where C_x denotes the chain transfer constant (the ratio between the particular chain transfer rate constant to the propagation rate constant, $\frac{k_{tr,x}}{k_p}$) where x can be monomer (M), solvent (S), initiator (I), or chain transfer agent (CTA). It can be seen that the rate of polymerization and molecular weight are inversely proportional. Thus, the simultaneous increase in the rate of polymerization and molecular weight is not possible in *homogeneous* free-radical chain reactions. For systems where branching does occur, Eq. 10 and 11 can be used for illustrative purposes only.

2.3.2 Characteristics and Advantages of Emulsion Polymerization

2.3.2.1 Heterogeneity

Heterogeneity is a distinctive characteristic of emulsion polymerization. Several phases can co-exist in an emulsion polymerization but the number of phases may change as the polymerization proceeds. The aqueous phase contains initiator, stabilizers, oligomers, micelles (when anionic stabilizer above a critical micellar concentration is used), and a small amount of water-soluble monomer(s). Monomer droplets (second phase) are stabilized by a stabilizer and dispersed by mixing in the aqueous phase. The third phase consists of stabilized polymer (latex) particles.

2.3.2.2 Three stages of emulsion polymerization

Harkins divided emulsion polymerization into three intervals (stages).(22) Although strictly not valid for all cases, it is a convenient picture whose simplified interpretation is given in Table 4. (23)

Table 6 Different Intervals of an Emulsion Polymerization (23)

Interval	Typical conversion range (%)	Micelles	Monomer droplets	Particle number	Particle size
I	0-10	present	present	increases	increases
II	10-40	absent	present	constant	increases
III	40-100	absent	absent	constant	~ constant

Interval I – The stabilizer is dissolved in water at a concentration above the critical micellar concentration. An excess of emulsifier molecules aggregate together to form colloidal clusters or micelles. Monomer is dispersed in droplets (diameter = 0.1-1 mm) that serve as monomer reservoirs. Monomer diffuses from the droplets through the water phase into the micelles driven by a concentration gradient. A small fraction of

monomer is dissolved in the water phase. Free radicals, generated in the water phase, can undergo several distinctive reactions in the water phase.(24,25)

1. Radicals can add monomer molecules present in water phase according to reactions (2) and (4). It is considered that when the number of monomer units added is about 7 (depending on the monomer system), the oligomer becomes hydrophobic and enters the organic phase (i.e. polymer particle or micelle).

2. Radicals can react with water-soluble impurities:

$$R^{\bullet}_{r,i} + WSI \xrightarrow{k_{zj}} P(WSI) \qquad (12)$$

where *P(WSI)* is a dead molecule and k_{zj} is the rate constant for reaction of water-soluble impurity, *j*, with monomer *i*-ended radical. Water-soluble impurities (e.g. oxygen) may cause an induction period by consuming large amounts of radicals.

3. The radicals may terminate upon encountering another radical (Eq. 4 and 5).

4. The initiator fragments may recombine. The efficiency factor, *f*, accounts for this phenomenon.

5. Radicals may be captured by monomer droplets. Droplet nucleation may occur under high shear (high rate of mixing) or other specific conditions such as in miniemulsion polymerizations.(26)

6. Radicals can be desorbed from the polymer particles. This phenomenon is usually a result of chain transfer to monomer, monomer-soluble impurity or chain transfer agent.

7. Desorbed radicals may be re-absorbed into the polymer particle.

8. Radicals may be captured by micelles.

9. Radicals may be captured by particles.

The "fate" of radicals in the organic phase (e.g. when the radical is captured by polymer particles, micelles or monomer droplets) is similar to that in homogeneous polymerizations. The radicals can undergo propagation (Eq. 3), termination (Eq. 4 and 5), or chain transfer reactions (Eq. 6 and 7). The concept of diffusion-controlled rate constants is applicable here. During this interval, the particle number, particle size and thus, the polymerization rate all increase with time.

Interval II – After approximately 15% conversion of the initially charged monomer, micelles are exhausted. No new particles are generated. Monomer diffuses from the monomer droplets, through the aqueous phase and into the latex particles, to maintain saturation swelling and support the propagation reaction.

Interval III – After approximately 40-60% conversion, the monomer droplets disappear, at which point the polymerization rate tends to decrease as the result of the decrease in monomer concentration inside the particles. During this stage, only the latex particles and the aqueous phase are present. The remaining monomer located in the latex particles is consumed.

2.3.2.3 Particle nucleation

Particle nucleation is an important aspect of emulsion polymerization. Three major nucleation mechanisms are possible: micellar, homogenous and droplet nucleation. Even though all three mechanisms can occur simultaneously, usually only one is dominant, depending on the monomer water solubility and stabilizer concentration.(24) In micellar nucleation, initiator radicals enter the monomer-swollen micelles to initiate the polymerization. Those micelles that capture radicals will become polymer particles while others will serve as a reservoir for the stabilization of formed particles. The formation of particles ceases at the end of interval I. Common to monomers with higher water solubility is homogeneous nucleation, where radicals generated in the water phase continue to grow, adding the monomer molecules located in the aqueous phase. When the growing oligomeric radical reaches a particular size (depending on the system), it becomes water insoluble and precipitates. These precipitated oligomeric radicals form primary particles. These will absorb stabilizer and monomer for stabilization and further growth, respectively. In the third mechanism, a radical may be captured by a monomer droplet to form a particle. This is less likely due to the difference in the surface/volume ratio of monomer droplets and monomer-swollen micelles but can be induced under some conditions. On the other hand, droplet nucleation is the dominant mechanism of nucleation in miniemulsion polymerizations.(26)

2.3.2.4 Advantages of emulsion polymerization

The rate of polymerization, R_p, and the number-average degree of polymerization for emulsion polymerization, $\overline{X}_n$, are given by

$$R_p = k_p[M]_p \bar{n} N / N_a \quad (13)$$

$$\overline{X}_n = k_p[M]_p \bar{n} N / R_I \quad (14)$$

where k_p is the propagation rate constant, $[M]_p$ is the monomer concentration inside the particle, $\bar{n}$ represents the average number of radicals per particle, N is the number of latex particles, N_a is Avogadro's number and R_I is the initiation rate. Note that Equation 14 is valid in the absence of branching and cross-linking. Otherwise, it should be used for illustrative purposes only. In general, the greatest advantage of emulsion polymerization is the ability to simultaneously increase both the polymerization rate and the molecular weight of polymer which is not possible in bulk or solution polymerizations. This is the biggest advantage of emulsion-based PSAs compared to solution-based ones. High molecular weight fractions are desirable for improved shear strength of PSAs. For solution-based PSAs, it is necessary to reduce the molecular weight in order to obtain a high solids content (>40%) which results in a decrease in shear strength.(27) For emulsion-based PSAs, there is no such limitation because the viscosity is not governed by the molecular weight distribution but rather by the particle size distribution. Thus, it is possible to obtain very high molecular weights. The reduced tack that accompanies high molecular weights can be improved by the addition of a chain transfer agent or tackifier. Latexes used in the PSA industry have 40 – 70% solids contents. For latexes of high solids contents (>60%) it is necessary to have bimodal or multimodal particle size distributions to ensure lower viscosity (< 500 mPa.s).(28) Considerable research effort is devoted to the preparation of these types of latexes.(29-34) Another advantage of emulsion polymerization is better heat transfer as a result of better temperature control due to the low viscosity of the reaction mixture. Furthermore, the health and environmental impact is lower, compared to solution polymerizations due to the absence of large amounts of organic solvents.

Emulsion polymerization monitoring and modeling. Ever increasing demands on product quality, process control and safety drive the development of new and improved polymerization monitoring techniques as well as comprehensive models.

Chien and Penlidis,(35) Hergeth,(36) Shork,(37) and Kammona et al.(38) critically reviewed up-to-date process monitoring techniques. Reviews on emulsion polymerization modeling are given by Dubé et al. (25), Gao and Penlidis (39), Penlidis et al.(40), and Saldivar et al. (41-43).

2.3.3 Emulsion Polymerization Components

The major components used in the production of emulsion-based PSAs and their approximate amounts are listed in Table 5.

Table 7 Emulsion Polymerization Components

COMPONENT		EXAMPLE	AMOUNT
MONOMERS	"Soft"	Alkyl esters e.g. BA, 2-EHA, EA	5-90%
	"Hard"	MMA, VAc, Sty	10-40%
	Polar	AA, MAA	2-20%
STABILIZER(S)	Electrostatic	Sodium dodecyl sulphate, sulfosuccinates	0-8%
	Steric	Hydroxyethyl cellulose, PVOH, starches	
	Surfmers	allyl amine salts of 1. alkyl benzene sulfonate or 2. phosphate ester	
BUFFER(S)		$CaCO_3$, $NaHCO_3$, Na_2CO_3	0-1%
INITIATOR(S)		Thermal (e.g. ammonium and potassium persulfate), Redox (persulfate/bisulfate systems)	Up to 3%
CHAIN TRANSFER AGENT(S)		Mercaptanes	0-3%
WATER		Distilled de-ionized	40-70%
ADDITIVES		See Table 6 for details	0.5-2%

* List of abbreviations provided at the end of the article.

2.3.3.1 Monomers

A wide variety of monomers can be polymerized by emulsion polymerization. Among them are butadiene, styrene, acrylonitrile, ethylene, vinyl chloride, vinyl acetate, vinylidene chloride, (meth)acrylic acid and its alkyl esters (e.g methyl, butyl, 2-ethyl hexyl) and others. The selection of monomers is governed by the intended latex end-use (e.g. paints, adhesives, sealants) and desired end-product properties (e.g. adhesive strength, minimum film forming temperature). Because end-products are usually specifically tailored formulations, compatibility with other latexes or common additives can also be tailored by appropriate monomer selection. The same reasoning applies to the processability of the polymer. The patent literature discloses a wide variety of main and modifying monomers used as emulsion-based PSAs: acrylic esters with alkyl groups having 4-17 C atoms (e.g. n-butyl acrylate, hexyl acrylate, isooctyl acrylate, 2-ethyl hexyl acrylate, isononyl acrylate, decyl acrylate), vinyl aromatic monomers (e.g. styrene, 3-methyl styrene, 4-propyl styrene, 4-cyclohexyl styrene, halogenated styrenes), vinyl esters (e.g. vinyl acetate, vinyl butyrate, vinyl propionate, vinyl isobutyrate, vinyl valerate, vinyl versitate), ethylene, acrylamide, carboxylic acids (e.g. (meth)acrylic acid, itaconic acid, fumaric acid) and others (e.g. cyclic and sulfonated monomers). PSAs based on acrylate copolymers are considered the most competitive PSAs when the balance between end-product properties, compatibility with additives and processability are considered. The main PSA properties that can be tailored by proper selection of monomers are tack, peel, and shear strength, which, in turn, are governed by, among other parameters, the glass transition temperature (T_g) and viscoelastic moduli of the polymer. The T_g and viscoelastic moduli are determined not only by the type of monomer but also by the sequence length distribution of the monomer units and the molecular weight of the polymer. The influence of T_g on the monomer selection is discussed here.

PSAs are required to be fluid at the bonding and application temperature. They must be permanently tacky and possess sufficient peel and shear resistance. Because no homopolymer possesses the appropriate combination of these properties, PSAs are obtained by co- or multicomponent emulsion polymerization. Even though it has been reported that the "optimal" T_g for a PSA is about –15 to –5°C, many commercial PSAs

have much lower T_g (i.e. as low as –60°C).(1) The patent literature discloses the main, so-called "soft" monomers as alkyl acrylates of 4-17 carbon atoms. Although large numbers of monomers are reportedly used in PSAs, the most commonly used are 2-ethylhexyl acrylate, n-butyl acrylate and ethyl acrylate. Their homopolymers have T_gs below 0°C and possess inherent tackiness but lack sufficient cohesive strength (i.e. shear strength). Thus, modifying or so-called "hard" monomers are added to enhance shear strength. Their homopolymers have T_gs above 0°C. The patent literature discloses the use of monomers such as the vinyl aromatic and vinyl ester monomers mentioned earlier, as well as ethylene and acrylamide. Monomers with functional groups are also added as modifying monomers. They act as cross-linking sites, thus improving peel and shear strength while simultaneously lowering the tack. Unsaturated carboxylic acids (e.g. acrylic and methacrylic acid, itaconic acid, fumaric acid, crotonic acid) are used for this purpose. Multifunctional monomers are added to induce cross-linking. Other monomers can be added to impart other application-specific PSA properties. Two ideal PSA formulations are often cited. One is an ideal formulation of acrylic PSA copolymers with 50-90 wt% main monomer, 10-40 wt.% modifying monomer, and 2-20 wt.% functional monomers.(44) The other is an ideal water-based PSA composed of 70-90 wt.% main monomer, 10-30 wt.% modifying monomer and 3-6 wt.% functional monomers.(1) Because there is no single adhesive that fits all applications, there is no ideal composition. Rather, these "base formulations" serve as a starting point when designing a PSA.

2.3.2 Stabilizers

There are two primary functions of a stabilizer in emulsion polymerization. One is to facilitate particle nucleation and the other is to stabilize the latex particles against flocculation as the polymerization proceeds. The biggest concern in PSA production is their effect on the final product properties. In the case of PSAs, they can reduce water resistance and can migrate to interfaces causing loss of tack, cloudiness at the surface and other undesired effects.(45)

There are three basic types of stabilizers employed in emulsion polymerization (23):

1. Electrostatic stabilizers: anionic or cationic soaps which prevent coagulation by electrostatic repulsion arising from the charges located on the particle surfaces and their associated electric double layers.
2. Polymeric (steric) stabilizers: which stabilize the particles via entropic repulsion caused by trying to pack two chains in the same space.
3. Electrosteric stabilizers: which display the characteristics of the previous two. These are rarely used in coating and adhesive applications and are often used in personal care products.(46)

Commonly employed stabilizers from group 1 are sodium dodecyl sulphate (SDS) and stabilizers from the Aerosol series (sodium dialkyl sulfosuccinates). The presence of stabilizer influences the kinetics of emulsion polymerization and ultimately the bulk film properties. It has been shown that, depending on the nature of the stabilizer and its interaction with the polymer, the peel strength of a PSA might be affected due to the easy migration of the small stabilizer molecules which are not strongly anchored to the particle surfaces.(48) In a series of papers on the adhesion of different latex films to different substrates, it was shown that SDS forms a relatively thick stabilizer layer at the adhesive-substrate interface where the rupture of the adhesive bond will easily propagate. (48-52) The thicker the layer, the easier the propagation. A plot of peel energy vs. stabilizer concentration can show either a minimum or maximum depending on the stabilizer used. In the case of SDS, maximum peel energy was observed at 3.5 wt.% at a constant low peel rate of 30 mm/min. (51)

Hydroxyethyl cellulose and poly(vinyl alcohol) (PVOH) are common polymeric stabilizers used at the industrial scale. PVOH is a product of hydrolysis of poly(vinyl acetate). It has been used as a stabilizer in emulsion polymerization reactions alone or in combination with electrostatic stabilizers such as SDS.(53) Lorenz and Daniels (54) have shown that EVA emulsions can be successfully applied as PSAs due to the excellent wet and residual tack induced by the PVOH as stabilizer. In addition, high shear stability of these latexes was observed. It is not unusual for PVOH stabilized latexes to exhibit

Newtonian flow even at high shear rates which makes them suitable for the high-speed applicators used in the adhesive industry.(54-56) These improved properties are the result of better particle-to-particle coalescence, which in turn leads to improved film clarity and water resistance, as well as residual tack and superior adhesion.(54) On the other hand, the inferior water resistance of PVOH stabilized latex films was also reported. Yuki et al. (56) showed that the morphology of films in the presence of PVOH is "canal-like PVOH in a polymer matrix" as opposed to "emulsifier islands in the matrix" when SDS is used. This canal-like structure allows easy diffusion of water into PVOH-containing films compared to films containing anionic stabilizers. Modified PVOH can offer better water resistance.(57)

The idea behind the development of so-called reactive or polymerizable stabilizers was to prevent the migration of the stabilizer by attaching it to the particle surface by covalent bonding. (58-61) Reactive stabilizers are incorporated in PSA formulations (62-65). Because these stabilizers are attached to the particle surface, they may offer better latex stability. Furthermore, better dry film characteristics were observed when these stabilizers were compared to conventional ones. Similar to reactive stabilizers atomic force microscopy has revealed that latex films prepared from PVOH stabilized emulsion have smoother surfaces compared to those produced using conventional stabilizers.(66) Polyethoxylated alkylphenyl phenyl ethers and polyethoxylated alkylphenyl phenyl ether sulfates are two families of polymerizable stabilizers.(28) Howe et al. (67) compared the performance of BA/MMA/AA/EHA-based PSAs, stabilized what by they defined as "non-migratory stabilizers", to those stabilized with conventional anionic stabilizers. The formulation employing polymerizable stabilizers showed higher shear strength, tack and reduced and slower whitening. Lu et al. (65) claimed that the unique combination of an ionic copolymerizable stabilizer and a water insoluble low molecular weight non-copolymerizable polymer introduced into a reaction mixture with a typical low T_g monomer (isooctyl acrylate), a high T_g monomer (VAc) and a polar monomer (AA) resulted in a water-based PSA with a unique set of desirable properties. The PSA showed high initial adhesion with controlled adhesion build-up. In addition, it exhibited good moisture resistance, good adhesion to low energy surfaces, high shear strength, and high solids content combined with low viscosity.

2.3.3.3. Initiators

In conventional emulsion polymerization, thermal and redox type initiators are used. Thermal initiators are mostly water-soluble (e.g. potassium or ammonium peroxodisulfate) but oil-soluble initiators (e.g. benzoyl peroxide, 2,2-azobis(isobutyronitrile)) have also been employed.(68) Persulfate initiators are usually employed at temperatures above 50°C and result in the formation of $SO_4^{-\bullet}$ radicals (Eq. 15).

$$S_2O_8^{2-} \xrightarrow{\Delta} 2SO_4^{-\bullet} \quad (15)$$

Sulfate radicals can react with water to produce HSO_4^- which alters the pH.

$$SO_4^{-\bullet} + H_2O \longrightarrow HSO_4^- + HO^\bullet \quad (16)$$

This can considerably reduce the initiator efficiency if the pH is less than 3. The increased acidity catalyzes the hydrolysis of some of the monomers (e.g. VAc, BA).(69) The hydrolysis of poly(vinyl acetate) produces acetic acid while the hydrolysis of poly(butyl acrylate) forms poly(acrylic acid) and butanol. These small molecules can act as plasticizers in a dry polymer film. For adhesive applications, this may be undesirable because these molecules can increase tack and reduce cohesive strength. Due to these reasons, a buffer is usually employed. Redox initiators can be employed at lower temperatures and when high molecular masses with low degrees of branching are desirable.(69) Common redox initiator systems are persulfate-bisulfate or hydrosulfite. In the production of emulsion-based PSAs, both types, thermal (70) and redox (65, 70, 71) as well as mixtures of initiators have been reported. In the preparation of high solids latexes, Schneider et al. (32) have shown that the choice of the initiator in a particular stage of reaction can affect stabilization and rate of reaction. In the preparation of BA/MMA/AA based high solids latexes for PSAs, these authors have stated that the oil-soluble initiator increased the reaction rate during a semi-batch reaction. They also reported better stabilization of homogeneously nucleated particles when persulfate initiators were used. Research has shown that persulfate initiator acts as an additional stablizer in emulsion polymerization and that it can also be used as the sole stabilizer.(72)

The benefits of using the initiator as the sole stabilizer for PSA formulations was not investigated, but one can speculate that it can be beneficial to reduce the concentration of small molecules present in the system (e.g. elimination of anionic stabilizers) that can undergo migration to interfaces and affect film formation properties and subsequently adhesion performance of PSAs. The use of inisurfs (i.e. molecules that combine initiator and surface-active properties) as well as surfmers (i.e. molecules that combine surface-active and monomer properties) is under investigation. For example, US Pat. No. 6,048,611 (65), the claim is that the utilization of surfmers was a major factor in the development of emulsion-based PSAs with improved performance.

2.3.3.4 Buffers

Due to possible hydrolysis reactions at acidic pH values, the presence of buffer in an emulsion polymerization is desirable. Usually $CaCO_3$, $NaHCO_3$ or Na_2CO_3 is employed. If the pH is too low, the decomposition rate of the initiator may accelerate and thus, the number of radicals and subsequently, conversion increases (69). In Sty/BA carboxylated latexes, the reaction mechanism and carboxyl group distribution depend on both the type of carboxylic acid used and the pH (73-78). Gajria and Vijayendran (79) found that feeding AA or MAA with monomer as opposed with water increased the concentration of carboxyl groups at the polymer particle surface of BA/VAc latexes. The effect of pH on mechanical properties (i.e ultimate elongation, ultimate strength and toughness) of emulsion terpolymers Sty/MMA/itaconic or methacrylic acid was investigated by Mendizabal et al. (74). At low pH values, more functional monomer was incorporated into the outer layer of particles, leading to higher rigidity and toughness. As essential pH regulators, buffers are employed in the production of emulsion-based PSAs. Except for the work of Brooks et al. (80), who found that NaOH used as a buffer for BA/VAc/MMA latexes can significantly affect PSA properties, no specific studies on the effect of buffer on PSA final properties were found.

2.3.3.5 Chain transfer agents (CTA)

CTAs are added to regulate the molecular weight development in an emulsion polymerization (Equations (6) and (7)). Although a large number of chemicals can act as a CTA (e.g aldehydes, chlorinated aliphatics, disulfides, amines and other carbonyl components) (81), generally, the most employed are substances from the thiol family. (82-86) In the PSA industry, dodecanethiol (dodecyl mercaptan), in a concentration range of 0.01-1 phm, is preferred (65, 87, 88). In this case, CTA is used to improve adhesion strength by reducing the cross-linking and formation of high molecular weight polymers. This will simultaneously reduce the cohesive strength of the PSA. Thus, the amount of CTA in a PSA formulation should be carefully chosen. Plessis et al. (85) investigated the effect of dodecanethiol on the kinetics, gel fraction, level of branching and sol molecular weight distribution in seeded semibatch emulsion where PBA particles were used as the seed. A pre-emulsified BA/AA (98/2 wt.%) mixture was fed along with the initiator solution during a semibatch step. They concluded that CTA strongly affected the gel content and weight-average molecular weight of the sol, while no influence on the kinetics or the level of branching was observed. These authors also developed a mathematical model to predict gel content vs. conversion for various concentrations of CTA. The model showed good agreement with the experimental data at low CTA concentrations (0-0.02 wt.%) but overpredicted the gel content as the CTA concentration increased (0.06-0.15 wt.%). Adhesive properties of the formed polymers were also tested. The shear strength increased as the gel fraction increased (i.e. lower CTA amount added) up to 32 wt.% gel. Samples with 55 wt.% gel showed a decrease in shear strength. Similar behaviour was observed for peel strength.

2.3.3.6 Dispersion medium (water)

Particle nucleation and stability in anionically stabilized emulsion polymerization can be affected by the presence of cations in natural water (69, 81). Thus, deionized and distilled water is used as a dispersing medium. In addition, while trace organic

components in water may have little influence on the kinetics due to their low concentration, the presence of oxygen is of utmost concern even at low concentrations. Oxygen acts as a free-radical scavenger and its presence leads to a delay in the start of polymerization (induction period), which in some cases, may be followed by a retardation period.(89) Thus, prior to polymerization, it is common to purge the reactor contents with nitrogen.

2.3.3.7 Additives

Additives are usually added to enhance the end product performance of emulsion polymers. For high performance formulations, it is necessary to have a knowledge of polymer properties (e.g. composition, molecular weight, rheology), the properties of the additive and the compatibility of the two. Different additives can be added to a latex depending on its end use. In Table 6, some of the most common additives which may affect PSA performance are summarized.

Table 8 Additives Commonly Used in PSA Formulations

ADDITIVE FAMILY	FUNCTION	REPRESENTATIVE
Tackifiers	To modify tackiness.	Rosin and rosin derivates, hydrocarbon resins, polyterpenes.
Peel Modifiers	To modify peel strength.	Polybutenes, silicones.
Wetting Agents	To modify surface tension.	Sulfosuccinates, Disulfosuccinates,
Rheology Modifiers	To modify latex viscosity.	Cellulose derivatives, PVOH, starch.
Cross-linking Agents	To ensure adequate shear strength.	Metal salts and oxides, polyfunctional aziridines.
Other additives: defoamers, fungicides, antioxidants, fillers etc.	Variety of functions.	

Tackifiers. These additives are specific to the use of latex as a PSA. Not only do the different classes of polymers have different tack levels (e.g. acrylates are considered inherently tacky while natural/synthetic rubbers have low tack levels), but also the same class of polymers can exhibit different tack levels depending on the chain structure and molecular weight.(1) Tackifiers are used to induce tackiness (e.g. in natural/synthetic-rubber based PSAs) or to enhance the tackiness of already inherently tacky polymers (e.g. in acrylate-based PSAs). Simultaneously, due to the interdependence of the three major PSA properties, the addition of a tackifier generally improves the peel strength but decreases the shear resistance and also influences other PSA characteristics (7). There are three important characteristics to consider when using a tackifier: its solubility in the polymer, its ability to modify the viscoelastic properties of the polymer, and the effect on the adhesive/substrate interfacial tension.(90) Generally, low molecular weight resins with a higher T_g than the base polymer (e.g. rosin (natural resin) and rosin derivates, hydrocarbon resins, polyterpene) are used as tackifiers.(91) Sensitivity to oxygen, incompatibilization at low temperatures, and aging resistance of adhesives are some of the problems associated with the use of resins. A combination of resins is also used for fine-tuning of the shear strength/tack balance.(28) Different aspects of tackification of acrylic-based PSAs (90-92) and natural rubber-based PSAs (93) have also been investigated.

Peel modifiers. In most cases, plasticizers, tackifiers and resins act as peel modifiers due to the interdependence of basic PSA properties, but special additives can be added to increase (e.g. polybutenes) or decrease (e.g. silicones) the peel strength of emulsion-based PSAs.

Wetting agents. High viscosity latexes will show better wetting and coverage of even low energy surfaces such as silicone release coatings or polyolefin films. On the other hand, some coating applications such as gravure and reverse gravure require low viscosity latexes to allow release from the gravure cells.(46) In these cases, the post-polymerization addition of a small amount of surface-active agent is common (94). The

purpose is to lower the surface tension of the PSA and thus, obtain better wetting of the substrate. Hence, the name of this class of additives: wetting agents. The most common wetting agents are sulfosuccinic acid esters. This class of agents can also influence the shear and peel strengths of the PSA and induce the water sensitivity of the PSA.(28,48) Thus, their amounts should be kept as low as possible. Apart from excellent wetting, especially under dynamic conditions, wetting agents have to show minimal foaming. Excessive foaming can be corrected with the addition of defoamers, which unfortunately can cause coating defects such as fish eyes, craters etc.(94)

Rheology modifiers. For a particular application, it is necessary for a latex to have a specified viscosity value or rheological behaviour. A decrease in PSA viscosity will affect wetting. Thus, when using conventional stabilizers, it is often necessary to incorporate thickeners to increase the viscosity of the latex. The addition of thickeners can also impart their migration through a carrier.(1) Starch, alginates, dextrin, PVOH and cellulose derivatives (e.g. hydroxyethyl cellulose) are used as thickeners. Polymeric thickeners such as copolymers of methacrylic acid and alkyl (meth)acrylates, polyvinylpyrrolidone or polyvinyl ethers are also used. Some stabilizers such as sulfosuccinates can act as thickeners.(1) In some cases, when high solids latexes are used as PSAs, it might be necessary to decrease the viscosity. It can be decreased by dilution with water, or if the high solids content has to be maintained, by the addition of a viscosity reducing agent (e.g. alkaline substances, carbamides, dicynadiamides).(1) The amount of thickener should be minimized because the water resistance of dried films will decrease with increasing thickener concentration. (28)

Cross-linking agents. A balanced level of cross-linking that will ensure good shear strength and adequate tack is necessary for PSAs. The major challenges are how to ensure the appropriate degree of cross-linking as well as the reproducibility of the process. In water-based acrylic PSAs, cross-linking occurs inside the particles due to chain transfer to polymer reactions during the emulsion polymerization reaction. (95, 96) In addition, external cross-linking agents may react with the functional groups of the bulk polymer. The most important class of external cross-linking agents for emulsion-based

PSAs are polyfunctional aziridines (e.g. Neocryl-CX100) followed by metal salts and oxides. External cross-linking occurs during the drying process. Water-soluble polyamide epichlorohydrin (Polycup, Hercules) is effective for carboxylated acrylic or SBR latexes. Czech (97) investigated cross-linking agents from seven different commercially available groups and their influence on the adhesive properties of 2-EHA/BA/VAc/Sty/AA emulsion-based PSAs. He concluded that zinc acetate and zirconium carbonate were not suitable cross-linkers for the given system. Excellent performance was obtained when aluminum acetylacetonate and a cross-linking agent from the propyleneimines family were used. The performance of the second cross-linking agent was superior to that of the first over a wide range of surfaces. Benedek and Heymans (1) advised a limited use of cross-linking agents in the form of water-soluble agents due to the fact that they may show only limited interaction with the bulk polymer and unlimited interaction with the aqueous medium.

Other additives. Defoamers are added to prevent encapsulation of air during the coating process in order to prevent the occurrence of coating defects in the PSA. Antioxidants and UV stabilizers can be added to improve the aging characteristics of the PSA. Pigments, plasticizers, antistatic agents, fungicides, and other additives such as fillers, colorants, anti-freezing agents, etc. can also be added to the PSA formulation to impart or enhance a particular property.

2.3.4 Latex Rheology

A latex during production, storage and application is subject to different stresses. Two recent overviews on latex rheology are presented by Shaller (98) and Fitch (99). They outlined different factors affecting latex rheology such as volume fraction of polymer, and particle size, shape and distribution. Also, theoretical relations governing latex rheology, such as Eistein's, Mooney's, and the Krieger-Dougherty equations were discussed by Shaller.(98) Fitch (99) outlined a concept of corresponding rheological states and four limiting viscosities which are defined by the Peclet number and the measurement method (i.e. shear or oscillatory).

As mentioned, polymer composition and molecular weight distribution do not have a significant effect on emulsion latex rheology compared to solution-based polymers. The post-polymerization changes in pH, the addition of water-soluble macromolecules, also called rheology modifiers, and the presence of surface active substances can affect latex rheology. Ideally, Newtonian flow, where the latex viscosity is not dependent on shear rates, is preferable. Such behaviour is observed with some PVOH-stabilized latexes at high solids contents.(100) This is also desirable for the application of latex as a PSA. A generalized non-Newtonian behaviour is presented in Figure (1).(98) A Newtonian plateau at low shear rates is denoted as zero shear viscosity. It is followed by a shear thinning region, where viscosity decreases with an increase in shear rate. The plateau at high shear rates is denoted as a high shear Newtonian plateau. In some cases, this region may be followed by a shear thickening behaviour where viscosity can increase again.

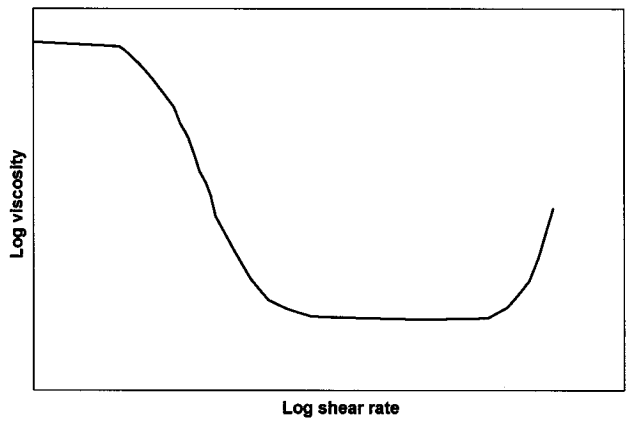


Figure 1 Generalized Flow Behaviour of Polymer Colloids (98)

One of the most important factors affecting latex rheology is the volume fraction of polymer. The viscosity of the latex increases indefinitely when the volume fraction of monodisperse, spherical particles approaches 0.74. As mentioned, latexes with solids contents from 40-70% are commonly employed in the PSA industry. High solids latexes will have lower shipping and drying costs and show better wetting of even low surface tension substrates such as silicone release paper. Thus, considerable research effort has been devoted to methods for preparing these types of latexes (29-34) while retaining low

viscosity. The main objective is to increase the maximum packing fraction of the particles by incorporating smaller particles into the interparticle space created by the larger particles. Common problems are the rheology of the reaction mixture and the colloidal stability. The most common methods for generating high solids latexes with multimodal particle size distributions involve multistage polymerization, the use of special stabilizers (30) and the use of miniemulsion polymerization (29). A method for producing concentrated emulsions with a dispersion phase volume fraction greater than 0.74 was proposed by Ruckestein.(101)

2.3.5 Latex Films

In most applications, latex is applied in the form of a thin film onto a substrate. The dry film properties, such as mechanical properties and permeability, are influenced by the film morphology, which is governed by the film formation process. Thus, an understanding of the film formation process and the structure-property relationships of latex films is of utmost importance in the design of high performance PSAs.

The film formation process (Figure 2) is the transformation of a polymeric dispersion into an isotropic polymeric film during drying. In the most general sense, this process involves three steps. The first stage, water evaporation, brings latex particles into close contact. A short period at a constant evaporation rate is followed by a decrease in the rate as the particles come into closer contact.(102) Winnik (103) and Richard (104) critically examined several drying models. The authors concluded that the proposed models are neither general nor complete and that recent advances in experimental techniques offer a potential for a better understanding of the film formation process and thus, the development of a more general model.

In the second stage, a void-free, mechanically weak structure is formed by the deformation of particles into polyhedral cells. Each cell consists of a hydrophobic particle core and a hydrophilic membrane formed from the species used to stabilize the latex.(105) This stage is governed by the ratio between driving and resisting forces to particle deformation.(104). Two factors are dominant: drying temperature and the T_g of the latex. The particle resistance to deformation decreases as the latex T_g decreases. The

deformation resistance will also decrease if the drying temperature is slightly higher than the T_g of the latex.(106) Determined by different methods (optical, crack- or knife-point), the temperature at which the particle deformation forces prevail is called the minimum film forming temperature (MFFT). A homogeneous, mechanically superior film will be formed when the latex is dried above the MFFT. Routh et al. (107, 108) examined the existing mechanisms of deformation and proposed a model that combines all existing mechanisms to predict the conditions under which each mechanism occurs.

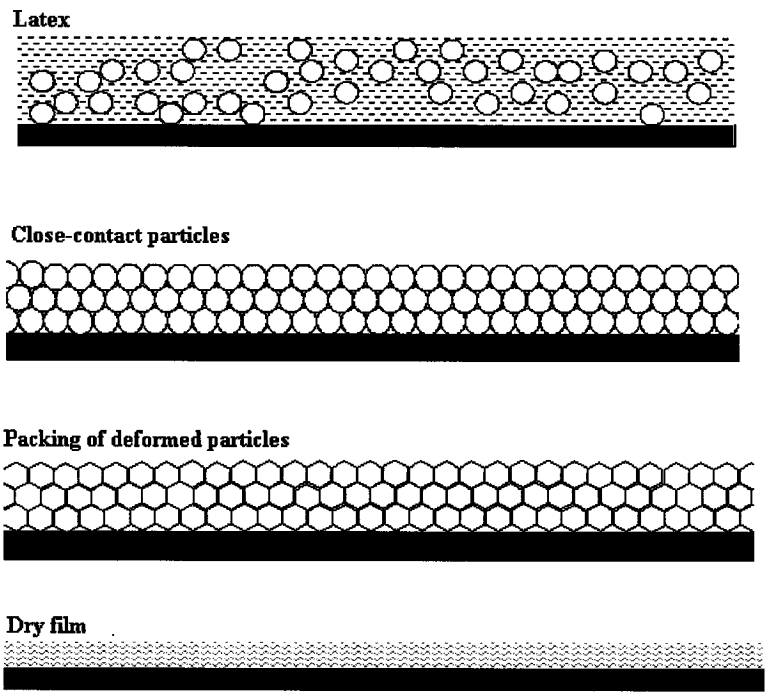


Figure 2 Film Formation Process (103)

In the final stage, a gradual further coalescence of the latex particles occurs. In this stage, the cohesive strength of the film is developed by the interdiffusion of polymer molecules across the boundary between adjacent particles or cells (103,104). The recent development of techniques such as transmission electron microscopy, small angle neutron scattering or direct non–radiative energy transfer has enabled the investigation of this final stage.(19, 110) The interface diffusion depends on the molecular weight of the polymer (111), particle structure (112), temperature (113) and

the presence of compounds acting as plasticizers (e.g. stabilizers, solvents). The movement of chains across the interfaces is usually described by the de Gennes' reptation model (103). The interdiffusion in the presence of cross-linkable compounds leads to the development of cross-linked film structures. Interest in gaining a better understanding of these structures is on the rise (19, 114-118). Zosel (115) illustrated that regardless of cross-linking mechanism (i.e. incorporation of bifunctional monomers in the recipe or the addition of salt metals to carboxylated latexes), latex films form heterogeneous networks. He also speculated that there are two limiting cases of network models: one where films are formed from pre-cross-linked particles without any additional cross-linking across particle boundaries, and the other where films are formed from uncross-linked particles which are cross-linked across particle boundaries during or after film formation, e.g. by hydrophilic bifunctional monomers. Based on the ideas of Zosel, Pinenq et al. (109) further investigated the mechanical properties of the films of four structured latexes: uncross-linked, fully cross-linked, core-crosslinked and shell-cross-linked latexes. Tobing and Klein (117) have shown that the utilization of as low as 1wt.% of isobutoxy methyl acrylamide (IBMA) in BA/AA or 2-EHA/AA emulsion-based PSAs will lead to improved PSA performance comparable to solvent-based PSAs from the same monomers. The formation of cross-links instead of simple entanglements across particle boundaries appeared to be responsible for these improvements.

The fate of stabilizer molecules during the film formation process has also been of interest due to their profound influence on film performance.(28, 112) It is generally accepted that anionic stabilizers (e.g. SDS) will be desorbed from the particles during stage two and carried away by thin channels of water still present between the particles towards the air-film or film-substrate interfaces. Small clusters of stabilizer molecules embedded into the film will give rise to water permeability through the dry film.(66) As discussed earlier, the migration of the stabilizer will also affect other properties, among them adhesive properties such as peel strength and tack.(49-53) Lam et al. (66) investigated the fate of the stabilizer using AFM and concluded that the films formed from reactive stabilizers exhibited smaller defects compared to the films from latexes stabilized with SDS. Mallegol at al. (119) investigated the origins and effects of stabilizer excess near the surface of emulsion-based PSAs. Using Rutherford backscattering

spectroscopy, the authors showed that the surface excess of Na, S, and K (from initiator, buffer, and/or stabilizers) can exist to a depth of 60 nm from the surface. The origin of this excess is chemical and physical in nature. The higher the concentration of carboxylic groups at the particle surface, the slower the desorption of water-soluble species. Physically, instead of a continuous structure upon water evaporation, the adjacent particles may form capillaries through which water-soluble species will travel to the film surface. The authors stated that the presence of stabilizer and other water-soluble moieties is the reason why they did not observe any particle coalescence using AFM after casting latexes (T_g = -45 °C) at room temperature. This is opposed to current film formation theories that predict rapid coalescence in such cases.

The film formation process will determine many of the latex film's properties. Among the most commonly investigated are mechanical properties (e.g. viscoelastic properties, tensile strength), thermal properties (e.g. transition temperatures, thermal stability) and permeability properties (e.g. permeability of water and solvents through the film). In addition to these, surface phenomena such as film surface topology or surface tension are of interest. Experimental techniques such as dynamic mechanical analysis (DMA) (120) or thermal techniques (e.g. differential scanning calorimetry (DSC) thermogravimetry (TG) alone or combined with FTIR spectroscopy) (121) are most commonly employed to evaluate bulk mechanical and thermal properties of latex films. Contact angle measurements and AFM are employed to investigate the surface characteristics. A review on the use of modern surface analysis methods in PSA development is given by Leiber et al. (122). AFM is increasingly used in the PSA industry for the examination of microparticle adhesion (123), surface roughness of individual latex particles (124), surface mapping, film formation (125, 126) and evaluation of adhesion and viscoelastic properties (127,128, 129). Hugel and Seitz (130) presented a more general review on the use of AFM for the investigation of molecular interactions, while Attard (131) concentrated on dynamic measurements and practical approaches to calibration and quantitative measurements of friction, adhesion and deformation. Paiva et al. (128) investigated the adhesive behaviour of tackified PSAs with AFM and concluded that a tackifier-enriched phase was responsible for adhesive performance PSAs because this domain showed a viscoelastic response. Mallegol et al.

(126) investigated emulsion-based acrylic PSAs by AFM and offered practical advice for AFM imaging of the soft and tacky surfaces. The authors recommended an increased free amplitude of tapping and the use of different tapping conditions and weaker cantilevers to avoid surface damage.

Comparisons of polymeric films obtained using different polymerization processes (e.g. solution and emulsion) or using different polymerization modes (e.g. batch or semi-batch) have also been reported. The Young's modulus of latex films were higher compared to those resulting from solution polymerization with the same composition while solution films showed better adhesion to a glass substrate.(48) As mentioned previously, differences in the reactivity ratios and water solubilities of monomers will influence the structure of the latex particles. In general, batch polymerization yields a heterogeneous particle structure, while a more uniform distribution is obtained when the semi-batch mode is employed. Thus, the films formed from these particles will be heterogeneous and homogenous in morphology, respectively, which can be confirmed using DMA. Aymonier et al. (132,133) investigated the influence of different feeding policies (e.g. commoner mixture, variable feed of individual monomers, or batch polymerization) on composition, particle morphology and tack of 2-EHA/MMA emulsion-based PSAs. They concluded that feeding the comonomer mixture ensured a homogeneous particle morphology that positively affected tack.

The mechanical properties of films prepared from latex mixtures (e.g. mixtures of homopolymers, different particles sizes, different particle morphologies, or latexes exhibiting particular properties such as high peel strength with those exhibiting high shear strength) are also of interest in the production of PSAs. Similar to copolymers obtained in batch emulsion polymerization, a mixture consisting of homopolymers will show two T_gs corresponding to each homopolymer. This serves as an indication that the physical properties of each homopolymer were not modified during the mixing and subsequent film formation.

2.4 PERFORMANCE CHARACTERISTICS OF EMULSION-BASED PSAs

2.4.1 Tack

Tack is defined as the property that enables an adhesive to form a bond of measurable strength with a surface of another material upon brief contact under light pressure (ASTM 2979-88) (134) or no pressure (PSTC-5) (135). Also called quick stick, quick adhesion, quick grab, initial adhesion, or wet tack, (1, 6) it is the most important property of an adhesive but the most difficult to measure (136). Tack is described in terms of indirect phenomena observed during the debonding process and thus, is not an intrinsic property.(6) Measured indirectly, it depends not only on the interfacial and bulk properties of the PSA and the properties of the carrier but also on the employed measurement method and conditions. Therefore, even though all methods are used to evaluate tack at low contact pressures and short contact times, the values obtained by different test methods should not be compared. This is due to the fundamental differences found among the tests or the subtle differences due to differing standard testing procedures.

2.4.1.1 Tack measurement methods

Four tack test methods are dominant in modern PSA technology: the rolling ball tack test (ASTM D 3121-94, PSTC-6), (137,138) the quick stick test (PSTC-5 (135); AFERA 4015), the loop tack test (TLMI LIB-1 and LIB-2; FINAT FTM-9) and the probe tack test (ASTM D2979-88) (134). Some variations of these methods such as the axisymmetric adhesion test (139) or the mechanical optical tack test (MOTT) (132,133, 140) are reported to have advantages over standard methods. Custom-made devices such as the one described in the work of Ben-Zion and Nussinovitch (141,142) are also common.

The rolling ball test was one of the earliest test methods used for tack measurements. A stainless steel ball of predefined dimensions is rolled down an inclined ramp on a strip of PSA. The distance that the ball travels before stopping is defined as

rolling ball tack. The shorter the distance, the higher the tack. Though widely used due to its simplicity, the test has a major disadvantage: the distance will depend not only on PSA properties but also on its anchorage to the carrier, the nature of the carrier surface, and the thickness of the adhesive layer.(1) On the other hand, Johnston (143) suggested that more care on the part of the experimenter would remedy this shortcoming. Another problem is associated with the fact that for some adhesives, the ball will not stop at the predefined length of the PSA strip.(6) Various authors have reported the reproducibility of the measurements to range from generally good (6) to very poor (144).

The loop tack and quick stick tests are essentially modified peel tests. In the loop tack test, a loop of PSP is formed with the PSA layer facing out and brought into contact with a substrate at a defined rate. The force required to immediately remove the loop with a defined speed is measured as loop tack. Different instruments can be used, such as an Instron Universal Tester (Instron, Massachusetts) or specially designed loop tack testers such as the LT-1000 (ChemInstruments, Ohio) and the LabMaster® Loop Tack Tester (Testing Machines Inc., New York). The observed loop tack value is also influenced by the flexibility or stiffness of the carrier. Reproducibility of this measurement is rated as good.(6)

For the quick stick test, a strip of PSA is placed on a flat stainless-steel plate test surface with no additional pressure (PSTC-5) or with the application of a light pressure (AFERA 4015). The strip is then peeled off at a defined rate at a 90^{o} angle. The measured peel force is recorded as the tack value. An Instron Universal Tester (Instron, Massachusetts) is used to perform this test. Residence times are relatively longer compared to other tack tests, but the resulting accuracy is high. It should be noted that the bigger the difference between the application conditions and the test conditions (i.e. one should simply lay down the tape and remove it immediately), the less useful the tests are.(6) Johnston (143) suggests that these two tests should be used only to compare PSPs with the same carrier flexibility. The reason is that the tape often applies itself to the surface with considerable pressure during the peeling process to a degree that depends on the flexibility of the backing.

For the probe tack test, the tip of a probe is brought into contact with a supported adhesive at a low pressure for a short time. The peak force of separation of the probe

from the adhesive is recorded as the probe tack. Compared to other tack tests, the influence of the mechanical characteristics of the carrier and adhesive thickness is reduced, although not completely eliminated. Reproducibility of this method is considered to be low.(144) Commercially available instruments usually referred to as Polyken tack testers include the LabMaster® Probe Tack Tester (Testing Machines Inc., New York) and the PT-500 Polyken™ Probe Tack Tester (ChemInstruments, Ohio).

Hammond (6) stated that, with substantial knowledge, each test can be interpreted in terms of the surface and bulk properties of the PSA interacting with those of a substrate. Benedek and Heymans (1) claimed that none of the tests alone is sufficient to characterize tack. Possibly due to the time and costs associated with using all of the methods, in most reported work only one or two method(s) are employed.

2.4.1.2 Factors affecting tack

Factors affecting tack (See Table 7) can be broadly divided into the following groups: chemical and physical characteristics of the adhesive, characteristics of the carrier, and measurement methods and conditions. One should recall that most factors are correlated and, in addition, affect not only tack but also the peel and shear strengths due to the interdependence of the PSA properties. These relationships are not necessarily synergistic.

Table 9 Some Factors Affecting Tack

FACTORS		TACK
CHEMICAL	"Soft" monomers	Increases
	"Hard" monomers	Decreases
	Polar monomers	Decreases
	Cross-linking agents	Decreases
	Tackifiers	Increases
	Stabilizers, buffers	Decreases
PHYSICAL	Adhesive layer thickness	Increases
	Carrier thickness/flexibility (loop tack)	Increases
	Dwelling time	Increases
	Temperature	Increases

As discussed earlier, the main component of a PSA is a soft monomer with a homopolymer of T_g below zero. The lower the T_g, the higher the tack at a wide range of testing temperatures. The inherently tacky nature of some acrylic homopolymers is directly connected to their low T_g values. Increases in the length of side chains up to a certain length will lower the T_g and thus, increase softness and tackiness. Although n-octyl acrylate has a lower T_g (-80°C), 2-ethylhexy acrylate (T_g = -70°C) and n-butyl acrylate (T_g = -54°C) are used most frequently. However, the cohesive strength of these homopolymers is not sufficient at typical application temperatures. Therefore, modifying monomers are added. These monomers will affect the peel and shear strength, increase the T_g of the copolymer and thus, lower the tack of the copolymer. Recent studies show that it is possible to incorporate a high T_g monomer to increase the shear strength with little or no influence on tack and peel strength.(117, 145) It should be taken into consideration that T_g depends on chain flexibility and that all factors affecting chain flexibility such as sequence length distribution, molecular weight distribution, and cross-linking density will also affect T_g. Benedek and Heymans (1) advised that the amount of hard monomer should be kept as low as possible in order to achieve a good balance of PSA properties. Aymonier et al. (133) studied the effect of MMA on tack in emulsion-based MMA/2-EHA copolymers over a wide range of compositions (0/100 to 100/0 wt.%) using a MOTT probe. The highest tack was observed for compositions of MMA/2-EHA 25/75 to 50/50, but residues on the probe indicated a low cohesive strength. Other compositions showed no tack. One limitation of this study was that the copolymers were obtained in batch polymerization mode resulting in heterogeneous copolymer compositions. This was due to the differences in the radical reactivity ratios and water solubilities of 2-EHA and MMA. Polymer particle morphologies obtained in the study ranged from MMA-to 2-EHA rich- shells. The influence of MMA on other PSA properties was not determined.

The addition of high T_g functional monomers such as AA, MAA or itaconic acid will also affect tack. A negative correlation between loop tack and MAA level was observed by Brooks et al. (80) for BA/VAc emulsion-based PSAs. Zosel (146) found that this was also valid for the addition of AA (5 wt.%) in 2-EHA/AA-based PSAs.

As discussed earlier, the presence and the nature of the stabilizers used in emulsion-based PSAs can influence tack. In general, a decrease in tack is observed with increasing stabilizer concentration. Unless covalently bonded to the particle surface, stabilizers have the tendency to migrate to the adhesive-air interface. This migration will influence the tackiness of the interfacial layer. On the other hand, Brooks et al. (80) reported that the influence of a proprietary stabilizer on tack of BA/VAc/MAA emulsion-based PSAs was low. Similarly, Lu et al. in US Pat. 6,048,611 (65) claimed that the use of a surfmer to obtain high solids content latexes resulted in high initial tack.

The lack of studies involving the investigation of the influence of particle and/or film morphology on PSA properties has been reported.(146) Zosel (146) has reported that a high tack level at low contact forces for emulsion-based poly (2-EHA), homopolymer decreased when AA was added (5 wt%). A difference in tack was observed when the same compositions were obtained by solution copolymerization. This was an indication that the particle structure and corresponding film morphology affected the tack. The two-phase structure of the emulsion-based copolymer exhibited higher stiffness and lower tack. As discussed earlier, particle structure is affected, among other factors, by the mode of polymerization. The effect of the polymerization mode on tack for the same overall MMA/2-EHA copolymer composition was investigated by Marcais et al. (140). The semi-batch mode led to a slightly lower tack compared to that in the batch mode.

The addition of tackifier, as expected, increases the loop tack and peel but decreases shear strength (92, 95). The effect of tackifier on T_g is similar to that of the addition of high T_g monomer. It increases T_g but, at the same time, will increase the molecular weight between entanglements, favourably influencing rheological properties. Benedek and Heymans (1) recommended the use of relatively low molecular weight base polymers and relatively high molecular weight tackifiers (when used) to achieve good tack. On the other hand, Satas (44) emphasized that low molecular weight polymers may exhibit high tack but their other properties are unacceptable (e.g. low shear holding power and cohesive peel) unless improved by cross-linking. He also demonstrated that an initial increase in tack with molecular weight will be followed by a decrease and levelling off. This is not surprising: at the short contact times that are employed in tack

experiments, tack is built up due to interdiffusion, which is inversely proportional to the second power of the molecular weight.

Another critical molecular weight parameter that influences viscoelastic behaviour and thus, PSA performance, is the molecular weight between entanglements, M_e. (95, 146,147) Zosel (148) showed that two polymers (polyisobutylene, PIB, and P(2-EHA) with almost identical properties (i.e. T_g, molecular weight), other than their M_e, exhibit different levels of tack. It was shown using DMA measurements, that higher tack levels were observed for the polymer with the lower storage modulus, G′, and thus, the higher M_e (M_e (PIB) = 8700 g/mol, M_e (P(2-EHA)) = 60000 g/mol). This is favourable to PSAs because a lower G′ plateau will ensure easy deformation, and thus, good contact with a substrate. Similarly, Tobing and Klein (95) showed that P(2-EHA) had a lower dynamic loss modulus, G″, and thus a higher M_e and higher tack compared to PBA. According to Zosel (148,147) the main effect of the entanglement length is on the phenomena called fibrillation or lamellation, which is essential for high tack. Fibrillation, also noticed in peel tests (149), is observed during the debonding stage where initial cavities on the interface grow and separate by thin fibrils (lamellas). Zosel (150) showed that polymers with M_e=1-1.5×10^4 g/mol exhibited fibrillation and good tack, while below this value they debonded homogeneously, showing lower tack. He connected this observation to the Dahlquist criterion: the shear modulus should not exceed 3×10^5 Pa in order to obtain good tack. This was calculated from the modulus suggested by Dahlquist, where M_e was about 1×10^4 g/mol and thus, the criterion could be connected to the transformation from a fibrillar to a homogeneous deformation.

Cross-linking will decrease tack due to a decrease in chain mobility, which is necessary for good tack.(1) As mentioned previously, the presence of cross-linking compounds is necessary for good shear holding power and peel strength. Thus, the addition of a cross-linking compound is not in question but the amount that will give a good balance between the three major PSA properties is. Satas (44) recommended a low cross-linking density because higher levels may yield a complete loss of tackiness. The overall picture for the formation of cross-linked latex films is not as simple as in the case of homogeneous film structures obtained from solution films. As described earlier, research efforts to investigate these network structures are ongoing. (109, 114-116)

As previously discussed, depending on the test method, the measured tack values may differ. Another factor affecting tack is the dwelling time or time of contact between the adhesive and the substrate (loop and quick stick tack) or the probe (probe tack). Temperature will affect the viscoelastic properties and subsequently, the tack. The thickness of the adhesive layer will influence flow conditions. An increase in thickness will increase the tack. Except for the probe tack method, the flexibility of the carrier is a factor in the determination of tack. A numerical analysis of loop tack tests performed by Plaut et. al (151) showed that the pull-off force increases with an increase in the stiffness of the backing and thickness of the adhesive layer.

2.4.1.3 Modeling tack

Brooks et al. (80) empirically modeled the tack of a BA/VAc/MAA based PSA with respect to emulsion polymerization variables (e.g. concentration of MAA, stabilizer, CTA, and buffer). They showed that the concentrations of MAA and buffer (NaOH) as well as the second order interactions between these factors were dominant in affecting loop tack.

Models of PSA performance as related to the viscoelastic properties have been under development since Dahlquist (152) defined a compressive creep compliance of 1×10^{-6}cm/dyne (at 1 sec at the application temperature) as a criterion for good wetting of the substrate by the PSA in short times. Usually, this criterion is interpreted in terms of oscillatory shear measurements as G' (1 rad/s) $< 3.3\times10^{5}$ Pa for good PSA performance. Recently, Christensen and Flint (153) raised the objection to this widely used interpretation of the original criterion. They stated that this criterion is rarely expressed in its original form: "the compressive creep compliance at the application temperature must be greater than 10^{-7} cm^2/dyne". Rather, it is transformed in terms of oscillatory shear data: "the complex shear modulus at 1 rad/s should not exceed 3.3×10^{5} Pa." This statement assumes that the ratio between extensional and complex shear viscosity is equal to 3, which might not be the case. Furthermore, Christensen and Flint (153) argue that the contribution from G'' is totally neglected, in most statements, which is reasonable if

$G' >> G''$. Further simplification of the original statement to $G' > 10^5$ Pa yields a different criteria compared to the original one proposed by Dahlquist.

Tse (154) suggested the following expression to relate adhesive performance (P) to the interfacial adhesion between the adhesive and the substrate (P_o), the term characterizing the bonding process (B) and rheological contributions (D), which represents energy dissipation in the adhesive during the debonding process:

$$P=P_oBD \quad (17)$$

Tse (154) determined that the contribution from P_o is small and constant (even when the concentration of tackifier is varied). The factor B is a function of bonding time and bonding pressure of the test and also on the plateau modulus of the PSA. It is also constant when the PSA fulfills the Dahlquist criterion. Thus, according to Tse, tack is proportional to the rheological properties according to

$$P=(\text{constant})D \quad (18)$$

The debonding frequency of the test is to be calculated using the following expression

$$\text{Test frequency} = 2\pi \text{ (Bond Rupture Speed)/(Bond Thickness) [rad/s]} \quad (19)$$

Using the bulk rheological properties, tack is then expressed as

$$\text{Tack}=(\text{constant})D= K_1 \log G''(\omega)+K_2 \quad (20)$$

where ω is the debonding frequency as calculated using Eq. (19), K_1 and K_2 are constants in lb_f/in and are highly correlated with values of 1.95 and –6.25, respectively, for a loop tack test. Tse (154) also presented some PSA design pathways using the proposed model.

2.4.2 Peel Strength

Resistance to peel is measured as the force required to peel away a strip of PSA coated material of standard dimensions from a standard surface at a constant pre-defined peel rate and angle. It is also called peel strength even in standard procedures (e.g. PSTC-

1), but some argue that the use of the term "adhesion" denotes a state in which two surfaces are held together rather than the force required to separate them.(155) Although adhesion terminology is addressed by an ASTM standard, ASTM D 907-94,(5) and is emphasized in textbooks,(3) misinterpretations such as this one are common (156).

In the determination of peel strength, not only is the value of the peel force of interest but also the mode of failure. Usually, what is desired is an adhesive failure (i.e. PSP is removed from the substrate with no macroscopic residues). A cohesive failure (i.e. residues are observed on the substrate), an unstable mode (a.k.a. "stick-slip" mode where the adhesive remains on the substrate but the peeling force shows oscillations of a small period and large amplitude) or an adhesive transfer (i.e. transfer of the adhesive from carrier to the test panel) are not desired. Satas (155) emphasized that peel, as just one specific type of failure, may not be related to other types of failure that can occur under performance conditions. Thus, peel strength and adhesive bond strength are not synonymous.

2.4.2.1 Peel strength measurement methods

The basic difference between the different peel tests suggested by different standards organizations (ASTM) or trade organizations (PSTC, TLMI, AFERA, FINAT) is in the peel angle. Two angles commonly employed are 180° (ASTM D3300 (157), PSTC-101 (158), FTM-1, AFERA 4001) and 90° (ASTM D6252 (159), PSTC-101 Method F (160), PSTC-14 (161)). The 90° angle peel test was suggested for PSPs with thick, rigid, brittle and easily torn carriers (162). Other differences among the above mentioned tests include: peeling rates (from static tests up to 300 mm/min), dwell time (0-24h), preparation of the substrate surface and sample, and the units in which the observed values should be reported. Peel tests are summarized by Muny (162). The values obtained using a peel test are strongly influenced by the physical characteristics of the carrier as well as the thickness of the carrier and the adhesive layer.(1, 163) The instruments that can be employed for peel strength measurements are an Instron Universal Tester (Instron, Massachusetts) or specialized instruments such as the AR-1500 Adhesion/Release Tester (ChemInstuments, Ohio), the LabMaster® Release and

Adhesion Tester (Testing Machines Inc., New York) or the SP 2000 Slip/Peel Tester (Imass, Massachusetts). The reproducibility for all of these tests is good.(155)

2.4.2.2 Factors affecting peel strength

Even though most of the factors affecting tack also influence peel strength, their influence is not necessarily in the same direction. Thus, the optimal value of a variable determined for tack is not necessarily optimal for peel. Shear holding power must also be considered. In Table 8 some of the factors affecting peel strength are outlined.

Incorporation of high T_g components will improve peel strength up to the point where the adhesive becomes too stiff and does not wet the surface and thus, decreases the peel strength.(1) Introduction of polar carboxylic acid groups increases the peel strength and the affinity towards polar surfaces as found in most commercial plastics (1) due to the changed interfacial rather than bulk properties of the adhesive (155). AA was stated as the most effective monomer to affect peel strength as well as the most commonly used (27, 155) but MAA has also been used (80,155, 163).

Table 10 Some Factors Affecting Peel Strength

FACTORS		PEEL STRENGTH
CHEMICAL	"Soft" monomers	Decrease
	"Hard" monomers	Shows maximum
	Polar monomers	Shows maximum
	Cross-linking agents	Shows maximum
	Tackifier	Shows maximum
	Stabilizers	Shows minimum/maximum
	Peel modifiers	Increases
PHYSICAL	Adhesive layer thickness	Increases
	Carrier thickness/flexibility	Shows maximum
	Dwelling time	Increases

Charmeau et al. (49) showed that the peel strength of the latex films of four different particle structures was always lower compared to the corresponding films cast

from solution polymers. This was due to the lower molecular movement and energy dissipation in the latex films, where a soft phase was embedded into a more rigid network. The influence of core-shell particle structures (soft-soft and hard-soft) on peel was investigated by Garrett et al. (164). They speculated that the peel strength of a soft core (PBA)-soft shell structure (PBA/AA) is controlled by the vol% of the shell rather than the total amount of AA. From the observed failure modes, it has also been suggested that the amount of PBA/AA reduces the peel strength of the bond to stainless steel and increases the peel strength in the bond to the carrier (Melinex) due to an increase in adhesive stiffness. This is consistent with the generally accepted belief that the introduction of carboxylic acid groups in low concentrations will improve peel strength.(155) On the other hand, all peel strength measurements becomes virtually zero when the particle cores are about 60% of the hard-soft particle structure due to the increased adhesive stiffness. This is testament to the complexity of the emulsion-based PSAs but also demonstrates the high potential for tailoring the desired properties.

Peel strength will exhibit a maximum or minimum vs. stabilizer concentration depending on the nature of the stabilizer.(47-52) At low peel rates stabilizer-free poly (ethylhexyl methacrylate), PEHMA, exhibits the same cohesive strength but higher adhesive strength compared to PEHMA polymerized in the presence of stabilizer.(47) This is an indication of the influence of the stabilizer on the interface rather than the bulk properties of the adhesive, although the stiffness of the adhesive must also be considered. Charmeau et al. (51) concluded that the stabilizer is concentrated at the film-substrate interface. It has been suggested that the increase of peel strength with concentration of stabilizer corresponds to the formation of a monolayer of stabilizer while a decrease in peel strength corresponds to the formation of a much thicker layer that will behave as a weak boundary layer. For the same stabilizer concentration, different layer thicknesses were observed for different stabilizers.

Peel strength exhibits a maximum where the average polymer molecular weight is concerned.(1, 155, 163) The transition from cohesive to adhesive failure in a peel test is observed in the region of maximum peel force vs. molecular weight.(155) Although tack and peel show a similar dependence of peel force on molecular weight, the position of the

maximums is different. The presence of low molecular weight chains and a broader molecular weight distribution will increase peel and tack, but may simultaneously negatively affect the shear strength.

Although CTA is usually employed to control molecular weight development some have found a small correlation between CTA level and peel strength. (80) Because the actual levels were not reported it is hard to comment on this observation but one possibility is that the selected levels were in a very close range and thus, any direct influence was not detected. On the other hand, Urban and Egan (28) described a high influence of the CTA on the peel strength of an acrylic dispersion. At a level of 0.2 phm of CTA, peel strength of the PSA investigated almost diminished. As discussed earlier, Plessis et al. (85) made similar observations.

In general, a low cross-link density is recommended for peel strength improvement.(155, 163) Zosel (146) emphasized that a very loose and imperfect network structure and a high percentage of uncross-linked material with a broad molecular weight distribution and a high degree of long chain branching, as found in acrylic emulsion polymers, gives a good balance between peel strength and tack. On the other hand, these morphologies are not easy to characterize. High cross-link densities will have the opposite effect: they tend to reduce peel strength. (1) This was illustrated by Plessis et al. (85) where an increase in gel content above 36 wt.% and the weight average molecular weight of the sol led to a decrease in peel strength of BA/AA emulsion-based PSAs. Tobing and Klein (117) reported a minimal influence of IBMA (a cross-linkable compound added in an amount $\leq$ 1 wt%) on peel strength of BA/AA or 2-EHA/AA emulsion-based PSAs.

Adhesive thickness is one of the factors influencing peel strength. Peel strength is an exponential function of adhesive thickness.(1, 153) Apart from thickness, the coating method will also have an influence on peel strength. Direct coating, due to better anchoring of the adhesive to the carrier, shows better peel strength compared to indirect coating methods.(1)

Characteristics of the carrier material (e.g. thickness and moduli) will also affect peel strength in a complex and not easily predictable manner, especially when tests are performed at a 180° angle (155). Satas (155) and Benedek and Heymans (1) emphasized

that the thickness influences the energy required to deform the backing and the moment arm, which in turn, are acting in opposite ways on the peel force. The increased thickness increases both factors. As a consequence, the peel force vs. carrier thickness will show a maximum at a certain thickness value. Peel strength is a direct function of the carrier moduli but an indirect function of the adhesive moduli.(1)

Sample preparation (e.g. drying time, pressure, temperature, humidity) can affect the peel strength. Dwell time is the time elapsed from application of the PSA to the substrate to the time of testing. It allows bond formation and it varies for different peel tests. Benedek and Heymans (1) showed that an increase in dwell time from 0-24h will almost double the observed peel strength of acrylic water-based PSAs. Temperature will influence peel force due to its influence on rheological properties of adhesives. The type of substrate will also influence the peel force. Lower forces are observed for polyester films compared to stainless steel and glass.(1) Some factors characteristic for a specific PSP can also affect peel (e.g. label laminate construction).

2.4.2.3 Modeling of peel strength

Modeling of peel strength has received more attention than that of tack or shear strength. On the other hand, most of the models are based on the viscoelastic properties of the PSA. Peel strength has been modeled using emulsion polymerization parameters such as the concentration of MAA, the concentration of stabilizer, CTA, and buffer.(80) Unfortunately, most of the results from a 180° peel test did not correlate well with these variables due to the inconsistency of the failure mode. The results observed for 90° peel, showed that the level of MAA, buffer and CTA were significant factors affecting the peel strength. In addition, second order interactions between the concentrations of MAA and CTA were significant.

Bulk rheological parameters (e.g moduli, complex viscosity, tan delta) of the PSA and its surface properties are identified as key parameters in PSA peel performance. Not only does the peel strength exhibit a similar peel rate and temperature dependence as the viscoelastic moduli (i.e. peel master curves can be obtained from time-temperature superposition in a way similar to the one employed for the generation of a modulus

master curve (165-167) but also different failure modes can be correlated to the different zones in a relaxation spectra. Gilbert et al. (168) showed that the cohesive mode of failure is related to the terminal zone of the relaxation spectra (lowest frequencies), the adhesive mode to the rubbery zone, while the stick slip and adhesive transfer modes are related to the glass transition zone and glassy behaviour at high frequencies, respectively.

While there is no doubt that the relationship between viscoelastic properties and peel strength exists, different approaches have been proposed in the past to describe it. There are three major points of concern when modeling peel strength based on viscoelastic data. Firstly, caution is recommended when DMA as a technique that involves low deformation rates is used for the modeling of the peel strength. The peel tests involving high deformation rates and DMA measurements obtained at high frequencies should be connected to the debonding (169, 170). Secondly, there is a question about which rheological parameters should be used for modeling of debonding: the shear storage modulus (G'), shear loss modulus (G''), both of them, or tan δ (phase angle). Usually, the answer depends on the assumed type of deformation taking place during the peel test. If the viscous contribution is considered dominant for the peel force, then G'' should be used. Due to the fact that G' is often higher than G'' over a broad range of frequencies (PSAs are rubbery materials), in most cases the contribution of G'' is ignored even when both moduli are used for modeling, which is not necessarily a good assumption.(153) In addition, one may ask whether peel strength is to be related to a discrete particular frequency, to a set of frequencies (154, 170) or to a spectrum of frequencies (153). All approaches are used, even though the selection of a discrete frequency in some studies has been criticized as completely arbitrary (171) or has been proven to neglect contributions from low frequencies that are significant during the peel test (153).

The Tse rheological model (154) (Eq. (17)) separated the bonding and debonding step in PSA adhesion and identified the connection between the plateau modulus, and bonding and high energy dissipation and debonding. Tse also determined the frequency of 435 (rad/s) as the test frequency to be related to the debonding step of the peel test using Eq. (19). Christensen and McKinley (172) found that the relationship between peel rate and test frequency was much stronger than the linear one proposed in Eq. (17). They

also found that the frequencies calculated using Eq. (18) were too high over the full range of peel rates. The explanation was that Eq. (18) does not take into the account the elastic contributions from the large time constants which cannot be neglected for the PSA studied in their work.

Yung (173) investigated the influence of the surface and bulk rheological characteristics of 13 different emulsion-based PSAs on peel strength. When the variation of the surface energy was small, the peel strength for all PSAs was proportional to the ratio of the shear loss at the debonding frequency to the shear storage modulus at the bonding frequency. He used the Tse model for the determination of the debonding frequency (435 rad/s) and stated that bonding was related to a frequency of 1 rad/s.

Chu (174) proposed that the PSA quality can be determined by the position of the value of G′ at two frequencies 0.1 and 100 rad/s (at 25 °C) vs. adhesive T_g determined as the peak position of tan δ. The values of G′ at 0.1 rad/s was related to bonding while that at 100 rad/s to debonding. For good PSA properties, lower G′ values at low frequencies favour bonding while higher values of G′ at higher frequencies indicate a higher resistance to debonding.

Similar to that by Chu (174), the model proposed by Chang (170) also suggested two frequencies of interests (0.01 and 100 rad/s) but, as opposed to Chu (174), the rheological master curves of both moduli (G′ and G″) were to be employed for the establishment of so-called "viscoelastic windows" (See Figure 3). Each window had the following coordinates (clockwise from the bottom left corner): G′ (0.01 rad/s), G″ (0.01 rad/s); G′ (100 rad/s), G″ (0.01 rad/s); G′ (100 rad/s), G″ (100 rad/s) and G′ (0.01 rad/s), G″ (100 rad/s). A plot of G′ vs. G″ was divided into four quadrants and a central region, each of which related to non-PSA, high shear PSA, removable PSA, cold-temperature PSA or general purpose PSA, respectively. From the position of the viscoelastic window of the tested PSA in a G′ vs. G″ plot, one can determine not only if the tested material is a good PSA, but also for which application it is most suitable. Peel strength is related to the bonding efficiency (values of G′ at 0.01 rad/s) and debonding strength (values of G′ and G″ at 100 rad/s). Thus, if the base of the window is lower, bonding is favoured and the higher the position of the top right corner, the higher will be the debonding strength (Figure 4.)

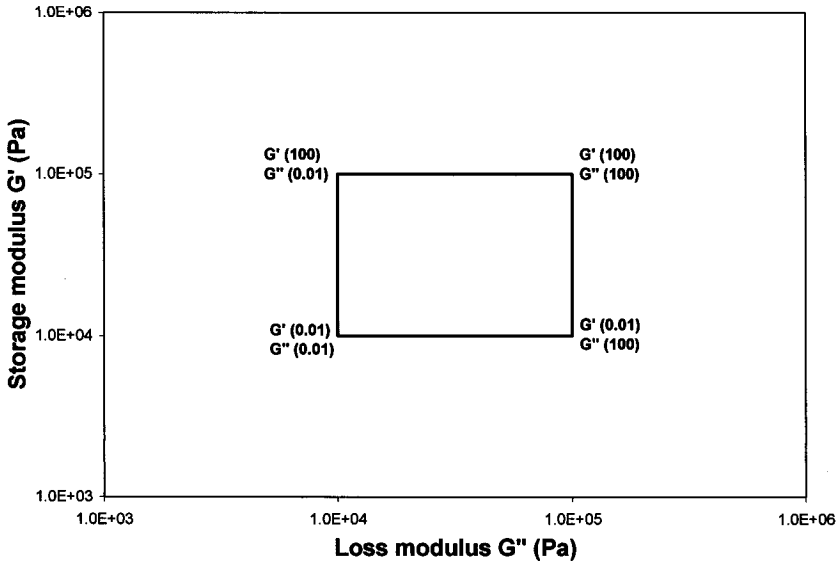


Figure 3 Viscoelastic Window Concept by Chang (170)

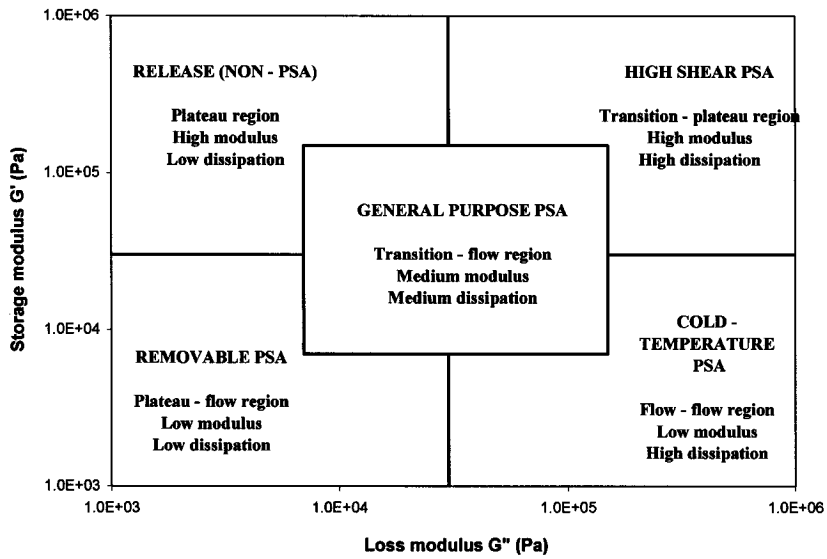


Figure 4 Generalized Concept of Viscoelastic Windows (170)

Modeling peel using mechanical properties such as tensile strength in an attempt to isolate the bulk properties of the adhesive itself has received much attention in the past. Most accepted is Kaeble's model (152, 155) in which the 180° peel strength is directly proportional to the width of the tape, adhesive thickness, squared value of the boundary stress and indirectly proportional to the tensile modulus of the adhesive. Dale et al. (175)

related the peel strength to results obtained by DMA and tensile strength measurements for a series of acrylic solution- and emulsion-based PSAs. The correlation between the peel strength and G′ (at 127°C) was lower for both observed modes of failure (adhesive and cohesive) of the emulsion-based PSA compared to the correlation between peel strength and tensile strength.

Uniaxial extension of a PSA during a peel test and its correlation to different viscoelastic parameters has received considerable attention.(153, 166, 167, 172) Yarusso (167) employed a generalized Maxwell model to describe the rheological behaviour of natural rubber based PSAs and used the response of the proposed model to the uniaxial extension to predict the peel force vs. peel rate behaviour of the PSA. Good predictions for the high rate region of the adhesive mode of failure, but poor ones for the cohesive mode and low rate region were obtained. Christensen et al. (153, 172) obtained nearly quantitative predictions of peel force using a non-linear model that incorporates strain hardening of a PSA during the peel test. Transient extensional viscosity was used to characterize strain hardening. Under low strains, transient extensional viscosity can be successfully predicted using DMA measurements, but it must be independently measured at high strains. Extensional viscosity of cross-linked and uncross-linked acrylic PSAs was also studied by Verdier et al.(166) Strain hardening was observed earlier in cross-linked acrylic PSAs which showed higher peel strengths compared to uncross-linked PSAs.

2.4.3 Shear Strength

PSAs are soft polymers prone to creep, the increase in strain with time after stress is applied and maintained constant. Although shear deformation under constant shearing stress or compressive strain under constant compressive stress or tensile strain under constant tensile stress can be measured, for PSA technology, shear deformation under constant shear stress is usually of interest. Shear resistance, also called shear holding power, is an indicator of the adhesive resistance to shearing forces. It is also referred to as the PSA's cohesive strength or simply cohesion.

2.4.3.1 Shear strength test methods

Similar to tack and peel, the determination of the shear holding power is also governed by standards: ASTM D3654 (176), PSTC-107 (177), FINAT FTM 8, AFERA 4012, TMLI LIC. The standard method to determine shear resistance is to measure the time required to pull a defined area of a PSA from a test panel under a constant load. As in other cases, different loads, areas and residence times are recommended by different standards, thus, caution is recommended when comparing reported values. In any static shear test it is important that the adhesive fails cohesively (i.e. leaves residue on both surfaces) so that it is certain that the internal strength of the adhesive is measured.(162) All standard tests are static tests, but shear resistance can also be determined using a faster, dynamic test where the force required to separate the joint is measured as shear resistance.

PSAs as thermoplastic materials are affected by temperature. Thus, an unofficial shear resistance test is in wide use.(162) It is called the shear strength failure temperature (SAFT) test and is used to assess the cohesive strength of a PSA for applications where the PSA will be subjected to heat. In the test, the same standard procedure is applied, but the samples are placed in a chamber and the temperature is increased at a pre-defined rate. (162)

2.4.3.2 Factors affecting shear strength

Shear resistance increases as the concentration of the high T_g component increases.(1) Introduction of polar groups at a level of 0.1-10 % (1) can significantly increase shear resistance, but the resulting enhanced chain interactions will increase the T_g and, in a poorly balanced PSA, result in insufficient tack at room temperature as well as unacceptable "stick-slip" and peel.(178) The presence of highly mobile small molecules (e.g. stabilizers, additives) will decrease the shear resistance. Some of the factors affecting shear strength are summarized in Table 9.

Table 11 Some Factors Affecting Shear Strength

FACTORS		SHEAR STRENGTH
CHEMICAL	"Soft" monomers	Decreases
	"Hard" monomers	Increases
	Polar monomers	Increases
	Cross-linking agents	Increases
	Tackifier	Decreases
	Stabilizers	Decreases
	Peel modifiers	Decreases
PHYSICAL	Adhesive layer thickness	Decreases
	Temperature	Decreases

Shear resistance increases with increasing molecular weight (44, 178). As the long linear molecules become entangled and the number of entanglements increases, the shear strength of the PSA increases.(178) The ratio M_w/M_e is also of interest. Tobing and Klein (95) showed that, regardless of the polymerization method used, PBA/AA copolymer showed higher shear strengths compared to P(2-EHA)/AA due to the higher M_w/M_e ratio. A broad molecular weight distribution will result in a lower shear resistance compared to a narrow one.(1) Most common acrylic PSAs have broad molecular weight distributions. The influence of particle and film morphology on shear resistance has been studied by Garrett et al. (164). They showed that the shear resistance of a soft core (PBA)-soft shell structure (PBA/AA) increased with an increase in the vol% of the shell. For the rigid core (PMMA)/allyl methacrylate)-soft shell (PBA/AA) the opposite effect was observed, i.e. shear resistance increased with an increased vol% of PBA/AA. Urban and Egan (28) demonstrated that the addition of AA as low as 2 phm will increase shear strength from less than 100 minutes to more than 1400 minutes.

Because cross-linking decreases the free movement of polymer chains, an increased cross-link density will positively affect the shear strength.(178) Regardless of the polymerization method, the increased gel content in acrylic PSAs will increase the shear strength.(95) As described previously, Plessis et al. (85) came to the same conclusion for emulsion-based PSAs. On the other hand, even PSAs with a high gel content due to network imperfections will show some non-recoverable creep.(178) Due to

its profound effect on tack and peel, the concentration of functional monomers that enable cross-linking should ensure a favourable, low cross-link density.(1)

An exponential decay in shear strength was observed when different substrates were compared. The highest shear strength was observed on a glass substrate (1h) and the lowest on PVC (0.2h). The carrier can also influence the shear strength. A lower shear strength was observed on paper compared to polar films. In addition, shear strength is improved when surface treated films are used.(1) The flexibility of the carrier is less important for the shear strength compared to the peel test, but dimensionally-stable carriers are preferred (e.g. PET). The time to failure of a sample is inversely proportional to the thickness of the adhesive layer.(178)

2.4.3.3 Modeling shear strength

Shear testing can be seen as a simple flow of material between parallel plates. Dahlquist (152) recognized that the time to failure in a shear test was proportional to the viscosity of the adhesive, among other factors. The complexity of the shear strength model will depend on the nature of the adhesive. When viscosity is independent of shear rate, the following model is suggested for time to failure, T:

$$T = \frac{H_o^2 w \eta}{2dMg} \tag{21}$$

where H_0 is the overlap in cm, d is the adhesive thickness, M is the load in g, η is the viscosity of PSA in poises, w the width in cm and g the gravitational constant. The model will lead to serious overestimation if applied to non-Newtonian fluids and thus, a more complex model was suggested for these PSAs.(152)

The relationship of shear resistance, i.e. holding time, to the rheological properties suffers from the same concerns as peel strength to the same properties. Different holding times are results of different time scales and deformation rates. Thus, Zosel (171) argued that a fixed frequency should be used to model different shear holding times. Rather, long holding times are related to the viscoelastic quantities at a low frequency and shorter holding times to the same quantities at a higher frequency. The test frequency is inversely proportional to the shear holding power (T) and adhesive thickness but directly

proportional to the length of overlap. Zosel (171) established an empirical model between the absolute value of the complex dynamic modulus, G*, (measured at the angular frequency equal to the shear test frequency) rather than its individual components, G′ and G″, with the shear holding time obtained in static and dynamic shear tests for a selected number of PSAs. Among these was an emulsion-based PBA. He stated that one of the problems with modeling the shear strength using rheological data is modeling of high viscosity PSAs or slightly cross-linked PSAs. This was motivation for the work of Vaynberg et al.(179) They successfully modeled the shear strength of a high viscosity emulsion-based PSA using the steady shear viscosity as opposed to the dynamic shear modulus as employed by Zosel.(171)

In terms of the proposed viscoelastic window concept (169, 170, 173, 174, 180), the higher the base of the window, which indicates the values of the plateau modulus, the better the shear, given that the Dahlquist criterion is satisfied (interpreted here as $G'=3\times10^4$ Pa). For the same position of the base of the window, the wider the base, the better the shear. The wider base indicates the higher degree of entanglement or higher cross-link density.(170) Given the same position and width, the shorter the window, the better the shear prediction.

Prediction of the shear holding power related to the factors affecting emulsion polymerization are rare. Brooks et al. (80) determined that MAA was a main factor affecting shear holding power of BA/VAc emulsion-based PSAs.

2.5 CONCLUSIONS

The main objective of this review was to highlight the recent advance in emulsion-based PSA technology. Emulsion polymerization as a technology for PSA production offers better environmental compliance compared to solvent technology and better energy efficiency compared to hot melt technology.

It is shown that the selection of components in the emulsion polymerization is of utmost importance for tailor-made PSA properties. The most general monomer selection would include monomer(s) with low T_g homopolymers (e.g. 2-EHA, BA…) and addition

of a high T_g monomers (e.g. styrene, MMA, VAc) for improved peel strength. Addition of multifunctional monomer(s) will increase shear strength and usually reduce tackiness of the final product. The selection of a stabilizer will govern not only the polymerization kinetics, but also the film formation and subsequent dry film properties. Negative consequences of stabilizer migration are increasingly solved with the use of reactive stabilizers. The selection of the stabilizer can also affect the rheological properties of the latex, which are important during the coating process. A variety of additives (e.g. tackifiers, peel modifiers, wetting agents, rheology modifiers) can be added for fine tuning of the final PSA properties. The selection and amount of a particular additive is governed by the desired properties of the final product.

Apart from the emulsion polymerization process itself, film formation is another important factor determining PSA properties. Considerable attention in this review was devoted to the investigation and modeling of film formation. Recent developments in microsopic techniques in general, and in particular, the development of AFM are offering new insights into the film formation process and adhesion process at the nano scale.

Factors affecting three major performance characteristics (e.g. tack, peel and shear strength) of a PSA were also reviewed. The influence of monomer selection, molecular weight, cross-linking, and other factors were outlined. In addition, recent advances in the modeling of these properties were presented.

The future will belong to health and environmentally benign, high performance adhesives that are multi-functional. That is, PSAs that do not simply adhere, but provide an additional functionality such as embedded colour coding, thermal conductivity, fire resistance, security, vibration absorption etc.(181) The biggest challenge is the development of intelligent adhesives, those capable of modifying themselves to bond to any substrate, while offering all the performance required. It is not hard to imagine that disperse systems can offer certain advantages in this quest for smart adhesives such as the encapsulation of magnetic materials, pigments, fire retardants and other materials into the particles. These advancements, combined with the advantages of dispersion polymerization, are powerful driving forces toward the development of tailor-made PSAs

that will have a low health and environmental impact and offer excellent and one day perhaps intelligent performance.

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Chapter 3

Jovanović R., Dubé M.A.
Screening Experiments for Butyl Acrylate/Vinyl Acetate Pressure-Sensitive Adhesives
(to be submitted)

the gel content of the emulsion latexes and the molecular weight of the soluble polymer fraction, as well as the monomer feed composition, were suspected to be among the most influential factors affecting the final PSA performance. In addition, it was possible to obtain balanced final properties using either sodium dodecyl sulphate or poly(vinyl alcohol) as surfactant but at different concentrations.

Key words: Pressure-sensitive adhesives, emulsion polymerization, modeling.

3.2 INTRODUCTION

Emulsion polymerization is used to obtain a variety of products such as paints, adhesives, polymers for transdermal drug delivery, etc. Among these products are pressure-sensitive adhesives (PSAs). These adhesives are viscoelastic materials that bond upon application of light pressure.(1) They are commonly part of tapes, labels, medical and cosmetic products.(2) It is estimated that 40% of PSAs are produced using emulsion polymerization.(3) This increase in the use of emulsion-based PSAs is due to the higher environmental compliance of emulsion-based processes as well as other advantages.(4) However, the performance of emulsion-based PSAs has been up to now considered less favourable compared to solution-based PSAs. The performance of PSAs is judged mainly on three major properties: peel and shear strength and tack of the final product.

Acrylic-based PSAs are commonly used due to their inherent tack, optical clarity, good resistance toward oxidation, UV radiation and relatively low cost.(1) However, due to the lack of a fine balance between tack, peel and shear strength, acrylic PSAs are usually obtained by polymerization of several monomers; terpolymers and higher are the most common. The base monomer is typically an acrylic, low T_g homopolymer (e.g. 2-ethylhexyl acrylate or butyl acrylate). The addition of a high T_g component (e.g. styrene, methyl methacrylate, vinyl acetate...) serves to improve peel and shear strength. The addition of multifunctional monomers (e.g. acrylic, methacrylic and itaconic acids) is also common. Other components can also be added, such as a variety of tackifiers, peel modifiers, cross-linking and wetting agents etc. (4)

While the majority of the patent literature mentions BA and VAc as possible components of PSAs, studies reporting the actual performance of such PSAs are rare. Brooks et al. investigated different factors affecting the performance of BA/VAc/methacrylic acid-based PSAs.(5) They reported a strong influence of methacrylic acid and the buffer (NaOH) on the final PSA properties. The major part of the study was devoted to the properties of PSAs obtained by blending different BA and VAc latexes.

Relationships between peel strength and composition of random BA/VAc solution-based copolymers were also reported by Chalykh et al. where various substrates were used to assess the strength of the joint in T-peel tests.(6) They observed an increase in T-peel strength of the adhesive joint when the BA content was increased.

The influence of molecular parameters on the performance of butyl acrylate/acrylic acid (BA/AA) emulsion- and solution-based copolymers was investigated by Tobing and Klein.(7) They concluded that solvent-based PSAs tend to outperform emulsion-based ones due to the presence of the continuous network formed after the evaporation of the solvent. On the other hand, the emulsion-based PSAs exhibited discrete microgels that were connected by entanglements. Regardless of the polymerization procedure used, the PSAs showed an increase in shear holding power as the gel content increased.

In this study, a range of BA/VAc polymers were synthesized in order to screen the system for application as a PSA. The influence of eight polymerization variables (i.e. BA/VAc ratio, weight fraction of AA, type and weight fraction of stabilizer, weight fraction of initiator and CTA, polymerization temperature and solids content) on final product properties of BA/VAc emulsion-based polymers was investigated. A resolution IV experimental design 2_{IV}^{8-4} with four center point replicates was used in order to obtain the information in a reasonable number of runs (16 + 4 = 20). The principal goal of the study was to develop empirical models for the determination of the most influential variables that will be used in further studies. The performance (i.e. peel and shear strength, tack) of the obtained polymers was tested on two different substrates, stainless steel and high density polyethylene (HDPE), as well as at two different thicknesses (30 and 70 μm).

3.2 EXPERIMENTAL PROCEDURES

Inhibitor was removed from the monomers used in this study using standard procedures.(9) Other reaction components were used without further purification: sodium dodoecyl sulphate (BHD), polyvinyl alcohol (Cevol), potassium persulphate (Aldrich), sodium bicarbonate (BHD), dodecanethiol (Aldrich) as well as the solvents (e.g. methanol (ACP Chemicals), tetrahydrofuran (THF, EM Science)) used for characterization.

All polymerizations were performed in an automatic reaction system LabMAX (Mettler-Toledo). The 1.2 L stainless steel reactor was equipped with a condenser, and feeding and sampling ports. Throughout the reaction, feed addition, reaction temperature and pH were continuously monitored. All VAc monomer and appropriate amounts of BA and AA along with other ingredients (stabilizer, water, part of the buffer and CTA) were charged to the reactor prior to the injection of initiator. The monomer feed consisting of the remaining BA/AA and CTA mixture was fed to the reactor simultaneously with the injection of initiator. The remaining buffer solution was used for pH control. Variable feed rates were used starting with high (3 g/min) to low (0.1 g/min) values. There was no feed during the last two hours of the reaction. Samples were periodically taken from the reactor for characterization.

Standard procedures were used for gravimetric analyses. Samples were left to evaporate until a constant weight was reached first at room conditions and later under strong vacuum at ~ 30°C. Gravimetry was based on the total mass of dry polymer.

Polymer compositions were calculated based on the residual monomer determined using gas chromatography. A gas chromatograph (Hewlett Packard 5710A) equipped with a flame-ionization detector (FID) and a glass column OW 351 (Chromatographic Specialists) was used. Injector and detector temperatures were 200 and 250°C, respectively, while the column temperature was programmed as follows: An isothermal step at 80°C for 4 min was followed by heating to 180°C with a heating rate of 8°C/min The final step was isothermal at 180°C for 20 min. Helium (35 mL/min) was the carrier

gas while air (300 mL/min) and hydrogen (30m/min) were supplied to the FID. Styrene was used as an internal standard. The injection volume was 1 μL.

Particle size distribution was determined using a BI-DCP (Brookhaven Instruments) disc centrifuge photosedimentometer. A mixture of water and methanol was used to prepare the gradient fluid. A narrow polystyrene standard was used to check the accuracy of the system prior to the determination of the particle size. Approximately 3 drops of latex were diluted in 3 mL of distilled de-ionized water and injected into the spinning disc (~10000 RPM). BI-DCP List software was used to calculate particle size distributions. Polymer densities used for calculations were weighted averages of homopolymer densities: d(pBA) = 1.026, d(pVAc) = 1.16, and d(AA) = 1.18.(8)

Gel content was determined using the membrane partitioning method.(7) A known amount of sample was heat sealed between two polytetrafluoroethylene membranes (pore size 2 μm, 47 mm diameter). Enclosed samples were shaken 72 hours in THF. Sealed pouches were then removed and air-dried until a constant weight was achieved. The gel content was determined based on the weight difference between the initial and final weight of the sample. Due to the presence of PVOH in some of the samples, the pouches were then further immersed in water and shaken for an additional 72 h to determine the water-soluble fraction. This was because PVOH is known to produce partially water-soluble polymers (18).

The cumulative number- and weight-average molecular weight distributions of THF-soluble polymers and THF-soluble fractions from the gel content determination were determined using a Waters Associates gel permeation chromatograph equipped with a Waters Model 410 refractive index detector. Three Waters Ultrastyragel packed columns (10^3, 10^4 and 10^6 Å) were installed in series. THF was filtered and used as the eluent at a flow rate of 0.3 mL/min at 38°C. Calibration of the instrument was performed with 10 polystyrene standards (SHODEX, Japan). All standards and samples were filtered prior to injection through 0.45μm filters to remove high molecular weight gel, if present. Millennium 32™ software (Waters) was used for data acquisition and manipulation. The Mark-Houwink, K and α, parameters used for the determination of the absolute cumulative number- and weight average molecular weights were previously reported. (9)

Meyer rods #30, 50, and 90 were used to cast latex onto 50 μm non-treated polyethylene terephthalate carriers (Mylar®, DuPont) to obtain dry film thicknesses of 30 and 70 μm. The films were conditioned for 24 h prior to testing at 23 ± 2°C and 50 ± 2% relative humidity prior to testing. Two films were cast per latex. Three specimens from each film were used for each adhesive test. A hierarchical design was used to test run-to-run and film-to-film differences. The analyses of the results have shown no film-to-film differences, therefore the average of six measurements was used in the analysis of the results.

All adhesive tests were performed according to standard test methods for PSAs.(10) PSTC-101, PSTC-16, and PSTC-107 were used for the determination of peel strength, loop tack and shear strength, respectively. A hand roller was used in all sample preparation. For PSTC-107, a 500 g load and a 2.5 cm × 2.5 cm test area were used with two substrates: stainless steel and HDPE. An Instron 1100 universal tester (Instron, Inc) was used to perform peel and loop tack tests.

Glass transition temperatures (T_g) of the final polymers were determined using a Seiko DSC 220C (Japan) differential scanning calorimeter. An empty, crimped aluminium pan was used as a reference. Approximately 10 μg was placed into a pre-weighed aluminum pan and heated to 120°C to eliminate any thermal history. The next step involved cooling the sample from 120 to -80°C followed by a 2 min isothermal step. The second heating from -80 to 120°C was used for the determination of the T_g. All heating and cooling steps were performed at a rate of 10°C/min. An empty aluminum pan was used as reference and for determination of the baseline that was subtracted from the samples.

3.4 RESULTS AND DISCUSSION

Experimental Design. The work reported herein is part of a larger study on structure-property relationships of PSAs. The intention was to investigate a number of factors affecting the performance of BA/VAc emulsion-based PSAs. Thus, the first step was a screening design where a wide range of the final PSA properties was to be

generated. For this purpose, a screening experimental design was employed. Eight variables were selected for the study based on their estimated influence on the latex and final product properties obtained from various literature sources. These eight variables and their levels ("-" for low , "0" for medium, and "+" for high level) are presented in Table 1.

The design was of resolution IV. Under the assumption of low influence of higher order interactions (e.g. three or more variables), this resolution enables the determination of the influence of main variables on the dependent variable. On the other hand, all two variable interactions will be confounded with at least one other two variable interaction.(11,12)

Table 1 Screening Design: Independent Variables and their Leveles

Independent variable	Level		
	-	0	+
A = BA/VAc wt/wt ratio*	95/5	90/10	80/20
B = Weight fraction of AA*	1	3	5
C = Weight fraction of Stabilizer*	2	4	6
D = Weight fraction of CTA*	0.05	0.5	1
E = Weight fraction of Initiator*	0.2	0.3	0.4
F = Temperature	60	70	80
G = Solids content**	30	40	50
H = Stabilizer type	SDS	PVOH	PVOH

*Weight fractions are based on the total weight of monomer mixture unless otherwise indicated
**Weight fraction of solids based on total weight of reaction mixture

From several subsets of the 2_{IV}^{8-4} design, which have maximum resolution, a minimum aberration design (11-13) (e.g. design with minimal number of main effects confounded with interactions of 3rd order, the minimum number of two-factor interactions confounded with interactions of order two, etc.) was selected for the proposed study. Four center point replicates (runs 17-20) were added. The design is presented in Table 2.
The following design generators were used: E=BCD, F=ACD, G=ABC, H=ABD.

An example of confoundings (aliases) are: A=CDF=BEF=BCG=DEG=BDH=CEH=FGH and AB=EF=CG=DH.

In order to eliminate external sources of variation, the runs were randomly performed.

Table 2 Screening Design

RUN	A	B	C	D	E= BCD	F= ACD	G= ABC	H= ABD
1	-	-	-	-	-	-	-	-
2	+	-	-	-	-	+	+	+
3	-	+	-	-	+	-	+	+
4	+	+	-	-	+	+	-	-
5	-	-	+	-	+	+	+	-
6	+	-	+	-	+	-	-	+
7	-	+	+	-	-	+	-	+
8	+	+	+	-	-	-	+	-
9	-	-	-	+	+	+	-	+
10	+	-	-	+	+	-	+	-
11	-	+	-	+	-	+	+	-
12	+	+	-	+	-	-	-	+
13	-	-	+	+	-	-	+	+
14	+	-	+	+	-	+	-	-
15	-	+	+	+	+	-	-	-
16	+	+	+	+	+	+	+	+
17	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0

Gravimetry. Gravimetric results indicated fast reaction rates in all reactions. Conversion vs. time data for a selected number of runs are shown in Figure 1. Fast polymerization rates observed in all runs were due to relatively high concentrations of BA (above 80 wt.%) in all recipes. The majority of the runs were completed successfully, with conversions of over 0.99 wt.fr. in most cases. GC analysis has shown no or very low levels of residual monomer in the final samples. On the other hand, four runs (i.e. runs 2, 3, 4 and 8) were not completed successfully. High concentrations of BA coupled with the

low CTA content in runs 2, 3, and 4 were the likely reason why a catastrophic coagulation occurred during these reactions. Both factors serve to increase gel formation.(15) In addition, runs 2 and 3 were high solids content runs which tends to compromise the latex stability. While run 8 did not coagulate during the reaction, it showed low shelf stability. These failed runs, coupled with the fact that several latexes showed low wetting of the PET surface during film casting, made the development of empirical models relating process conditions to final product properties impossible.

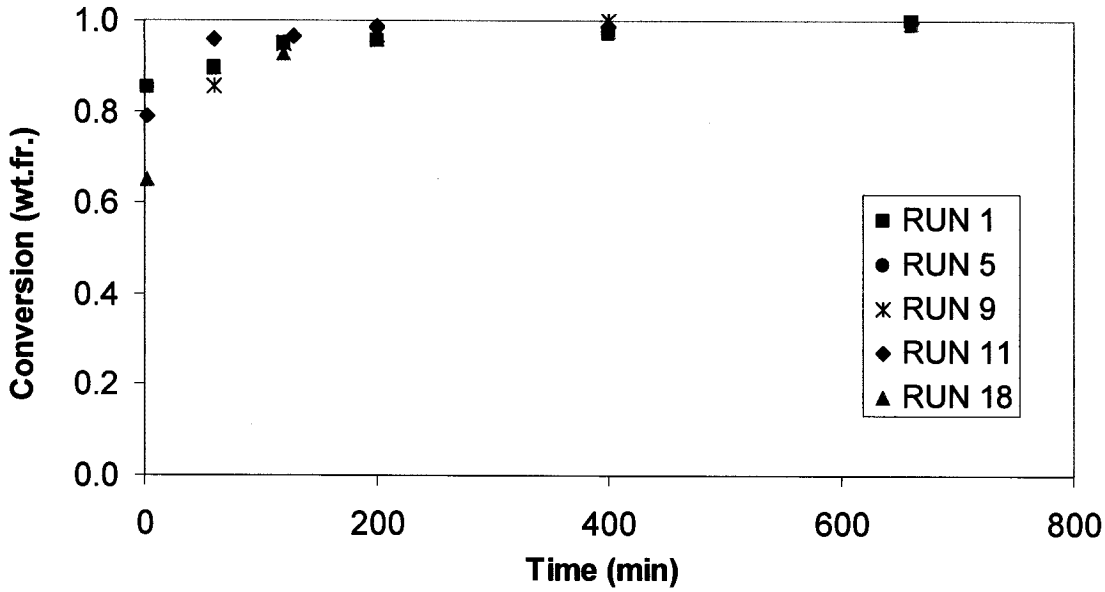

Figure 1 Conversion vs. Time for selected runs

pH monitoring. The addition of small amounts of AA in industrial emulsion polymerization recipes has been found to be beneficial for colloidal stability.(15) In addition, the presence of AA improves the shear and peel strength of the final PSA. On the other hand, the partitioning of AA in the water and organic phase will be strongly influenced by the pH of the reaction mixture.(16) In the BA/Sty/AA system, AA was found to be equally distributed between the water and organic phases when the pH was between 2 and 4.(16) An increased pH of 6 and higher resulted in the presence of AA mainly in the water phase. Furthermore, at a pH = 6-7, the AA propagation rate decreased. Given this prior knowledge, in this study the pH was maintained between 3.5

and 4.5 to maximize the incorporation of AA into the polymer particles. However, the distribution of AA between the aqueous phase, the interior and the surface of the particles was not determined.

Particle size distributions. Number-average particle diameters of the final latex samples are shown in Table 3. All samples showed monomodal particle size distributions. Relatively larger particles were observed for the runs where PVOH was used as the stabilizer compared to those where SDS was employed. Average particle sizes for the center point replicates have shown no statistically significant differences, indicating that the replication of the experimental conditions was successfully achieved.

Table 3 Weight Average Particle Diameters

RUN	d_w (nm)	PDI	RUN	d_w (nm)	PDI
1	179 ± 52	1.19	**13**	351 ± 117	1.27
5	283 ± 75	1.16	**14**	298 ± 96	1.22
6	373 ± 99	1.09	**15**	236 ± 82	1.35
7	384 ± 56	1.05	**16**	344 ± 92	1.17
9	397 ± 59	1.12	**17**	558 ± 192	1.24
10	189 ± 56	1.20	**18**	592 ± 174	1.25
11	193 ± 68	1.30	**19**	585 ± 218	1.27
12	356 ± 93	1.08	**20**	591 ± 220	1.22

PDI: polydispersity index

Glass transition temperatures. One of the most important factors affecting the performance of PSA is T_g. T_g will affect the major adhesive properties by dictating the softness necessary for flow of the adhesive and thus, bonding of the adhesive with the surface. It will also affect the flexibility of the adhesive over a range of temperatures. However, Benedek (1) warned that while T_g is a good predictor, it is not an absolute measure of the adhesive's suitability as a PSA. T_g's observed in this study are presented in Figure 2.

In all final samples, only one transition was observed, confirming that samples of homogeneous compositions were obtained. The highest T_g was observed for run 6 due to

its lower BA content and increased level of PVOH, which is a high T_g-component (T_g ~ 80°C) that can increase the overall T_g. The center point replicate runs also had relatively high T_gs compared to other runs, due to the same reasons. However, run 9, also with PVOH as stabilizer, showed the lowest T_g, possibly due to a higher BA and lower AA content. Overall, the T_g span for all runs was between -49.7 to -36.4°C.

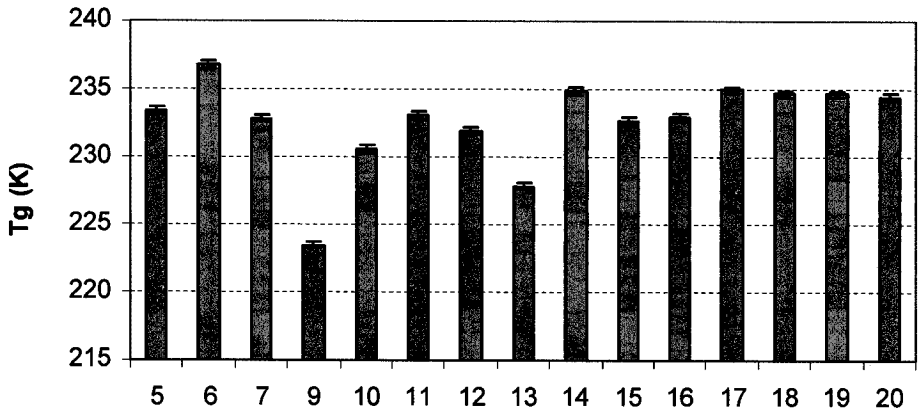

Figure 2 Glass transition temperatures

Gel content and molecular weight distributions. It has been shown that the gel content is one of the most important factors affecting PSA performance. Increased gel content and molecular weight between entanglements will increase the shear strength of a PSA while at the same time decreasing tack.(17) Gel fractions determined after removing THF- and water-soluble fractions at room temperature are presented in Figure 3. Four replicates were used in the determination of the gel content.

In the systems used in this study, a major contributor to the formation of gel fraction was the BA monomer. A high BA content can lead to "backbiting" during the polymerization, resulting in the formation of terminal double bonds that can further undergo polymerization and form branches and cross-links.(14)

In addition, low CTA levels in some recipes are expected to enhance this effect up to the point where one can even expect catastrophic coagulation, as occurred in runs 2, 3, and 4. An additional factor in gel formation is the presence of PVOH. It is known that partially hydrolized PVOH has three potential grafting sites.(18) Hydrogen atoms from tertiary C-H bonds on the backbone or from the methyl side chain in partially hydrolized

PVOH are prone to transfer, especially to VAc monomer. Grafting of VAc on these sites will leave terminal double bonds that can undergo further polymerization and lead to branching or possible cross-linking. The formed polymer is partially water-soluble, partially solvent-soluble and partially insoluble (gel).(18)

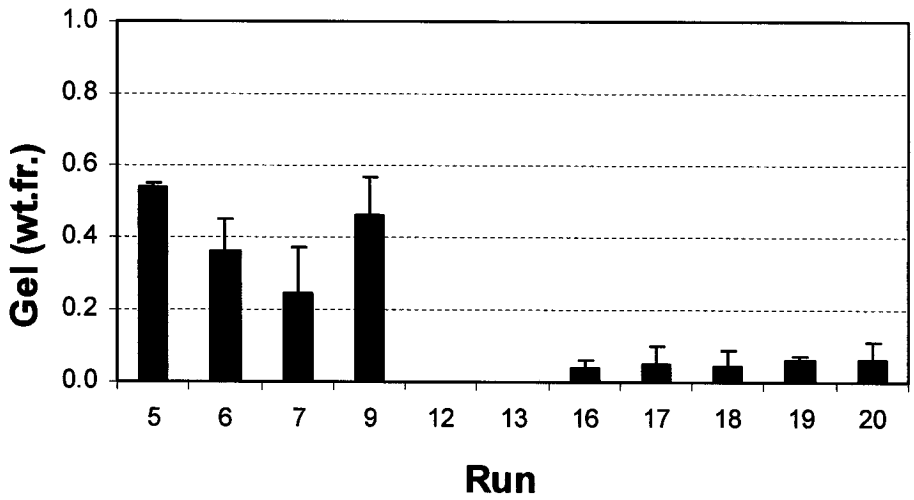

Figure 3 Gel content

In this study, the highest gel content was observed for run 5, which was not surprising given the high BA and PVOH content. The proof that factors other than type and concentration of monomer(s) and stabilizer(s) can promote gel formation lie in the fact that the high gel contents were also observed in run 9 where SDS was used as stabilizer. On the other hand, despite the use of PVOH as stabilizer, center point replicates (run 17-20) have shown relatively low gel content. The same is valid for run 16, which had the highest PVOH weight fraction but a low BA content. All these differences will affect the final product performance.

Not only the gel content, but the molecular weight of the soluble polymer fraction will affect adhesive performance. Thus, an attempt to determine these quantities was also made (Figure 4). The lowest molecular weights of the THF-soluble fraction were observed for run 5 while the highest were in run 9. However, given the relatively high error in the determination of molecular weight distributions of copolymers and branched

polymers when only a refractive index detector is used, these observed differences might not be statistically significant.

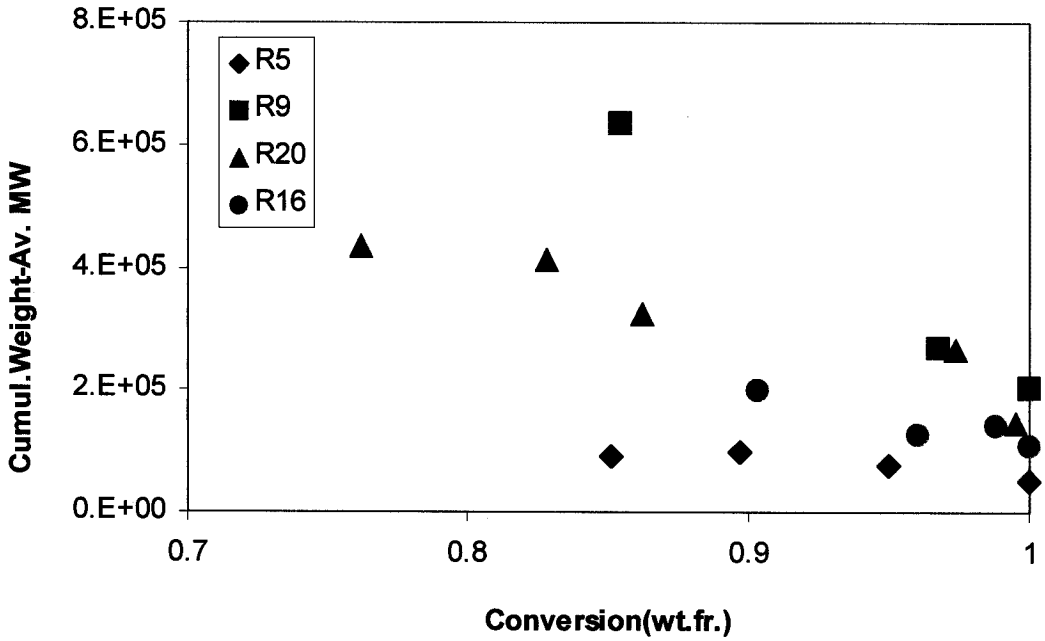

Figure 4 Cumulative average molecular weights of THF - soluble fraction

Adhesive performance. Three major performance indicators: loop tack, peel strength and shear strength were measured for all final latex samples. The latex was coated onto a PET carrier and dried prior to testing. During the coating procedure, it was found that low solid content latexes stabilized with SDS do not wet the PET surface, leading to retraction from the PET surface and poor film formation. Runs 1, 14, and 15 exhibited this behaviour and were excluded from subsequent adhesive performance evaluation. It is possible to remedy this shortcoming by the addition of thickeners to increase the viscosity as well as the post-polymerization added surfactants and wetting agents. However, the introduction of additional components, especially if they are low molecular weight substances that can easily migrate to the interfaces, could negatively impact adhesive performance.(4) On the other hand, runs of similar solid contents with PVOH as stabilizer (i.e. runs 6, 7 and 12) formed continuous films.

Two films were cast from each final latex sample because all specimens needed for the three adhesive tests could not be obtained from only one film. Thus, a hierarchical design was employed to test for run-to-run and film-to-film differences. A fully nested (hierarchical) analysis of variance (ANOVA) was performed to provide an estimate of the variance components. In all cases, there were no statistically significant film-to-film differences while, as expected, the run-to-run differences were significant at the 0.05 level and were the major contributors to the total variability. An example of these calculations for different tests, different substrates and adhesive thicknesses is presented in Table 4.

Table 4 Examples of Fully Nested ANOVA Outputs

	LoopTack_SS30		Shear_SS70		Peel_HDPE70		Shear_HDPE30	
	F(p)	% total	F/p	% total	F/p	% total	F/p	% total
Run	289.5 (0.00)	92.09	287.694 (0.00)	98.25	152.826 (0.00)	97.18	254.853 (0.00)	99.87
Film	0.242 (0.99)	0	11.284 (0.259)	0.15	1667 (0.207)	0.51	0.667 (0.677)	0
Error	-	7.91	-	1.60	-	2.30	-	0.13

F=F test, p= p-value (significant difference if $p<0.05$)
% total = % of total variability attributable to the component

Loop tack as a measurement of final PSA performance is presented in Figure 5. Two failure modes, adhesive and cohesive, were observed, but regardless of the substrate or adhesive thickness, the type of failure for a particular run remained consistent. On the stainless steel substrate, the best performance was observed in runs 9 and 5. These adhesives showed moderate tack but, the more preferable, adhesive failure. Runs 11, 12 and 13 showed higher tack on the stainless steel substrate but the mode of failure was cohesive. This could be linked to the fact that these runs did not contain any gel. The absence of gel enabled fast bonding; however, there was no inherent cohesive strength in the adhesives for clean removal. The absence of gel could be further linked to a high concentration of CTA used in these runs, thus making the CTA level among the most important among the investigated variables.

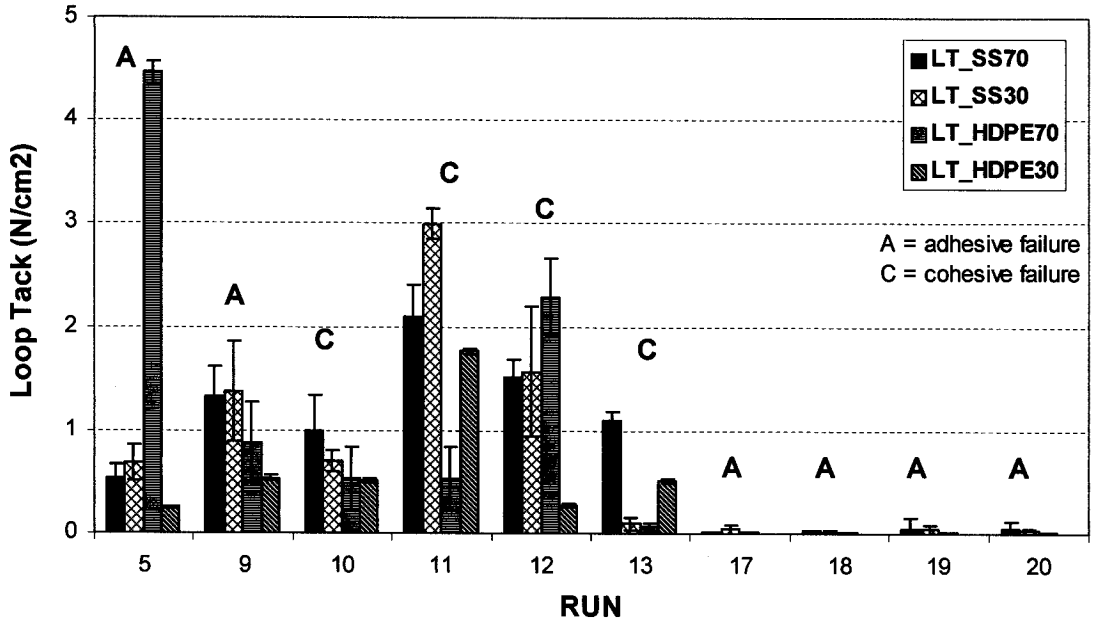

Figure 5 Loop tack for different substrates and adhesive thickness investigated

Run 9 had a lower loop tack compared to runs 11, 12, and 13, but enough gel content to enable adhesive failure. This run also had high amounts of CTA but PVOH was used as stabilizer as opposed to SDS (run 10 and 11), a higher BA content compared to run 12 (also PVOH stabilizer) and a lower concentration of PVOH compared to run 13. When T_g's were compared, run 9 had the lowest T_g value of all runs. This low T_g value, combined with an increased gel content, contributed to superior performance under loop tack testing conditions. Runs 6, 7, and 16 did not exhibit any tack. This might be due to their relatively high gel content and also to their relatively higher T_g values. Under these conditions, due to its relatively stiff chains, the adhesive is not able to wet the surface of the substrate by the adhesive. The loop tack of the center point replicates on all substrates was low. The relatively high T_g values were also responsible for such behaviour. Similar performances were observed on the HDPE substrate; however, an interesting behaviour was observed for run 5. Run 5 exhibited a significantly higher loop tack on HDPE substrate, not only compared to the other runs, but also compared to that on the SS substrate. Loop tack measured on HDPE was lower compared to that on the SS substrate. All runs showed a similar type of failure on both substrates. Without the help of at least an empirical model, it is not possible to point out which of the investigated variables has

the highest influence on any of the observed behaviours. In our case, only reasonable speculations about the influence of the particular variables are possible because the development of an empirical model was prevented by the coagulations already mentioned and the influence of the solids content on film casting. An additional obstacle to modeling was the presence of different failure modes. On the other hand, the purpose of the screening design has been completely fulfilled. Using this design, we have generated a wide range of final properties that will guide further experimental efforts in the determination of the most influential variables on the properties of BA/VAc emulsion-based PSAs.

Peel strength was also measured on the same substrates using the same adhesive thicknesses as for the loop tack tests. These results are presented in Figure 6.

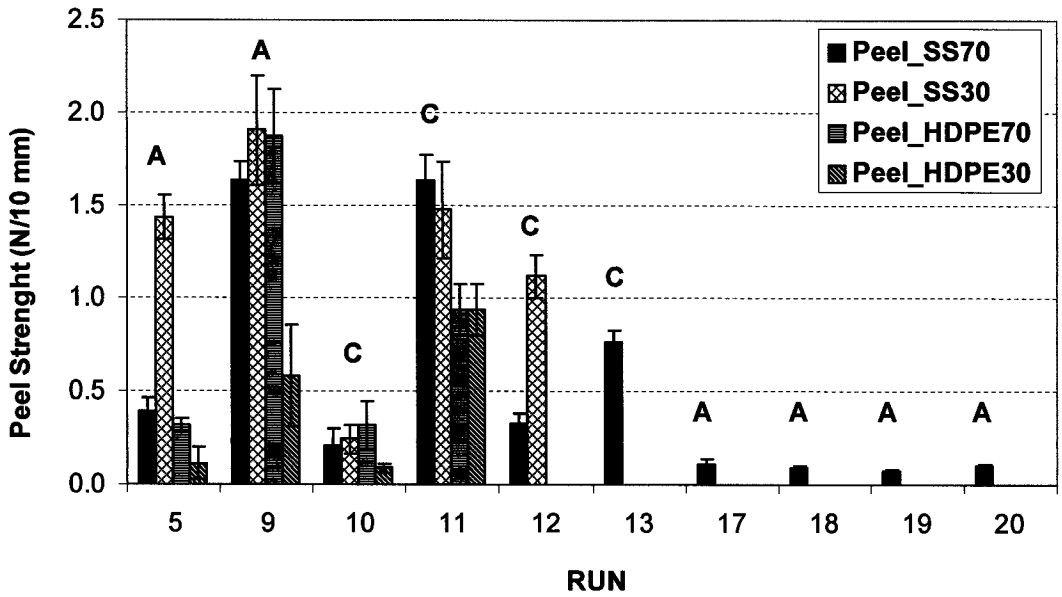

Figure 6 Peel strength

Overall, the peel strength of the investigated adhesives was low. Runs 6, 7, and 16 did not exhibit any peel strength. Given that their loop tack performance was low, this was not surprising. The performance on the HDPE substrate was considerably lower or even non-existent for most of the runs (i.e. runs 12, 13, 17, 18, 19 and 20). Again, the performances of runs 9 and 5 were the best. Run 9 showed an interesting behaviour where its peel strength on HDPE substrate (70 μm) was almost as high as that on SS when the adhesive

thickness was 30 μm. It is known that the acrylates can exhibit a good adhesion to even low energy substrates such as HDPE. However, more work is necessary to address which factor has contributed to such behaviour. Runs 10, 11, 12, and 13 showed comparable strengths but with cohesive failure, thus indicating the lack of cohesive strength. While a low T_g and the absence of gel enabled adhesion, the lack of gel simultaneously caused a lack of cohesive strength during debonding. In most cases, on the stainless steel substrate, the performance was better under lower thickness conditions.

The shear strength of the adhesives in this study is presented in Table 5. Reported values are in minutes.

Table 5 Shear Strength

RUN	Shear_SS70			Shear_SS30			Shear_HDPE70			Shear_HDPE30		
	Average	*St.Dev.*		*Average*	*St.Dev.*		*Average*	*St.Dev.*		*Average*	*St.Dev.*	
5	order of several weeks - had to be removed due to the capacity of the shear tester											
9	1204.9	148.7	a	1390.8	45.2	a	1757.8	258.9	a	1761.1	183.0	a
10	1.1	0.1	c	2.2	0.4	c	1.5	0.3	c	0.9	0.1	c
11	2.8	0.6	c	5.6	0.2	c	3.6	0.4	c	2.5	0.2	c
12	1.5	0.9	c	5.6	0.2	c	0.0	0.0	c	*	*	*
13	4.8	2.0	c	7.4	0.3	c	1.3	0.2	c	*	*	*
17	295.6	15.1	a	5.8	0.5	a	2.1	0.5	a	*	*	*
18	281.9	29.9	a	6.2	0.4	a	2.5	0.5	a	*	*	*
19	279.8	30.6	a	6.1	0.4	a	2.7	0.5	a	*	*	*
20	298.9	21.6	a	6.4	0.5	a	2.6	0.5	a	*	*	*

reported values are in minutes; a =adhesive failure, c = cohesive failure.

For example, in the SS70 tests, all samples could be divided into three general categories according to their exhibited shear strength. First, the high shear strengths observed for runs 5 and 9, respectively. This can be attributed to the high gel content observed in these samples. They exhibited enough cohesive strength due to the presence of a high molecular weight network but also relatively good balance with other properties such as tack, which was influenced by the lower T_g and molecular weight of the sol compared to the other runs. It can be speculated that the monomer feed composition and CTA content were among the major factors influencing such behaviour. The second group had moderate shear strength. These are runs 17-20 (center point replicates). They exhibited moderate shear strength coupled with a relatively low loop tack and peel on the SS

substrate and a poorer performance on the HDPE substrate. Due to their higher stiffness, they did not exhibit strong tackiness but the existence of some network structure contributed to a higher shear strength compared to that in the third group of samples. The third group had very low or no shear strength: runs 6, 7, 10, 11, 12, 13 and 16. Obviously, it is not only enough that the samples have sufficient gel content to ensure sufficient shear strength, but also the appropriate T_g and adequate molecular weight of the sol fraction. While runs 10-13 did bond to the substrate and almost immediately cohesively debonded, runs 6, 7, and 16, similar to their peel test behaviour, did not even bond to the substrate. Under these experimental conditions, properties such as gel content, molecular weight of the soluble fraction and T_g were such that they contributed to the high stiffness of the chains, thus reducing their ability to flow and wet the surface in the short times used in these standard test conditions. One can only speculate that these are the most influential factors, given that the empirical modeling was not possible.

Figure 7 is a spider plot of several responses for the four adhesives with distinctive performances: good runs 5 (SDS stabilizer) and 9 (PVOH stabilizer), adequate but poor cohesive strength (run 11), and low performance run 16 on stainless steel substrate for 70 μm thickness.

BA, AA, and PS denote the BA and AA contents in the final polymer, and the number-average diameter of the particles, respectively. All values presented are normalized values obtained by dividing a particular value with the highest observed values among the runs. It appears that the differences in gel fraction and molecular weight in the sol that are influenced by the level of CTA and selection of monomers and substrates have the largest influence on PSA performance. For example, only a slightly lower BA content, the absence of gel and the relatively moderate molecular weights of the sol are connected with very low performance (run 16). These, on the other hand, are connected at least with the BA and CTA levels in the feed (independent variables in this study).

The performance of run 11 was not unexpected. With zero gel content but the highest number-average molecular weight, run 11 had good peel strength and tack, which was governed by the mobility of the chains in contact with the substrate. However,

cohesive failure in these two tests and the non-existent shear strength were governed by the lack of any gel fraction.

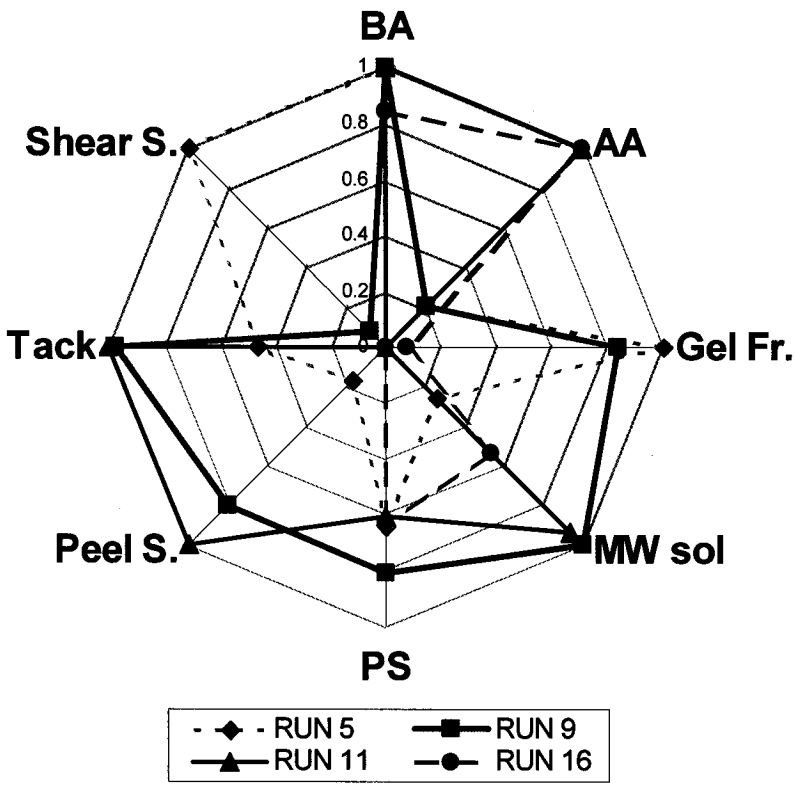

Figure 7 A spider plot of selected responses for selected adhesives

A relatively small difference was observed in the gel contents between runs 5 and 9 but a larger difference appeared in the molecular weights of the soluble fractions. Run 5 outperformed run 9 in shear strength. However the peel and tack was better for run 9. While both runs had the same compositions, the type and concentration of the surfactant was different. Also, run 5 had lower amounts of CTA, which could have contributed to the gel formation and subsequent excellent shear strength.

3.5 CONCLUSIONS

In this work an experimental design was used to determine the effects of eight variables on the properties of BA/VAc emulsion-based PSAs. Due to the fact that some of the 20 runs coagulated and that, in addition, some latexes showed low wettability of the PET surface, empirical modeling of the PSA properties was not possible. However, the screening design fulfilled its purpose to generate a wide range of final properties in a series of experiments. The results obtained here will be used in the decision making process for further experimental designs. The possible experimental spaces to be investigated should be close to the conditions of runs 5, 9 or even the center point replicates.

The polymerization rates of all runs showed similar behaviour: very fast kinetics was observed due to the high BA contents. The T_g's of the obtained final polymers were in the range from -49.7 to -36.4°C. The gel contents ranged from no gel to over 50% gel and led to a wide range of observed behaviours in all three adhesive tests. The molecular weight of the soluble fraction was also shown to be important because some of the runs had similar gel contents but different molecular weight distributions of the soluble fraction. The adhesive performance ranged from bad (no tack, no shear and peel strength as in run 16), to intermediate, where all cohesive failures were observed (runs 10, 11, 12, and 13), to very good (runs 5 and 9). Similar trends in the performance of all runs were observed when tested on SS while, in general, the performance on HDPE was less favourable. One can speculate that the observed differences in the adhesive behaviour are due to the influence of the monomer feed compositions and the CTA concentration. The monomer feed composition has a strong effect on T_g, which in turn strongly influences the final adhesive properties – stiffness of the chains will affect the wetting of the surface of the substrate by the adhesive. The CTA had a strong effect on the gel content and the molecular weight of the soluble fraction, which in turn affected not only the ability of the adhesive to wet the surface but also its cohesive strength. It is clear that the right balance between gel content and the molecular weight of the soluble fraction should be achieved (run 5 and run 9). Runs 10-13 had shown good wetting but lacked cohesive strength. When runs 5 and 9 were compared, it was obvious that a relatively good balance could be

achieved using a different type and concentration of stabilizer. Either SDS or PVOH, under the right conditions, could be used to obtain a good balance of PSA properties.

In future experimentation, it will be interesting to explore the experimental spaces around run 5 and/or run 9 or even the center point replicates with a reduced number of variables compared to that used in this design. Indications are that monomer feed compositions, CTA level and stabilizer concentrations are variables of great interest in future experimentations. Solid contents should remain as high as possible (preferably around 50%) to eliminate the wettability problems during the film casting stage.

3.6 ACKNOWLEDGEMENTS

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Chapter 4

Jovanović R., Dubé M.A.
Empirical Modeling of Butyl Acrylate/Vinyl Acetate/Acrylic Acid Emulsion-Based Pressure-Sensitive Adhesives
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EMPIRICAL MODELING OF BUTYL ACRYLATE/VINYL ACETATE/ACRYLIC ACID EMULSION-BASED PRESSURE-SENSITIVE ADHESIVES

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4.1 ABSTRACT

Butyl acrylate/vinyl acetate/acrylic acid (BA/VAc/AA) emulsion latexes were produced in a semi-batch mode. The objective was to generate polymers with properties favouring their application as pressure-sensitive adhesives. The influence of the individual monomer concentrations on final properties such as glass transition temperature (T_g), peel strength, shear strength and tack was investigated. To obtain the maximum amount of information in a reasonable number of runs, a constrained three-component mixture design was used to define the experimental conditions. Latexes were coated onto a polyethylene terephthalate carrier and dried. Different empirical models (e.g. linear, quadratic and cubic mixture models) governing the individual properties (i.e. T_g, peel adhesion, shear resistance and tack) were developed and evaluated. In the given experimental region, no single model was found to fit all of the responses (i.e. the final properties). However, in all models the most significant factor affecting the final properties was the AA concentration, followed by the VAc concentration.

Key words: butyl acrylate, vinyl acetate, emulsion polymerization, adhesion, structure-property relationships.

4.2 INTRODUCTION

Pressure-sensitive adhesives (PSAs) are viscoelastic materials that adhere upon application of slight pressure.[1] Different technologies can be used for the production of PSAs, but increasingly the interest is to utilize environmentally friendly processes, such as water-borne and curing technologies, that do not use large amounts of organic solvents.[2] Regardless of the production method, the basis for a PSA is a polymer with a low glass transition temperature (T_g), usually 2-ethylhexyl acrylate (T_g= -70°C) or butyl acrylate ([BA], T_g= -54°C). The low T_g component enables the PSA to flow and wet the substrate surface.[1] Acrylates are inherently tacky and posses good oxidative and radiation stability but have low shear or peel strength. Thus, they are polymerized with a variety of monomers for which their homopolymers have a high T_g (e.g. methyl methacrylate, styrene, vinyl acetate [VAc]) and/or carry additional functional groups (e.g. acrylic and methacrylic acid [MAA]). Due to its complexity, the relationship between process parameters, T_g and final PSA performance has been a subject of a number of studies.[3-6] Comparison of the different methods for T_g measurement is also of interest[3,7], as is the development of T_g models.[8-10]

Selection of the monomers and the polymer composition are probably the most important in a set of many variables that can affect the performance of water-based PSAs. With ever increasing product performance requirements, the need for understanding the relations between polymer microstructure and the final product properties of PSAs is increasing. Although VAc is usually mentioned in the patent literature as one of the monomers that can be used in a PSA formulation,[11,12] there are few studies investigating the factors affecting BA/VAc-based adhesives. The peel strength of a range of BA/VAc copolymers on a range of substrates was investigated and modeled by Chalukh et al.[13] They found that peel strength showed a maximum with increasing peel rates. Brooks et al.[14] conducted a series of experiments where BA/VAc/MAA latexes were blended in order to obtain a desired combination of tack, shear strength and peel strength and concluded that blending often leads to a non-balanced product. Thus, the authors suggested that semi-batch emulsion polymerization might be a better mode for obtaining

the desired balance of properties. They investigated the effects of four factors, surfactant (proprietary blend), buffer (NaOH), polar monomer (methacrylic acid) and chain transfer agent (dodecyl mercaptan), on the performance of BA/VAc/MAA emulsion-based PSAs. The most influential factor was the level of MAA, whereas the surfactant level had no effect.

In this study, a series of BA/VAc/AA latexes was synthesized and their performance as PSAs was investigated. Polyvinyl alcohol, used as the sole stabilizer, and other components in the PSA formulation were kept constant. The objective was to perform a systematic investigation of the influence of individual monomers BA, VAc and AA on the final performance of emulsion-based PSAs. Next, the determination of an optimal operating region was attempted. A constrained three-component mixture design was used to determine the ratios of the three monomers in the region of interest. The measured responses were T_g, loop tack, peel strength and shear strength. Subsequently, an empirical model was derived and the contour lines for the responses were generated over the investigated region.

4.3 EXPERIMENTAL PROCEDURES

Butyl acrylate (Aldrich), vinyl acetate (Aldrich), acrylic acid (AA), ammonium persulfate (Aldrich), n-dodecyl mercaptan (Aldrich), calcium bicarbonate, polyvinyl alcohol (average molecular weight=22000, degree of hydrolysis=88%), sodium bicarbonate (Aldrich), toluene (Aldrich) were used as received. All reactions were performed in a 1L jacketed glass reactor equipped with condenser, temperature probe, sampling port and stirrer. Experimental conditions are outlined in Table 1. All of the components, apart from the monomers and initiator, were charged to the reactor initially. The monomers were then fed at a variable decreasing rate (1.8 to 0 g/min) starting simultaneously with the injection of the initiator solution. All reactions were performed at 60°C with a stirring speed of 200 rpm. The pH of the reaction was not monitored continuously but in a study under similar conditions, a decrease in pH from 6 to 4 over the course of the reaction was observed.

Table 1 Experimental Conditions

Run	BA/VAc/AA (wt. %/wt. %/wt. %)	Other components (phm*)
F6	95/5/0	PVOH = 6 CTA = 1 Initiator = 0.17 Buffer = 0.17 Water = 137
F7	70/25/5	
F8	82.5/17.5/0	
F9	80/15/5	
F10	81.25/16.25/2.5	
F11	70/30/0	
F12	92.5/5/2.5	
F13	81.25/16.25/2.5	
F14	90/5/5	
F15	70/27.5/2.5	
F16	81.25/16.25/2.5	
F17	81.25/16.25/2.5	

* parts per hundreds of monomer

Conversion was followed using gravimetry and residual monomer content was determined by gas chromatography using a modified ASTM D4747-87 procedure. A gas chromatograph (Hewlett Packard 5890 Series II) with a flame-ionization detector (FID) was used. Nitrogen (35 mL/min) was the carrier while air (300 mL/min) and hydrogen (30m/min) were supplied to the FID. A DB Wax capillary column (J&W Scientific, California) was used. Methyl methacrylate was used as an internal standard.

Glass transition temperature, T_g, was determined using differential scanning calorimetry (DSC). A SETARAM® DSC 131 (Scientific and Industrial Equipment, KFP Group) was used. All samples were subjected to two heating/cooling cycles from -80°C to 110°C. The first cycle was used to remove any previous thermal history of the sample and the results of the second cycle were used for the determination of T_g. Approximately 4 mg of the sample were used for the analysis. SETASOFT® software was used for the determination of T_g.

Particle size analysis was conducted using an Autosizer Lo-C (Malvern Instruments) equipped with a Series 7032 Multi-8 Correlator. All analyses were performed at 90° angle at room temperature. Latex samples were diluted prior to particle size determination. Prior to coating the latex onto a carrier, particle agglomerates were

removed using a size #30 mesh. Latexes were coated using a wire-rod #30 onto a 50 μm polyethylene terephthalate carrier (Mylar®, DuPont) and dried at room temperature to give a dry film of 30 μm thickness. The films were conditioned 24h prior to testing at 23 ± 2°C and 50 ± 2% relative humidity. Stainless steel panels were used as substrates in all tests. All tests were performed according to the Test Methods for Pressure Sensitive Tapes (Pressure Sensitive Tape Council, PSTC).

PSTC 1 – Test method A (180° peel) was used for peel adhesion testing. A 25.4 mm × 300 mm specimen was cut and laminated against a stainless steel substrate using a 2040 g rubber coated roller. Dwell time was 1 min. The testing speed of the tensile tester (Instron Inc.) was 300 mm/min. The average force per 10 mm to peel the specimen from the substrate was reported. Six specimens were tested per sample.

PSTC 7 – Test method A was used to test shear adhesion. A specimen of 12 mm × 150 mm was cut. A 12.7 mm × 12.7 mm area of the specimen was laminated onto a stainless steel substrate using a 2040 g rubber coated roller. A 500 g weight was placed at the end of the specimen. Time to failure was recorded automatically using Labview™ software (National Instruments). Six specimens were tested for each sample.

PSTC 6 – Standard test method was used to measure loop tack. A specimen of 25.4 mm × 177.8 mm was cut. A loop with the adhesive facing outside was formed and 25.4 mm was masked using a masking tape and placed in the upper grip of the tensile tester (Instron Inc.). The loop was then brought into contact with the substrate mounted onto a loop tack fixture inserted into the bottom grip. When the loop covered an area of 25.4 mm × 25.4 mm, the upper grip was brought up at a crosshead speed of 300 mm/min. The maximum force per surface area necessary to detach the specimen was recorded as the loop tack. Six specimens were tested per sample.

4.4 RESULTS AND DISCUSSION

In order to obtain maximum information about the influence of individual monomers on PSA performance, a three-component mixture design was used. Three

monomers BA, VAc, and AA were considered as components of a mixture and all other components in the polymerization recipe were kept constant. Based on previous knowledge, it was assumed that certain compositions were not of importance for the desired application of the final polymers as PSAs. Thus, the following consistent constraints (wt %) were used in the design: 70<BA<95, 5<VAc<30, and 0<AA<5. As a result, a total of 12 runs (8 + 4 center point replicates) was performed.

In general, special cubic polynomial model for a three-component mixture can be written as:

$$E(y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} x_i x_j + \sum_{i<j<k}^{q} \sum \sum \beta_{ijk} x_i x_j x_k \quad (1)$$

where E(y) is the expected value of the response, q is number of components in the mixture, β's are the fitted parameters in the model and x is the weight percentage of a mixture component. Thus, four runs performed at the design vertices were used for the estimation of linear blending terms (β_i), four edge midpoints for the estimation of binary blending terms (β_{ij}), and four center point replicate runs were used for the estimation of ternary (β_{ijk}) blending terms and to perform error analysis. The objective function used for parameter estimation was the least squares function. Parameters in all models are presented along with 95% confidence intervals.

Selected runs (four vertices and a center point of the experimental design) are shown in Figure 1. Similar conversion vs. time curves were observed for other runs.
All runs showed a characteristic increase of the polymerization rate with an increase in BA fraction in the reaction mixture. For example, the lowest polymerization rates were observed for runs F7, F11, and F15, all with 70 wt% BA in the monomer mixture, whereas the fastest rates were observed for runs F6, F12, and F14 where the BA content was 95, 92.5, and 90 wt%, respectively. Given that the propagation rate of BA is higher than that of VAc, this behaviour was expected. To ensure consistency in the subsequent steps (e.g. film casting and thickness) it was important to ensure that all polymerizations were completed above 98%. There were no significant differences in conversion observed between the four replicated runs.

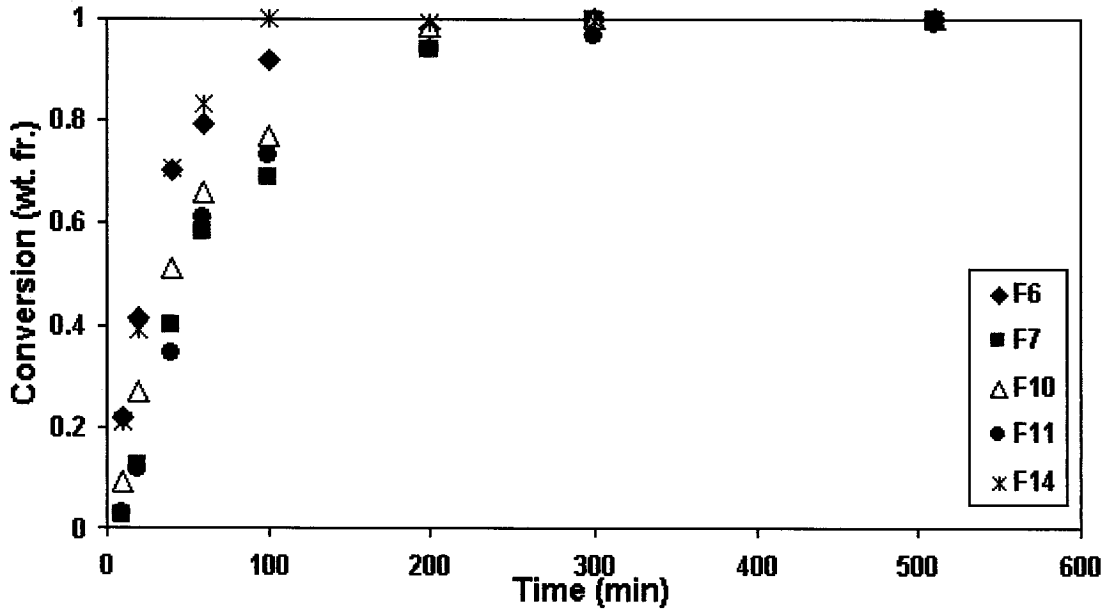

Figure 1 Conversion vs. time: Selected runs

All observed particle size distributions were monomodal and broad (PDI=0.5 to 1). In Figure 2, the particle size development is shown for selected runs (i.e. 4 vertices and 1 center point replicate). All other runs exhibited similar trends in particle size development with time.

In general, particle size increased from approximately 100 nm to approximately 550 nm over the course of the reaction. This should indicate that some particle agglomeration has occurred in the sample. This is a common problem when steric stabilizer is used.

Glass transition temperature is one of the most important factors affecting PSA performance. Thus, in this work, T_g was determined for each final polymer latex. When the amounts of all other components in the polymerization recipe are kept constant, the final observed value should be dependent only on the ratio of monomers in the recipe. Only one transition was observed in the temperature range from -80°C to 110°C for all final samples indicating the presence of a homogeneous polymer. T_g values for all runs are shown in Table 2. Although the T_g is a range of temperatures rather than a single temperature where different segmental motions will take place, for modeling purposes, T_g

was considered as a single temperature in this study. The variation of T_g values determined was in the range of 226 K (Run F6) to 241.7 K (Run F7).

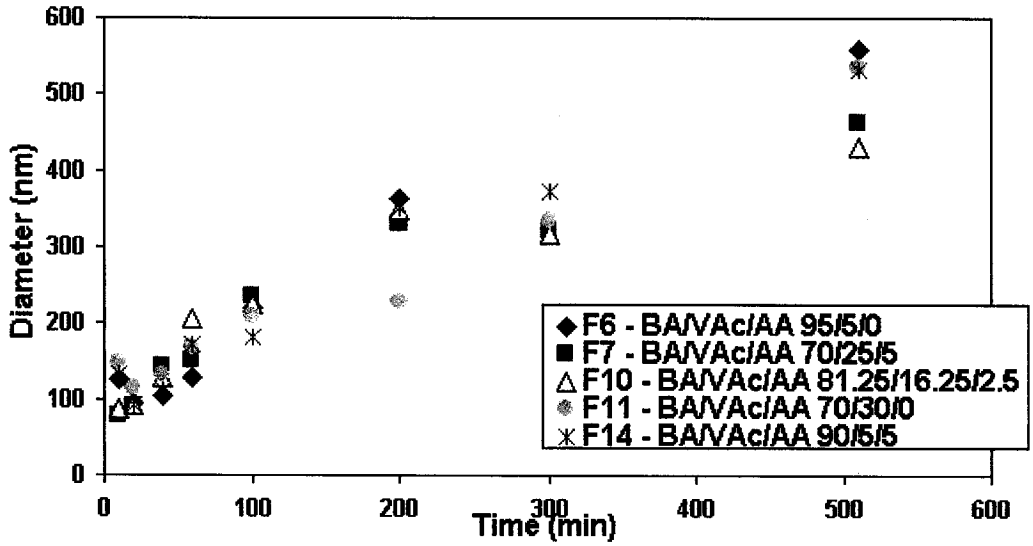

Figure 2 Selected particle size developments

Table 2 Experimental Results

RUN	T_g** (K)	Loop Tack (N/6.45 cm^2)	Peel Strength (N/10mm)	Shear Strength (h)
F6	225.9	0.04 ± 0.008	0.01 ± 0.016	17.77 ± 1.23
F7	241.5	0.91 ± 0.115	1.98 ± 0.244	-
F8	230.4	0.70 ± 0.107	0.53 ± 0.069	0.54 ± 0.068
F9	238.1	2.24 ± 0.322	1.13 ± 0.296	12.0 ± 3.113
F10	235.4	2.38 ± 0.265	1.51 ± 0.373	0.09 ± 0.041
F11	240.7	2.16 ± 0.333	1.26 ± 0.564	1.71 ± 0.881
F12	231.2	1.61 ± 0.288	1.33 ± 0.269	2.41 ± 0.303
F13	234.7	2.33 ± 0.250	1.58 ± 0.138	3.07 ± 0.293
F14	234.1	1.12 ± 0.209	0.45 ± 0.117	5.33 ± 1.623
F15	241.7	2.19 ± 0.144	3.81 ± 0.161	16.78 ± 1.123
F16	235.8	2.11 ± 0.124	1.67 ± 0.361	0.06 ± 0.026
F17	237.8	2.47 ± 0.286	2.04 ± 0.210	0.12 ± 0.045

*All failures in adhesive tests were cohesive.
** Standard deviation for T_g measurements was determined for a single sample to be 1.07 degrees

The lowest T_g's were observed for polymers with high BA content such as F6 and F12, which was expected due to the low T_g of BA homopolymer (-52°C). The highest T_g

values were observed for polymers richer in VAc such as F7, F11 and F15 with 25, 30, and 27.5 wt. % VAc, respectively in the monomer mixture. This was due to the fact that VAc homopolymer has a T_g=32°C.

Despite the existence of various mechanistic models to predict T_g such as the Fox[8] or Gordon-Taylor models[9], in this work, T_g was modeled empirically. A stepwise regression was used in the selection of the model starting with a special cubic mixture model with seven parameters and ending with a linear mixture model (three parameters). The model selection was based on trends in the residuals, lack of fit tests, the precision of the parameter estimates, and the adjusted R^2 value. The following linear mixture model was found to provide the best fit based on the criteria described above:

$$E(T_g) = (2.2418 \pm 0.0318)\,(BA) + (2.7360 \pm 0.1459)\,(VAc) + (3.6036 \pm 0.7639)\,(AA) \quad (2)$$

No trends in the residuals were observed and there was no lack of fit for this model. The adjusted R^2=0.9021. The amount of AA was found to be the most influential factor affecting T_g followed by the amount of VAc. Given the relatively high T_g of AA homopolymer (T_g= 379.15 K), the addition of even a small weight percentage of AA to a base polymer can affect T_g considerably. The model was subsequently used to generate contours of constant T_g over the investigated region of interest (Figure 3).

One of the more general models for prediction of T_g is the Fox model (Eq. (3)) where T_g is the overall T_g and T_{gi} is the T_g of homopolymer i, where i varies from 1 to n.

$$\frac{1}{T_g} = \frac{1}{T_{g1}} + \frac{1}{T_{g2}} + \ldots + \frac{1}{T_{gn}} \quad (3)$$

Using T_{g1} (pBA)=221.15 K, T_{g2} (pVAc)=301.15 K and T_{g3} (pAA)=379.15 K for the T_g's of BA, VAc and AA homopolymers, respectively, the overall T_g's using the Fox model were obtained and compared to the measured values. Both the Fox model and our empirical model (Eq. (2)) displayed no lack of fit. However, our empirical model showed a slightly better fit to the data as revealed by the adjusted R^2 and F values. For both models, the critical F value was F(6,3,0.05) = 8.94 whereas the adjusted R^2 values were 0.9021 and 0.6650 and the F values were 1.415 and 6.085, for the empirical (Eq. (2)) and Fox models (Eq. (3)), respectively.

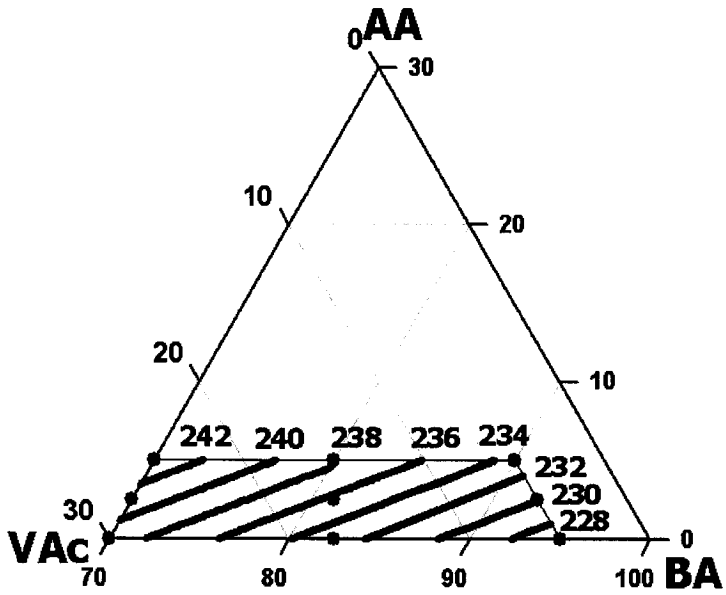

Figure 3 T_g contour lines over the region of interest

The better fit using the empirical model can be explained by the fact that the observed variations in T_g were in a very narrow range (less than 20 K). In addition, it is not unusual for the Fox model to differ from experimental values due to the fact that it does not account for the dependence of T_g on molecular weight or on the segmental distribution of monomer units in the polymer chain. Regardless, it is one of the most common models used for the prediction of polymer T_g.

For the determination of loop tack, six specimens from two different film samples were tested. Prior to any analysis, a hierarchical experimental design was used to investigate run-to-run and film-to-film differences. The analysis of variance and variance components in Table 3 were obtained using a fully nested analysis of variance in MINITAB software v.13.1 (Minitab, Inc). Because the analysis of variance showed no film-to-film differences, the average of six measurements were reported as a single value of loop tack (see Table 2).

All samples showed cohesive failure, leaving a residue on the stainless steel substrate. In general, lower loop tack values were observed probably due to the use of

PVOH as stabilizer, which can have the ability to migrate to the adhesive-air interface during drying and thus, reduce tack.

Table 3 Fully Nested Analysis of Variance and Variance of Components for Loop Tack

Fully Nested ANOVA	**Source**	**DF**	**SS**	**MS**	**F-calculated**	**F-tabulated**
	Run	11	42.5685	3.8699	71.677	4.2
	Film	12	0.6479	0.0540	1.064	1.99
	Error	48	2.4352	0.0507		
	Total	71	45.6515			
Variance Components	**Source**	**Variance Component**		**% of Total**	**St. Deviation**	
	Run	0.636		92.47	0.797	
	Film	0.001		0.16	0.033	
	Error	0.051		7.38	0.225	
	Total	0.688		0.829		

DF=degrees of freedom, SS=Sum of Squares, MS=Mean Square

In addition, other small molecules present in the recipe, such as buffer, can also negatively affect tack. The same procedure used to model T_g was used to model tack as well as peel and shear strength. Using stepwise regression beginning with the special cubic model and ending with the linear mixture model, the same model discrimination rules as were used in the T_g modeling were applied. The model showing the best fit was the special cubic mixture model:

E(Loop Tack) =

$$\begin{aligned}&(0.0015 \pm 0)\,(BA) + (0.2802 \pm 0.2423)\,(VAc) - (11.0350 \pm 4.8486)(AA)\\ &- (0.003 \pm 0)\,(BA)(VAc) + (0.1156 \pm 0.0551)\,(BA)\,(AA)\\ &- (0.0879 \pm 0.0636)\,(VAc)(AA) + (0.0028 \pm 0)\,(BA)(VAc)(AA)\end{aligned} \quad (4)$$

All other models showed lack of fit and/or displayed trends in the residuals. The adjusted $R^2 = 0.9226$ for the special cubic mixture model. No trends in the residuals nor lack of fit was found for this model which was therefore used to generate contours of constant loop tack for the investigated experimental region (see Figure 4).

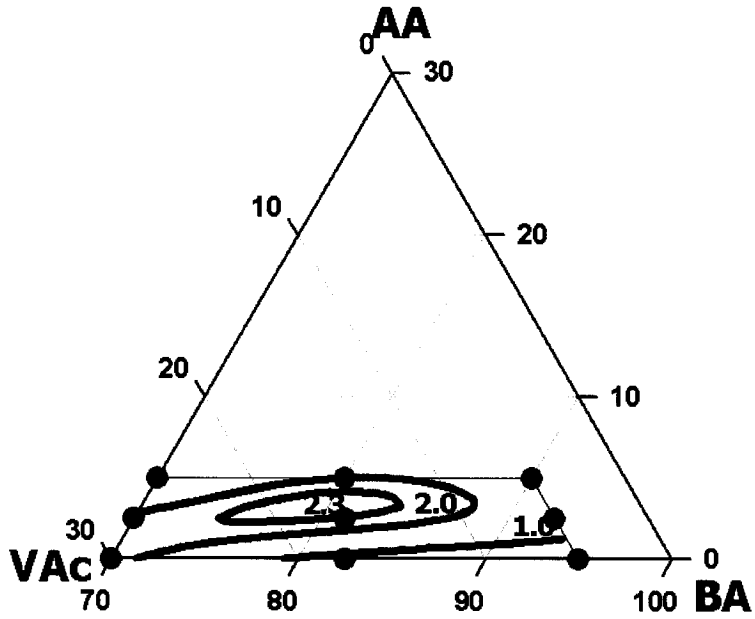

Figure 4 Loop tack contour lines over the region of interest

The most influential component, by far, affecting loop tack was AA, of which increased amounts served to reduce the loop tack. This is likely due to the increased possibility of grafting or cross-linking reactions which are known to reduce loop tack.[1] Other minor effects include a binary synergistic effect of BA and AA on loop tack. The binary parameter indicates that a blend of BA and AA produced higher loop tack values than would have been expected by simply averaging the values for the pure blends. The addition of a small fraction of AA in combination with BA, which can be considered as a major "tack carrier", will produce higher loop tack. It can be speculated that the binary interaction is such that the BA effect dominates that of the AA. On the other hand, the other minor parameters suggested that when AA and VAc, or BA and VAc were combined, the resulting adhesive had a lower loop tack value than would have been expected by averaging the values produced by the single-component blend. The binary parameter describing the combination of AA and VAc, which resulted in lower loop tack, is consistent with the fact that both components individually are considered as tack reducing monomers because of the increase in T_g linked to their reduced segmental motion. These small range motions are essential for good loop tack.[1] It was interesting

to find that there was a small, yet significant, tertiary synergistic effect between the components. When all three components were combined, the resulting adhesive had higher loop tack than would have been expected by simply averaging the single-component blends. Given that the tertiary synergistic effect is positive it can be speculated that BA was the dominant component under the conditions studied.

It can be seen that the loop tack response surface has a maximum located in the middle of the investigated region. Moving further away from those compositions would lead to reduced tack.

Similar to the tack, peel strength was also investigated using six specimens that originated from two films (three specimens per film) for each run. Again applying a hierarchical design, film-to-film and run–to-run differences were tested. Results of this analysis are shown in Table 4.

Table 4 Fully Nested Analysis of Variance and Variance of Components for Peel Strength

	Source	DF	SS	MS	F-calculated	F-tabulated
Fully Nested ANOVA	**Run**	11	61.9705	5.6337	71.768	4.2
	Film	12	0.9420	0.0785	1.038	1.99
	Error	48	3.6287	0.0756		
	Total	71	66.5411			

	Source	Variance Component	% of Total	St. Deviation
Variance Components	**Run**	0.926	92.36	0.962
	Film	0.001	0.10	0.031
	Error	0.076	7.54	0.275
	Total	1.002	1.001	

DF=degrees of freedom, SS=Sum of Squares, MS=Mean Square

Analysis of variance showed that there were no film-to-film differences and thus, reported peel strength values are the averages of six measurements. All samples exhibited a cohesive failure mode with the lowest observed values at higher BA content. Using the same procedure as for loop tack, peel strength was modeled.

In this case, the best predictions were obtained using a quadratic mixture model:

E(Peel strength) =

$$(0.0026 \pm 0)\,(BA) + (0.3055 \pm 0.2444)\,(VAc) - (18.6921 \pm 7.0846)\,(AA) - (0.0037 \pm 0)\,(BA)(VAc) + (0.1963 \pm 0.0779)\,(BA)(AA) + (0.2031 \pm 0.0779)(VAc)(AA) \quad (5)$$

There were no trends in the residuals nor lack of fit for this model. The adjusted R^2 was 0.9111. The most influential factor, by far, was wt. fraction of AA in the mixture. Although statistically significant, the other effects were quite minor in comparison.

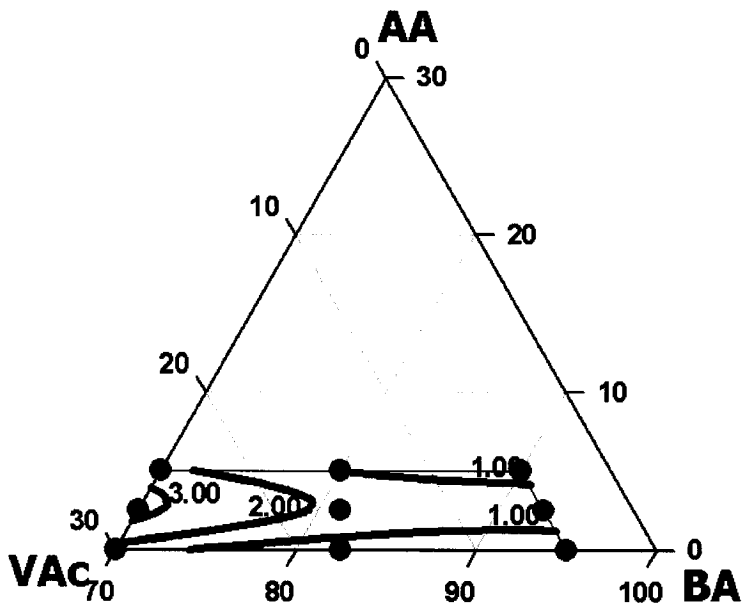

Figure 5 Peel strength contour lines over the investigated region

For example, when combined, BA and AA, as well as VAc and AA, had binary synergistic effects on the peel strength of the adhesive. The binary blend of these components produced higher peel strength values compared to the values obtained by averaging the pure blends. A positive VAc-AA binary effect on peel strength is not surprising given that both homopolymers serve to increase peel strength.[1] On the other hand, the binary parameter for BA and VAc showed lower peel strengths than would be expected by averaging the single-component blends. It can be speculated that in this binary combination, BA could be a dominant component given that BA homopolymer

does not exhibit sufficient peel strength.[1] Model predictions are shown in Figure 5 and indicate that the highest peel strength is in the region of low BA wt. fractions in the mixture. Contour lines indicate the existence of a local maximum in that region.

An average of six shear strength measurements was represented by a single point in Table 3 after the analysis of variance had shown no film-to-film differences. Detailed results of nested ANOVA and components of variances are shown in Table 5. Similar to peel strength and loop tack, the experimental results were used to model shear strength over the investigated region using a stepwise regression strategy for model selection. The model that showed the best fit to the experimental data was a quadratic mixture model with an adjusted R^2= 0.9402:

$$\begin{aligned} E(\text{Shear strength}) = {} & (0.3083 \pm 0.0842)(BA) + (4.0967 \pm 1.8149)(VAc) \\ & + (106.418 \pm 57.1062)\,(AA) - (0.0675 \pm 0.0318)(BA)(VAc) \\ & - (1.1729 \pm 0.6056)(BA)(AA) - (0.7239 \pm 0.5649)(VAc)(AA) \end{aligned} \quad (6)$$

The most influential factor affecting shear strength was AA monomer. The addition of AA provided additional potential grafting or cross-linking sites. These, in addition to BA backbiting reactions[15] and grafting of VAc to PVOH[16], perhaps contributed to the formation of a network necessary for the higher shear strength of the adhesive. Other significant yet lesser effects on shear strength include the combined BA-VAc effect.

The decrease in shear strength when BA and VAc are combined can be explained by the dominance of BA in this term. However, when BA and AA were combined, the resulting shear strength of the adhesive was lower than that expected by simply averaging the single-component blends. This indicates that BA is dominant for this binary parameter. The shear strength contour lines, presented in Figure 6, indicate the existence of a minimum in the investigated region.

Table 5 Fully Nested Analysis of Variance and Variance of Components for Shear Strength

	Source	DF	SS	MS	F-calc.	F-tab.
Fully Nested ANOVA	**Run**	10	2766.0435	276.6043	147.138	4.2
	Film	11	20.6789	1.8799	1.095	1.99
	Error	44	75.5144	1.7162		
	Total	65	2862.2368			

	Source	Variance Component	% of Total	St. Deviation
Variance Components	**Run**	45.787	96.28	6.767
	Film	0.055	0.11	0.234
	Error	1.716	3.61	1.310
	Total	47.558	6.896	

DF=degrees of freedom, SS=Sum of Squares, MS=Mean Square

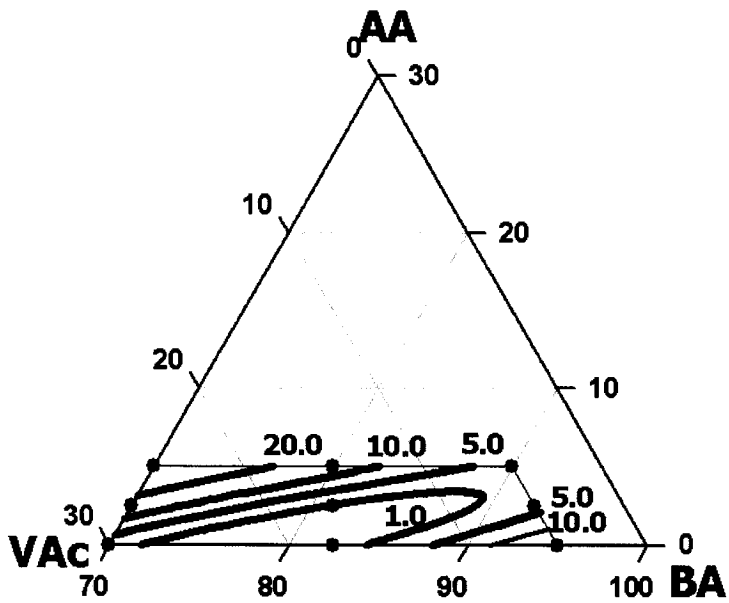

Figure 6 Shear contour lines

After modeling all responses individually, their contour lines were overlaid on the same plot (Figure 7) to obtain a region of optimal adhesive performance in the investigated region. From Figure 7 it can be seen that there was no single area in the investigated region where all responses (i.e. tack, peel strength, shear strength) were at

their maximum value. Given the nature of PSAs this is not surprising. Usually, the final performance is a matter of a trade-off where certain properties are favored at the expense of others. For example, a feasible operating region to obtain higher peel and shear strength of the investigated adhesives would be in the vicinity of lower BA content (70-80 wt%) with greater than 20 wt% VAc and at 2.5-5% AA. On the other hand, highest loop tack values would be in the vicinity of the centre of the investigated region. Thus, suboptimal regions observed from the overlaid plot can serve as a guide for the selection of the appropriate terpolymer composition for the final PSA application of interest.

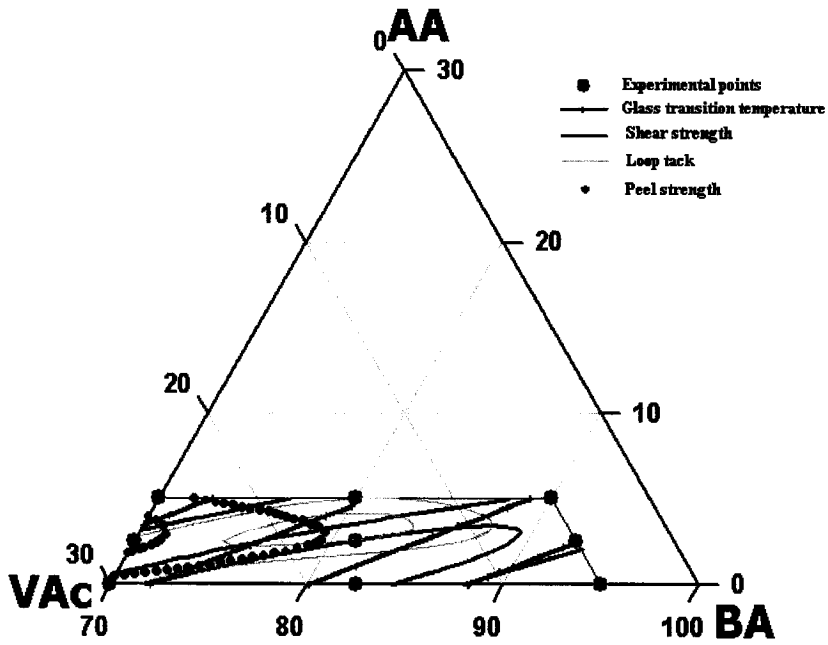

Figure 7 Overlapped plot of four responses

4.5 CONCLUSIONS

In this work, a series of BA/VAc/AA latexes were synthesized. Using a constrained mixture design, the influence of individual monomers on the final performance was investigated while all other components in the recipe were kept

constant. In total, 12 runs (8 runs and 4 replicates) were performed. T_g, loop tack, peel strength and shear strength were analyzed and empirical models were developed. Modeling was performed using stepwise regression starting with a special cubic model (seven parameters) and ending with a linear model (three parameters). Model selection was based on lack of fit tests, trends in residuals, the precision of parameter estimates and adjusted R^2 values. The best predictions of T_g were obtained using a linear mixture model. Peel and shear strength were modeled using quadratic models while loop tack was modeled using a special cubic model. In all cases, the wt. fraction of AA was the most influential factor followed by the wt. fraction of VAc. Contour plots were generated for each response and revealed the existence of minima in the investigated experimental region for loop tack and shear strength, while a maximum was observed for peel strength.

Even though not directly measured for the polymers obtained in this study, it is known that there is a considerable amount of grafting occurring especially of the VAc monomer on PVOH.[16] In addition, intra-molecular cross-linking is known to occur in BA-rich systems.[15] Because in all cases cohesive failure was observed, it is likely that additional cross-linking would be necessary to improve shear strength. However, this improvement should be carefully considered, given that an increase in the cross-link density negatively influences tack.

When all responses were overlapped, no single area was found where all responses showed the optimal maximum values. This indicated the existence of sub-optimal regions. Thus, the design for the final performance might involve a trade-off between certain properties. On the other hand, this situation can be used to our advantage if one of the adhesive performance properties is favored in a certain application compared to another. In this case, the appropriate monomer mixture can be easily identified using the response surfaces.

4.6 ACKNOWLEDGEMENTS

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Chapter 5

Jovanović R., Dubé M.A.
Butyl Acrylate/Vinyl Acetate Emulsion-Based Pressure-Sensitive Adhesives: Empirical Modeling of Final Properties
(to be submitted)

BUTYL ACRYLATE/VINYL ACETATE EMULSION-BASED PRESSURE-SENSITIVE ADHESIVES: EMPIRICAL MODELING OF FINAL PROPERTIES

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5.1 ABSTRACT

An investigation of a variety of factors affecting the adhesive performance of BA/Bac emulsion-based PSAs was performed as part of a larger systematic study. The influence of the amounts of acrylic acid, chain transfer agent and anionic stabilizer on polymer microstructural properties and final adhesive performance on stainless steel and high density polyethylene substrates was investigated using a Box-Behnken experimental design for 15 runs. The resulting data were empirically modeled.

For each final adhesive property (i.e. loop tack, shear and peel strength), different models were found to fit the data. Similar models for loop tack and peel strength were found to be adequate for different PSA thicknesses on the same substrate. The shear strength models were similar regardless of the substrate or thickness of the adhesive (e.g. in all models, AA and CTA as well as their second order interactions were the significant factors.)

AA and SDS had significant effects on loop tack as did the AA-SDS and CTA-SDS two-factor interactions. Given the nature of SDS, it is expected that these effects result from the ability of SDS to migrate to the adhesive/carrier and adhesive/air interface.

Quadratic peel strength models were found to adequately describe the data for SS substrate cases with a noticeable absence of any interaction parameters. On the other hand, the only models found to fit the data obtained using HDPE substrates were linear. However, despite not showing lack of fit, the HDPE models were able to explain only

60% of variation in the data. Given the nature of these results it would be recommended to use larger data sets.

The empirical models developed for shear strength showed the highest consistency between different substrates and adhesive thicknesses. The dominant factor among the three investigated was the amount of CTA. This result is related to the influence of CTA on gel formation. Gel or network structure is necessary for good cohesive strength. In all models, CTA was present as a significant factor, which relates to its importance in tailoring the properties of the PSAs.

5.2 INTRODUCTION

Emulsion-based pressure-sensitive adhesives (PSA) are replacing solvent-borne counterparts at an increasing rate. More than 40% of the PSA market belongs to emulsion-based products.(1) Given the increasing pressure from the public and policy makers on environmental compliance of PSA products, the percentage of emulsion-based PSAs will continue to rise in the future. Thus, it is not surprising that there is increasing interest to develop new products and processes based on emulsion polymerization technology as well as to improve existing ones. In that quest, it is important to systematically investigate a variety of PSA systems, identify important variables that will affect final properties and establish empirical, or more preferably, mechanistic models that will describe PSA behaviour.

Although the major factors affecting PSA properties are mostly identified for solvent and hot melt adhesives, a systematic approach is needed when emulsion-based PSAs are considered. While a number of studies have investigated either tack or peel or shear for a variety of emulsion-based PSAs,(2-6) rare are the ones that have investigated all three of these important indicators of final performance simultaneously.(7-9)

The BA/VAc system has been far less investigated for PSA properties compared to other systems. One such study emphasized blending of a variety of BA and VAc latexes, but part of the study was dedicated to the investigation of factors affecting BA/VAc compolymers as well.(10) They concluded that the most influential factor

affecting PSA properties was the amount of methacrylic acid used. A similar conclusion was obtained by Jovanovic and Dubé (11) in an investigation of the influence of monomer feed composition for a series of BA/VAc/AA emulsion-based PSAs. Using a three-component mixture design, they similarly found that the amount of AA was the most influential monomer affecting loop tack, shear and peel strength of the investigated PSAs.

There are various mechanistic models that are able to predict polymer microstructural properties from the reaction operating variables.(12) On the other hand, there is a considerable lack of even empirical models connecting reaction variables (e.g. feed composition, concentration and type of stabilizer(s), temperature...) and/or polymer microstructural properties (e.g. polymer composition, molecular weight distribution, particle size distribution) to final PSA performance (e.g. tack, peel and shear strength).

The study presented herein, is part of an ongoing attempt to investigate variables affecting final performance of various emulsion-based PSAs. Previously, a screening design was used to determine the influence of several variables on the final properties of BA/VAc PSAs.(13) Results from the screening study indicated that the BA/VAc ratio and the amount of CTA were among the most influential factors affecting the final PSA performance. In another study, where only the influence of the three monomers on the final performance were investigated (14), AA was found to be the most important among the monomers at different monomer compositions. In that study, all other factors were kept constant including the concentration of poly(vinyl alcohol), PVOH, that was used as a sole stabilizer.

In the study reported herein, sodium dodecyl sulphate (SDS) was used as a sole stabilizer. The objective of the study was to investigate the influence of three variables: AA, CTA and SDS concentration on the final properties (i.e. loop tack, shear and peel strength). Furthermore, empirical models were developed to predict the final PSA properties. The performance of the obtained polymers was tested on two different substrates: stainless steel (SS) and high density polyethylene (HDPE) as well as at two different thicknesses (30 and 70 μm).

5.3 EXPERIMENTAL PROCEDURES

All reaction components excluding monomers were used without further purification: SDS (BHD), PVOH (Cevol), potassium persulphate (Aldrich), sodium bicarbonate (BHD), dodecanethiol (Aldrich) as well solvents (e.g. methanol (ACP chemicals), tetrahydrofuran (THF, EM Science)) used for characterization. Inhibitor was removed from the monomers used in this study using standard procedures previously described.(15)

All polymerizations were performed in a LabMAX automatic reaction system (Mettler-Toledo). Throughout the reaction, feed addition, reaction temperature and pH were continuously monitored. All VAc monomer and appropriate amounts of BA and AA along with other ingredients (i.e. stabilizer, water, part of the buffer and CTA) were charged to the reactor prior to the injection of initiator. The monomer feed, consisting of the remaining BA/AA and CTA mixture, was fed to the reactor simultaneously with the injection of initiator. The remaining buffer solution was used for pH control. Variable feed rates were used starting with high (3 g/min) to low (0.1 g/min) values. There was no feed during the last two hours of the reaction. Samples were periodically taken from the reactor for characterization.

Standard gravimetric analyses were used to calculate monomer conversion. Samples were left to evaporate until a constant weight was reached first at room conditions and later under strong vacuum at ~ 30°C. Gravimetry was based on the total mass of dry polymer.

Polymer compositions were calculated based on the residual monomer determined using gas chromatography. A gas chromatograph (Hewlett Packard 5710A) equipped with a flame-ionization detector (FID) and a glass column OW 351 (Chromatographic Specialists) was used. Injector and detector temperatures were 200 and 250°C, respectively, while the column temperature was programmed as follows: An isothermal step at 80°C for 4 min was followed by heating to 180°C (heating rate = 8°C/min). The final step was isothermal at 180°C for 20 min. Helium (35 mL/min) was the carrier while air (300 mL/min) and hydrogen (30 m/min) were supplied to the FID. Styrene was used as an internal standard. The injection volume was 1 μL.

Particle size distribution was determined using a 90Plus particle size analyzer (Brookhaven Instruments Corp). Approximately 3-5 drops of latex were diluted with distilled de-ionized water and a 5mL cuvette was inserted into the cell for measurement. 90Plus particle sizing software (V. 2.25) was used to calculate particle size distributions.

Gel content was determined using the membrane partitioning method. A known amount of sample was heat sealed between two polytetrafluoroethylene membranes (pore size 0.2 μm, 47 mm diameter). Enclosed samples were shaken for 72 hours in THF. Sealed pouches were air-dried until a constant weight was achieved. The difference between the initial and final weight of the sample was used to calculate the gel content.

Meyer rods were used to cast latex onto 50 μm non-treated polyethylene terephthalate carriers (Mellinex®, DuPont) to obtain dry film thicknesses of 30 and 70 μm. The films were conditioned for 24 h prior to testing at 23 ± 2°C and 50 ± 2% relative humidity prior to testing. Two films were cast per latex. Three specimens from each film were used for each adhesive test.

Glass transition temperatures (T_g) of the final polymers were determined using a Seiko DSC 220C (Japan) differential scanning calorimeter. Approximately 10 μg was placed into a pre-weighed aluminum pan. The first step in the thermal program was heating to 120°C to eliminate any thermal history. The next step involved cooling the sample from 120 to -80°C (cooling rate = 10°C/min) followed by a 2 min isothermal step. The second heating from -80 to 120°C (heating rate = 10°C/min) was used for the determination of T_g. An empty aluminum pan was used as reference and for determination of the baseline that was subtracted from the samples.

All adhesive tests were performed according to standard test methods for PSAs.(16) PSTC-101, PSTC-16, and PSTC-107 were used for the determination of peel strength, loop tack and shear strength, respectively. An Instron 1100 universal tester (Instron, Inc) was used to perform peel and loop tack tests. A hand roller was used in all sample preparation. For PSTC-107, a 500 g load and a 1.25 cm × 1.25 cm test area were used with two substrates (SS and HDPE).

5.4 RESULTS AND DISCUSSION

The study reported herein is a part of a systematic investigation of variables affecting the final properties of BA/VAc emulsion-based PSAs. In a screening design, we identified the BA/VAc feed composition of 95/5 wt/wt% and the amount of CTA as important variables affecting the final adhesive performance measured as loop tack, peel and shear strength.(13) However, in that study, model adequacy was not achieved in the development of empirical models to predict the PSA properties. In another series of experiments, a three-component mixture design was followed to investigate the influence of the individual monomers BA, VAc, and AA on the final adhesive properties. All other components in the recipe were kept constant, including the concentration of PVOH as sole stabilizer for the system. Empirical models developed based on these experiments have shown that AA was the most important monomer affecting all three final adhesive properties.(14) Based on the results of these two studies, in the study reported herein, we have investigated the influence of AA, CTA and SDS concentration on the final properties. Having already established that the amount of AA monomer is important in PVOH-based recipes, we kept it as a variable in this experimental design. In order to better quantify the importance of CTA in the investigated system, CTA was selected as one of the variables. In addition, the influence of SDS was of interest as opposed to that of PVOH. PVOH is a polymer (weight-average molecular weight of the PVOH used in the previous study was 22000), whereas SDS is a small molecule which can easily migrate to the substrate-adhesive and/or adhesive-carrier interfaces and thus affect adhesion.(5, 17-19) From the previous screening design, we selected the run with the best PSA performance and have chosen to investigate the experimental space around those reaction conditions while accounting for the three variables of interest. A Box-Behnken design was developed: three variables were investigated at three levels ("-, 0, +" as low, medium and high level, respectively) in 12 runs. In addition, three center-point replicate runs were conducted for error analysis. The experimental design is presented in Table 1.

Kinetics and polymer microstructural properties. Similar to the two previous studies, all runs were completed above 0.99 weight fraction conversion. Due to a high

BA concentration in the reaction mixture, the observed reaction rates in all experiments were high. The analyses of the residual monomer content showed no or low levels of residual monomers in the final polymer. Particle sizes obtained in the study are shown in Figure 1.

Most of the runs exhibited narrow particle size distributions with polydispersity indices ranging from 0.1-0.4. Certain runs had considerably smaller particle sizes (i.e. runs 201, 203, 205, 207 and 209). Particles in these runs grew by approximately 60 nm over the course of the reaction. Given that the gravimetric, GC and continuous pH monitoring during these reactions did not indicate any abnormalities, it is possible that during these reactions, particle nucleation continued throughout the reaction, generating a significant number of smaller particles. Measurements were repeated on several independent specimens and the obtained results were reproducible.

Table 1 Experimental Design

Run	AA	CTA	SDS	Levels			
1	-	-	0				
2	+	-	0	AA	-	0	+
3	-	+	0		1	3	5
4	+	+	0				
5	-	0	-	CTA	-	0	+
6	+	0	-		0.05	0.425	0.8
7	-	0	+				
8	+	0	+	SDS	-	0	+
9	0	-	-		4	6	8
10	0	+	-	All amounts are wt.% based on total BA/VAc monomer.			
11	0	-	+				
12	0	+	+				
13	0	0	0				
14	0	0	0				
15	0	0	0				

Glass transition temperature is one of the most significant factors affecting the performance of PSAs. PSAs are low T_g polymers that must be able to flow and wet the surface of the substrate at the application temperature to enable the formation of the adhesive bond. T_g's obtained under investigated experimental conditions are reported in

Figure 2. Given that all runs had a high BA content, the observed glass transitions in the range between -38 to -49°C were not unexpected.

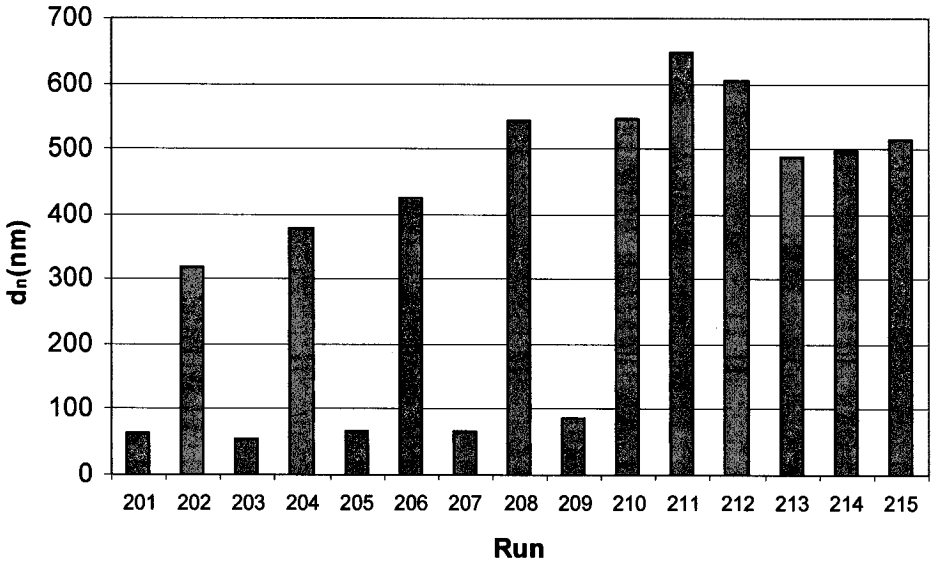

Figure 1 Series 200: Average particle sizes

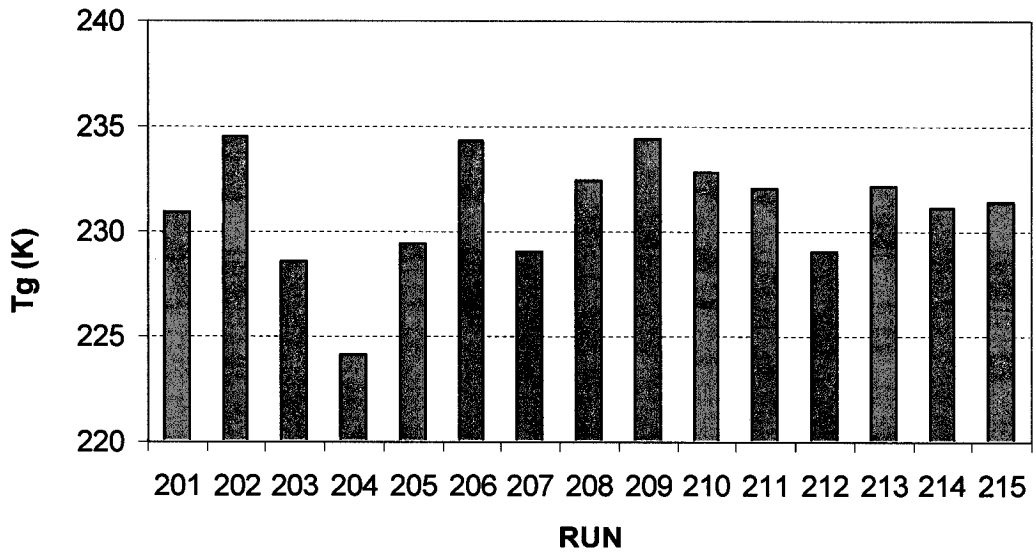

Figure 2 Glass transition temperatures

The observed changes in T_g are mainly due to changes in the amounts of AA and SDS in the recipe as shown by an empirical model (Equation 1). A negative synergistic

effect of AA and CTA was also observed. Although there was no trend in the residuals and no significant lack of fit (P-value 0.068), the model was able to predict only 71.9% of the variability in the data. In the model, standard errors are reported along with the parameters.

$$\text{Predicted value } (T_g) = (230 \pm 2.605) + (3.51 \pm 1.359)(AA) - (0.531 \pm 0.3061)(SDS) - (0.360 \pm 0.2441)(AA^2) - (2.07 \pm 0.4922)(AA)(CTA) \quad (1)$$

This is consistent with the results of the previously reported study on the effect of different monomers on the Tg of the BA/VAc/AA system. The amount of AA was the most significant variable affecting the T_g among the three monomers.(14)

Having a low T_g and being able to flow at the application temperature are not the only requirements for PSAs. In most cases, PSAs have to be removed without leaving residues on the surface of the substrate. In other words, the failure mode of the PSA is of extreme importance. While greater flexibility of the chains favours the flow and wetting of the substrate, at the same time it limits the clean removal of the adhesive from the substrate. In the later case, it is necessary to form a network structure to limit the free movement of the chains and thus, increase the cohesive strength of the PSAs. Thus, in this study, we have determined the gel content of the final polymer samples. These results are presented in Figure 3.

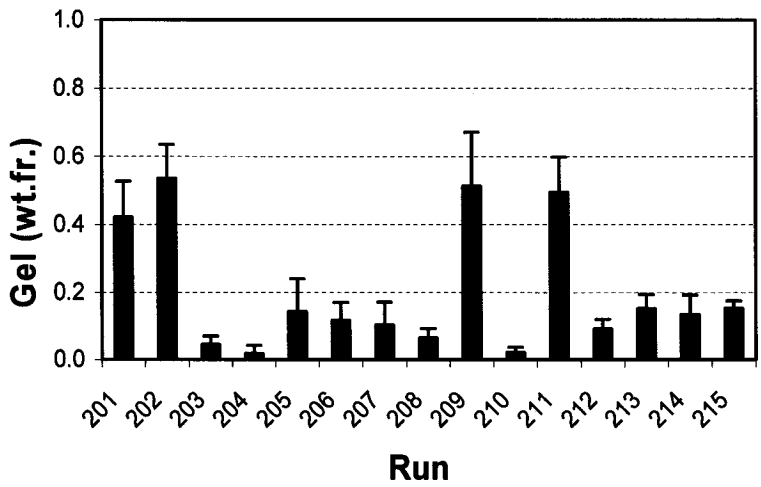

Figure 3 Gel content

In all samples a certain amount of gel was observed. This can be attributed to a relatively high BA content in all recipes. It is known that the gel in BA polymerizations is a result of chain transfer to polymer and subsequent propagation to double bonds and/or termination by combination.(20) An empirical model (Equation 2) was developed using MINITAB®. The standard errors are reported along with the parameters. The model was able to predict 97.3% (adjusted R^2) of the variability in the data.

$$\begin{aligned}\text{GelContent} = {} & (0.440 \pm 0.0448) + (0.0682 \pm 0.0254)\,(\text{AA}) - (1.30 \pm 0.1151)\,(\text{CTA}) - \\ & (0.0079 \pm 0.0039)\,(\text{AA})^2 + (0.9940 \pm 0.1107)\,(\text{CTA})^2 \\ & -(0.0473 \pm 0.0200)\,(\text{AA})(\text{CTA}) \end{aligned} \quad (2)$$

Equation 2 shows that the amount of CTA has the greatest (and negative) influence on the gel content. This can be explained by the high amount of radical transfer to CTA that generates shorter chains, which do not contribute to network formation. On the other hand, the presence of AA positively affected gel formation. The amount of SDS was not found to influence the gel content. A small yet significant effect of the binary combination of AA and CTA was found. The effect on gel content is negative, which suggests the dominance of CTA in this binary term. The observed gel content at the lower CTA content was similar to the levels observed in other studies. For example, Plessis et al. (21) investigated seeded BA/AA emulsion polymerizations and found that the gel content varied from 55-0% when CTA was changed from 0-0.15% based on total monomer.

A cautionary note should be also made on the method of gel content determination. Used in several studies as the preferred method compared to solvent extraction (7-9), the gel partitioning method has advantages such as no likelihood of additional cross-linking in the samples due to the increased temperatures which are usually employed in solvent extraction, higher safety compared to the solvent extraction method and less time consumption. However, in our experience, the error in measurement can be considerably high, despite our precautions and consistency in the procedure. The recommendation concerning this method is that at least several replicates should be run simultaneously to ensure accuracy of the results.

The determination of the molecular weights of the sol fractions was attempted but the molecular weights were extremely high and beyond the operating capacity of the GPC.

Adhesive properties. The final adhesive performance of the obtained polymers was measured on two different substrates: SS and HDPE. The adhesive performance was investigated at two different thicknesses 30 and 70 μm. In all figures and text, the combinations of substrate and thicknesses are denoted using the following notation: e.g. SS30 denotes a test conducted on stainless steel substrate where the adhesive thickness on the carrier was 30 μm. Three major PSA performance indicators were determined: loop tack, peel and shear strength.

For the determination of all final adhesive performances including loop tack, two films were cast from each final latex in order to obtain the number of specimens per test recommended by PSTC standards. The first step in the result analyses was to test for run-to-run and film-to-film differences using a hierarchical analysis of variance test. The tests were preformed using MINITAB® software.

Table 2 Fully Nested ANOVA for LT_SS70

	Source	DF	SS	MS	F	P
Fully Nested ANOVA	**Run**	14	20.4796	1.4628	155.797	0.000
	Film	15	0.1408	0.0094	0.490	0.936
	Error	60	1.1487	0.0191		
	Total	89	21.7692			
	Source	**Variance Component**		**% of Total**		**St. Deviation**
Variance Components	**Run**	0.242		92.68		0.492
	Film	0.003		0.00		0.000
	Error	0.019		7.32		0.138
	Total	0.261		0.511		

DF=degrees of freedom, SS=Sum of Squares, MS=Mean Square

For all four series of tests, there were significant run-to-run differences and no film-to-film differences. The major component that contributed to the total variation was run-to-run variation. An example of a fully nested ANOVA is presented in Table 2. Similar results were obtained for the other three substrate/thickness combinations. Thus,

in all subsequent model developments and calculations, an average of six measurements was used.

Loop tack results for both substrates and thicknesses are shown in Figure 4.

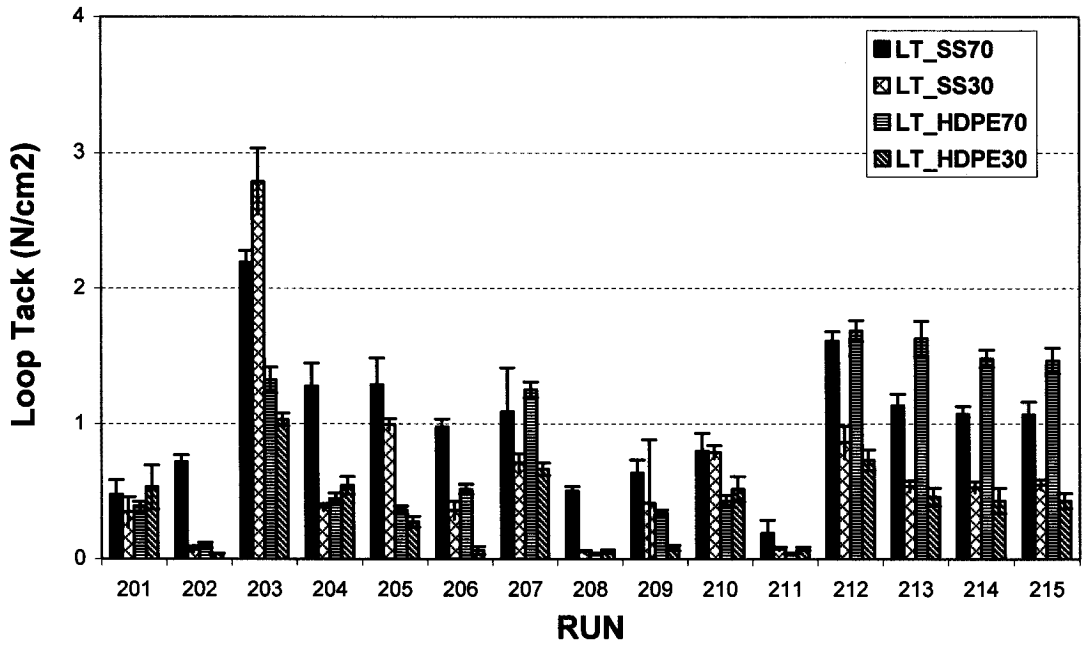

Figure 4 Loop tack

In almost all cases, the loop tack for the SS70 runs was the highest followed by SS30 and HDPE70 and HDPE30. This is not unexpected since SS is a high-energy substrate that favours adhesion, while HDPE is a low-energy substrate that does not. Nonetheless, the loop tack in runs 212 to 215 was higher for HDPE70 measurements even when compared to SS70 measurements. It is known that acrylic-based adhesives can show good adhesion to even low-energy substrates (22). The results for runs 213-215 are replicates of the same experimental conditions. The commonality with run 212 is the medium level of AA used. In all cases, the amount of CTA and SDS was either high or medium for both variables. All runs showed similar particle size distributions, T_g values (approx. -43°C) and gel contents (between 8-15%). Thus, it might be speculated that the ratio of CTA and SDS might be of interest for future investigation. For SS measurements the performance was better when the adhesive thickness was higher (70 μm) except for

run 203. This particular run might be an outlier. Run 203 also exhibited the highest loop tack under SS30, SS70, HDPE30 measurement conditions. Its T_g (-44.6°C) value was the second lowest observed and its gel content among the lowest (2.4%). Similar to SS, the overall loop tack performance on HDPE substrate was better when a thicker adhesive film was used. In all cases, the observed mode of failure was adhesive, which enabled the subsequent modeling. Model discrimination was based on trends in residuals, lack of fit, significance of parameter estimates as well as adjusted R^2 values. There was no single model found to predict all responses. The loop tack models are presented in Table 3. The standard errors for the parameters are not included in order to to shorten the expressions. In some cases, although not significant, some parameters were included in a model to preserve the model hierarchy. These cases are clearly marked. While there was no single model to fit all measurement conditions, there was a certain similarity between the models governing loop tack on SS and HDPE substrates regardless of the thickness.

In general, the models of loop tack on SS substrate were less accurate compared to that for HDPE. In both cases, LT_SS70 and LT_SS30 models displayed lack of fit at α=0.05. In addition, for LT_SS30 all models showed lack of fit even at α=0.01 unless two observations (202 and 203) were removed from the set. Upon removal of these observations, the LT_SS30 model showed fit only at α=0.01. However, LT_HDPE models showed no lack of fit at α=0.05 and were able to predict over 90% of the variation in the data.

In all cases, the major factors affecting loop tack were found to be SDS and AA concentrations. The CTA concentration did not affect loop tack. It might be speculated that under these conditions, the contribution to tackiness mainly comes from the adhesive composition (high BA content) while CTA only indirectly influenced the loop tack by influencing the gel content rather than the molecular weight of the sol. A positive synergistic effect of CTA and SDS was observed on both substrates and for both thicknesses. It is not surprising that SDS, either as a linear or quadratic term, plays a significant role in the determination of the loop tack. As a small molecule, it is possible for SDS to migrate to the interfaces and affect adhesion. (5, 17-19)

In the LT_SS70 model, the most influential factors were the AA-SDS and CTA-SDS interaction terms rather than the linear or quadratic terms. In the LT_SS30 a reduced quadratic model was found to provide the best fit to the data at α=0.01.

Table 3 Loop Tack Models

Empirical Model LT_SS70: **$LT\_SS70 = -0.611 - 0.282\ (AA)(SDS) + 0.359\ (CTA)(SDS)$**			
Adjusted R^2	Regression p-value	Lack of fit p-value	Observations removed
86.7%	0.000	0.038	-
Empirical Model LT_SS30: **$LT\_SS30 = 1.19 - 0.137\ (SDS) - 0.0155\ (AA)^2 - 0.135\ (AA)(SDS) + 0.196\ (CTA)(SDS)$**			
Adjusted R^2	Regression p-value	Lack of fit p-value	Observations removed
94.7%	0.000	0.017	202, 203
Empirical Model LT_HDPE70: **$LT\_HDPE70 = -4.91 - 1.15\ (AA) + 1.48\ (SDS) - 0.129\ (AA)^2 - 2.89\ (CTA)^2 - 0.115\ (SDS)^2 - 0.0853\ (AA)(SDS) + 0.574\ (CTA)(SDS)$**			
Adjusted R^2	Regression p-value	Lack of fit p-value	Observations removed
93.4%	0.000	0.210	-
Empirical Model LT_HDPE30: **$LT\_HDPE30 = -1.53 + 0.628\ (AA) - 0.00349\ (AA)^{2*} + 0.531\ (CTA)^2 - 0.0452\ (SDS)^2 - 0.0224\ (AA)(SDS) + 0.0431\ (CTA)(SDS)$**			
Adjusted R^2	Regression p-value	Lack of fit p-value	Observations removed
98.2%	0.000	0.132	-

* Denotes a parameter that is included in the model only to preserve model hierarchy. Significance $p<0.05$

The best fits for the LT_HDPE70 and LT_HDPE30 models were also of the reduced quadratic form. Here, all three quadratic terms were found to be significant in both models apart from AA in LT_HDPE30. This factor was not significant but it was retained only to maintain model hierarchy (i.e. to retain all three quadratic terms).

Similar to loop tack, the peel strength modeling required testing of run-to-run and film-to-film differences. An example of such results is presented in Table 4 for Peel_SS70. The contribution of film-to-film variation to the total variation was negligible. Similar results were obtained for the other three measurement conditions. Once it was established that there were no film-to-film differences, six measurements

were averaged for use in the analyses of the results. The results for both substrates and adhesive thicknesses are presented in Figure 5.

Table 4 Fully Nested ANOVA for Peel_SS70

	Source	DF	SS	MS	F	P
Fully Nested ANOVA	Run	14	224.7899	16.0564	261.442	0.000
	Film	15	0.9212	0.0614	0.493	0.935
	Error	60	7.4719	0.1245		
	Total	89	233.1830			
	Source	Variance Component		% of Total	Standard Deviation	
Variance Components	Run	2.666		95.54	1.633	
	Film	-0.021		0.00	0.000	
	Error	0.125		4.46	0.353	
	Total	2.790		1.670		

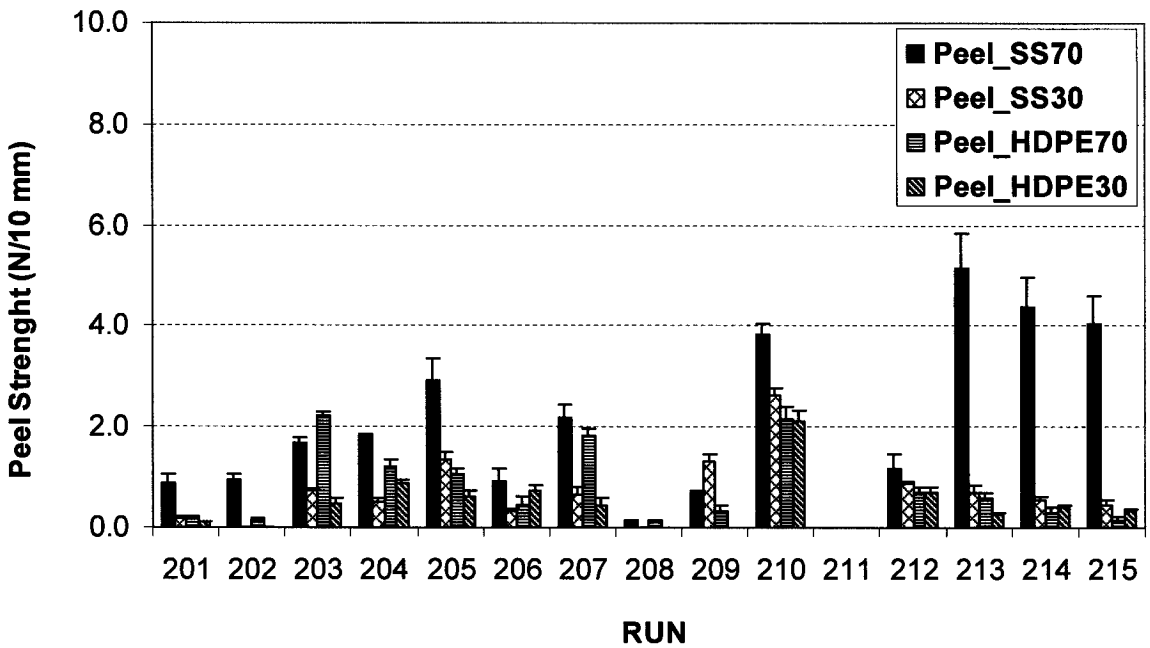

Figure 5 Peel strength results

In general, moderate or low peel results were obtained in this study. The best performance was observed for the SS substrate when the adhesive thickness was 70μm. It is known that the peel strength increases and displays a plateau as the adhesive thickness increases.(22) Run 210 exhibited an interesting balanced behaviour for both substrates and thicknesses. This run had a high level of CTA and moderate AA levels, which resulted in a moderate T_g and that enabled the bonding to the substrate. A low gel content ensured enough cohesive strength so that the adhesive could be removed from the surface of the substrate with no residues. Run 211 showed no peel strength. Given that this run had the same polymer composition as run 210 and a similar T_g value, the most likely reason for the lack of peel strength is the amount of SDS used in this particular recepie. The amount of SDS in run 211 was two times that used in run 210.

Table 5 Peel Strength Models

Empirical Model Peel_SS70: **Peel_SS70 =** **$-12.4 + 2.05\,(AA) + 12.0\,(CTA) + 4.05\,(SDS) - 0.383\,(AA)^2 - 11.7(CTA)^2 - 0.362\,(SDS)^2$**			
Adjusted R^2 75.6%	Regression p-value 0.005	Lack of fit p-value 0.320	Observations removed -
Empirical Model Peel_SS30: **Peel_SS30 =** **$5.32 + 0.493\,(AA)^* - 1.59\,(SDS) - 0.104\,(AA)^2 + 1.28\,(CTA)^2 + 0.111\,(SDS)^2$**			
Adjusted R^2 76.5%	Regression p-value 0.002	Lack of fit p-value 0.114	Observations removed -
Empirical Model Peel_HDPE70: **Peel_HDPE70 = 1.13 - 0.213 (AA) + 1.87 (CTA) - 0.0877 (SDS)***			
Adjusted R^2 61.3%	Regression p-value 0.003	Lack of fit p-value 0.158	Observations removed -
Empirical Model Peel_HDPE30: **Peel_HDPE30 = 0.761 - 0.0038 (AA) + 1.36 (CTA) - 0.143 (SDS)**			
Adjusted R^2 58.1%	Regression p-value 0.005	Lack of fit p-value 0.038	Observations removed -

* Denotes a parameter that is included in the model only to preserve model hierarchy. Significance $p<0.05$

As was the case for loop tack, modeling was possible because all runs exhibited the same type of failure: adhesive failure. No model was found to fit all responses, however, in this case, modeling of the peel strength on SS substrate was more accurate

compared to modeling on the HDPE substrate. This is possibly due to the fact that most runs exhibited very low peel strength on the HDPE substrate.

Models (Table 5) developed for the SS substrate were able to describe approximately 76% of the variation in the data, while models for the HDPE substrate were able to describe only ~50% of the variation. In addition, HDPE30 displayed significant lack of fit at α=0.05. Both peel models for HDPE substrate were linear in all parameters. Inclusion of other parameters such as second order interactions or quadratic terms, further decreased adjusted R^2 values and led to model inadequacy. It is likely that the peel strength on the low-energy HDPE substrates requires a larger data set for improved model predictions. On the other hand, models for the SS substrate were better able to predict the variation in the data set. Both models were reduced quadratic models. All three quadratic parameters were significant whereas the interaction parameters were not for both models. CTA was found to be the most influential parameter affecting the peel strength. However, the dependence was not linear. Addition of AA positively affected peel strength but again the nature of the influence was not linear in both SS cases. The significance of the SDS terms indicates that during the synthesis, particular attention should be devoted to its level and possibly that of other low molecular components (e.g. initiator, buffers etc). It is advisable to replace SDS with other polymeric or reactive stabilizers to minimize this migration. (11)

A similar procedure was used to analyze the results for shear strength. A fully nested ANOVA was used to test for film-to-film differences (Table 6) and after establishment of the fact that there were none, further modeling was performed.

The shear strengths of the adhesives obtained in this study are shown in Table 7. The adhesives exhibited a wide range of shear strengths on both substrates and both thicknesses. Apart from a few runs, the shear strength was measured on the order of minutes rather than hours. Higher shear strength values for both substrates and adhesive thicknesses were observed for runs 201, 202, 209 and 211. When these runs were compared, all, apart from run 203, exhibited relatively higher T_g values (approximately -38°C). It has to be emphasized that the range of the observed T_gs was not very wide. In terms of gel content, these four runs contained significantly larger amounts of gel (approximately 50%) compared to all other runs (approximately 10%).

Table 6 Fully Nested ANOVA for Shear_SS30

	Source	DF	SS	MS	F	P
Fully Nested ANOVA	Run	14	72462221.22	5175872.94	1351.570	0.000
	Film	15	57442.91	3829.52	1.178	0.313
	Error	60	195069.54	3251.15		
	Total	89	72714733.67			

	Source	Variance Component	% of Total	Standard Deviation
Variance Components	**Run**	862007.236	99.60	928.443
	Film	192.789	0.02	13.885
	Error	3251.159	0.38	57.019
	Total	865451.185	930.296	

Table 7 Shear Strength

RUN	Shear_SS70		Shear_SS30		Shear_HDPE70		Shear_HDPE30	
	Average	*St.Dev.*	*Average*	*St.Dev.*	*Average*	*St.Dev.*	*Average*	*St.Dev.*
201	14.2	0.7	27.4	1.4	261.8	54.5	10.5	4.8
202	134.6	17.8	9.9	0.6	2.9	0.6	1.6	0.1
203	9.1	1.0	0.2	0.2	0.2	0.1	0.0	0.0
204	0.2	0.0	3.9	0.3	0.5	0.0	0.6	0.1
205	1.3	0.2	1.5	0.1	4.9	0.8	1.3	0.2
206	8.4	1.2	5.4	0.2	8.2	0.6	3.2	0.2
207	0.8	0.1	0.6	0.1	0.6	0.1	0.8	0.2
208	1.0	0.1	1.1	0.1	2.6	0.3	0.6	0.3
209	799.4	77.6	3602.9	224.7	956.8	260.4	1063.5	132.7
210	2.7	1.0	0.6	0.1	0.3	0.0	0.4	0.1
211	35.9	4.2	20.2	8.9	1339.6	159.6	105.4	24.7
212	5.1	0.1	1.0	1.2	0.4	0.1	0.5	0.1
213	1.1	0.1	3.0	0.7	2.4	0.4	1.5	0.3
214	1.1	1.0	1.7	0.9	2.2	0.5	1.5	0.1
215	1.2	0.1	2.7	0.8	2.7	0.4	1.6	0.1

The development of empirical models for shear strength on the SS substrate was more complicated compared to that for the HDPE substrate (Table 8). At first, no model was found to fit the data even at α=0.01. In all cases, the highest observed values were regarded as outliers and worsened the fit. Upon removal of runs 202 and 209 for Shear_SS70 and run 202 for Shear_SS30, modeling was possible. In both cases, the models were able to describe approximately 90% of the variability in the reduced data sets. Both exhibited no lack of fit at α=0.01. In both models for the SS substrate, the most important variable affecting shear strength was the amount of CTA. The significance of

quadratic terms indicates that the influence of CTA on shear strength is not linear in nature. The amount of AA and the synergistic effect of CTA and AA were also found to be significant in both cases. Finding that CTA and AA are the most significant factors affecting the shear strength is not surprising given the influence of these reaction variables on the development of gel content, which in turn governs the cohesive strength of the adhesive.

Table 8 Shear Models

Empirical Model Shear_SS70: **Shear_SS70 = 15.5 + 7.72 (AA) - 93.4 (CTA) - 0.014 $(AA)^2$ - $(114\ CTA)^2$ - 13.5 (AA)(CTA)**			
Adjusted R^2 87.0%	Regression p-value 0.001	Lack of fit p-value 0.068	Observations removed 202, 209
Empirical Model Shear_SS30: **Shear_SS30 = 35.9 - 3.67 (AA) - 102 (CTA) + 63.4 $(CTA)^2$ + 7.14 (AA)(CTA)**			
Adjusted R^2 90.4%	Regression p-value 0.000	Lack of fit p-value 0.049	Observations removed 209
Empirical Model Shear_HDPE70: **Shear_HDPE70 = 1053 - 61.5 (AA) - 3408 (CTA) + 2548 $(CTA)^2$ - 103 (AA)(CTA)**			
Adjusted R^2 99.7%	Regression p-value 0.000	Lack of fit p-value 0.045	Observations removed -
Empirical Model Shear_HDPE30: **Shear_HDPE30_1 = 12.4 - 1.88 (AA) - 28.2(CTA) + 12.4 $(CTA)^2$ + 3.56 (AA)(CTA)**			
Adjusted R^2 74.7%	Regression p-value 0.003	Lack of fit p-value 0.059	Observations removed -

Regardless of the substrates or thicknesses, empirical models developed for shear strength were most similar in terms of the significant parameters compared to the other models developed for peel strength or loop tack. For peel strength and loop tack, similarity in the significant parameters existed only between the models developed for similar substrates. For shear strength, the performance on SS and HDPE substrate was dependent only on AA and CTA variables, and their linear, quadratic or synergistic effects. The most dominant factor was the amount of CTA.

5.5 CONCLUSIONS

A Box-Behnken experimental design was used to investigate the influence of AA, CTA and SDS on the adhesive properties of BA/VAc emulsion-based PSAs. Indications fromscreening design experiments were that these might be the most influential variables when all other factors were kept constant.

Reaction kinetics in all cases were fast given the high BA content in all runs. Conversion vs. time data showed, in most cases, completion to over 99%. The solid content of the latexes was 50%. In most cases, no residual monomer was detected using GC. The ranges of the particle sizes were between approximately 100 to well above 500 nm.

A wide range of gel contents was observed from 50% for runs with 0.05% CTA to 2% for runs with 0.08% CTA based on total monomer. However, a large standard deviation was observed for these measurements.

An empirical model has shown that the most influential variable affecting T_g was the amount of AA. Adhesive performance in the form of loop tack, peel and shear strengths was investigated on two different substrates using two different adhesive thicknesses. In all cases, it was necessary to conduct a fully nested ANOVA analysis to investigate the significance of film-to-film variation, due to the fact that the required number of samples was not possible to obtain by using one film alone. In all cases, there were no statistically significant differences between the films. Therefore, the average of six runs was used for model building. In general, for all three properties, different models were found to fit the data. Another general trend was the similarity of the models developed for different thicknesses on the same substrate. The exception was the shear strength where all four models were similar regardless of the substrate or thickness of the adhesive film. For the loop tack models, AA and SDS main effects as well as AA-SDS and CTA-SDS two-factor interactions were found to be significant factors. Given the nature of SDS as a small molecule, it is expected that its migration to the adhesive-substrate interface can affect the properties measured in short times such as loop tack.

Peel strength models developed for SS substrates were quadratic models with a noticeable absence of interaction parameters. While the only models found to fit the data

obtained on HDPE substrates were linear, they were able to explain only 60% of the variation in the data. These results suggest that larger data sets be used.

The empirical models developed for shear strength showed the highest consistency between different substrates and adhesive thicknesses. The dominant factor among the three investigated factors is the amount of CTA. Given its influence on gel formation, it is necessary to adjust the amount of CTA during the reaction stage to obtain the desired shear strength performance.

In general, in all models, the CTA was present as a variable, which indicates the importance of this parameter in tailoring the properties of the PSAs. In addition to the polymer composition, which was previously found to be a dominant factor, this is probably the second biggest variable affecting the properties of the final performance characteristics of BA/VAc emulsion-based adhesives.

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Chapter 6

Jovanović R., Dubé M.A.
Butyl Acrylate/Vinyl Acetate Miniemulsion Polymerization: A Study on Compartmentalization
Macromolular Chemistry and Physics
205: 258-265 (2004)

6.2 INTRODUCTION

Various free radical and non-radical polymerizations can be performed in miniemulsion.[1] Miniemulsion polymerization offers unique challenges as well as possibilities compared to conventional emulsion polymerization. Kinetics and applications of miniemulsion polymerization have been investigated intensively over several decades and have been recently reviewed by several authors.[1-4] Conceptual and kinetic investigations of miniemulsion polymerization once dominated the research in the field, but today, concerns about the production of high solids contents latexes with low viscosity [5-7] or the design of hybrid particles involving encapsulation of various compounds (e.g. pigments,[8] liquids [9] or polymers[10]) or the surface coating of particles[11] are of increasing interest.

Wu and Schork[12] compared conventional and miniemulsion polymerizations of BA/VAc, among other systems, and concluded that the rate of polymerization in all cases was higher for conventional emulsion. More BA was incorporated into the copolymer throughout the reaction in conventional emulsion compared to the miniemulsion case. In a series of studies by Delgado et al.[13-16], it was found that the rate of polymerization in miniemulsion showed greater dependence on the initiator concentration compared to conventional emulsion polymerizations. Also, the number of particles showed an almost linear dependence on initiator concentration, whereas for conventional emulsion polymerizations, no dependence was observed.

The occurrence of mass transfer between particles in a miniemulsion polymerization appears to be a point of controversy and highly system dependent. Ideally, once monomer droplets are formed and nucleated, no monomer transfer occurs between the polymer particles.[17] On the other hand, Rodriguez et al.[18] concluded that during the emulsion polymerization of BA/Sty/2-ethylhexyl acrylate, monomer transfer does occur. This behaviour seemed to stem from the fact that not all monomer droplets were nucleated, and those non-nucleated droplets became monomer reservoirs similar to their role in conventional emulsion polymerizations.[2,18] Delgado et al.[15] developed a mathematical model for monomer transport and applied it to a BA/VAc 50/50 mol/mol miniemulsion polymerization. In addition, the type and concentration of hydrophobe used

can affect monomer transfer as Rodriguez et. al[18] showed for the Sty/MMA system. When comparing BA/VAc conventional and miniemulsion polymerization, Wu and Shork[12] concluded that the rate of polymerization for the conventional case is always higher than that observed in miniemulsions due to the retardation effect of the hydrophobe on monomer transfer from the non-nucleated droplets to the polymer particles. They concluded that monomer transfer does occur but is not as significant as in conventional emulsions, especially for highly water-insoluble monomers. Similarly, Landfester et al.[17] have shown that in the miniemulsion polymerization of styrene, the final particle size and distribution are identical to the initial monomer droplet size and distribution, indicating that no mass transfer occurs. The determination of the monomer droplet size and distribution could be a challenge due to the fact that most of the techniques require dilution, which could lead to a change in the size of the droplets. Ouzineb et al.[19] investigated monomer transfer that involved the preparation of Sty/butyl methacrylate (BMA) miniemulsions and blends of miniemulsions of Sty and BMA. Using differential scanning calorimetry and attenuated total reflectance - Fourier transform infrared spectroscopy they showed that no significant mass transfer occurred between the particles.

One can consider the monomer droplets in a miniemulsion polymerization to be small independently operating nanoreactors.[1] This implies that miniemulsions could be extremely useful for a variety of applications where one can use particles as "particular property carriers." For example, one particle population can "carry" high molecular weights that govern shear strength in an adhesive application, while the other can "carry" low molecular weights that improve tack. Thus, the appropriate balance of particle "property carriers" could render a product with a balanced shear strength and tackiness, which is usually subject to a trade-off in conventional emulsion-based adhesive products.

The objective of this study was to investigate the possibility of monomer transfer during polymerization. Two procedures were used to prepare the miniemulsions. In the first procedure, monomers were mixed together, sonicated, and polymerized. In the other, each monomer was homogenized separately, and the sonicated pre-mixtures were combined in the desired ratio and polymerized. At the beginning, in the first case,

monomer droplets contained both monomers while in the second case the droplets contained either BA or VAc monomer depending on their origin.

6.3 EXPERIMENTAL PROCEDURES

Reagents. Inhibitor was removed from BA (Aldrich) and VAc (Aldrich) according to previously described procedures.[20] Other reagents (e.g. sodium dodecyl sulphate (EM Science), octadecyl methacrylate (ODMA) (Aldrich), Triton X405 (Aldrich), dodecyl mercaptan (Aldrich), ammonium persulphate (Aldrich) and solvents used for characterization such as d-chloroform , tetrahydrofuran (THF, EM Science) and methanol (ACP Chemicals) were used without further purification. Distilled-deionized water was used in all experiments.

Polymerization procedure. Preparation of the miniemulsions was performed a day prior to polymerization according to the following procedure. The aqueous phase containing water, Triton X405, and SDS was mixed using a magnetic stirrer. The monomer mixture containing dodecyl mercaptan and ODMA was prepared in a separate flask also using a magnetic stirrer. Once the components were completely dispersed, the contents of both flasks were combined and mixed for approximately 1h. A Fisher Scientific 550 sonic dismembrator at 30% power, Level 9 for 1 min was used for sonication. The mixture was simultaneously cooled in an ice bath and well mixed while undergoing sonication. For the purpose of this study, "miniemulsion" denotes a procedure where both monomers were mixed in the desired ratio and sonicated together. "Miniemulsion blend" denotes a procedure where miniemulsions of individual monomers were prepared and sonicated separately. These were mixed in the desired ratio prior to polymerization. A schematic representation of the preparation procedures is given in Figure 1. Experimental conditions are outlined in Table 1.

All reactions were performed in a 1.2L Labmax™ (Mettler Toledo) glass reactor equipped with a condenser, feed and sampling ports, and an anchor stirrer. Stirring speed (200 rpm) and temperature (60°C) were automatically controlled using Camille™

software (Mettler Toledo).

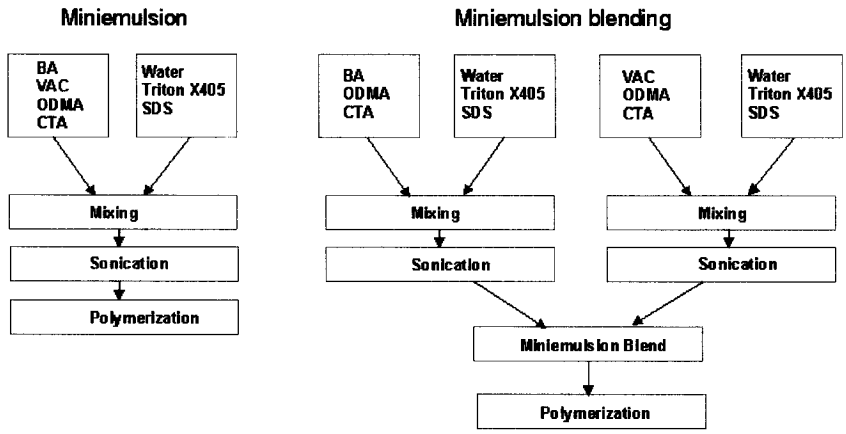

Figure 1 Miniemulsion preparation procedure

Table 1 Experimental Conditions

Notation		BA/VAc (wt/wt-%)	Other components (phm*)
Miniemulsion Blend	M1	50/50	Triton X 405: 2.68 SDS: 0.16 Initiator: 0.09 CTA: 3.00 ODMA: 1.92 Water: 151
	M2	95/5	
	M3	85/15	
	M4	65/35	
Miniemulsion	C1	50/50	
	C2	95/5	
	C3	85/15	
	C4	65/35	

* (phm - parts per hundred parts monomer)

Conversion. Conversion was followed using gravimetry and was based on total polymer.

ATR-FTIR spectroscopy. All reactions were monitored in-line using the ReactIR™ 1000 (ASI Applied Systems, Mettler Toledo), which uses Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy. This monitoring

system was prevously described in detail.[20,21] All spectra were collected using 128 scans at a resolution of $4cm^{-1}$, for an optimal signal-to-noise ratio. Reaction mixture prior to additon of the initiator was collected as a background and the collection of the reaction spectra was started simulteaneosly with the injection of the initiator.

Copolymer Composition. Cumulative copolymer compositions were determined using a Bruker AMX—500 Fourier transform ^1H—NMR spectrometer. The analyses were carried out in deuterated chloroform (~2(w/v) solution) at room temperature. The relative amounts of monomer bound into the polymer were estimated using the areas under the appropriate absorption peaks: BA (4.0 ppm) representing the $-OCH_2$ group and VAc (4.9 ppm) representing the α-hydrogen. Using areas under the peaks, the fractions of BA and VAc monomers bound into the polymer were calculated.[22]

Molecular weight. A Waters gel permeation chromatograph (GPC) equipped with a refractive index detector was used for the determination of the molecular weight distribution of the latexes. Three Waters Ultrastyragel columns (10^3, 10^4 and 10^6 Å) were used in series. THF was used as the eluent at a flow rate of 0.3 mL/min at 38°C. Polystyrene standards (SHODEX) with molecular weights between $1.3x10^3$ to $3.15x10^6$ g mol^{-1} were used for calibration. Standards and samples were prepared in THF and filtered prior to injection through 0.45 μm filters to remove high molecular weight gel, if present. The injection volume was 200 μL. Millennium32™ software (Waters) was used for data acquisition and analysis. The universal calibration method was used with Mark-Houwink constants for BA and VAc as reported in previous work.[20]

Particle size. Particle size analysis was conducted using a disc ultracentrifuge photosedimentometer, BI-DCP (Brookhaven Instruments). LIST start was used and a mixture of methanol and water was used as a gradient fluid. Latex samples were diluted prior to injection. BI-DCP software was used to analyze collected data.

Adhesive properties. Prior to coating the latex onto a carrier, particle agglomerates were removed using a size #30 mesh. Latexes were coated using a wire-rod

#30 onto a 50 μm polyethylene terephthalate carrier (Mylar®, DuPont) and dried at room temperature to give a dry film of 30 μm thickness. The films were conditioned 24h prior to testing at 23 ± 2°C and 50 ± 2% relative humidity. Stainless steel panels were used as substrates in all tests. All tests were performed according to the Test Methods for Pressure Sensitive Tapes (Pressure Sensitive Tape Council, PSTC).[23] PSTC 1, PSTC 7, and PSTC 6 standards were used for the determination of peel strength, shear strength and loop tack, respectively.

6.4 RESULTS AND DISCUSSION

Conversion. Conversion data for all miniemulsion and miniemulsion blend runs are shown in Figures 2 to 5. The lowest polymerization rate was observed for BA/VAc 50/50 wt/wt.-%. An increase in polymerization rate with BA content was observed for all reactions regardless of the miniemulsion preparation procedure used. Similar observations were found in bulk and conventional BA/VAc emulsion polymerizations.[22] This behavior was expected, given the difference in the propagation rate constants of the BA and VAc monomers and their reactivity ratios (r_{BA}=5.93, r_{VAc}=0.026).[22] Although determination of the individual rate constants for these polymer systems remains a challenge even with the pulsed laser polymerization technique, the propagation rate constants for BA and VAc have been estimated at k_p(BA) = 40400 L mol^{-1} s^{-1} and k_p(VAc) = 6600 L mol^{-1} s^{-1}, respectively, at 55°C.[24]

Conversions were also compared for each BA/VAc composition between the two different miniemulsion procedures. Apart from the BA/VAc 50/50 wt/wt run, there was no difference in the observed rates of polymerization between the two miniemulsion procedures.

Particle size. Particle sizes for all runs are shown in Figures 2-5. In all cases, broad, monomodal particle size distributions were observed. Polydispersity index for final samples were in the range from 1.10-1.45. As already discussed in the experimental section, all data were obtained using a BI-DCP disc ultracentrifuge photosedimentometer. Schneider and McKenna[25] pointed out that the determination of particle size

distributions of soft particles (i.e. polymers of low T_g) using centrifugation may cause particles to coalesce and flocculate. Although some of the particles examined in this study are "soft" particles no flocculation was observed during the measurements.

In general, no differences in particle sizes were observed between runs at the same BA/VAc ratio obtained using different preparation procedures. In an ideal compartmentalized situation, particle size would not differ from the initial size of the monomer droplets and no changes in particle size throughout the polymerization would be observed. At BA/VAc ratios of 65/35, 85/15 and 95/5 wt/wt, particle size remained almost unchanged, indicating that true miniemulsion polymerization was occurring. The BA/VAc 50/50 wt/wt run showed less of an increase: from 250 to 317 nm. That order of particle size increase has been reported in some VAc miniemulsion homopolymerizations.[26]

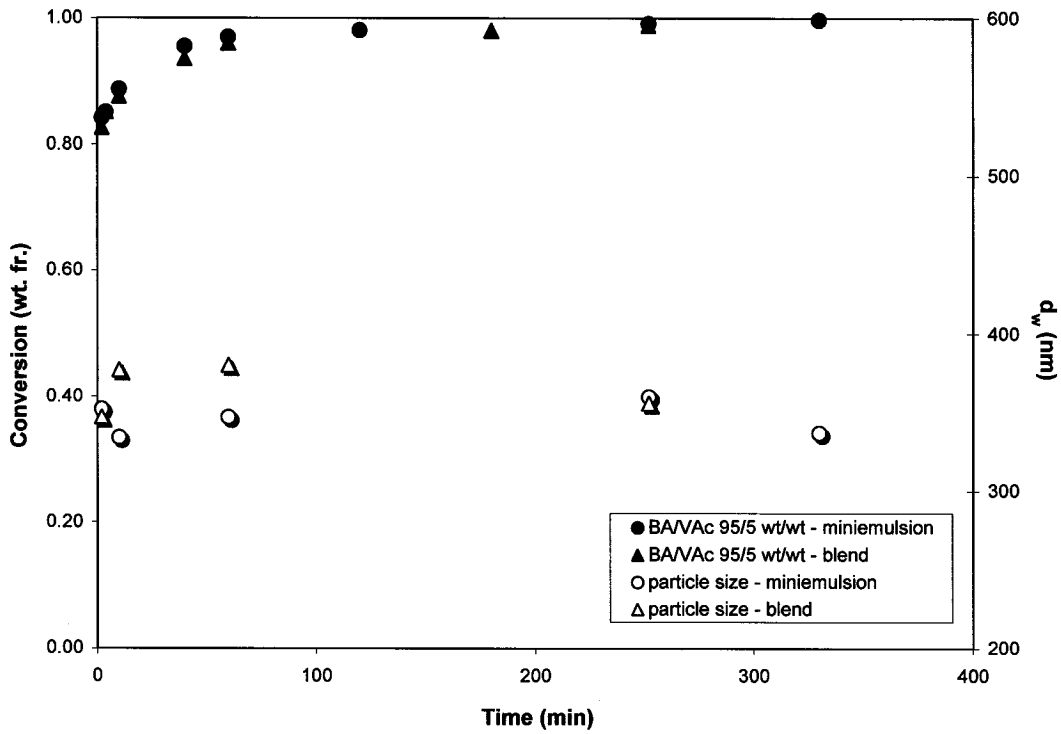

Figure 2 Conversion and particle size for BA/VAc 95/5 wt/wt runs

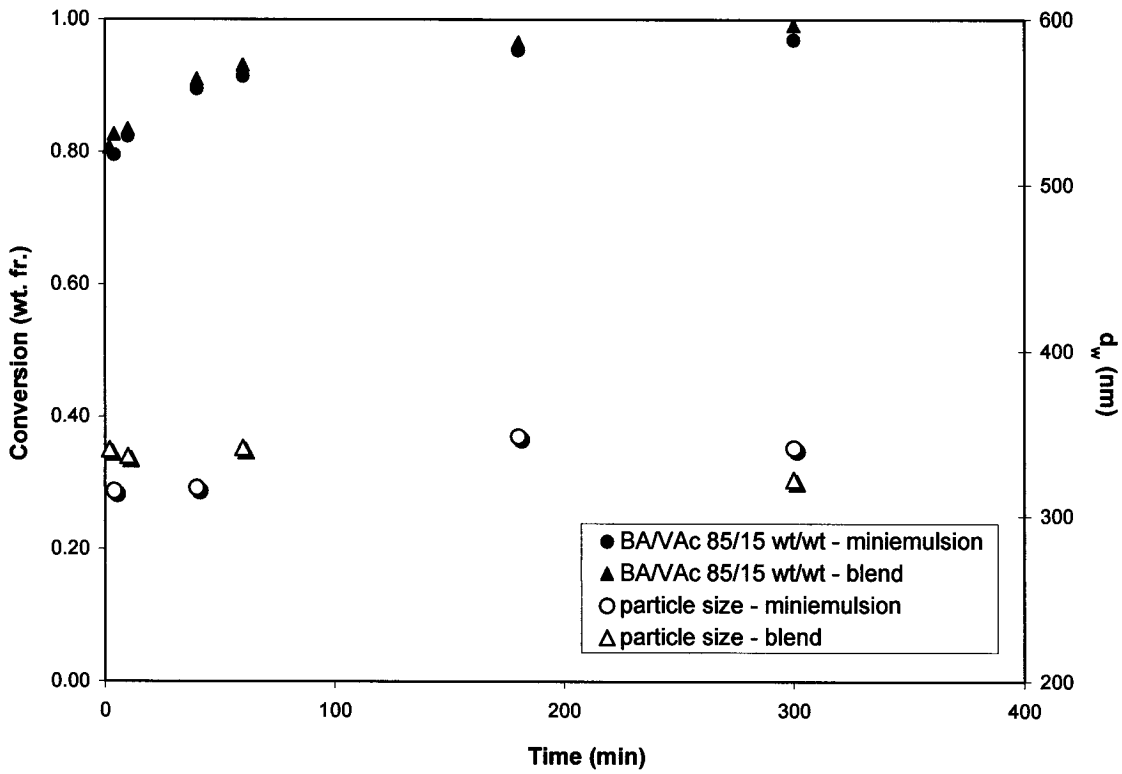

Figure 3 Conversion and particle size for BA/VAc 85/15 wt/wt runs

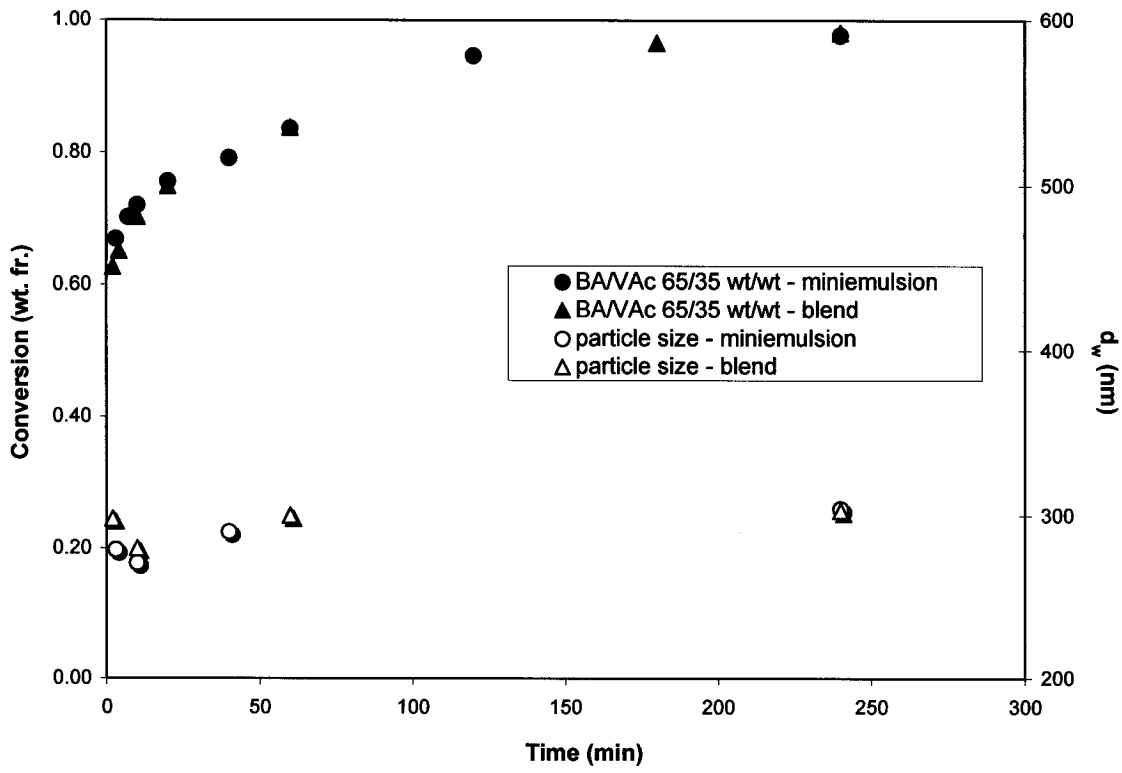

Figure 4 Conversion and particle size for BA/VAc 65/35 wt/wt runs

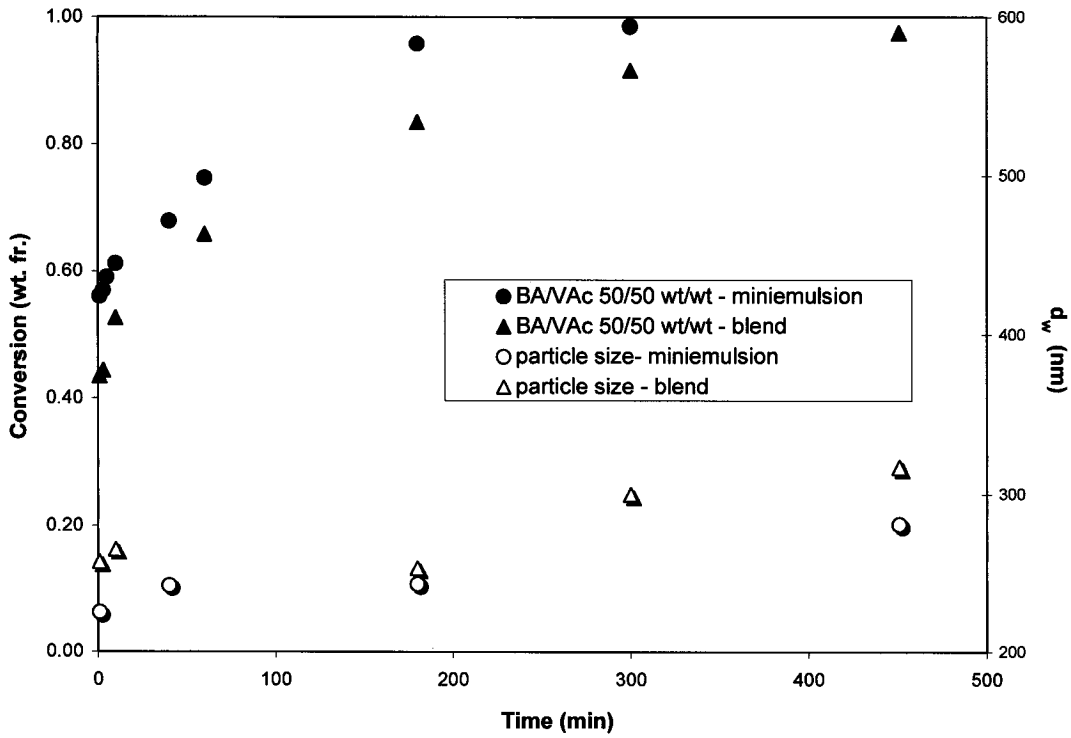

Figure 5 Conversion and particle size for BA/VAc 50/50 wt/wt runs

It can be speculated, that a portion of the droplets, especially at a BA/VAc ratio of 50/50, remained non-nucleated and served as monomer reservoirs during the polymerization. Thus, monomer transfer was likely to be occurring and the particles did not preserve their identity from the onset of reaction to completion, but rather changed with time regardless of the presence of ODMA as hydrophobe. On the other hand, one would expect mass transfer to be more pronounced in the runs where miniemulsions of the two monomers were blended due to the fact that the polymerization started from non-equilibrium. Those are the exact conditions that would favor mass transfer and thus, lead to a larger difference in particle number and size than those observed here. Less particle growth was observed with the decreased level of VAc, which correlates with the fact that VAc is the more water soluble of the two monomers, which enables easier VAc transfer through the water phase.

A means of suppressing monomer transfer is through the use of a hydrophobe. In their mathematical model for monomer transport, Delgado at al.[14] used hexadecane as a

hydrophobe and sodium hexadecyl sulfate as surfactant. The model predicted that under the given conditions and at a BA/VAc 50/50 mol/mol ratio, monomer transfer occurred. In this work, ODMA was used as a hydrophobe and a combination of anionic (SDS) and non-ionic (Triton X 405) surfactants were used. One indication from our determination of monomer transfer during miniemulsion polymerization is that for a similar BA/VAc molar ratio and our hydrophobe/surfactants combination, monomer transfer also occurs.

Copolymer Composition. Cumulative copolymer compositions for all runs are shown in Figures 6-9. In all figures, solid lines are trend-lines and not model predictions. The drifts in the cumulative copolymer compositions were typical for batch polymerization of monomers of different radical reactivity ratios (i.e. r_{BA}=5.93, r_{VAc}=0.026[22]). The smallest drift was observed for BA/VAc 95/5 wt/wt whereas, in all other cases, BA was consumed at a much faster rate compared to VAc. As the reaction proceeded, the cumulative copolymer composition approached the composition of the initial monomer feed.

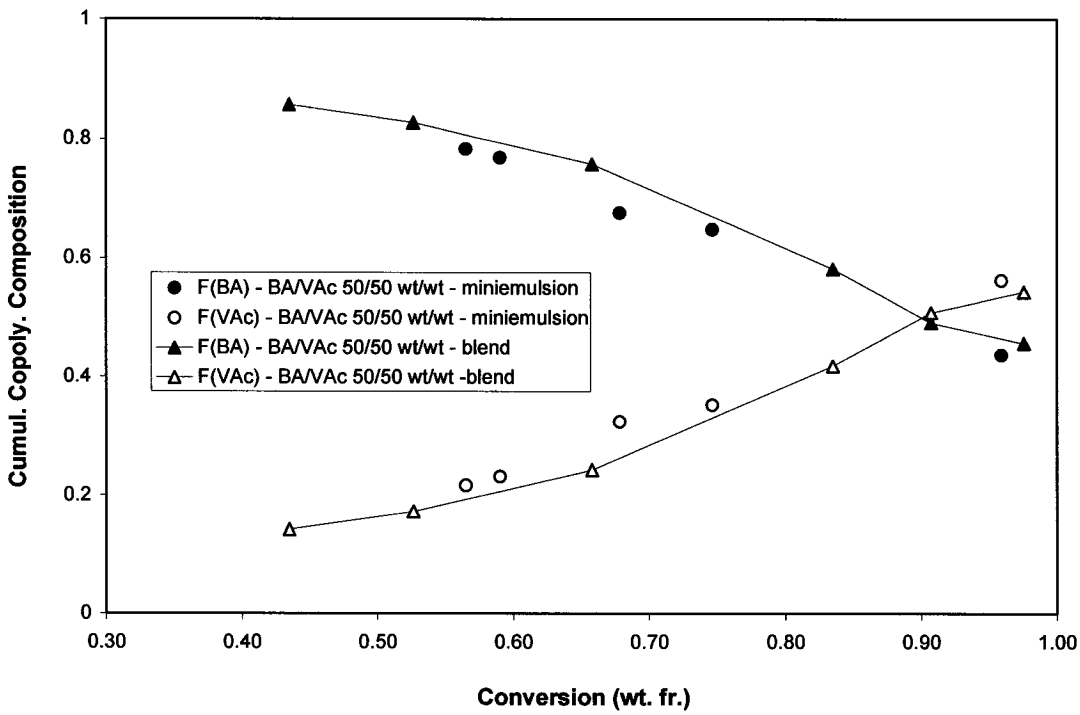

Figure 6 Cumulative copolymer composition: BA/VAc 50/50 wt/wt runs

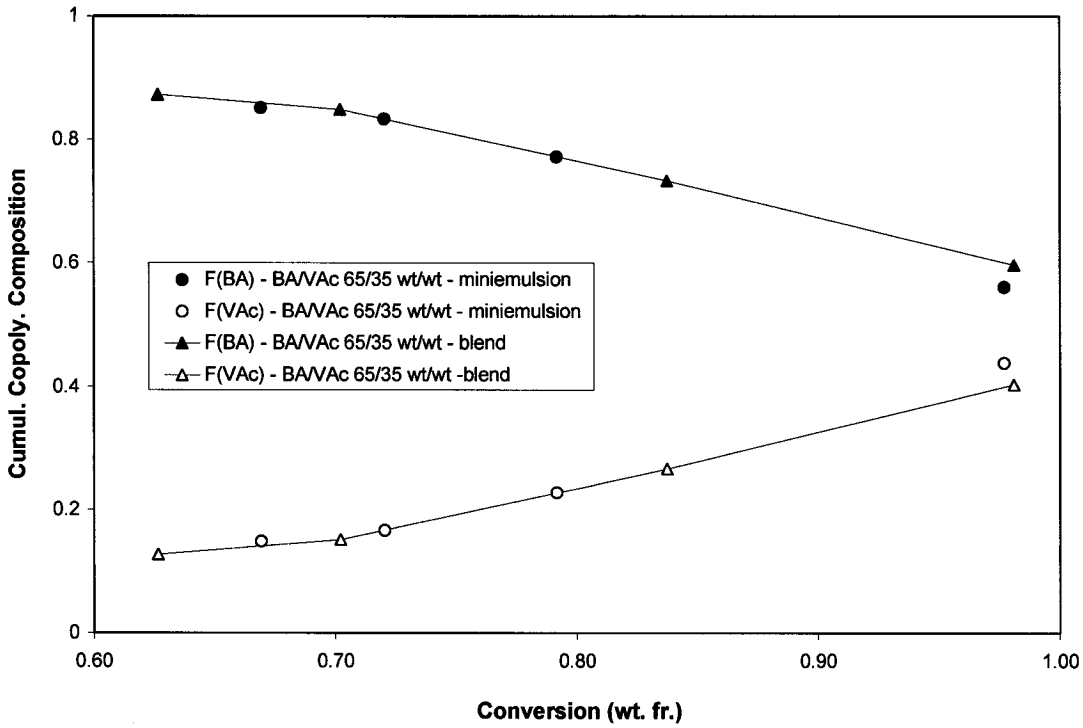

Figure 7 Cumulative copolymer composition: BA/VAc 65/35 wt/wt runs

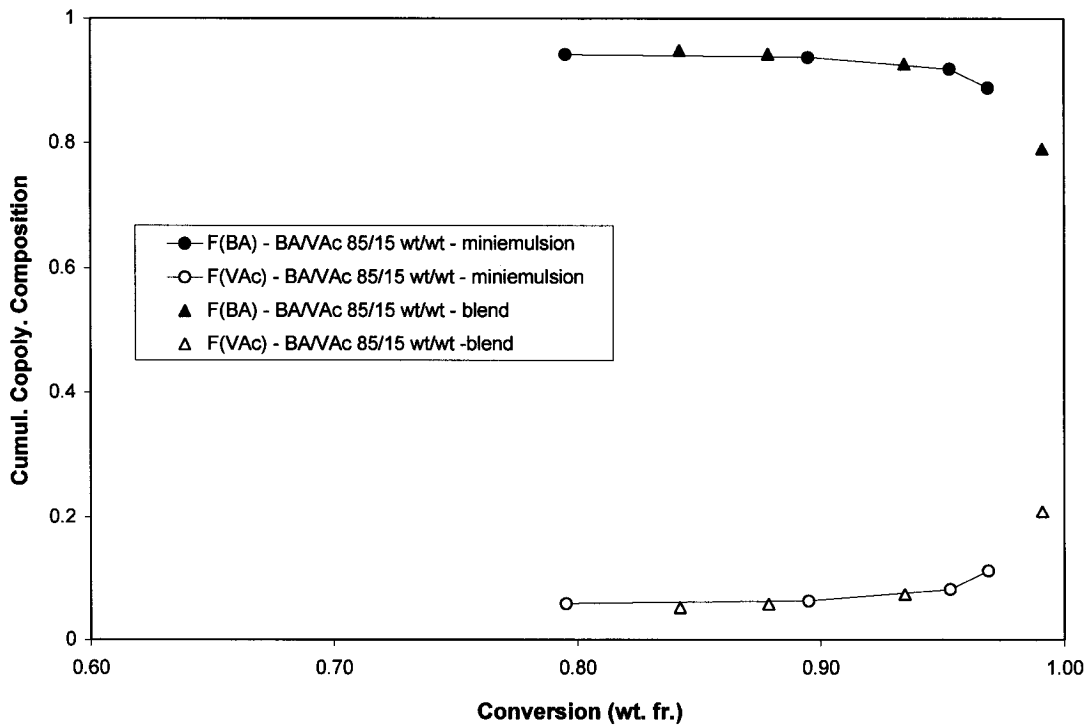

Figure 8 Cumulative copolymer composition: BA/VAc 85/15 wt/wt runs

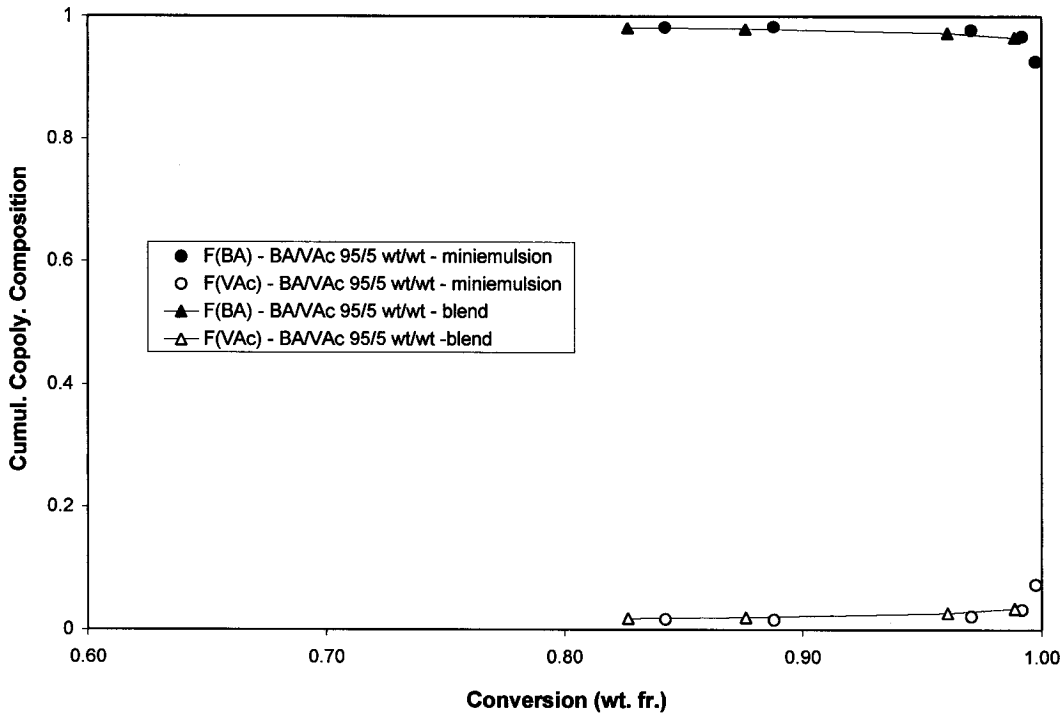

Figure 9 Cumulative copolymer composition: BA/VAc 95/5 wt/wt runs

There were no differences between runs when comparing the different miniemulsion preparation procedures. According to model predictions by Delgado et al.[14] BA/VAc copolymer composition is quite insensitive to the value of the mass transfer coefficient when it is greater than a certain threshold value, which, in turn, is a function of the number and size of the monomer droplets. This supports our suspicion that regardless of the preparation procedure, monomer transfer does occur.

Molecular weights. For the sake of brevity, the molecular weight development is shown in Figures 10 for the two extreme copolymer compositions studied, BA/VAc 50/50 and 95/5 wt/wt. Similar trends were observed for other compositions. Due to the relatively high CTA concentrations employed (3 phm), the average molecular weights were low. There were no differences in the molecular weights between the runs obtained by the two different preparation procedures.

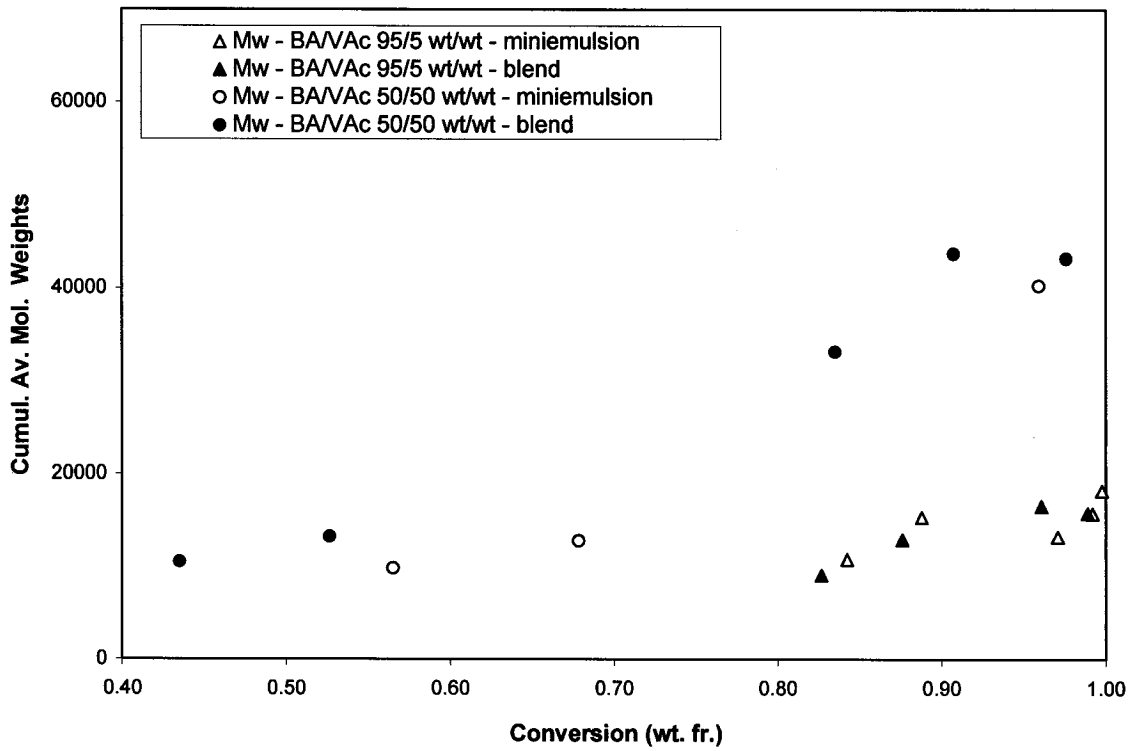

Figure 10 Cumulative average molecular weight vs. conversion: BA/VAc 50/50 and 95/5 wt/wt runs

The similarities in polymerization rate, copolymer composition or average molecular weights for the two procedures cannot be used to draw conclusions about the potential mass transfer between particles. Therefore, all reactions were also monitored in-line using ATR-FTIR spectroscopy. In our previous work, the same instrument was utilized for the investigation of monomer compartmentalization in the Sty/butyl methacrylate system.[19] The basis for the utilization of ATR-FTIR spectroscopy is the fact that homopolymers have different spectral signatures, especially in the fingerprint region of the mid-IR spectra (~1800-700 cm^{-1}). Peak assignments for these regions are given in detail in Jovanovic and Dubé (2001).[20] This region for homopolymers of BA and VAc is shown in Figure 11. Ideally, polymers formed by the two different miniemulsion procedures should have different spectral signatures. If a miniemulsion blend procedure is used and compartmentalization takes place, then the miniemulsion should contain two particle populations: one consisting of BA homopolymers and the other, VAc homopolymers.

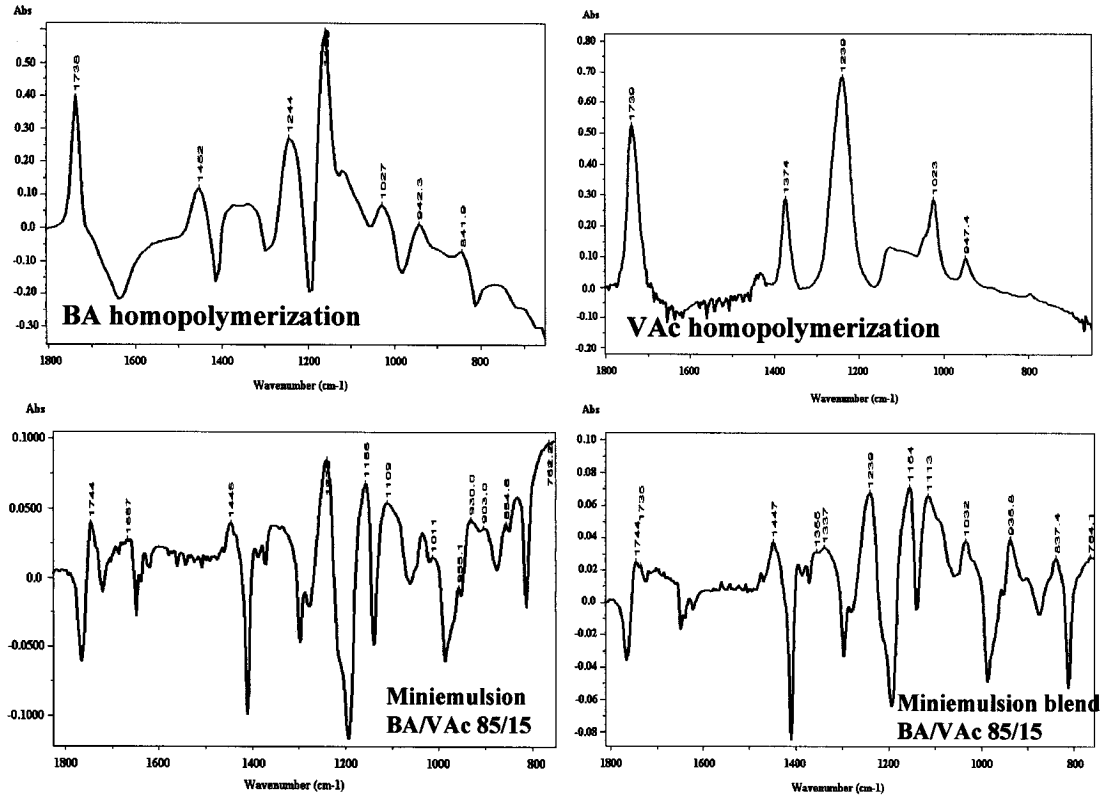

Figure 11 Spectra of homopolymers (a,b) , miniemulsion and VAc on (c) and miniemulsion blend (d) of BA

The polymerization reactions would take place independently in the two particle populations and the resulting spectra (Figure 11) would resemble the summation of the spectra of the two homopolymers. In addition, these spectra would be different from that obtained if both monomers were present in each particle when a conventional copolymerization takes place (Figure 11).

For the purposes of this study when the two procedures were compared, the position, appearance or disappearance of peaks at certain wavenumbers is of interest rather than their intensities.

Thus, if monomer transfer does not occur, the two spectra should differ in certain characteristic absorbances. In Figure 12, overlapped fingerprint regions for BA/VAc 85/15 wt/wt miniemulsions obtained by the two procedures are shown. It can be seen that there are no differences, suggesting that compartmentalization did not take place. It

should be pointed out that the differences in the absorbance observed are due to differences in the concentration of the individual components in the mixture.

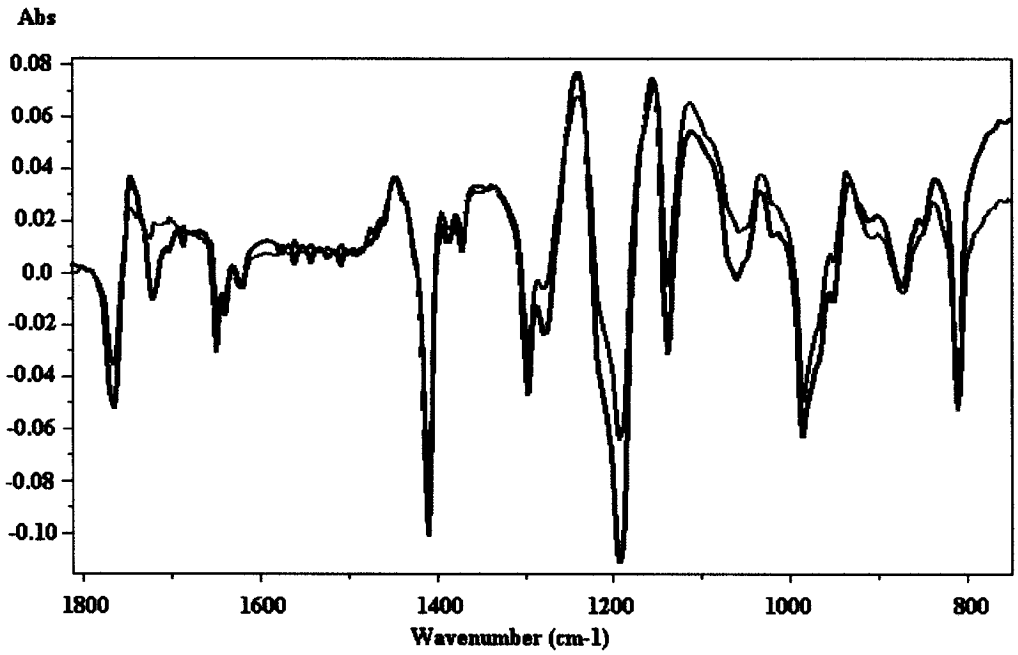

Figure 12 Comparison of the spectra of miniemulsion polymerizations obtained by two different procedures (BA/VAc 85/15 wt/wt)

For all other compositions and run conditions in this study, all of the characteristic peaks were present in the fingerprint region of the spectra. Thus, one can conclude that compartmentalization did not take place under the current conditions for the BA/VAc system. On the other hand, in previous work on the Sty/butyl methacrylate system, distinct differences between the two procedures were found when the fingerprint regions of the polymerizations were compared.[19] It is likely that the high water solubility of VAc is responsible for this behaviour. The VAc monomer could easily have diffused through the water phase and entered the BA-rich particles despite the presence of a hydrophobe (i.e. ODMA). It should be noted that Sty is far less soluble in water compared to VAc (Sty=0.027 wt% and VAc=2.5 wt% at 25°C). Therefore, Sty monomer should be less prone to diffusion through the water phase, especially in the presence of a hydrophobe. In our previous work, two different miniemulsion procedures for the Sty/butyl methacrylate

system yielded different spectral signatures. The fact that the BA/VAc system behaved differently indicates that compartmentalization (monomer transfer) in miniemulsion polymerization could be highly system-dependent. Monomer systems containing highly water-soluble monomers could be more prone to monomer transfer regardless of the presence of a hydrophobe.

Adhesive properties. Given the fact that CTA was used in a relatively high amount in the recipe, a balanced adhesive performance was not obtained. All samples showed no peel and shear strength. For the loop tack, the highest value of 0.4 Ncm^{-2} was observed for the BA/VAc 95/5 wt/wt run. One source for property improvement could be the addition of a polar monomer (e.g. acrylic or methacrylic acid) and some multifunctional monomer(s). Despite these observations, given appropriate conditions, the idea of mixing particles as carriers of different relevant properties is still intriguing.[27]

6.5 CONCLUSIONS AND RECOMMENDATIONS

In this work, reaction kinetics and polymer properties resulting from two different BA/VAc miniemulsions were investigated. In one procedure, the monomers were mixed, sonicated and polymerized together. In the other, two miniemulsions, each containing one monomer, were prepared separately and mixed prior to polymerization. There are few reported studies utilizing a similar procedure.[19] The objective was to investigate the possibility of monomer transfer during polymerization.

In all cases, similar results for the rate of polymerization were obtained, regardless of the procedure employed. The only distinguishable differences in conversion vs. time data were observed for the BA/VAc 50/50 wt/wt run, but these were only minor. Trends in the particle size data for runs with a lower VAc content indicated that true miniemulsion polymerization conditions were observed. On the other hand, for runs with a higher VAc content (35-50 wt%), particle size data suggested that non-nucleated monomer droplets served as monomer reservoirs during the course of the reaction, despite the presence of a hydrophobe. Copolymer compositions and average molecular

weights were indistinguishable for all runs regardless of the preparation procedure used. These similarities cannot be used as indicators of compartmentalization during the polymerization reaction. ATR-FTIR spectroscopy was therefore used to investigate possible monomer transfer. In our case, both procedures had similar spectral signatures regardless of the feed composition. There were no differences or shifts in wavenumbers of characteristic peaks indicating that in each case, there was monomer transfer between the particles regardless of the presence of the hydrophobe. In BA/VAc 85/15 and 95/5 wt/wt runs, the fingerprint regions of the reaction spectra indicated that mass transfer occurred despite maintaining an almost constant particle size throughout the reaction regardless of the procedure. One can speculate that VAc, a more water-soluble monomer, is prone to diffusion in the water-phase despite the presence of a hydrophobe. Thus, when miniemulsion blending was used, VAc was able to diffuse through the water phase into the BA-rich particles. In that case, instead of two simultaneous homopolymerizations, a copolymerization was taking place in a way similar to that in the non-blended system. As a result, similar spectral signatures were observed for the two polymerization procedures. Given these results and those from a previous study, it can be concluded that compartmentalization is highly system-dependent with monomer solubility playing a major role.

As a follow up to the work presented here, the following two paths are possible: The addition of polar and/or multifunctional monomers to improve shear and peel strength; different initiators (e.g. redox initiator) or combination of initiators as well as different combinations of surfactant/hydrophobe can be used in order to reduce the high initial polymerization rate and still obtain high conversion. These new combinations could also lead to a reduction in the use of CTA, leading to more appropriate CTA concentrations for the intended adhesive applications.

6.6 ACKNOWLEDGEMENTS

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Chapter 7

General Discussion and Conclusions

This study is part of an ongoing trend that is oriented towards the establishment of emulsion polymerization technologies in PSA markets. To be able to surpass the performance of PSAs obtained from other technologies such as hot melt or solution polymerization, our understanding of the important variables affecting the final performance properties (e.g. tack, shear and peel strength) must increase.

The selection of the emulsion-based technology for the study was intentional and based on the current trend towards environmentaly friendly technologies that is directed by policy makers as well as by public opinion. Emulsion-based technologies and products are continuously improving and gaining considerable market share in the PSA industry. Thus, emulsion-based PSAs are the subject of intense reaserch in academia and industry.

In Chapter 2 we summarized the most important contemporary research results in the area of emulsion polymerization as a means for PSA production. Though systematic in some areas such as the emulsion polymerization process itself, the knowledge of emulsion-based PSAs is scattered. The need for an integration of existing areas of knowledge such as the polymerization process, inherent polymer properties and final performance properties was recognized and addressed in this work. Thus, the first part of the study was the accumulation, selection, integration and presentation of the existing knowledge on the subject of emulsion-based PSAs in general.

In the next phase of the work, we proceeded with the selection of a particular system where this integrated, systematic approach would be tested. Selection of BA/VAc monomers for PSAs was based on the fact that the literature revealed that this system has high potential as a PSA. The objective was to investigate the most influential factors affecting the inherent polymer and final product properties of BA/VAc emulsion-based PSAs. The ultimate objective was the development of models that would bridge three areas of knowledge: 1. Polymerization process, 2. Inherent polymer properties and 3. PSA performance.

As described in Chapter 3, we started with an investigation of eight variables that were judged to have a possible effect on the inherent and final performance properties. These included the BA/VAc ratio, amounts of AA, CTA, initator, amounts and type of

stabilizer, polymerization temperature and solids content. These factors were investigated in 20 runs using a screening design. The screening design fulfilled its purpose due to the fact that a wide range of properties was generated. These ranged from excellent tack, shar and peel strength (run 9 and run 5) to non-existent adhesion performance (run 11). Indications were that the BA/VAc ratio of 95/5 was the most favourable monomer ratio for balanced adhesive performance. Next, it was judged that one of the most important variables was the amount of CTA, that in turn governs the amount of gel in the final samples as well as the properties of the sol fraction. These have influence on short-term bonding and debonding processes that occur during tack, shear, and peel tests. Both stabilizers used, namely SDS and PVOH, have shown similar PSA performance. However, due to the coagulation of several runs and the differences in the mode of failure in all three adhesive tests, model development was not possible. Thus, these conclusions needed further verification. In the next design step, it was necessary to reduce the number of investigated variables:: one where SDS was used as stabilizer and another where PVOH was used as stabilizer.

In Chapter 4, the results of the investigation of BA/VAc PSA properties were reported when PVOH was used as a sole stabilizer for the system. The objective was to investigate the influence of the individual monomers BA, VAc and AA on the final product properties in order to better understand the behaviour of this system as a PSA. Similar to the previous study, the ultimate objective was model development. To address the influence of the monomers, a three-component mixture design was used. All three components were highly constrained since the accumulated knowledge pool has shown that certain compositions are not of interest as PSAs. The results have shown that the most important among the three monomers is AA. It was the most significant factor in the tack, shear and peel strength models as well as in an empirical T_g model. Its influence, however, was different and opposite on different final product properties. Contour plots were generated for each response and revealed the existence of minima in the investigated experimental region for loop tack and shear strength, while a maximum was observed for peel strength. Overlapping of contour plots did not result in an optimal operating condition but rather in a sub-optimum. The major contribution of the work was model development and the generation of contour plots that could be used in the

determination of sub-optimal operating regions as well as for further improvement of PSAs.

In the subsequent study reported in Chapter 5, SDS was used as a stabilizer and its concentration was varied in the experimental design because it was likely that SDS was one of the factors affecting adhesive performance. As a small molecule it can easily migrate to the film/carrier or film/air interface and thus affect the PSA performance. In addition to the amount of SDS, another variable investigated was AA. It was found that this was the most significant among the monomers when PVOH was used and was therefore of interest in its influence when SDS was used as stabilizer. In addition, it was important to compare the influence of AA to other factors. In addition, to AA and SDS, CTA was selected as the third variable to be investigated. All three variables were investigated in 15 runs using a Box-Behnken design. In this case, all runs showed an identical type of failure since they were "daughters" of run 5 from the screening design. Empirical modeling was possible. Similar to the three-component mixture models, there was no single model able to fit the data but rather several different ones. The most important characteristic was that for peel and tack there was similarity in the parameters that comprised the model when the two different substrates were compared at different thicknesses. The only models that contained the same parameters at both thichkesses and substrates were shear strength models. Here AA and CTA main effects and their interaction were the most significant parameters. However, in all peel and shear strength models, CTA was present as a significant parameter either as a linear, quadratic or second-order interaction (usually with AA). This confirmed our suspicion that CTA was among the most influential parameters affecting the performance of BA/VAc copolymers when the polymer composition is fixed. This can be used in tailor-made approaches in PSA development.

Finally, in this work, some alternative ways of producing PSAs were investigated. The idea was to test the possibility of compartmentalization in BA/VAc miniemulsions. If it existed, the compartmentalization would mean that each particle represents a nanoscale independent reactor during the polymerization. This could improve our ability to tailor-make PSAs. For example, one could add more CTA in one particle population to favour the development of small chains necessary for the instantaneous bonding of PSA,

and cross-linker in another particle population to increase shear strength. Thus, a balanced end performance would be controlled during the synthesis of the PSA and more factors affecting the performance could be controlled independently. To confirm the absence/presence of compartmentalization we used two procedures for the preparation of miniemulsions. In one procedure, the monomers were mixed, sonicated and polymerized together. In the other, two miniemulsions, each containing one monomer, were prepared separately and mixed prior to polymerization.

In all cases, copolymer compositions and average molecular weights were indistinguishable for all runs regardless of the preparation procedure used. These similarities could not be used as indicators of compartmentalization during the polymerization reaction. ATR-FTIR spectroscopy was therefore used to investigate possible monomer transfer. In our case, both procedures had similar spectral signatures regardless of the feed composition. There were no differences or shifts in wavenumbers of characteristic peaks, indicating that in each case, there was monomer transfer between the particles regardless of the presence of the hydrophobe. In BA/VAc 85/15 and 95/5 wt/wt runs, the fingerprint regions of the reaction spectra indicated that mass transfer occurred despite maintaining an almost constant particle size throughout the reaction regardless of the procedure. One can speculate that VAc, a more water-soluble monomer, is prone to diffusion in the water-phase despite the presence of a hydrophobe. Finally, the absence of compartmentalization for this particular system might not be a general observation. Thus, further studies are needed.

Future work regarding BA/VAc emulsion-based PSA should include the following:

1. In general, low shear values were obtained for most of the adhesives tested in this study. These were observed with PVOH but also with SDS stabilized systems. To obtain more balanced final properties, the addition of supplementary cross-linkers may be necessary but in a limited amount to avoid the loss of tack. Thus, one can design a series of experiments where different types and amounts of cross-linkers should be investigated. An additional factor in this study would be the amount of CTA, since this is the most important factor whose effect is opposed to that of the crosslinker. Model development for such systems would also be of interest.

2. Regarding PVOH stabilized systems, it is recommended that the performance of these adhesives be tested when different molecular weights and degrees of hydrolization are used since these could possibly have an influence on grafting and cross-linking. Thus, a variation in gel content could be expected.

3. In general, improvements in viscosity were not necessary for the investigated system if the solid content was above 40% when SDS was used and above 30% when PVOH was used. However, it could be of interest to test the influence of different types and concentration of thickeners on adhesive properties since these are commonly used in industry.

4. Further improvement in modeling of this and other systems is necessary. The models developed in this study are empirical in nature. They are a big step forward in terms of modeling of BA/VAc emulsion-based PSAs, however, the development of mechanistic models for this and other emulsion-based systems linking reaction conditions, inherent polymer and final product properties would offer a "quantum leap" in PSA design. Given the nature of PSAs, a large amount of highly reproducible data is necessary for the development of such models.

Appendix A

Sample Calculations and Additional Figures and Tables For Chapters 3-6

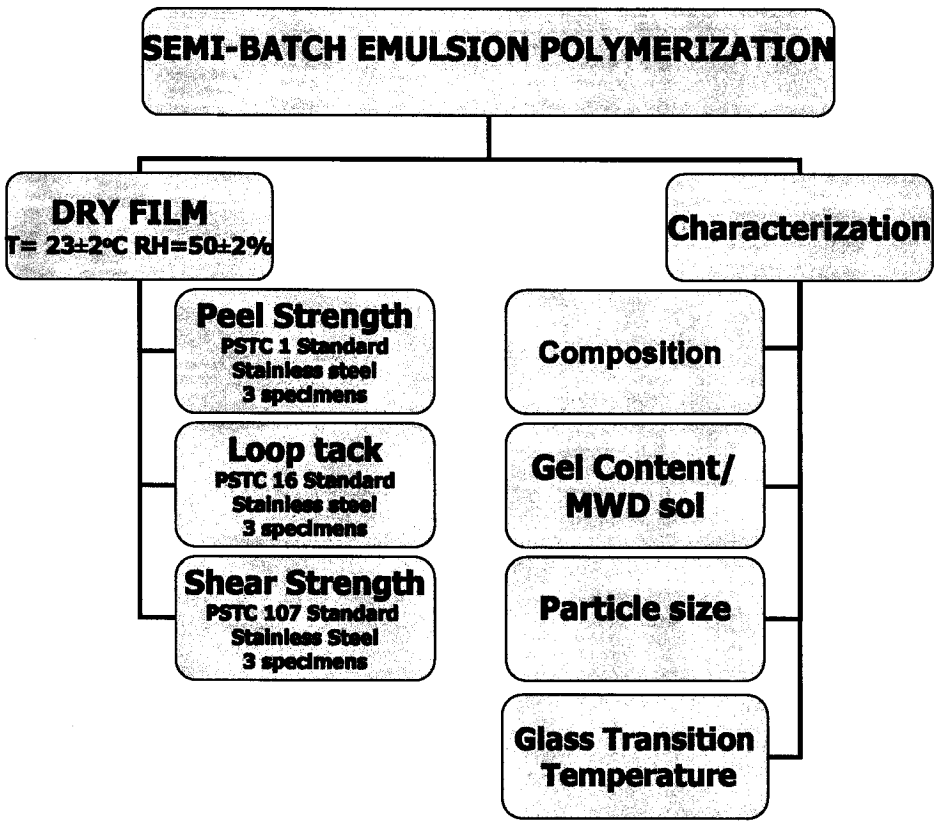


Figure 1 A general experimental procedure followed throughout the work

SAMPLE CALCULATIONS AND SUPPORT DOCUMENTATION FOR CHAPTER 3

RUN 5

27-Jul-03

Initial reactor load		
Component	Weight (g)	Wt. fract.
SDS	14.0157	0.0491
Buffer	0.6073	0.0021
Water	224.7337	0.7873
BA	34.1397	0.1196
VAc	11.4746	0.0402
AA	0.4628	0.0016
CTA	0.0229	0.0001
Total	285.4567	1.0000

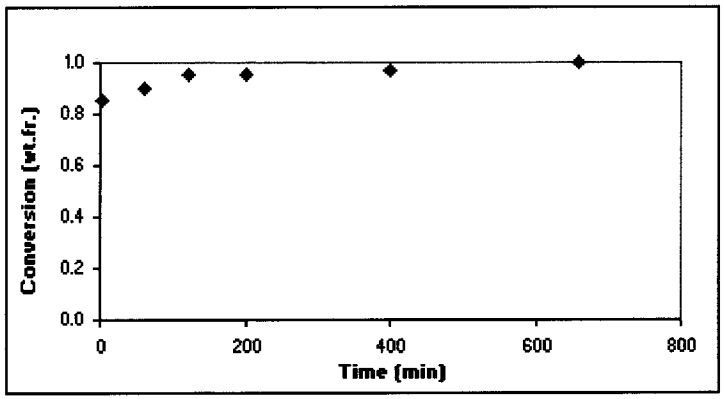
Initial feed composition		
Total fed (g):		46.1000
Component	Weight (g)	Wt. fract.
BA	74.1000	0.7406
VAc	24.9056	0.2489
AA	1.0044	0.0100
CTA	0.0498	0.0005
Total	100.0598	1.0000

Balance B2: Neet monomer feed		
Feed rate: Variable		
Comp.	Weight (g)	Wt. fract.
BA	244.3799	0.9775
VAc	0.0000	0.0000
AA	5.4958	0.0220
CTA	0.1273	0.0005
Total	250.0030	1.0000

Initiator feed		
Feed rate:		
Comp.	Weight (g)	Wt. fract.
Initiator	1.7520	0.0529
Water	31.3792	0.9471
Total	33.1312	1.0000
Total add:	19.8620	

Balance B1: Buffer feed		
Feed rate:		
Comp.	Weight (g)	Wt. fract.
Buffer	10.4790	0.0455
Water	220.0460	0.9545
Total	230.5250	

Gravimetry					
Sample	Time (min)	Empty Pan	Sample o	Dry	Solids
1	3	1.228	2.683	1.789	0.209
2	60	1.261	2.549	2.123	0.338
3	120	1.240	2.037	2.046	0.396
4	200	1.247	1.080	1.735	0.452
5	400	1.239	0.432	1.459	0.509
6	660	1.252	0.511	1.514	0.513



	Balance	Balance	Individual Components in the Feed coming from Balance B2								Total	Total	Monomer	Other	Solids	Conversion
Time	B2	B1	BA	VAc	AA	CTA	INI	SDS	Buff	Water w/ Buf	Water	Weight	wt.fr.	wt.fr.		
3	7.70	0.00	41.6665	11.4746	0.6320	0.0269	1.0503	14.0157	0.6073	0.0000	224.7337	294.2070	0.1828	0.0534	0.2090	0.8515
60	71.30	0.00	103.8360	11.4746	2.0301	0.0592	1.0503	14.0157	0.6073	0.0000	224.7337	357.8070	0.3279	0.0440	0.3382	0.8973
120	97.20	0.00	129.1534	11.4746	2.5995	0.0724	1.0503	14.0157	0.6073	0.0000	224.7337	383.7070	0.3733	0.0410	0.3957	0.9503
200	138.50	0.00	169.5245	11.4746	3.5074	0.0935	1.0503	14.0157	0.6073	0.0000	224.7337	425.0070	0.4341	0.0371	0.4520	0.9558
400	187.40	1.70	217.3247	11.4746	4.5824	0.1184	1.0503	14.0157	0.6846	1.6227	226.3564	477.2297	0.4890	0.0333	0.5087	0.9722
660	187.70	6.50	217.6179	11.4746	4.5889	0.1185	1.0503	14.0157	0.9028	6.2045	230.9382	486.9115	0.4799	0.0330	0.5131	1.0003

Figure 2 Recipe and Gravimetric results for Run 5 (Chapter 3)

RUN 9

03-Aug-03

Reactor loading prior to reaction		
Component	**Weight**	**wt. fr.**
PVOH	2.8977	0.0081
Buffer	0.3053	0.0009
Water	324.3700	0.9094
BA	21.4457	0.0601
VAc	7.1942	0.0202
AA	0.1739	0.0005
CTA	0.2861	0.0008
Total	356.6730	1.0000

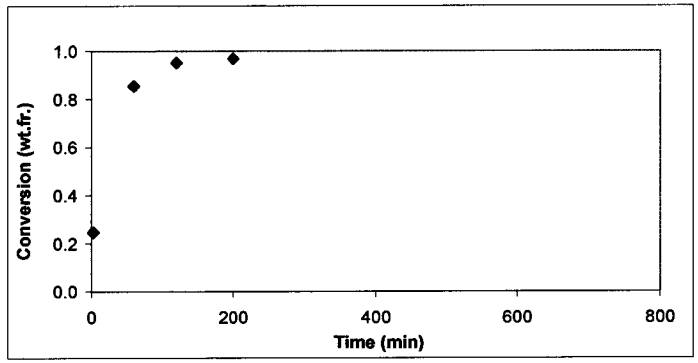
Initial feed composition		
Total fed (g):		**29.1000**
Component	**Weight**	**Wt. fract.**
BA	51.6492	0.7370
VAc	17.3263	0.2472
AA	0.4189	0.0060
CTA	0.6891	0.0098
Total	70.0835	1.0000

Balance 2: Neet monomer feed		
Feed rate: Variable		
Comp.	**Weight (g)**	**Wt. fract.**
BA	166.4963	0.9793
VAc	0.0000	0.0000
AA	1.8277	0.0108
CTA	1.6873	0.0099
Total	170.0113	1.0000

Balance 2: Initiator feed		
Feed rate:		10g@1min
Comp.	**Weight (g)**	**Wt. fract.**
Initiator	0.8694	0.0279
Water	30.2866	0.9721
Total	31.1560	1.0000
Total added:	19.8608	

Balance 1: Buffer feed		
Feed rate:		
Comp.	**Weight (g)**	**Wt. fract.**
buffer	10.4790	0.0455
Water	220.0460	0.9545
Total	230.5250	

Gravimetry					
Sample	**Time (min)**	**Empty**	**Sample only**	**Dry**	**Solids**
1	3	1.245	1.154	1.285	0.035
2	60	1.236	1.411	1.507	0.192
3	120	1.241	1.105	1.516	0.249
4	200	1.244	1.491	1.675	0.290
5	400	1.244	1.851	1.831	0.317
6	660	1.234	3.151	2.240	0.319



Time	B2	B1	BA	VAc	AA	CTA	INI	SDS	Buff	Water w/ buffer	Water	Total	Monomer wt.fr.	Other wt.fr.	Solids	Conversion
3	5.50	0.00	26.8320	7.1942	0.2331	0.3407	0.5542	2.8977	0.3053	0.0000	324.3700	362.7272	0.0944	0.0113	0.0346	0.2466
60	60.10	0.00	80.3032	7.1942	0.8200	0.8826	0.5542	2.8977	0.3053	0.0000	324.3700	417.3272	0.2116	0.0111	0.1919	0.8543
120	82.10	0.00	101.8483	7.1942	1.0565	1.1009	0.5542	2.8977	0.3053	0.0000	324.3700	439.3272	0.2506	0.0111	0.2493	0.9506
200	105.40	0.00	124.6666	7.1942	1.3070	1.3322	0.5542	2.8977	0.3053	0.0000	324.3700	462.6272	0.2879	0.0110	0.2896	0.9678
400	117.40	0.00	136.4185	7.1942	1.4360	1.4513	0.5542	2.8977	0.3053	0.0000	324.3700	474.6272	0.3056	0.0110	0.3168	1.0007
660	117.40	0.00	136.4185	7.1942	1.4360	1.4513	0.5542	2.8977	0.3053	0.0000	324.3700	474.6272	0.3056	0.0110	0.3192	1.0087

Figure 3 Recipe and Gravimetric results for Run 9 (Chapter 3)

RUN 11

06-Aug-03

Reactor loading prior to reaction		
Component	**Weight**	**wt. fr.**
SDS	4.8445	0.0171
Buffer	0.2478	0.0009
Water	230.2579	0.8141
BA	3.8219	0.0135
VAc	38.3359	0.1355
AA	3.8165	0.0135
CTA	1.5257	0.0054
Total	282.8502	1.0000

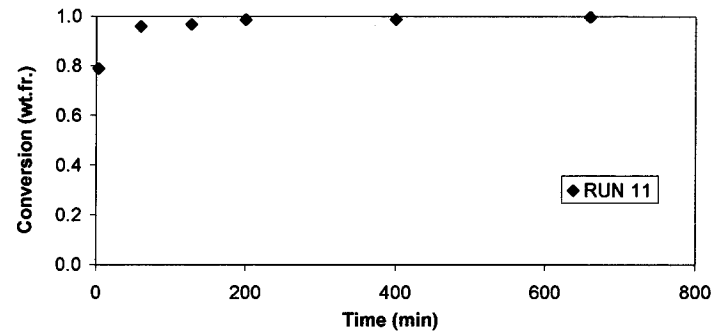
Initial feed composition		
Total fed (g):		**47.5000**
Component	**Weight (g)**	**Wt. fract.**
BA	2.4200	0.0805
VAc	24.2743	0.8071
AA	2.4166	0.0803
CTA	0.9661	0.0321
Total	30.0770	1.0000

Balance 2: Neet monomer feed		
Feed rate: Variable		
Comp.	**Weight (g)**	**Wt. fract.**
BA	243.7161	0.9373
VAc	0.0000	0.0000
AA	13.7006	0.0527
CTA	2.5990	0.0100
Total	260.0157	1.0000

Balance 2: Initiator feed		
Feed rate:		
Comp.	**Weight (g)**	**Wt. fract.**
Initiator	0.7270	0.0242
Water	29.3345	0.9758
Total	30.0615	1.0000
Total added:	19.9666	

Balance 1: Buffer feed		
Feed rate:		
Comp.	**Weight (g)**	**Wt. fract.**
buffer	10.4790	0.0455
Water	220.0460	0.9545
Total	230.5250	

Gravimetry					
Sample	**Time (min)**	**Empty**	**Sample only**	**Dry**	**Solids**
1	3	1.244	1.567	1.487	0.155
2	60	1.245	1.937	1.866	0.321
3	120	1.236	2.487	2.173	0.377
4	200	1.250	1.045	1.705	0.436
5	400	1.244	0.743	1.610	0.494
6	660	1.241	1.583	2.030	0.498



Time	B2	B1	BA	VAc	AA	CTA	INI	SDS	Buff	Water w/ buffer	Water	Total	Monomer wt.fr.	Other wt.fr.	Solids	Conversion
3	5.70	0.00	9.1645	38.3359	4.1168	1.5827	0.4829	4.8445	0.2478	0.0000	249.7416	308.5168	0.1673	0.0232	0.1552	0.7888
60	72.20	0.00	71.4959	38.3359	7.6208	2.2474	0.4829	4.8445	0.2478	0.0000	249.7416	375.0168	0.3132	0.0209	0.3210	0.9585
128	106.20	0.00	103.3645	38.3359	9.4123	2.5873	0.4829	4.8445	0.2478	0.0000	249.7416	409.0168	0.3695	0.0200	0.3770	0.9663
200	144.30	0.00	139.0761	38.3359	11.4199	2.9681	0.4829	4.8445	0.2478	0.0000	249.7416	447.1168	0.4223	0.0191	0.4355	0.9859
400	196.90	0.00	188.3788	38.3359	14.1914	3.4939	0.4829	4.8445	0.2478	0.0000	249.7416	499.7168	0.4821	0.0181	0.4938	0.9867
660	196.90	0.00	188.3788	38.3359	14.1914	3.4939	0.4829	4.8445	0.2478	0.0000	249.7416	499.7168	0.4821	0.0181	0.4984	0.9961

Figure 4 Recipe and Gravimetric results for Run 11 (Chapter 3)

RUN 20

21-Aug-03

Reactor loading prior to reaction		
Component	**Weight**	**wt. fr.**
PVOH	7.6385	0.0230
Buffer	0.2876	0.0009
Water	280.1582	0.8441
BA	24.2266	0.0730
VAc	18.7010	0.0563
AA	0.6419	0.0019
CTA	0.2305	0.0007
Total	331.8843	1.0000

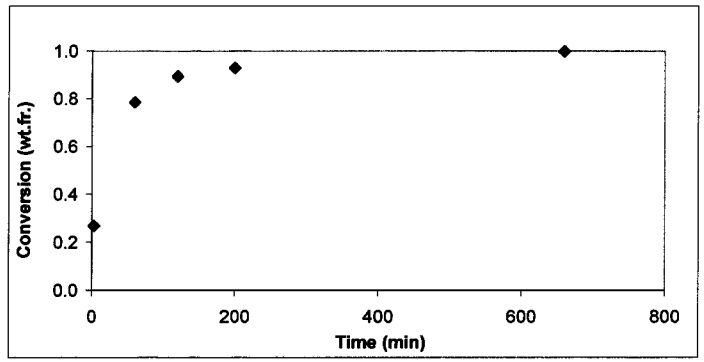
Initial feed composition		
Total fed (g):		**43.8000**
Component	**Weight**	**Wt. fract.**
BA	49.9745	0.5531
VAc	38.5763	0.4270
AA	1.3241	0.0147
CTA	0.4755	0.0053
Total	90.3504	1.0000

Balance 2: Neet monomer feed		
Feed rate: Variable		
Comp.	**Weight (g)**	**Wt. fract.**
BA	182.7450	0.9618
VAc	0.0000	0.0000
AA	6.3033	0.0332
CTA	0.9512	0.0050
Total	189.9995	1.0000

Balance 2: Initiator feed		
Feed rate:		10g@1min
Comp.	**Weight (g)**	**Wt. fract.**
Initiator	0.8596	0.0285
Water	29.3476	0.9715
Total	30.2072	1.0000
Total added:	19.9207	

Balance 1: Buffer feed		
Feed rate:		
Comp.	**Weight (g)**	**Wt. fract.**
buffer	10.4790	0.0476
Water	220.0460	0.9545
Total	230.5250	

Gravimetry					
Sample	**Time (min)**	**Empty**	**Sample only**	**Dry**	**Solids**
1	3	1.249	1.545	1.342	0.061
2	60	1.250	1.082	1.486	0.218
3	120	1.246	1.395	1.661	0.298
4	200	1.243	1.522	1.781	0.354
5	400	1.251	2.005	2.057	0.402
6	660	1.246	1.619	1.894	0.400



Time	B2	B1	BA	VAc	AA	CTA	INI	SDS	Buff	Water w/ buffer	Water	Total	Monomer wt.fr.	Other wt.fr.	Solids	Conversion
3	4.30	0.00	28.3624	18.7010	0.7846	0.2520	0.5669	7.6385	0.2876	0.0000	299.5120	356.1050	0.1344	0.0246	0.0605	0.2677
60	59.60	0.00	81.5510	18.7010	2.6191	0.5289	0.5669	7.6385	0.2876	0.0000	299.5120	411.4050	0.2500	0.0219	0.2182	0.7849
120	95.90	0.00	116.4650	18.7010	3.8234	0.7106	0.5669	7.6385	0.2876	0.0000	299.5120	447.7050	0.3104	0.0206	0.2978	0.8929
200	130.70	0.00	149.9363	18.7010	4.9779	0.8848	0.5669	7.6385	0.2876	0.0000	299.5120	482.5050	0.3598	0.0194	0.3537	0.9289
400	148.30	0.00	166.8643	18.7010	5.5618	0.9730	0.5669	7.6385	0.2876	0.0000	299.5120	500.1050	0.3822	0.0189	0.4019	1.0022
660	148.30	0.00	166.8643	18.7010	5.5618	0.9730	0.5669	7.6385	0.2876	0.0000	299.5120	500.1050	0.3822	0.0189	0.4004	0.9982

Figure 5 Recipe and Gravimetric results for Run 20 (Chapter 3)

Example calculations for Run 5 at 3 min:

$$\text{Solids} = \frac{\text{Dry} - \text{Empty Pan}}{\text{Sample}} = \frac{1.789 - 1.228}{2.683} = 0.209$$

$$\text{Conversion} = \frac{\text{Solids} - \text{Wt.fr.of Other (e.g.CTA, INI, BUFFER)}}{\text{Wt.fr.of Monomer}} = \frac{0.2090 - 0.0534}{0.1828} = 0.8515$$

$$\text{Wt.fr.of Monomer} = \frac{(\text{BA} + \text{VAc} + \text{AA})}{\text{Total Weight}} = \frac{4.6665 + 11.4746 + 0.6320}{294.2070} = 0.1828$$

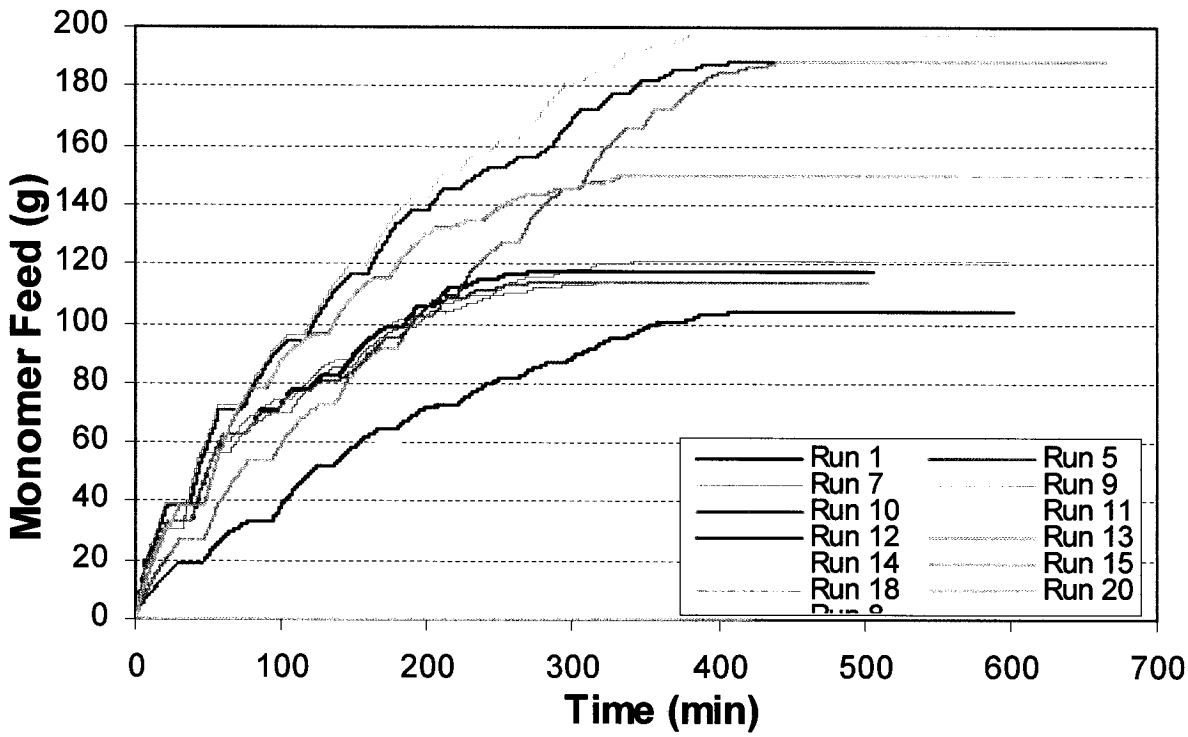


Figure 6 Monomer Feed Profiles (Chapter 3)

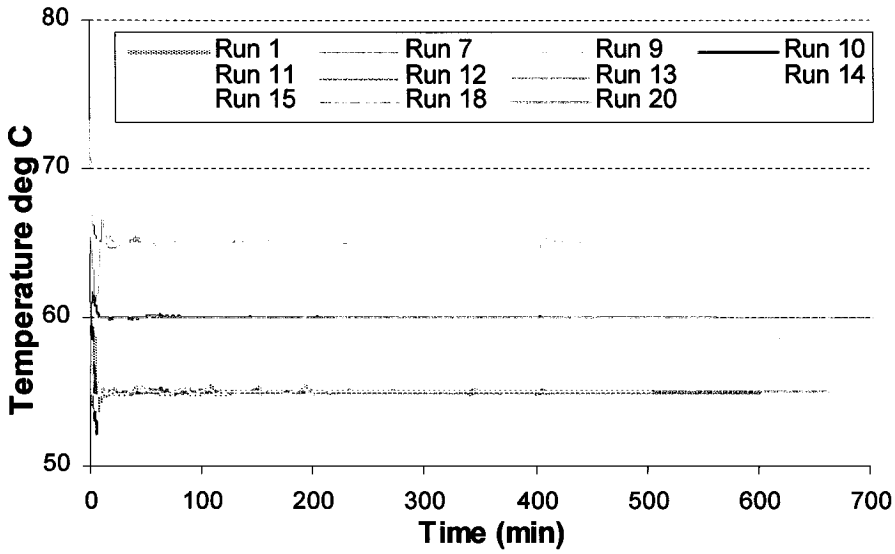


Figure 7 Temperature profiles for selected runs (Chapter 3)

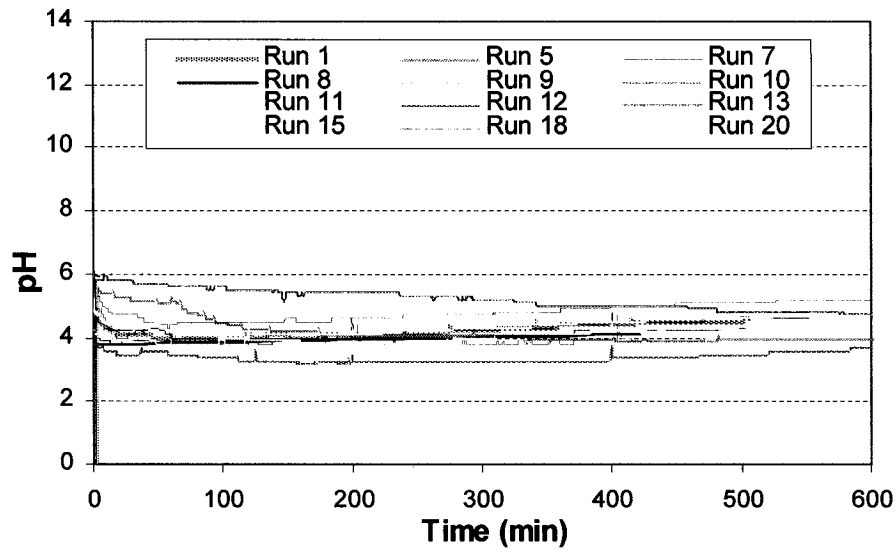


Figure 8 pH profiles for selected runs (Chapter 3)

Example of GC calibration curves used for determination of polymer composition

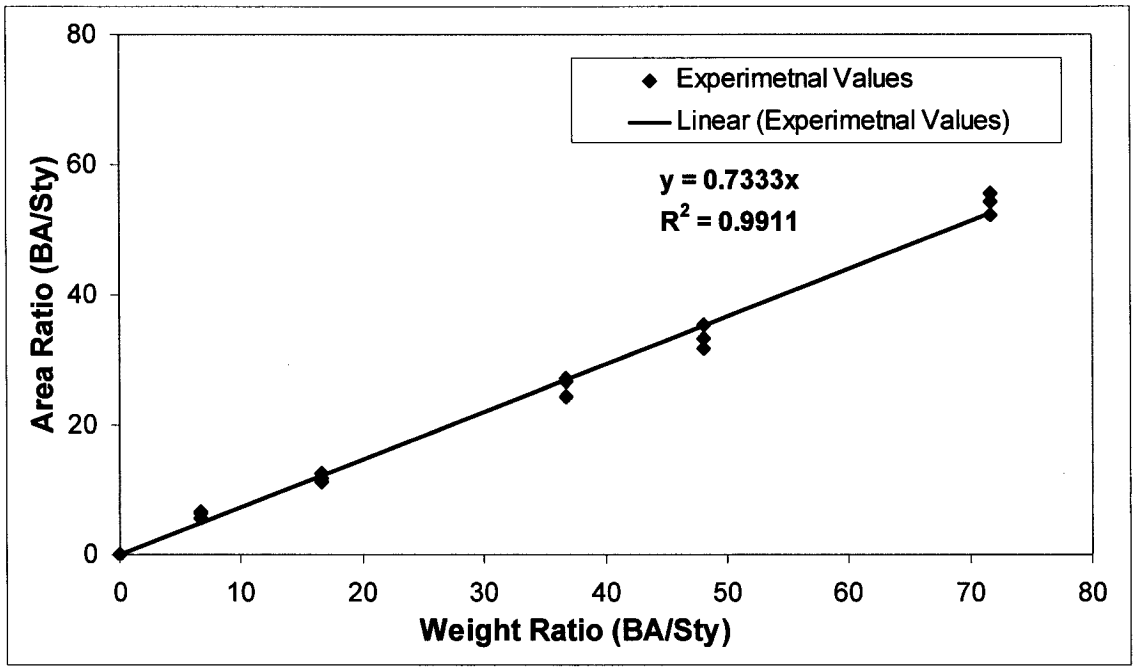


Figure 9 Butyl acrylate GC calibration curve used in Chapters 3 and 5

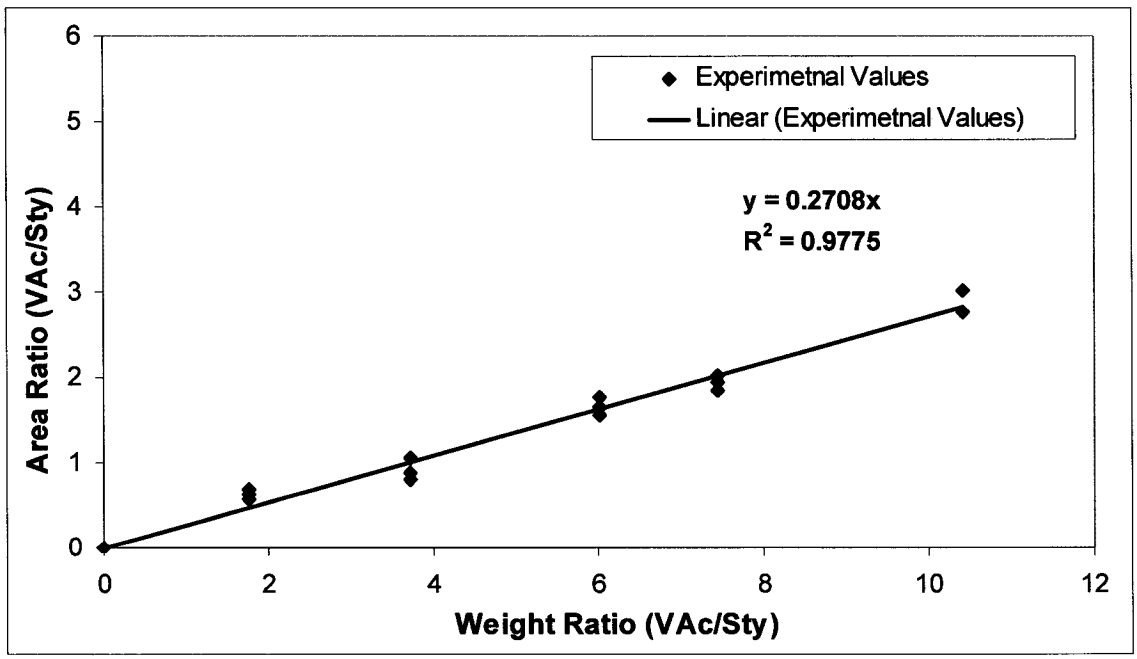


Figure 10 Vinyl acetate GC calibration curve used in Chapters 3 and 5

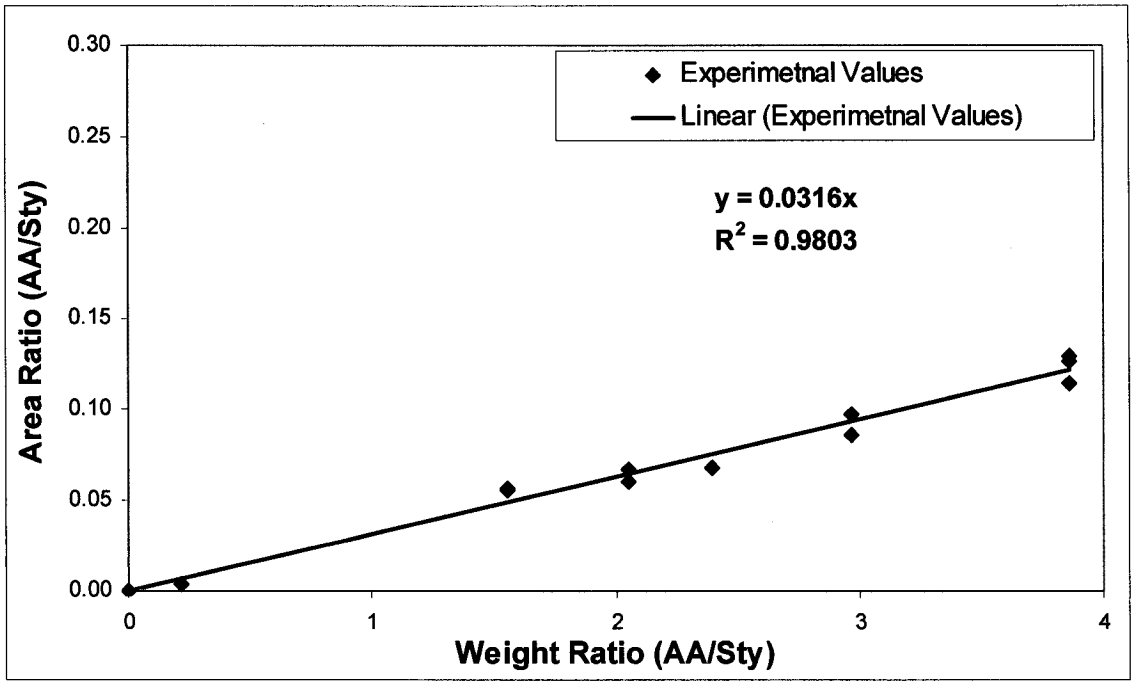


Figure 11 Acrylic acid GC calibration curve used in Chapters 3 and 5

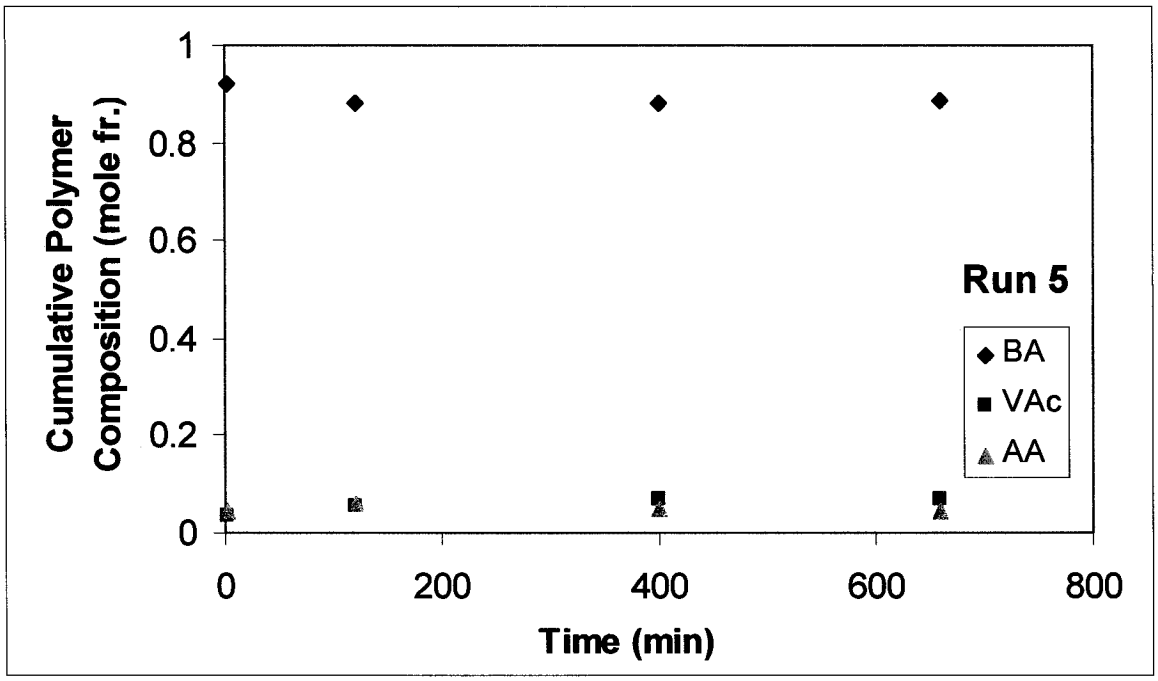


Figure 12 Cumulative polymer composition Run 5 (Chapter 3)

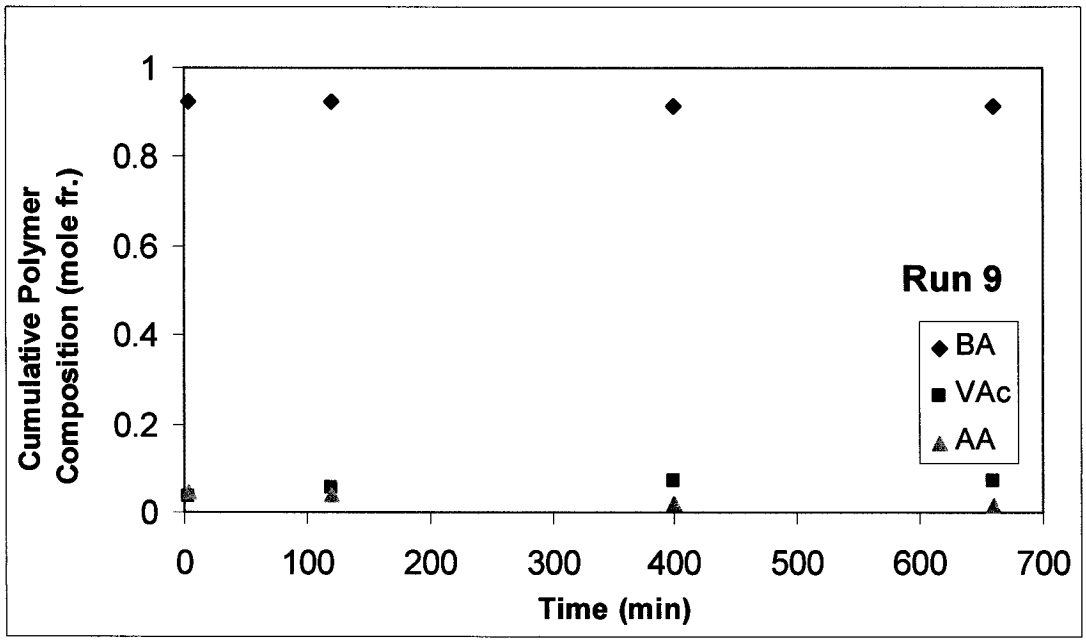


Figure 13 Cumulative polymer composition Run 9 (Chapter 3)

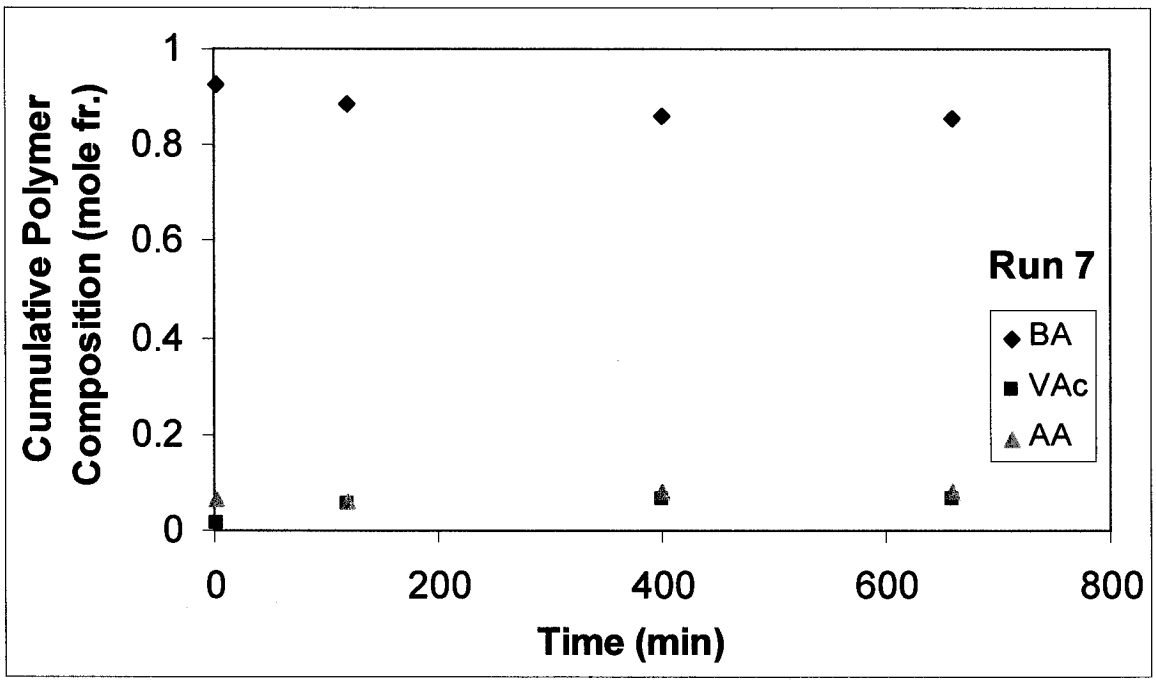


Figure 14 Cumulative polymer composition Run 7 (Chapter 3)

An example of determination of glass transition temperature (Run 17 in Chapter 3) is given in Figures A6 and A7.

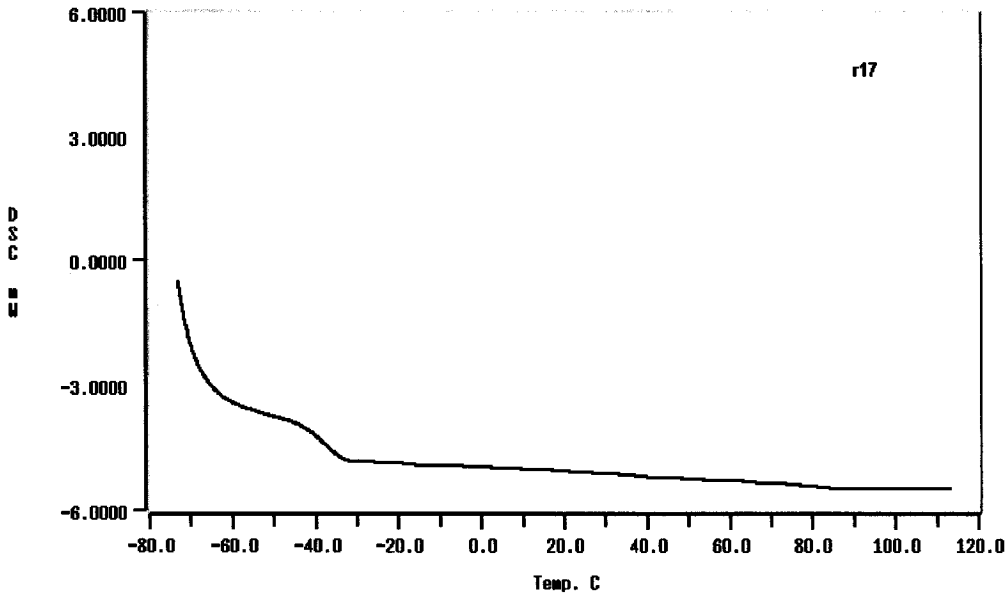


Figure 15 Full temperature range -80 to 120°C for Tg determination

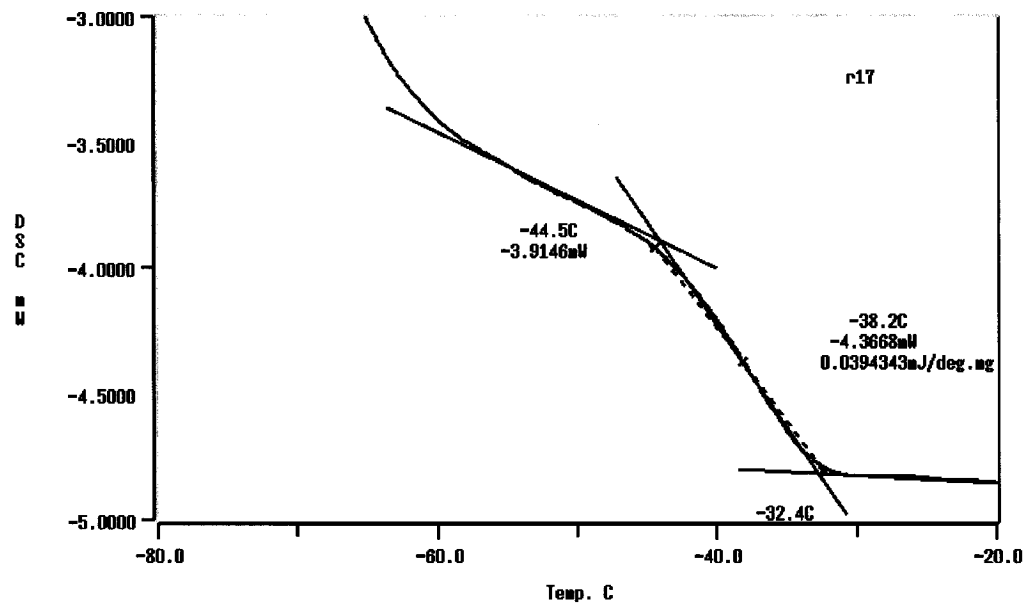


Figure A7

Figure 16 Enlarged area of interest for T_g determination along with T_g value Run 17 (Chapter 5)

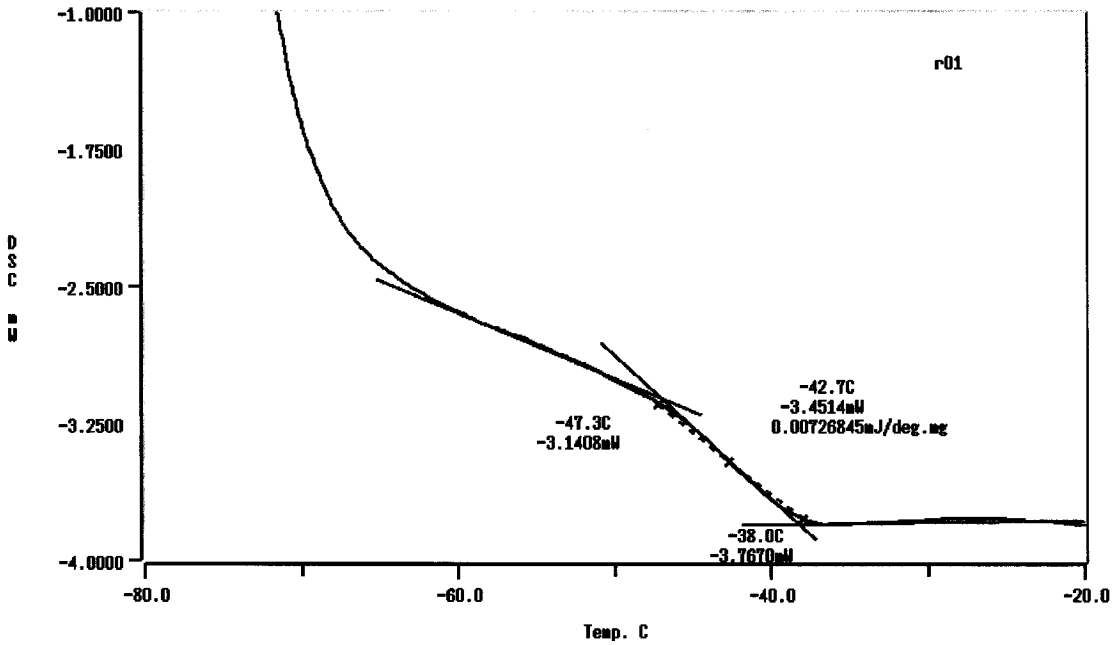


Figure 17 Glass transition temperature Run 1 (Chapter 3)

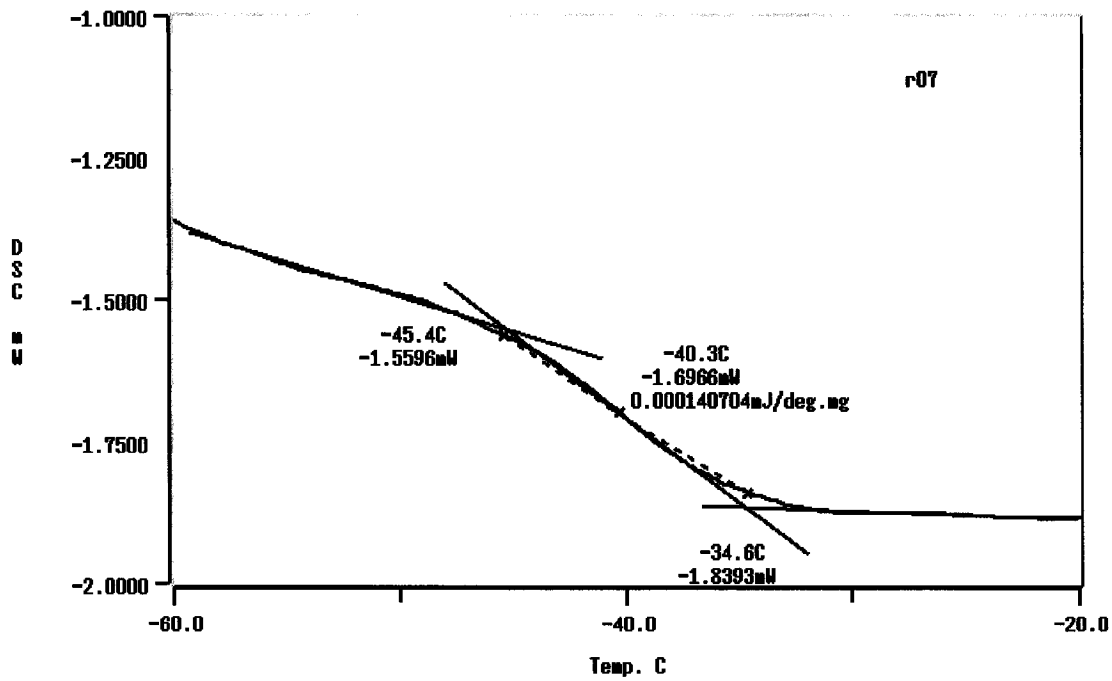


Figure 18 Glass transition temperature Run 7 (Chapter 3)

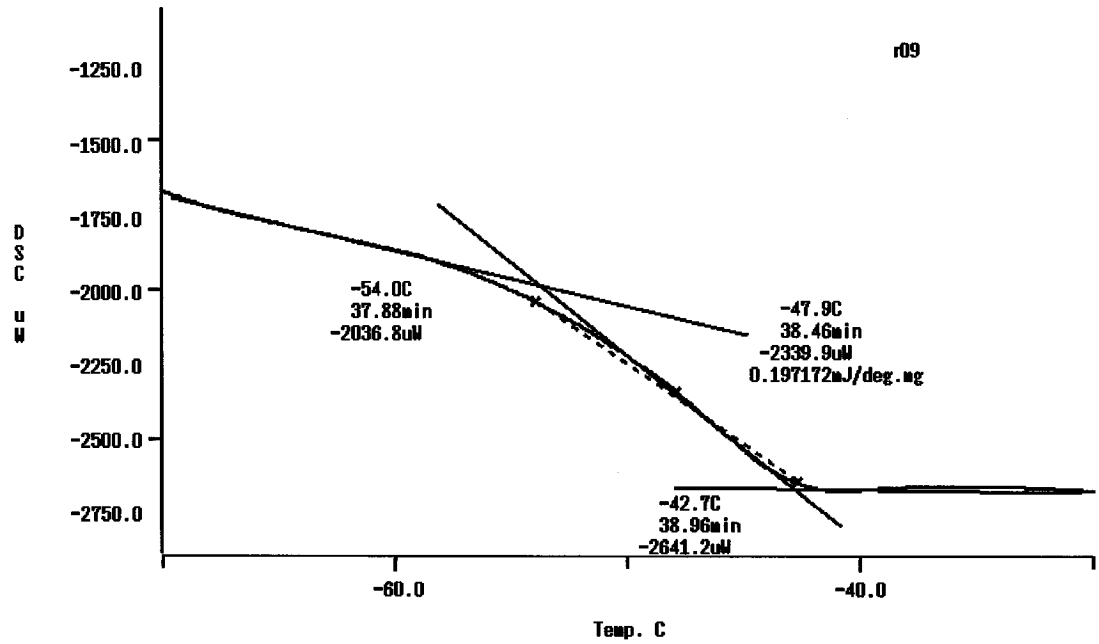


Figure 19 Glass transition temperature Run 9 (Chapter 3)

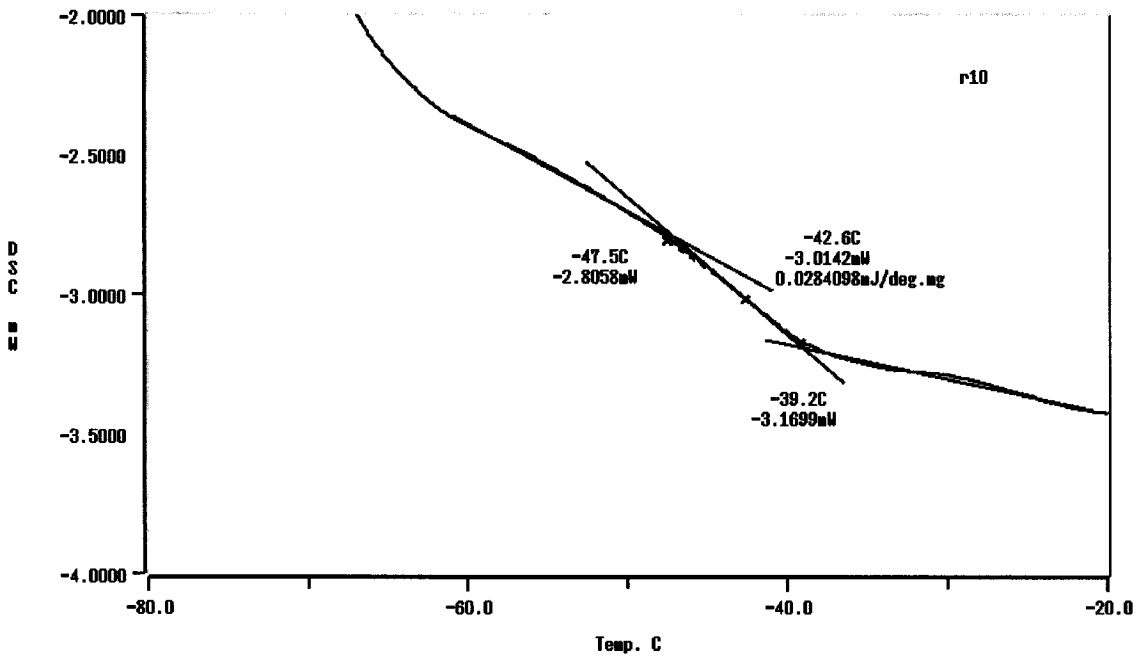


Figure 20 Glass transition temperature Run 10 (Chapter 3)

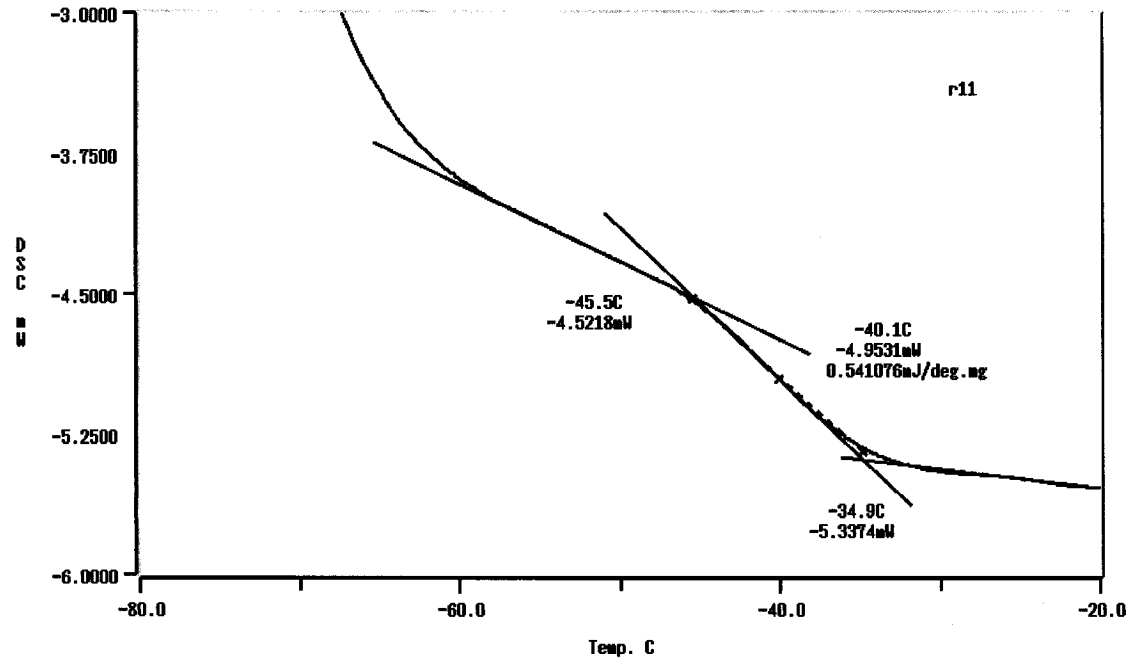


Figure 21 Glass transition temperature Run 11 (Chapter 3)

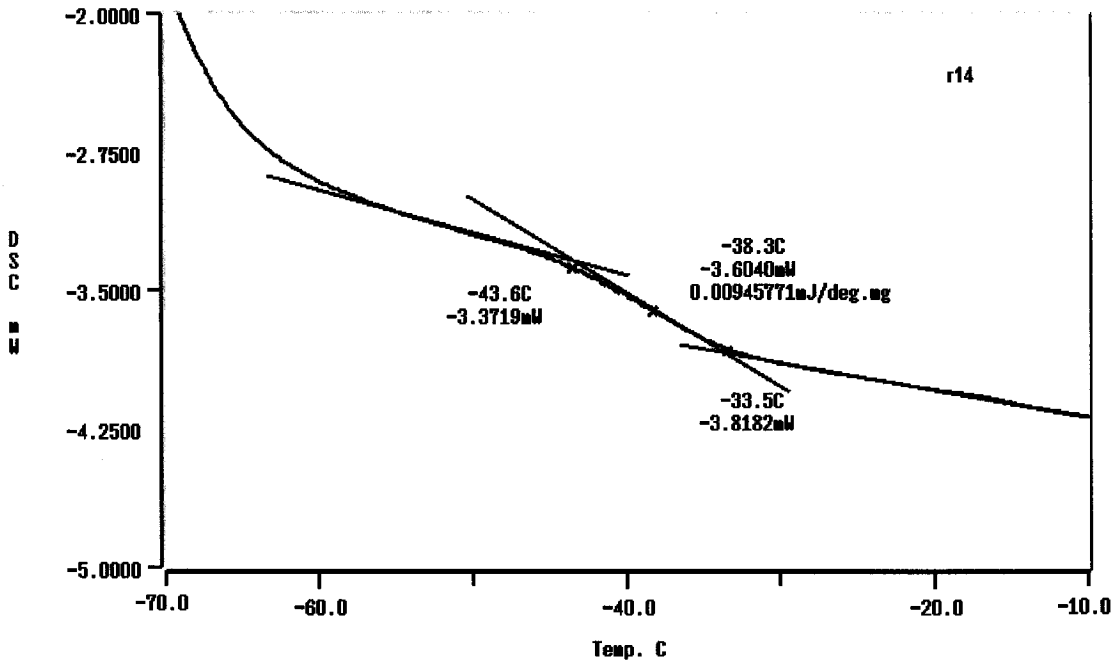


Figure 22 Glass transition temperature Run 14 (Chapter 3)

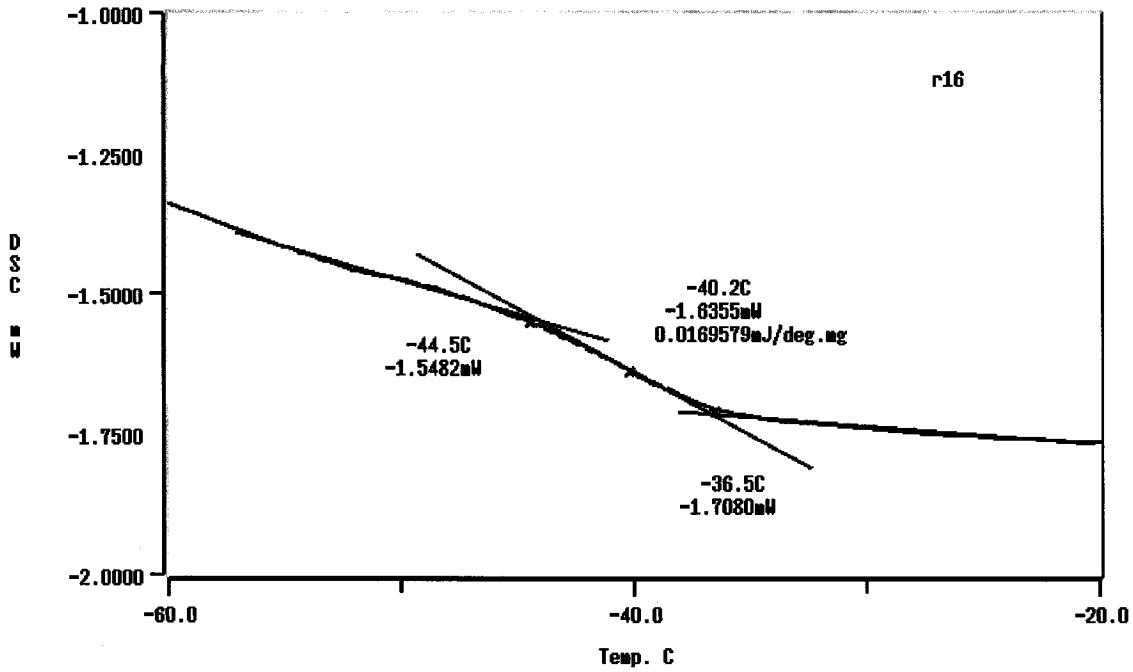


Figure 23 Glass transition temperature Run 16 (Chapter 3)

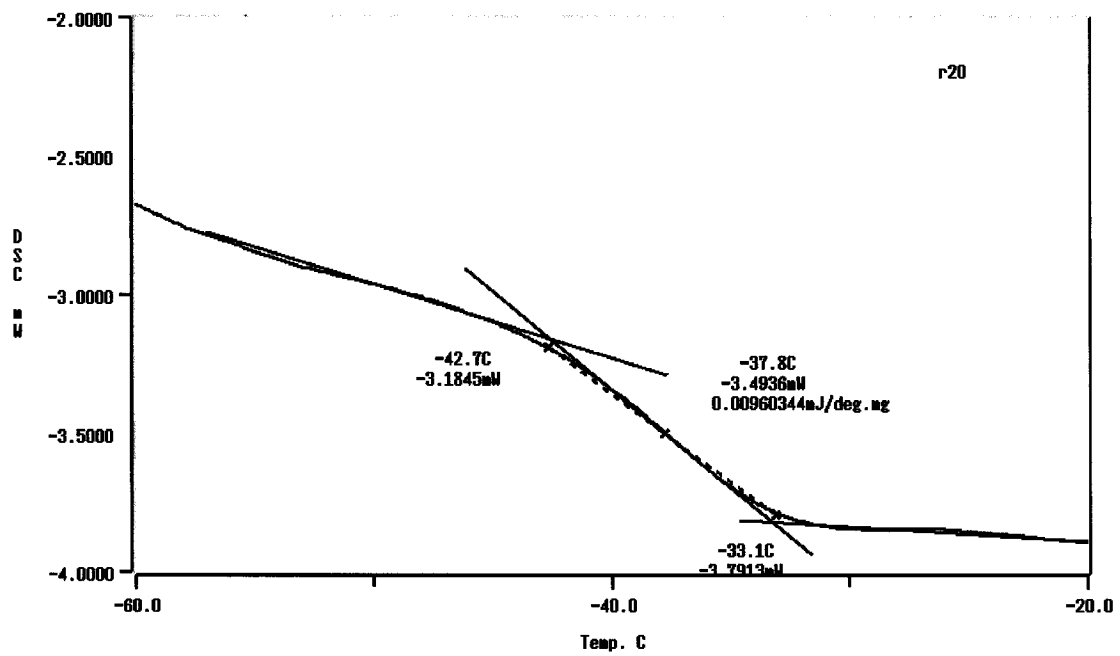


Figure 24 Glass transition temperature Run 20 (Chapter 3)

Table 1 Peel Strength Determination Summary (Chapter 3)

Sample ID		SS70 (N/10mm)	Peel Average	St.Dev		SS30 (N/10mm)	Peel Average	St.Dev.		HDPE70 (N/10mm)	Peel Average	St.Dev.		HDPE30 (N/10mm)	Peel Average	St.Dev.
R5.1.1	1.713	0.4283			6.1651	1.5413			1.2126	0.3031			1.1232	0.2808		
R5.1.2	1.2588	0.3147			6.0056	1.5014			1.247	0.3117			0.3514	0.0878		
R5.1.3	1.3027	0.3257			5.1733	1.2933			1.5755	0.3939			0.3473	0.0868		
R5.2.1	1.4039	0.351			6.1608	1.5402			1.1371	0.2843			0.4496	0.1124		
R5.2.2	1.6884	0.4221			5.1474	1.2868			1.2289	0.3072			0.2537	0.0634		
R5.2.3	2.0198	0.505	0.3911	0.0735	5.767	1.4418	1.4341	0.1173	1.2209	0.3052	0.3176	0.0386	0.1565	0.0391	0.1117	0.0865
R9.1.1	6.1162	1.529			7.2826	1.8207			7.1278	1.782			0.1565	0.0391		
R9.1.2	6.0826	1.5206			8.4585	2.1146			5.8799	1.47			3.2749	0.8187		
R9.1.3	6.999	1.7498			7.293	1.8232			8.1095	2.0274			2.674	0.6685		
R9.2.1	6.8683	1.7171			5.6096	1.4024			7.0556	1.7639			2.6618	0.6655		
R9.2.2	6.3419	1.5855			8.9861	2.2465			8.7367	2.1842			2.5678	0.642		
R9.2.3	6.8408	1.7102	1.6354	0.1023	8.0577	2.0144	1.9036	0.2963	8.0268	2.0067	1.8723	0.2534	2.5854	0.6464	0.58	0.2731
R10.1.1	0.7097	0.1774			1.2219	0.3055			2.2264	0.5566			0.5017	0.1254		
R10.1.2	0.623	0.1558			0.8463	0.2116			1.0479	0.262			0.3017	0.0754		
R10.1.3	0.4357	0.1089			0.5059	0.1265			1.4472	0.3618			0.3148	0.0787		
R10.2.1	0.7144	0.1786			0.939	0.2348			0.7714	0.1928			0.2891	0.0723		
R10.2.2	1.0843	0.2711			1.4109	0.3527			1.0057	0.2514			0.3319	0.083		
R10.2.3	1.4267	0.3567	0.2081	0.0899	0.9679	0.242	0.2455	0.0782	1.0757	0.2689	0.3156	0.13	0.3778	0.0945	0.0882	0.0198
R11.1.1	6.4461	1.6115			6.1479	1.537			10.197	2.5493			4.2556	1.0639		
R11.1.2	6.8381	1.7095			7.6784	1.9196			8.9017	2.2254			3.3895	0.8474		
R11.1.3	6.1348	1.5337			6.343	1.5858			9.4461	2.3615			3.8141	0.9535		
R11.2.1	7.247	1.8117			5.2515	1.3129			9.3164	2.3291			3.4243	0.8561		
R11.2.2	6.8381	1.7095			4.9812	1.2453			8.9017	2.2254			3.1715	0.7929		
R11.2.3	5.7689	1.4422	1.6364	0.1344	4.9812	1.2453	1.4743	0.2629	8.0818	2.0204	2.2852	0.1759	4.5632	1.1408	0.9424	0.1364
R12.1.1	1.3518	0.3379			5.1177	1.2794			**********				**********			
R12.1.2	1.6921	0.423			4.29	1.0725										
R12.1.3	1.0598	0.2649			4.0925	1.0231										
R12.2.1	1.2462	0.3116			4.3316	1.0829										
R12.2.2	1.3486	0.3372			4.975	1.2437										
R12.2.3	1.1853	0.2963	0.3285	0.0538	4.0408	1.0102	1.1186	0.1147								

R13.1.1	2.8828	0.7207			**********
R13.1.2	3.1972	0.7993			
R13.1.3	2.917	0.7292			
R13.2.1	2.7597	0.6899			
R13.2.2	3.4949	0.8737			
R13.2.3	3.1019	0.7755	0.7647	0.0663	
R17.1.1	0.4518	0.113			
R17.1.2	0.5415	0.1354			
R17.1.3	0.3391	0.0848			
R17.2.1	0.4761	0.119			
R17.2.2	0.3385	0.0846			
R17.2.3	0.5678	0.142	0.1131	0.0244	
R18.1.1	0.3367	0.0842			
R18.1.2	0.3872	0.0968			
R18.1.3	0.3283	0.0821			
R18.2.1	0.39	0.0975			
R18.2.2	0.4163	0.1041			
R18.2.3	0.3428	0.0857	0.0917	0.0089	
R19.1.1	0.3504	0.0876			
R19.1.2	0.2928	0.0732			
R19.1.3	0.3087	0.0772			
R19.2.1	0.2915	0.0729			
R19.2.2	0.2744	0.0686			
R19.2.3	0.2957	0.0739	0.0756	0.0065	
R20.1.1	0.3597	0.0899			
R20.1.2	0.3559	0.089			
R20.1.3	0.3977	0.0994			
R20.2.1	0.4558	0.1139			
R20.2.2	0.3592	0.0898			
R20.2.3	0.4688	0.1172	0.0999	0.0128	

Table 2 Loop tack determination for all runs LT_SS30 (Chapter 3)

Sample ID	Reading	Range (N)	Loop Tack (N/cm^2)	Average	St.Dev.	Description of failure
R5.1.1	0.3	12.56	0.5842			adhesive
R5.1.2	0.42	12.56	0.8179			adhesive
R5.1.3	0.32	12.56	0.6231			adhesive
R5.2.1	0.6	5	0.4651			adhesive
R5.2.2	0.48	12.56	0.9347			adhesive
R5.2.3	0.38	12.56	0.7400	0.6942	0.170211	adhesive
R9.1.1	0.7	12.56	1.3631			adhesive
R9.1.2	0.68	12.56	1.3242			adhesive
R9.1.3	0.67	12.56	1.3047			
R9.2.1	1	12.46	1.9318			adhesive
R9.2.2	0.9	12.56	1.7526			adhesive
R9.2.3	0.14	25	0.5426	1.3698	0.480187	adhesive
R10.1.1	0.38	12.56	0.7400			cohesive
R10.1.2	0.17	25	0.6589			cohesive messy
R10.1.3	0.22	25	0.8527			cohesive
R10.2.1	0.14	25	0.5426			cohesive
R10.2.2	0.19	25	0.7364			cohesive
R10.2.3	0.18	25	0.6977	0.7047	0.102537	cohesive
R11.1.1	0.77	25	2.9845			cohesive messy
R11.1.2	0.76	25	2.9457			cohesive messy
R11.1.3	0.78	25	3.0233			cohesive messy
R11.2.1	0.84	25	3.2558			cohesive messy
R11.1.2	0.76	25	2.9457			cohesive messy
R11.2.3	0.73	25	2.8295	2.9974	0.142236	cohesive messy
R12.1.1	0.2	25	0.7752			cohesive messy
R12.1.2	direct reading		2.1000			cohesive messy
R12.1.3	0.35	25	1.3566			cohesive not messy
R12.2.1	0.25	25	0.9690			cohesive not messy
R12.2.2	0.5	25	1.9380			cohesive not messy
R12.2.3	0.59	25	2.2868	1.5709	0.627473	cohesive not messy
R13.1.1	0.51	2.45	0.1937			cohesive not messy
R13.1.2	0.39	2.45	0.1481			cohesive
R13.1.3	0.13	5	0.1008			adhesive
R13.2.1	0.06	2.45	0.0228			adhesive
R13.2.2	0.12	2.45	0.0456			adhesive
R13.2.3	0.21	2.45	0.0798	0.0985	0.063905	adhesive
R17.1.1	0.04	2.45	0.0152			adhesive
R17.1.2	0.05	2.45	0.0190			adhesive
R17.1.3	0.11	2.45	0.0418			adhesive
R17.2.1	0.04	2.45	0.0152			adhesive
R17.2.2	0.15	2.45	0.0570			adhesive
R17.2.3	0.35	2.45	0.1329	0.0468	0.045433	adhesive
R18.1.1	0.04	2.45	0.0152			adhesive
R18.1.2	0.07	2.45	0.0266			adhesive
R18.1.3	0.05	2.45	0.0190			adhesive

R18.2.1	0.06	2.45	0.0228			adhesive
R18.2.2	0.11	2.45	0.0418			adhesive
R18.2.3	0.06	2.45	0.0228	0.0247	0.009226	adhesive
R19.1.1	0.19	2.45	0.0722			adhesive
R19.1.1	0.19	2.45	0.0722			adhesive
R19.1.3	0.04	2.45	0.0152			adhesive
R19.2.1	0.14	2.45	0.0532			adhesive
R19.2.2	0.03	2.45	0.0114			adhesive
R19.2.3	0.12	2.45	0.0456	0.0449	0.0456	adhesive
R20.1.1	0.1	2.45	0.0380			adhesive
R20.1.2	0.07	2.45	0.0266			adhesive
R20.1.3	0.1	2.45	0.0380			adhesive
R20.2.1	0.09	2.45	0.0342			adhesive
R20.2.2	0.11	2.45	0.0418			adhesive
R20.2.3	0.15	2.45	0.0570	0.0393	0.010097	adhesive

$$\text{Loop Tack} = \frac{\text{Reading} \times \text{Range (N)}}{6.25\text{cm}^2} = \frac{0.3 \times 12.56}{6.25} = 0.5842 \ (\text{Ncm}^{-2})$$

Table 3 Loop tack determination for all runs LT_SS70 (Chapter 3)

Sample ID	Reading	Range	Tack (N)	Tack (N/cm^2)	Average	St.Dev.	Description of failure
R10.1.1	0.69	12.56	8.6664	1.343628			cohesive messy
R10.1.2	0.44	12.56	5.5264	0.856806			cohesive messy
R10.1.3	0.46	12.56	5.7776	0.895752			cohesive
R10.2.1	0.76	12.56	9.5456	1.479938			cohesive
R10.2.2	0.28	12.45	3.486	0.540465			cohesive messy
R10.2.3	0.43	12.56	5.4008	0.837333	0.99232	0.351304	messy cohesive
R11.1.1	0.6	25	15	2.325581			cohesive
R11.1.2	0.83	12.56	10.4248	1.616248			cohesive
R11.1.3	0.97	12.56	12.1832	1.888868			cohesive
R11.2.1			13.56	2.102326			cohesive
R11.2.2	0.61	25	15.25	2.364341			cohesive
R11.2.3			14.87	2.305426	2.100465	0.297173	cohesive messy
R12.1.1	0.8	12.56	10.048	1.557829			cohesive
R12.1.2	0.61	12.56	7.6616	1.187845			suspiious
R12.1.3	0.81	12.56	10.1736	1.577302			cohesive messy
R12.2.1	0.83	12.56	10.4248	1.616248			cohesive
R12.2.2	direct reading		10.48	1.624806			cohesive
R12.2.3	0.8	12.56	10.048	1.557829	1.52031	0.16536	cohesive no trace
R13.1.1	0.51	12.56	6.4056	0.993116			cohesive no trace
R13.2.1	direct reading		7.63	1.182946			cohesive no trace
R13.2.2	0.57	12.56	7.1592	1.109953			cohesive no trace
R13.2.3	0.29	25	7.25	1.124031	1.102512	0.079489	
R16.1.1	0	2.45	0	0			no tack whatsoever
R16.1.2	no tack	2.45	0	0			doesn't grab the surface

R16.1.3	no tack	2.45	0	0			
R16.2.1	0	2.45	0	0			clear no tack at all
R16.2.2	0	2.45	0	0			no tack
R16.2.3	no tack	2.45	0	0			
R16.2.4	0	2.45	0	0	0	0	no tack
R17.1.2	0.04	2.45	0.098	0.015194			
R17.1.3	0.04	2.45	0.098	0.015194			clean (adhesive) but weak
R17.2.1	0.03	2.45	0.0735	0.011395			
R17.2.2	0.05	2.45	0.1225	0.018992			clear almost no tack
R17.2.3	0.04	2.45	0.098	0.015194	0.015194	0.002686	
R18.1.1	0.09	2.45	0.2205	0.034186			
R18.1.2	0.09	2.45	0.2205	0.034186			
R18.1.3	0.11	2.45	0.2695	0.041783			
R18.2.1	0.09	2.45	0.2205	0.034186			clear almost no tack
R18.2.2	0.09	2.45	0.2205	0.034186			
R18.2.3	0.05	2.45	0.1225	0.018992	0.03292	0.007469	clean but almost no force
R19.1.1	0.07	2.45	0.1715	0.026589			
R19.1.2	0.03	2.45	0.0735	0.011395			cohesive
R19.1.3	0.7	2.45	1.715	0.265891			
R19.2.1	0.06	2.45	0.147	0.022791			
R19.2.2	0.05	2.45	0.1225	0.018992			clean but almost no force
R19.2.3	0.02	2.45	0.049	0.007597	0.058876	0.101661	cohesive
R20.1.1	0.05	2.45	0.1225	0.018992			cohesive
R20.1.2	0.04	2.45	0.098	0.015194			cohesive
R20.1.3	0.09	2.45	0.2205	0.034186			cohesive
R20.2.1	0.5	2.45	1.225	0.189922			cohesive
R20.2.2	0.01	5	0.05	0.007752			cohesive
R20.2.3	0.05	2.45	0.1225	0.018992	0.047506	0.0703	
R5.1.1	0.21	12.56	2.6376	0.40893			clean adhesive
R5.1.2	0.23	12.56	2.8888	0.447876			clean adhesive
R5.1.3	0.21	12.56	2.6376	0.40893			clean adhesive
R5.2.1	0.38	12.56	4.7728	0.739969			clean
R5.2.2	0.28	12.56	3.5168	0.54524			clean
R5.2.3	0.33	12.56	4.1448	0.642605	0.532258	0.136403	clean adhesive
R6.1.1	0	2.45	0	0			oscilates around zero
R6.1.2	0.01	2.45	0	0			no tack
R6.1.3	0	2.45	0	0			doesn't grab the surface
R6.1.4	no force	2.45	0	0			doesn't grab the surface
R6.2.1	no force	2.45	0	0			doesn't grab the surface
R6.2.2	no force	2.45	0	0			doesn't grab the surface
R6.2.3	0	2.45	0	0	0		doesn't grab the surface
R7.1.1	0	2.45	0	0			cohesive
R7.1.2	0.08	2.45	0	0			low tack
R7.1.3	0	2.45	0	0	0	0	cohesive
R9.1.1	0.79	12.56	9.9224	1.538357			clear
R9.1.2	0.74	12.56	9.2944	1.440992			clear
R9.1.3	0.71	12.56	8.9176	1.382574			clear, no residue
R9.2.1	0.74	12.56	9.2944	1.440992			clear
R9.2.2	0.7	12.56	8.792	1.363101			clear
R9.2.3	0.38	12.56	4.7728	0.739969	1.317664	0.289529	clear

Table 4 Loop tack determination for all runs LT_HDPE 70 (Chapter 3)

Sample ID	Reading	Range	Loop Tack (N/cm^2)	Average	St.Dev.	Description of failure
R5.1.1	0.17	12.56	0.3310			adhesive
R5.2.1	0.18	12.56	0.3505			adhesive
R5.1.3	0.13	12.56	0.2531			adhesive
R5.2.1	0.14	12.56	0.2726			adhesive
R5.2.2	0.14	12.56	0.2726			adhesive
R5.2.3	0.28	12.56	0.5452	4.461747	0.108537	adhesive
R9.1.1	0.44	12.56	0.8568			adhesive
R9.1.2	0.39	12.56	0.7594			adhesive
R9.1.3	0.61	12.56	1.1878			adhesive
R9.2.1	0.49	2.45	0.1861			adhesive
R9.2.2	0.55	12.56	1.0710			adhesive
R9.2.3	0.64	12.56	1.2463	0.8846	0.390336	adhesive
R10.1.1	0.25	12.56	0.4868			cohesive
R10.1.2	0.45	12.56	0.8763			cohesive
R10.1.3	0.27	12.56	0.5258			cohesive
R10.2.1	0.28	12.56	0.5452			messy
R10.2.2	0.35	12.56	0.0000			cohesive
R10.2.3	0.39	12.56	0.7594	0.5323	0.30184	cohesive
R11.1.1	0.88	12.56	1.7136			cohesive
R11.1.2	direct reading		2.2000			cohesive messy
R11.1.3	direct reading		2.5000			cohesive messy
R11.2.1	0.55	25	2.1318			cohesive messy
R11.2.2	0.62	25	2.4031			cohesive messy
R11.2.3	0.72	25	2.7907	2.2899	0.366864	cohesive messy
R12.1.1	0.09	2.45	0.0342			adhesive
R12.1.2	0.06	2.45	0.0228			adhesive
R12.1.3	0.09	2.45	0.0342			adhesive
R12.2.1	0.15	2.45	0.0570			adhesive
R12.2.2	0.26	2.45	0.0988			adhesive
R12.2.3	0.32	2.45	0.1216	0.0614	0.040013	adhesive
R13.1.1	0.1	5	0.0775			adhesive
R13.1.2	0.1	5	0.0775			adhesive
R13.1.3	0.07	5	0.0543			adhesive
R13.2.1	0.05	5	0.0388			adhesive
R13.2.2	0.08	5	0.0620			adhesive
R13.2.3	0.05	5	0.0388	0.0581	0.017506	adhesive
R17.1.1	0.03	2.45	0.0114			adhesive
R17.1.2	0.03	2.45	0.0114			adhesive
R17.1.3	0.04	2.45	0.0152			adhesive
R17.2.1	0.045	2.45	0.0171			adhesive
R17.2.2	0.02	2.45	0.0076			adhesive
R17.2.3	0.03	2.45	0.0114	0.0123	0.003344	adhesive

R18.1.1	0.03	2.45	0.0114			adhesive
R18.1.2	0.02	2.45	0.0076			adhesive
R18.1.3	0.02	2.45	0.0076			adhesive
R18.2.1	0.03	2.45	0.0114			adhesive
R18.2.2	0.03	2.45	0.0114			adhesive
R18.2.3	0.035	2.45	0.0133	0.0104	0.002326	adhesive
R19.1.1	0.02	2.45	0.0076			adhesive
R19.1.2	0.035	2.45	0.0133			adhesive
R19.1.3	0.035	2.45	0.0133			adhesive
R19.2.1	0.035	2.45	0.0133			adhesive
R19.2.2	0.025	2.45	0.0095			adhesive
R19.2.3	0.04	2.45	0.0152	0.0120	0.002859	adhesive
R20.1.1	0.02	2.45	0.0076			adhesive
R20.1.2	0.06	2.45	0.0228			adhesive
R20.1.3	0.03	2.45	0.0114			adhesive
R20.2.1	0.04	2.45	0.0152			adhesive
R20.2.2	0.03	2.45	0.0114			adhesive
R20.2.3	0.03	2.45	0.0114	0.0133	0.005236	adhesive

Table 5 Loop tack determination for all runs HDPE_SS30 (Chapter 3)

Sample ID	Reading	Range	Loop Tack (N/cm^2)	Average	St.Dev.	Description of Failure
5.1.1	0.12	12.56	0.233674			adhesive
5.1.2	0.13	12.56	0.253147			adhesive
5.1.3	0.13	12.56	0.253147			adhesive
5.2.1	0.12	12.56	0.233674			adhesive
5.2.2	0.14	12.56	0.27262			adhesive
5.2.3	0.13	12.56	0.253147	0.249902	0.014659	adhesive
9.1.1	0.3	12.56	0.584186			adhesive
9.1.2	0.28	12.56	0.54524			adhesive
9.1.3	0.27	12.56	0.525767			adhesive
9.2.1	0.26	12.56	0.506295			adhesive
9.2.2	0.27	12.56	0.525767			adhesive
9.2.3	0.28	12.56	0.54524	0.538749	0.026605	adhesive
10.1.1	0.26	12.56	0.506295			cohesive
10.1.2	0.27	12.56	0.525767			cohesive
10.1.3	0.26	12.56	0.506295			cohesive
10.2.1	0.28	12.56	0.54524			cohesive
10.2.2	0.26	12.56	0.506295			cohesive
10.2.3	0.26	12.56	0.506295	0.516031	0.016292	cohesive
11.1.1	0.46	25	1.782946			cohesive
11.1.2	0.46	25	1.782946			cohesive
11.1.3	0.45	25	1.744186			cohesive
11.2.1	0.45	25	1.744186			cohesive
11.2.2	0.45	25	1.744186			cohesive
11.2.3	0.46	25	1.782946	1.763566	0.02123	cohesive
12.1.1	0.13	12.56	0.253147			adhesive

12.1.2	0.14	12.56	0.27262			adhesive
12.1.3	0.15	12.56	0.292093			adhesive
12.2.1	0.14	12.56	0.27262			adhesive
12.2.2	0.16	12.56	0.311566			adhesive
12.2.3	0.14	12.56	0.27262	0.279111	0.020111	adhesive
13.1.1	0.26	12.56	0.506295			adhesive
13.1.2	0.26	12.56	0.506295			adhesive
13.1.3	0.28	12.56	0.54524			adhesive
13.2.1	0.26	12.56	0.506295			adhesive
13.2.2	0.27	12.56	0.525767			adhesive
13.2.3	0.27	12.56	0.525767	0.519276	0.0159	adhesive

SAMPLE CALCULATIONS AND SUPPORT DOCUMENTATION FOR CHAPTER 5

RUN 201

19-Feb-04

Initial feed composition

Component	Weight	Wt. fract.
SDS	14.0157	0.0491
Buffer	0.6073	0.0021
Water	224.7337	0.7873
BA	34.1397	0.1196
VAc	11.4746	0.0402
AA	0.4628	0.0016
CTA	0.0229	0.0001
Total	285.4567	1.0000

Initial feed composition

Total fed (g): 46.1000

Component	Weight	Wt. fract.
BA	74.1000	0.7406
VAc	24.9056	0.2489
AA	1.0044	0.0100
CTA	0.0498	0.0005
Total	100.0598	1.0000

Balance 2: Neet monomer feed

Feed rate: Variable

Comp.	Weight (g)	Wt. fract.
BA	244.3799	0.9775
VAc	0.0000	0.0000
AA	5.4958	0.0220
CTA	0.1273	0.0005
Total	250.0030	1.0000

Balance 2: Initiator feed

Feed rate:

Comp.	Weight (g)	Wt. fract.
Initiator	1.7520	0.0529
Water	31.3792	0.9471
Total	33.1312	1.0000

Total added: 19.8620

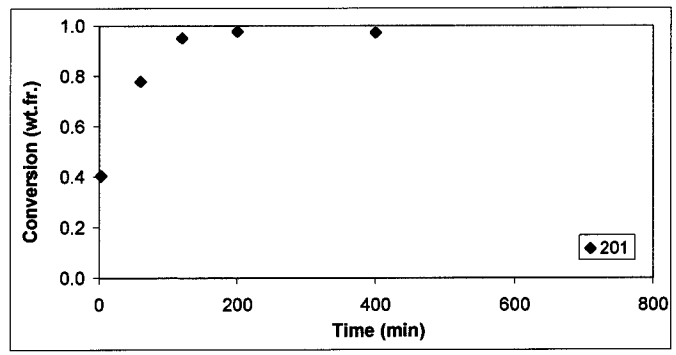
Balance 1: Buffer feed

Feed rate:

Comp.	Weight (g)	Wt. fract.
buffer	10.4790	0.0455
Water	220.0460	0.9545
Total	230.5250	

Gravimetry

Sample	Time (min)	Empty	Sample only	Dry	Solids
1	3	1.228	2.683	1.569	0.127
2	60	1.261	2.549	2.023	0.299
3	120	1.240	2.037	2.046	0.396
4	200	1.247	1.080	1.745	0.461
5	400	1.239	0.432	1.459	0.509
6	660	1.252	0.511	1.514	0.513



Time	B2	B1	BA	VAc	AA	CTA	INI	SDS	Buff	Water w/ buffer	Water	Total	Monomer wt.fr.	Other wt.fr.	Solids	Conversion
3	7.70	0.00	41.6665	11.4746	0.6320	0.0269	1.0503	14.0157	0.6073	0.0000	224.7337	294.2070	0.1828	0.0534	0.1270	0.4029
60	71.30	0.00	103.8360	11.4746	2.0301	0.0592	1.0503	14.0157	0.6073	0.0000	224.7337	357.8070	0.3279	0.0440	0.2990	0.7777
120	97.20	0.00	129.1534	11.4746	2.5995	0.0724	1.0503	14.0157	0.6073	0.0000	224.7337	383.7070	0.3733	0.0410	0.3957	0.9503
200	138.50	0.00	169.5245	11.4746	3.5074	0.0935	1.0503	14.0157	0.6073	0.0000	224.7337	425.0070	0.4341	0.0371	0.4613	0.9771
400	187.40	1.70	217.3247	11.4746	4.5824	0.1184	1.0503	14.0157	0.6846	1.6227	226.3564	477.2297	0.4890	0.0333	0.5087	0.9722
660	187.70	6.50	217.6179	11.4746	4.5889	0.1185	1.0503	14.0157	0.9028	6.2045	230.9382	486.9115	0.4799	0.0330	0.5131	1.0003

Figure 25 General Recipe used in Chapter 5 (Changes in AA, SDS and CTA were indicated in Table 1/Chapter 5)

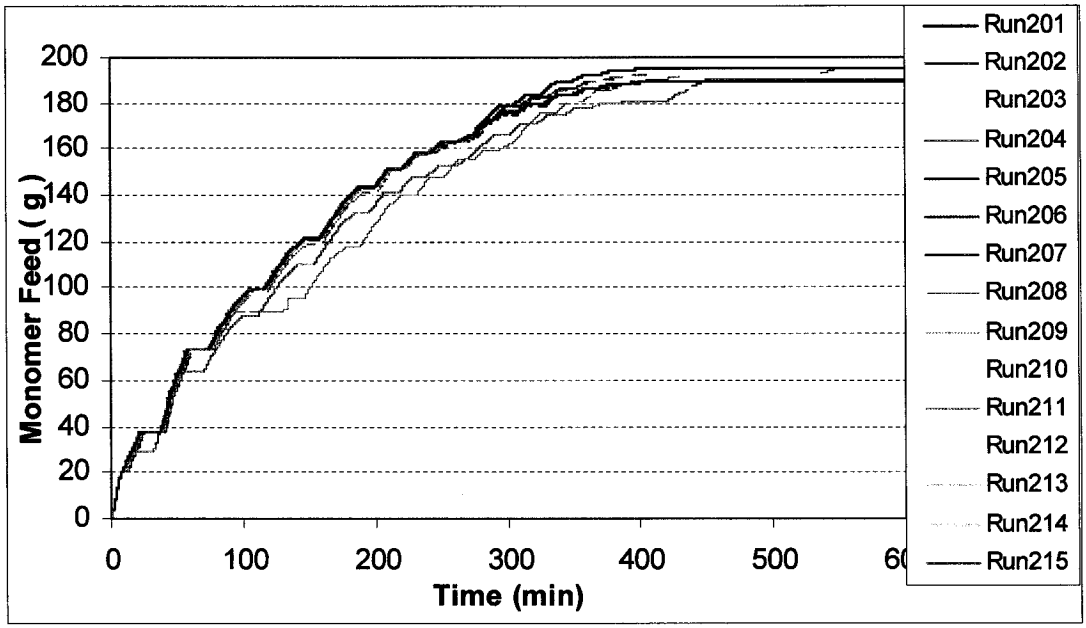


Figure 26 Monomer feed profiles (Chapter 5)

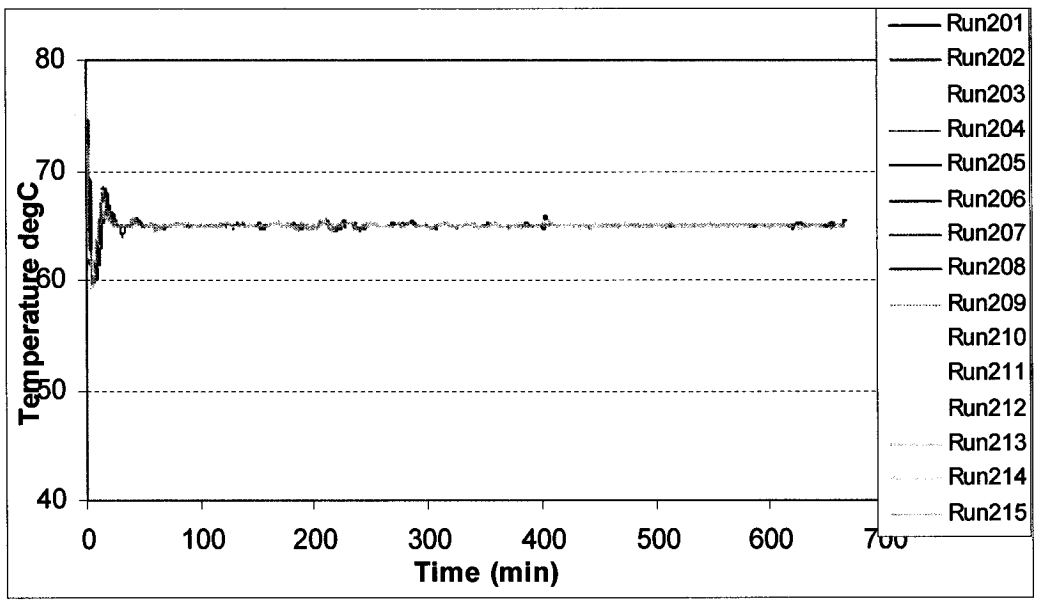


Figure 27 Temperature profiles (Chapter 5)

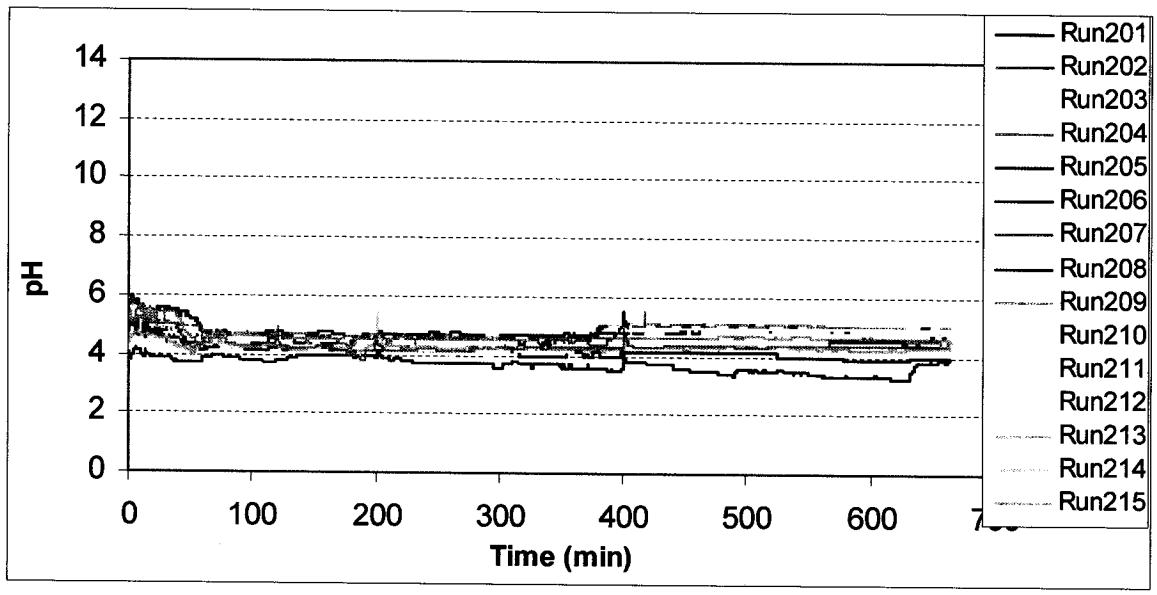


Figure 28 pH profiles (Chapter 5)

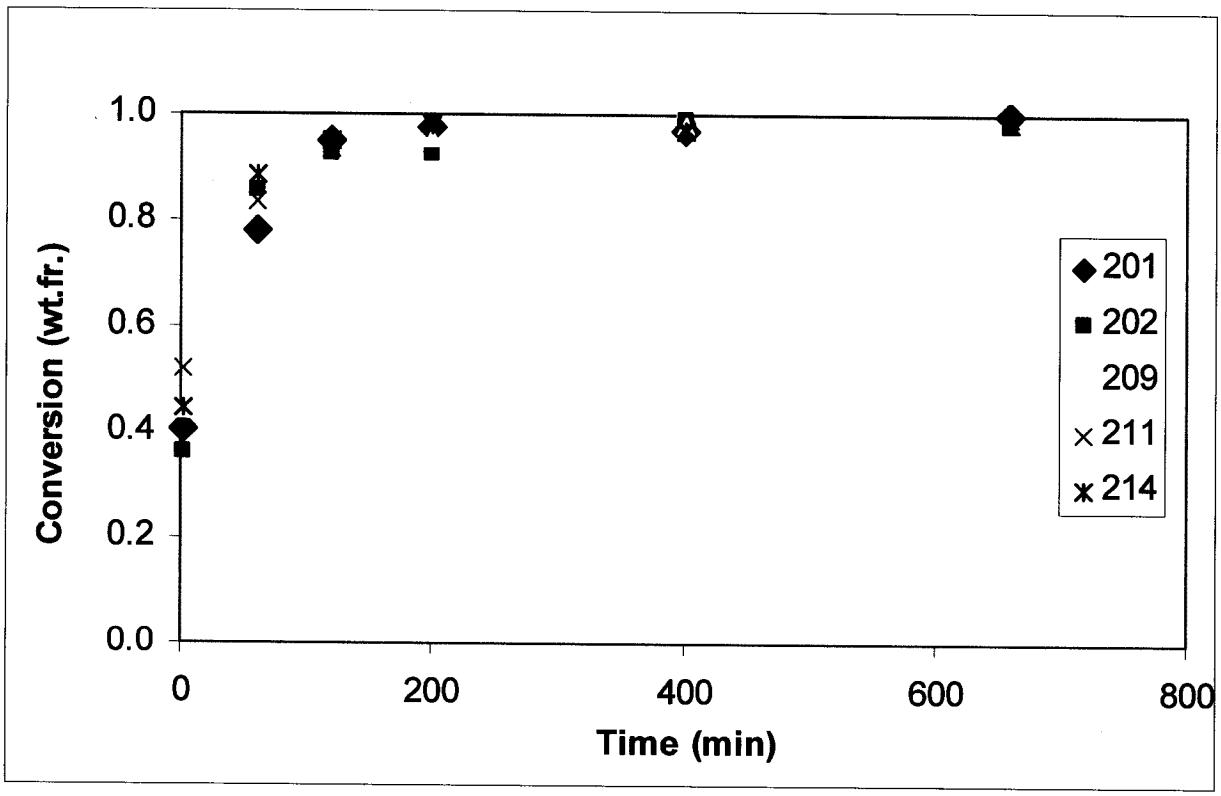


Figure 29 Conversion vs. time for selected runs (Chapter 5)

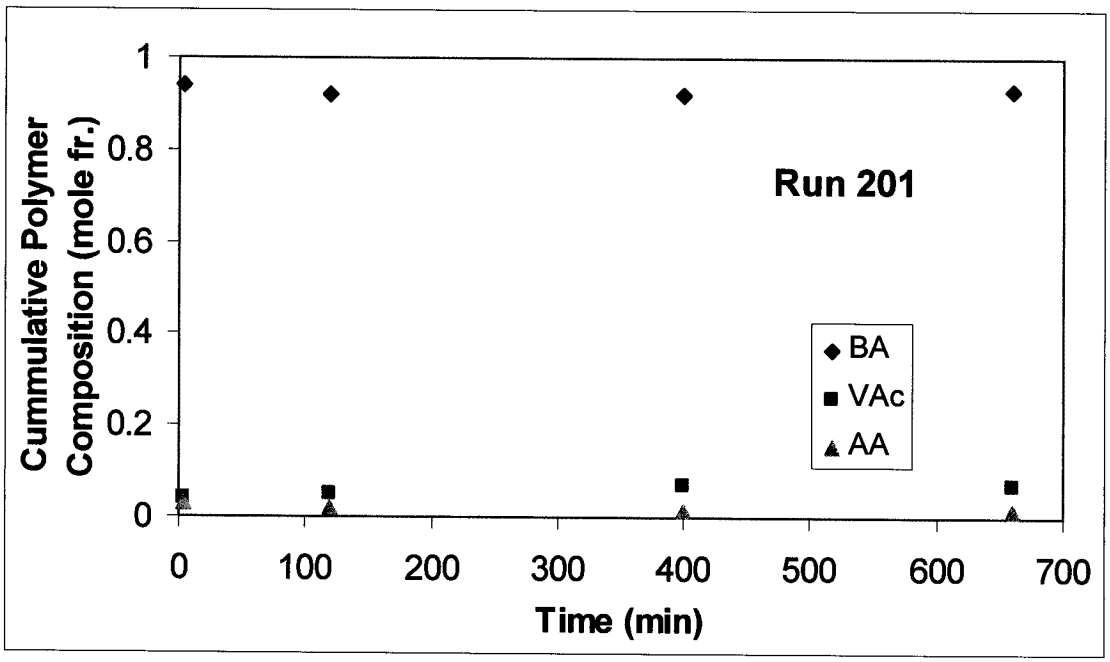


Figure 30 Cumulative polymer composition Run 201 (Chapter 5)

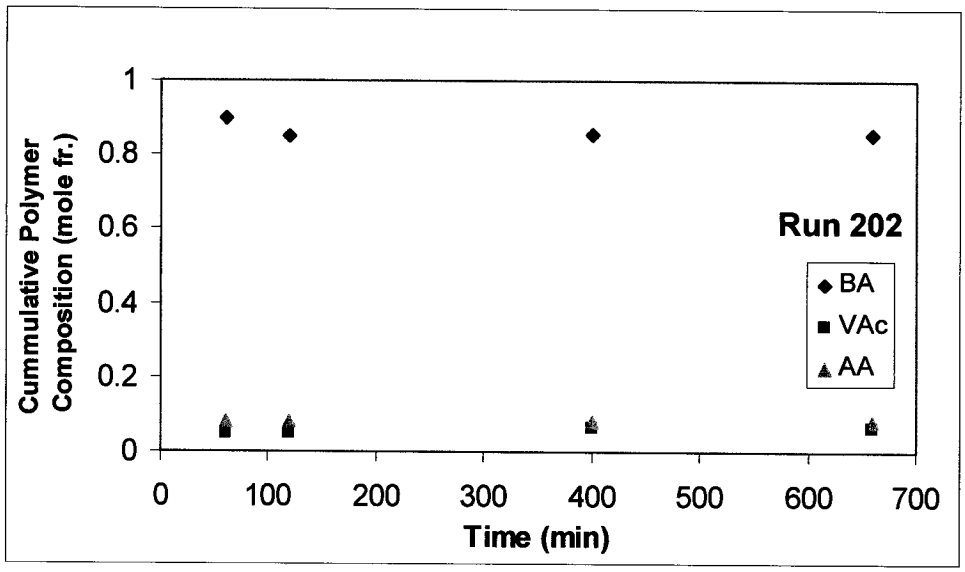


Figure 31 Cumulative polymer composition Run 202 (Chapter 5)

An example of peel strength measurements (Run 205 Peel SS70– Chapter 5). The following notation was used Run.Film.Specimen. (i.e. 205.1.1 denotes run 205, film 1, specimen 1)

Table 6 Results for six specimens used for the determination of peel for run 205 (SS70)

205.1.1		205.1.2		205.1.3		205.2.1		205.2.2		205.2.3	
Length (mm)	Force (N)	Length (mm)	Force (N)	Length (mm)	Force (N)	Length (mm)	Force (N)	Length (mm)	Force (N)	Length (mm)	Force (N)
0	0	-2.59	-0.1	0.733	0.047	-0.66	0.047	0.729	-0.05	1.462	0.048
0.801	10.72	9.608	11.71	6.667	13.81	7.971	14.12	2.222	10.54	2.924	3.605
8.924	10.92	12.24	11.81	10.4	13.47	11.97	14.21	4.443	9.951	7.241	10.57
12.97	10.72	15.73	11.86	12.6	13.57	17.29	14.21	4.443	9.755	10.13	10.52
15.41	10.77	22.75	11.86	15.6	13.66	19.29	14.21	8.123	9.508	15.2	10.62
21.89	10.77	26.24	11.86	19.3	13.62	21.94	14.12	9.581	9.412	20.26	10.62
24.33	10.77	28.87	11.76	27.47	13.66	25.94	14.02	13.3	9.313	23.15	10.62
28.37	10.82	34.08	11.71	32.67	13.71	30.6	13.93	18.47	9.313	31.11	10.48
34.05	10.82	37.57	11.66	35.64	13.71	34.57	14.02	21.42	9.313	33.28	10.43
38.14	10.82	40.2	11.71	37.87	13.71	37.91	14.02	25.1	9.264	38.35	10.38
40.58	10.82	43.69	11.71	41.57	13.71	42.57	14.02	30.27	9.264	42.7	10.48
46.26	10.87	48.94	11.71	43.81	13.71	45.89	14.02	38.39	9.264	47.02	10.62
49.5	10.87	51.57	11.81	48.27	13.62	51.2	14.02	41.35	9.216	52.08	10.62
53.54	10.87	54.2	11.81	54.21	13.62	55.86	14.02	46.52	9.165	55.72	10.62
56.78	10.82	56.79	11.76	60.14	13.62	57.86	14.02	51.69	9.165	61.5	10.62
61.66	10.77	59.42	11.71	64.61	13.62	59.86	13.88	56.86	9.216	65.85	10.57
65.71	10.82	64.67	11.71	68.31	13.52	64.51	13.97	59.81	9.264	69.45	10.62
68.95	10.82	68.16	11.71	72.78	13.57	67.17	14.02	62.76	9.264	72.34	10.62
71.39	10.87	70.79	11.76	75.75	13.57	70.48	13.97	67.21	9.264	77.41	10.67
77.07	10.92	74.28	11.76	81.68	13.62	75.83	13.97	70.16	9.264	83.94	10.62
84.39	10.92	76.91	11.81	84.65	13.52	77.8	13.97	73.11	9.264	88.97	10.57
90.04	10.92	80.4	11.81	89.85	13.57	83.8	14.07	82.73	9.117	96.21	10.57
93.32	10.96	83.89	11.86	92.81	13.57	87.8	13.97	90.85	9.313	100.6	10.72
99.8	11.01	89.14	11.71	98.78	13.62	91.11	13.88	97.48	9.412	103.5	10.72
104.6	10.96	98.75	11.86	102.5	13.57	93.77	13.83	101.9	9.46	109.9	10.67
107.9	10.96	103.1	11.86	106.2	13.57	98.43	13.83	106.4	9.508	117.2	10.67
111.2	10.96	106.6	11.91	109.9	13.57	101.1	13.88	110.8	9.508	122.3	10.72
116	10.96	109.2	11.91	112.9	13.57	107.7	13.88	113.7	9.508	125.9	10.67
120.9	10.96	114.5	11.86	121.1	13.57	112.4	13.78	122.6	9.508	129.5	10.67
125.8	10.96	118.8	11.86	126.3	13.47	115.7	13.83	127	9.559	133.8	10.67
129.8	10.96	123.2	11.86	129.2	13.38	120.4	13.88	134.4	9.559	138.9	10.72
132.3	10.96	126.7	11.86	133.7	13.38	124.4	13.93	137.4	9.559	143.9	10.72
137.1	10.92	131.1	11.81	138.9	13.47	131.7	13.97	143.3	9.607	148.3	10.72
140.4	10.96	138	11.76	144.8	13.47	137	14.02	150.7	9.508	151.2	10.72
149.3	10.96	142.4	11.71	148.5	13.47	140.3	13.97	157.3	9.607	157	10.72
155.8	10.96	146.8	11.71	156.7	13.33	145	13.93	162.5	9.704	159.1	10.82
164.7	10.96	149.4	11.76	158.9	13.28	148.3	13.97	175.8	9.803	165	10.87
167.9	10.96	152	11.76	164.1	13.23	153	14.02	181.7	9.704	172.2	10.87
175.2	10.96	155.5	11.71	167.8	13.23	155.6	13.97	185.4	9.559	180.1	10.87
198	0.048	159	11.71	177.5	13.28	160.3	13.93	197.9	0.048	182.3	10.82
		166	11.66	179.7	13.23	163.6	13.88			198.2	0.195
		172.1	11.71	182	13.23	168.3	13.88				

		180	11.71	196.8	0.096	172.9	13.83		
		186.1	11.71			177.6	13.83		
		194	11.52			182.9	13.83		
		196.6	0			189.5	13.69		
						200.2	0.24		
Average	**10.91**		**11.77**		**13.51**		**13.93**	**9.418**	**10.66**

Table 7 Peel Strength Summary (Chapter 5)

Run	Film	Spec	Peel_SS70				HDPE30				HDPE70				SS30			
			Force	N/10mm	Av.	St.Dev	Force	N/10mm	Av.	St.Dev	Force	N/10mm	Av.	St.Dev	Force	N/10mm	Av.	St.Dev
201	1	1	2.929	0.7322			0.415	0.104			0.854	0.2136			0.725	0.1813		
201	1	2	2.793	0.6982			0.406	0.101			0.791	0.1977			0.954	0.2385		
201	1	3	3.33	0.8326			0.42	0.105			0.423	0.1058			0.709	0.1771		
201	2	1	4.913	1.2282			0.447	0.112			0.908	0.227			0.708	0.1771		
201	2	2	3.225	0.8063			0.411	0.103			0.785	0.1963			0.441	0.1102		
201	2	3	3.628	0.9069	0.867	0.192	0.42	0.105	0.105	0.004	0.647	0.1618	0.184	0.044	0.455	0.1139	0.166	0.048
202	1	1	3.831	0.9578			0	0			0.561	0.1404			0	0		
202	1	2	3.94	0.9851			0	0			0.414	0.1034			0	0		
202	1	3	4.221	1.0552			0	0			0.463	0.1158			0	0		
202	2	1	4.163	1.0406			0	0			0.668	0.1671			0	0		
202	2	2	3.392	0.8481			0	0			0.73	0.1826			0	0		
202	2	3	3.601	0.9001	0.965	0.08	0	0	0	0	0.4	0.1001	0.135	0.034	0	0	0	0
203	1	1	7.482	1.8705			2.117	0.529			9.115	2.2788			2.946	0.7364		
203	1	2	6.344	1.5859			1.635	0.409			9.295	2.3238			3.154	0.7885		
203	1	3	7.153	1.7883			1.406	0.351			8.486	2.1215			2.691	0.6728		
203	2	1	6.704	1.676			1.783	0.446			8.807	2.2016			2.953	0.7382		
203	2	2	6.366	1.5916			2.547	0.637			8.883	2.2207			2.702	0.6755		
203	2	3	6.493	1.6233	1.689	0.116	2.2	0.55	0.487	0.104	8.942	2.2354	2.23	0.069	2.824	0.706	0.72	0.044
204	1	1	7.499	1.8748			3.25	0.812			4.656	1.1641			1.987	0.4966		
204	1	2	7.118	1.7796			3.506	0.876			5.605	1.4013			2.2	0.55		
204	1	3	7.014	1.7536			3.367	0.842			4.594	1.1484			1.885	0.4714		
204	2	1	7.274	1.8186			3.614	0.904			5.228	1.3071			2.438	0.6095		
204	2	2	7.611	1.9028			4.036	1.009			3.897	0.9744			1.87	0.4675		
204	2	3	7.09	1.7724	1.817	0.06	3.642	0.91	0.892	0.068	4.502	1.1254	1.187	0.149	1.615	0.4037	0.5	0.072
205	1	1	10.91	2.7263			2.163	0.541			4.691	1.1727			5.932	1.4831		
205	1	2	11.77	2.9415			1.901	0.475			4.004	1.001			6.341	1.5851		
205	1	3	13.51	3.3787			2.372	0.593			3.705	0.9262			4.76	1.1899		
205	2	1	13.93	3.4834			2.59	0.648			4.258	1.0645			5.265	1.3162		
205	2	2	9.418	2.3544			2.977	0.744			4.875	1.2188			5.388	1.3469		
205	2	3	10.66	2.6653	2.925	0.436	2.87	0.718	0.62	0.104	4.266	1.0666	1.075	0.108	4.821	1.2052	1.354	0.155
206	1	1	2.719	0.6798			2.39	0.597			1.827	0.4567			1.2	0.3		
206	1	2	4.993	1.2482			2.916	0.729			1.157	0.2892			1.397	0.3491		

206	1	3	3.13	0.7824			3.305	0.826			2.111	0.5277			1.621	0.4053		
206	2	1	4.993	1.2482			3.386	0.846			0.836	0.2089			1.357	0.3392		
206	2	2	2.744	0.686			2.784	0.696			2.463	0.6157			1.207	0.3018		
206	2	3	2.931	0.7328	0.896	0.275	2.369	0.592	0.715	0.109	2.451	0.6129	0.452	0.17	1.423	0.3557	0.342	0.039
207	1	1	9.037	2.2593			1.161	0.29			7.703	1.9258			3.376	0.844		
207	1	2	10.13	2.5319			1.674	0.419			6.982	1.7456			2.62	0.6549		
207	1	3	7.473	1.8682			2.466	0.616			7.168	1.792			2.943	0.7357		
207	2	1	9.615	2.4037			2.48	0.62			7.558	1.8896			1.871	0.4678		
207	2	2	7.823	1.9558			1.518	0.38			6.251	1.5628			2.187	0.5469		
207	2	3	8.785	2.1962	2.203	0.255	1.628	0.407	0.455	0.134	7.801	1.9504	1.811	0.145	2.765	0.6913	0.657	0.134
208	1	1	0.612	0.1529			0	0			0.571	0.1428			0	0		
208	1	2	0.435	0.1089			0	0			0.426	0.1064			0	0		
208	1	3	0.382	0.0954			0	0			0.394	0.0986			0	0		
208	2	1	0.345	0.0862			0	0			0.427	0.1066			0	0		
208	2	2	0.484	0.1209			0	0			0.473	0.1182			0	0		
208	2	3	0.382	0.0954	0.11	0.024	0	0	0	0	0.394	0.0986	0.112	0.017	0	0	0	0
209	1	1	2.841	0.7103			0	0			1.827	0.4566			5.718	1.4294		
209	1	2	2.875	0.7187			0	0			1.468	0.367			4.799	1.1997		
209	1	3	2.875	0.7187			0	0			1.012	0.253			6.11	1.5276		
209	2	1	2.756	0.6889			0	0			0.801	0.2002			4.422	1.1056		
209	2	2	2.357	0.5894			0	0			1.777	0.4441			5.262	1.3156		
209	2	3	2.776	0.694	0.687	0.049	0	0	0	0	1.369	0.3423	0.344	0.102	5.417	1.3541	1.322	0.153
210	1	1	15.91	3.9769			9.106	2.276			9.37	2.3425			10.77	2.6935		
210	1	2	14.45	3.6134			7.446	1.862			8.166	2.0416			10.99	2.7466		
210	1	3	14.75	3.6868			9.542	2.385			8.113	2.0282			10.24	2.5602		
210	2	1	16.62	4.1543			8.966	2.241			10.08	2.5202			11.34	2.8356		
210	2	2	15.37	3.8437			7.577	1.894			8.877	2.2193			9.673	2.4183		
210	2	3	14.46	3.6138	3.815	0.219	7.788	1.947	2.101	0.226	7.189	1.7972	2.158	0.257	9.79	2.4475	2.617	0.168
211	1	1	0	0			0	0			0	0			0	0		
211	1	2	0	0			0	0			0	0			0	0		
211	1	3	0	0			0	0			0	0			0	0		
211	2	1	0	0			0	0			0	0			0	0		
211	2	2	0	0			0	0			0	0			0	0		
211	2	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
212	1	1	6.537	1.6344			2.958	0.739			2.529	0.6322			3.697	0.9243		
212	1	2	3.675	0.9189			3.586	0.896			3.491	0.8728			3.423	0.8558		
212	1	3	4.345	1.0862			2.684	0.671			2.519	0.6299			3.415	0.8537		

212	2	1	4.363	1.0908			2.436	0.609			2.957	0.7393			3.574	0.8936		
212	2	2	5.492	1.3729			2.363	0.591			3.03	0.7575			3.404	0.8511		
212	2	3	3.574	0.8936	1.166	0.286	2.668	0.667	0.696	0.112	2.34	0.5849	0.703	0.107	3.509	0.8772	0.876	0.029
213	1	1	18.63	4.6567			0.821	0.205			2.337	0.5843			2.675	0.6688		
213	1	2	20.39	5.0981			1.001	0.25			2.063	0.5157			3.133	0.7832		
213	1	3	21.19	5.2985			1.169	0.292			2.583	0.6458			2.005	0.5013		
213	2	1	23.12	5.7808			1.316	0.329			2.087	0.5217			3.174	0.7934		
213	2	2	16.18	4.0453			0.995	0.249			3.012	0.753			2.27	0.5676		
213	2	3	23.72	5.9295	5.135	0.706	0.977	0.244	0.262	0.043	1.722	0.4305	0.575	0.113	3.292	0.8231	0.69	0.133
214	1	1	16.57	4.1416			1.751	0.438			1.274	0.3184			1.963	0.4908		
214	1	2	16.47	4.1187			1.499	0.375			1.626	0.4065			2.165	0.5413		
214	1	3	16.48	4.1188			1.573	0.393			1.033	0.2582			2.485	0.6213		
214	2	1	22.09	5.5234			1.531	0.383			0.806	0.2016			1.605	0.4013		
214	2	2	17.52	4.3795			1.378	0.344			0.906	0.2264			2.458	0.6146		
214	2	3	15.81	3.9524	4.372	0.58	1.684	0.421	0.392	0.033	1.616	0.4041	0.303	0.089	2.434	0.6085	0.546	0.088
215	1	1	14.92	3.7301			1.283	0.321			0.539	0.1348			1.801	0.4502		
215	1	2	16.25	4.0614			1.188	0.297			0.414	0.1035			1.348	0.3369		
215	1	3	19.89	4.9725			1.292	0.323			0.916	0.2291			2.254	0.5635		
215	2	1	17.3	4.3238			1.296	0.324			0.403	0.1007			1.132	0.2829		
215	2	2	15.23	3.8071			1.467	0.367			0.477	0.1191			1.761	0.4402		
215	2	3	13.34	3.3349	4.038	0.565	1.234	0.309	0.323	0.024	0.863	0.2157	0.15	0.057	2.045	0.5114	0.431	0.105

Table 8 Loop Tack SS70 (Chapter 5)

RUN	Film	Spec	Reading	Scale	Tack (N)	Tack (N/cm^2)	Average	St.Dev.	Failure
201	1	1	0.24	12.56	3.0144	0.4673			adhesive
201	1	2	0.21	12.56	2.6376	0.4089			adhesive
201	1	3	0.2	12.56	2.512	0.3895			adhesive
201	2	1	0.25	12.56	3.14	0.4868			adhesive
201	2	2	0.35	12.56	4.396	0.6816			adhesive
201	2	3	0.22	12.56	2.7632	0.4284	0.4771	0.1065	adhesive
202	1	1	0.35	12.56	4.396	0.6816			adhesive
202	1	2	0.35	12.56	4.396	0.6816			adhesive
202	1	3	0.34	12.56	4.2704	0.6621			adhesive
202	2	1	0.37	12.56	4.6472	0.7205			adhesive
202	2	2	0.41	12.56	5.1496	0.7984			adhesive
202	2	3	0.39	12.56	4.8984	0.7594	0.7173	0.0529	adhesive
203	1	1	0.54	25	13.5	2.0930			adhesive
203	1	2	0.57	25	14.25	2.2093			adhesive
203	1	3	0.6	25	15	2.3256			adhesive
203	2	1	0.55	25	13.75	2.1318			adhesive
203	2	2	0.55	25	13.75	2.1318			adhesive
203	2	3	0.58	25	14.5	2.2481	2.1899	0.0875	adhesive
204	1	1	0.78	12.56	9.7968	1.5189			adhesive
204	1	2	0.55	12.56	6.908	1.0710			adhesive
204	1	3	0.62	12.56	7.7872	1.2073			adhesive
204	2	1	0.6	12.56	7.536	1.1684			adhesive
204	2	2	0.65	12.56	8.164	1.2657			adhesive
204	2	3	0.74	12.56	9.2944	1.4410	1.2787	0.1701	adhesive
205	1	1	0.77	12.56	9.6712	1.4994			adhesive
205	1	2	0.63	12.56	7.9128	1.2268			adhesive
205	1	3	0.59	12.56	7.4104	1.1489			adhesive
205	2	1	0.51	12.56	6.4056	0.9931			adhesive
205	2	2	0.72	12.56	9.0432	1.4020			adhesive
205	2	3	0.75	12.56	9.42	1.4605	1.2885	0.1987	adhesive
206	1	1	0.45	12.56	5.652	0.8763			adhesive
206	1	2	0.52	12.56	6.5312	1.0126			adhesive
206	1	3	0.51	12.56	6.4056	0.9931			adhesive
206	2	1	0.53	12.56	6.6568	1.0321			adhesive
206	2	2	0.52	12.56	6.5312	1.0126			adhesive
206	2	3	0.48	12.56	6.0288	0.9347	0.9769	0.0596	adhesive
207	1	1	0.53	12.56	6.6568	1.0321			adhesive
207	1	2	0.35	12.56	4.396	0.6816			adhesive
207	1	3	0.75	12.56	9.42	1.4605			adhesive
207	2	1	0.4	12.56	5.024	0.7789			adhesive
207	2	2	0.6	12.56	7.536	1.1684			adhesive
207	2	3	0.73	12.56	9.1688	1.4215	1.0905	0.3226	adhesive
208	1	1	0.67	5	3.35	0.5194			adhesive
208	1	2	0.69	5	3.45	0.5349			adhesive
208	1	3	0.61	5	3.05	0.4729			adhesive
208	2	1	0.69	5	3.45	0.5349			adhesive

208	2	2	0.65	5	3.25	0.5039			adhesive
208	2	3	0.59	5	2.95	0.4574	0.5039	0.0325	adhesive
209	1	1	0.34	12.56	4.2704	0.6621			adhesive
209	1	2	0.28	12.56	3.5168	0.5452			adhesive
209	1	3	0.37	12.56	4.6472	0.7205			adhesive
209	2	1	0.29	12.56	3.6424	0.5647			adhesive
209	2	2	0.4	12.56	5.024	0.7789			adhesive
209	2	3	0.29	12.56	3.6424	0.5647	0.6394	0.0965	adhesive
210	1	1	0.34	12.56	4.2704	0.6621			adhesive
210	1	2	0.33	12.56	4.1448	0.6426			adhesive
210	1	3	0.41	12.56	5.1496	0.7984			adhesive
210	2	1	0.45	12.56	5.652	0.8763			adhesive
210	2	2	0.5	12.56	6.28	0.9736			adhesive
210	2	3	0.44	12.56	5.5264	0.8568	0.8016	0.1288	adhesive
211	1	1	0.13	12.56	1.6328	0.2531			adhesive
211	1	2	0.06	12.56	0.7536	0.1168			adhesive
211	1	3	0.18	12.56	2.2608	0.3505			adhesive
211	2	1	0.05	12.56	0.628	0.0974			adhesive
211	2	2	0.1	12.56	1.256	0.1947			adhesive
211	2	3	0.07	12.56	0.8792	0.1363	0.1915	0.0965	adhesive
212	1	1	0.78	12.56	9.7968	1.5189			adhesive
212	1	2	0.85	12.56	10.676	1.6552			adhesive
212	1	3	0.85	12.56	10.676	1.6552			adhesive
212	2	1	0.81	12.56	10.174	1.5773			adhesive
212	2	2	0.87	12.56	10.927	1.6941			adhesive
212	2	3	0.81	12.56	10.174	1.5773	1.6130	0.0657	adhesive
213	1	1	0.57	12.56	7.1592	1.1100			adhesive
213	1	2	0.66	12.56	8.2896	1.2852			adhesive
213	1	3	0.59	12.56	7.4104	1.1489			adhesive
213	2	1	0.55	12.56	6.908	1.0710			adhesive
213	2	2	0.6	12.56	7.536	1.1684			adhesive
213	2	3	0.54	12.56	6.7824	1.0515	1.1392	0.0842	adhesive
214	1	1	0.58	12.56	7.2848	1.1294			adhesive
214	1	2	0.59	12.56	7.4104	1.1489			adhesive
214	1	3	0.56	12.56	7.0336	1.0905			adhesive
214	2	1	0.53	12.56	6.6568	1.0321			adhesive
214	2	2	0.52	12.56	6.5312	1.0126			adhesive
214	2	3	0.53	12.56	6.6568	1.0321	1.0743	0.057	adhesive
215	1	1	0.6	12.56	7.536	1.1684			adhesive
215	1	2	0.53	12.56	6.6568	1.0321			adhesive
215	1	3	0.5	12.56	6.28	0.9736			adhesive
215	2	1	0.52	12.56	6.5312	1.0126			adhesive
215	2	2	0.62	12.56	7.7872	1.2073			adhesive
215	2	3	0.52	12.56	6.5312	1.0126	1.0678	0.0957	adhesive

Table 9 Loop Tack SS30 (Chapter 5)

RUN	Film	Spec	Reading	Scale	Tack (N/cm^2)	Average	St.Dev.	Failure
201	1	1	0.23	12.56	0.4479			adhesive
201	1	2	0.12	12.56	0.2337			adhesive
201	1	3	0.13	12.56	0.2531			adhesive
201	2	1	0.26	12.56	0.5063			adhesive
201	2	2	0.16	12.56	0.3116			adhesive
201	2	3	0.18	12.56	0.3505	0.3505	0.10807	adhesive
202	1	1	0.05	12.56	0.0974			adhesive
202	1	2	0.03	12.56	0.0584			adhesive
202	1	3	0.05	12.56	0.0974			adhesive
202	2	1	0.04	12.56	0.0779			adhesive
202	2	2	0.03	12.56	0.0584			adhesive
202	2	3	0.02	12.56	0.0389	0.0714	0.023583	adhesive
203	1	1	0.72	25	2.7907			adhesive
203	1	2	0.84	25	3.2558			adhesive
203	1	3	0.68	25	2.6357			adhesive
203	2	1	0.71	25	2.7519			adhesive
203	2	2	0.66	25	2.5581			adhesive
203	2	3	0.71	25	2.7519	2.7907	0.243909	adhesive
204	1	1	0.18	12.56	0.3505			adhesive
204	1	2	0.2	12.56	0.3895			adhesive
204	1	3	0.19	12.56	0.3700			adhesive
204	2	1	0.22	12.56	0.4284			adhesive
204	2	2	0.2	12.56	0.3895			adhesive
204	2	3	0.19	12.56	0.3700	0.3830	0.026605	adhesive
205	1	1	0.53	12.56	1.0321			adhesive
205	1	2	0.54	12.56	1.0515			adhesive
205	1	3	0.51	12.56	0.9931			adhesive
205	2	1	0.5	12.56	0.9736			adhesive
205	2	2	0.48	12.56	0.9347			adhesive
205	2	3	0.51	12.56	0.9931	0.9964	0.041613	adhesive
206	1	1	0.15	12.56	0.2921			adhesive
206	1	2	0.15	12.56	0.2921			adhesive
206	1	3	0.2	12.56	0.3895			adhesive
206	2	1	0.24	12.56	0.4673			adhesive
206	2	2	0.19	12.56	0.3700			adhesive
206	2	3	0.18	12.56	0.3505	0.3602	0.066036	adhesive
207	1	1	0.39	12.56	0.7594			adhesive
207	1	2	0.41	12.56	0.7984			adhesive
207	1	3	0.39	12.56	0.7594			adhesive
207	2	1	0.34	12.56	0.6621			adhesive
207	2	2	0.33	12.56	0.6426			adhesive
207	2	3	0.34	12.56	0.6621	0.7140	0.06594	adhesive
208	1	1	0.05	5	0.0388			adhesive
208	1	2	0.07	5	0.0543			adhesive
208	1	3	0.09	5	0.0698			adhesive
208	2	1	0.08	5	0.0620			adhesive

208	2	2	0.07	5	0.0543			adhesive
208	2	3	0.07	5	0.0543	0.0556	0.010304	adhesive
209	1	1	0.22	12.56	0.4284			adhesive
209	1	2	0.18	12.56	0.3505			adhesive
209	1	3	0.17	12.56	0.3310			adhesive
209	2	1	0.25	12.56	0.4868			adhesive
209	2	2	0.22	12.56	0.4284			adhesive
209	2	3	0.24	12.56	0.4673	0.4154	0.4673	adhesive
210	1	1	0.4	12.56	0.7789			adhesive
210	1	2	0.36	12.56	0.7010			adhesive
210	1	3	0.42	12.56	0.8179			adhesive
210	2	1	0.43	12.56	0.8373			adhesive
210	2	2	0.42	12.56	0.8179			adhesive
210	2	3	0.41	12.56	0.7984	0.7919	0.048747	adhesive
211	1	1	0.11	5	0.0853			adhesive
211	1	2	0.08	5	0.0620			adhesive
211	1	3	0.12	5	0.0930			adhesive
211	2	1	0.11	5	0.0853			adhesive
211	2	2	0.08	5	0.0620			adhesive
211	2	3	0.1	5	0.0775	0.0775	0.012971	adhesive
212	1	1	0.4	12.56	0.7789			adhesive
212	1	2	0.46	12.56	0.8958			adhesive
212	1	3	0.44	12.56	0.8568			adhesive
212	2	1	0.55	12.56	1.0710			adhesive
212	2	2	0.37	12.56	0.7205			adhesive
212	2	3	0.44	12.56	0.8568	0.8633	0.119828	adhesive
213	1	1	0.25	12.56	0.4868			adhesive
213	1	2	0.3	12.56	0.5842			adhesive
213	1	3	0.26	12.56	0.5063			adhesive
213	2	1	0.3	12.56	0.5842			adhesive
213	2	2	0.27	12.56	0.5258			adhesive
213	2	3	0.28	12.56	0.5452	0.5387	0.040223	adhesive
214	1	1	0.29	12.56	0.5647			adhesive
214	1	2	0.25	12.56	0.4868			adhesive
214	1	3	0.28	12.56	0.5452			adhesive
214	2	1	0.3	12.56	0.5842			adhesive
214	2	2	0.25	12.56	0.4868			adhesive
214	2	3	0.27	12.56	0.5258	0.5323	0.040223	adhesive
215	1	1	0.29	12.56	0.5647			adhesive
215	1	2	0.25	12.56	0.4868			adhesive
215	1	3	0.3	12.56	0.5842			adhesive
215	2	1	0.3	12.56	0.5842			adhesive
215	2	2	0.28	12.56	0.5452			adhesive
215	2	3	0.28	12.56	0.5452	0.5517	0.036257	adhesive

Table 12 Loop Tack HDPE70 (Chapter 5)

Run	Film	Spec	Reading	Range	Loop Tack (N/cm^2)	Average	St.Dev.	Failure
201	1	1	0.51	5	0.3953			adhesive
201	1	2	0.58	5	0.4496			adhesive
201	1	3	0.44	5	0.3411			adhesive
201	2	1	0.51	5	0.3953			adhesive
201	2	2	0.49	5	0.3798			adhesive
201	2	3	0.48	5	0.3721	0.3889	0.035833	adhesive
202	1	1	0.16	5	0.1240			adhesive
202	1	2	0.14	5	0.1085			adhesive
202	1	3	0.14	5	0.1085			adhesive
202	2	1	0.15	5	0.1163			adhesive
202	2	2	0.11	5	0.0853			adhesive
202	2	3	0.09	5	0.0698	0.1021	0.020461	adhesive
203	1	1	0.69	12.56	1.3436			adhesive
203	1	2	0.64	12.56	1.2463			adhesive
203	1	3	0.74	12.56	1.4410			adhesive
203	2	1	0.61	12.56	1.1878			adhesive
203	2	2	0.72	12.56	1.4020			adhesive
203	2	3	0.68	12.56	1.3242	1.3242	0.094599	adhesive
204	1	1	0.24	12.56	0.4673			adhesive
204	1	2	0.26	12.56	0.5063			adhesive
204	1	3	0.2	12.56	0.3895			adhesive
204	2	1	0.21	12.56	0.4089			adhesive
204	2	2	0.23	12.56	0.4479			adhesive
204	2	3	0.24	12.56	0.4673	0.4479	0.042663	adhesive
205	1	1	0.45	5	0.3488			adhesive
205	1	2	0.43	5	0.3333			adhesive
205	1	3	0.47	5	0.3643			adhesive
205	2	1	0.51	5	0.3953			adhesive
205	2	2	0.43	5	0.3333			adhesive
205	2	3	0.52	5	0.4031	0.3630	0.030388	adhesive
206	1	1	0.25	12.56	0.4868			adhesive
206	1	2	0.27	12.56	0.5258			adhesive
206	1	3	0.28	12.56	0.5452			adhesive
206	2	1	0.24	12.56	0.4673			adhesive
206	2	2	0.26	12.56	0.5063			adhesive
206	2	3	0.29	12.56	0.5647	0.5160	0.03643	adhesive
207	1	1	0.67	12.56	1.3047			adhesive
207	1	2	0.64	12.56	1.2463			adhesive
207	1	3	0.61	12.56	1.1878			adhesive
207	2	1	0.65	12.56	1.2657			adhesive
207	2	2	0.68	12.56	1.3242			adhesive
207	2	3	0.61	12.56	1.1878	1.2528	0.057327	adhesive
208	1	1	0.05	5	0.0388			adhesive
208	1	2	0.06	5	0.0465			adhesive

208	1	3	0.05	5	0.0388			adhesive
208	2	1	0.05	5	0.0388			adhesive
208	2	2	0.05	5	0.0388			adhesive
208	2	3	0.06	5	0.0465	0.0413	0.004003	adhesive
209	1	1	0.44	5	0.3411			adhesive
209	1	2	0.44	5	0.3411			adhesive
209	1	3	0.42	5	0.3256			adhesive
209	2	1	0.4	5	0.3101			adhesive
209	2	2	0.48	5	0.3721			adhesive
209	2	3	0.46	5	0.3566	0.3411	0.021926	adhesive
210	1	1	0.25	12.56	0.4868			adhesive
210	1	2	0.24	12.56	0.4673			adhesive
210	1	3	0.23	12.56	0.4479			adhesive
210	2	1	0.21	12.56	0.4089			adhesive
210	2	2	0.2	12.56	0.3895			adhesive
210	2	3	0.19	12.56	0.3700	0.4284	0.046081	adhesive
211	1	1	0.05	5	0.0388			adhesive
211	1	2	0.06	5	0.0465			adhesive
211	1	3	0.05	5	0.0388			adhesive
211	2	1	0.05	5	0.0388			adhesive
211	2	2	0.05	5	0.0388			adhesive
211	2	3	0.04	5	0.0310	0.0388	0.004903	adhesive
212	1	1	0.8	12.56	1.5578			adhesive
212	1	2	0.87	12.56	1.6941			adhesive
212	1	3	0.92	12.56	1.7915			adhesive
212	2	1	0.87	12.56	1.6941			adhesive
212	2	2	0.85	12.56	1.6552			adhesive
212	2	3	0.88	12.56	1.7136	1.6844	0.076665	adhesive
213	1	1	0.93	12.56	1.8110			adhesive
213	1	2	0.83	12.56	1.6162			adhesive
213	1	3	0.79	12.56	1.5384			adhesive
213	2	1	0.81	12.56	1.5773			adhesive
213	2	2	0.76	12.56	1.4799			adhesive
213	2	3	0.9	12.56	1.7526	1.6292	0.127791	adhesive
214	1	1	0.77	12.56	1.4994			adhesive
214	1	2	0.75	12.56	1.4605			adhesive
214	1	3	0.78	12.56	1.5189			adhesive
214	2	1	0.79	12.56	1.5384			adhesive
214	2	2	0.78	12.56	1.5189			adhesive
214	2	3	0.7	12.56	1.3631	1.4832	0.064486	adhesive
215	1	1	0.75	12.56	1.4605			adhesive
215	1	2	0.73	12.56	1.4215			adhesive
215	1	3	0.85	12.56	1.6552			adhesive
215	2	1	0.74	12.56	1.4410			adhesive
215	2	2	0.72	12.56	1.4020			adhesive
215	2	3	0.73	12.56	1.4215	1.4670	0.094331	adhesive

Table 13 Loop Tack HDPE30 (Chapter 5)

RUN	Film	Spec	Reading	Range	Tack (N/cm^2)	Average	St.Dev.	Failure
201	1	1	0.32	12.56	0.623132			adhesive
201	1	2	0.11	12.56	0.214202			adhesive
201	1	3	0.34	12.56	0.662078			adhesive
201	2	1	0.29	12.56	0.564713			adhesive
201	2	2	0.31	12.56	0.603659			adhesive
201	2	3	0.27	12.56	0.525767	0.532258	0.162766	adhesive
202	1	1	0.1	2.45	0.037984			adhesive
202	1	2	0.11	2.45	0.041783			adhesive
202	1	3	0.09	2.45	0.034186			adhesive
202	2	1	0.12	2.45	0.045581			adhesive
202	2	2	0.12	2.45	0.045581			adhesive
202	2	3	0.1	2.45	0.037984	0.040517	0.0046	adhesive
203	1	1	0.26	25	1.007752			adhesive
203	1	2	0.28	25	1.085271			adhesive
203	1	3	0.25	25	0.968992			adhesive
203	2	1	0.26	25	1.007752			adhesive
203	2	2	0.27	25	1.046512			adhesive
203	2	3	0.28	25	1.085271	1.033592	0.04694	adhesive
204	1	1	0.32	12.56	0.623132			adhesive
204	1	2	0.26	12.56	0.506295			adhesive
204	1	3	0.23	12.56	0.447876			adhesive
204	2	1	0.31	12.56	0.603659			adhesive
204	2	2	0.27	12.56	0.525767			adhesive
204	2	3	0.29	12.56	0.564713	0.54524	0.065169	adhesive
205	1	1	0.12	12.56	0.233674			adhesive
205	1	2	0.14	12.56	0.27262			adhesive
205	1	3	0.17	12.56	0.331039			adhesive
205	2	1	0.15	12.56	0.292093			adhesive
205	2	2	0.12	12.56	0.233674			adhesive
205	2	3	0.15	12.56	0.292093	0.275866	0.037793	adhesive
206	1	1	0.05	12.56	0.097364			adhesive
206	1	2	0.03	12.56	0.058419			adhesive
206	1	3	0.03	12.56	0.058419			adhesive
206	2	1	0.03	12.56	0.058419			adhesive
206	2	2	0.01	12.56	0.019473			adhesive
206	2	3	0.05	12.56	0.097364	0.06491	0.029317	adhesive
207	1	1	0.32	12.56	0.623132			adhesive
207	1	2	0.35	12.56	0.68155			adhesive
207	1	3	0.33	12.56	0.642605			adhesive
207	2	1	0.32	12.56	0.623132			adhesive
207	2	2	0.35	12.56	0.68155			adhesive
207	2	3	0.38	12.56	0.739969	0.665323	0.045111	adhesive
208	1	1	0.09	5	0.069767			adhesive
208	1	2	0.04	5	0.031008			adhesive
208	1	3	0.08	5	0.062016			adhesive

208	2	1	0.07	5	0.054264			adhesive
208	2	2	0.07	5	0.054264			adhesive
208	2	3	0.08	5	0.062016	0.055556	0.013352	adhesive
209	1	1	0.09	5	0.069767			adhesive
209	1	2	0.07	5	0.054264			adhesive
209	1	3	0.13	5	0.100775			adhesive
209	2	1	0.14	5	0.108527			adhesive
209	2	2	0.1	5	0.077519			adhesive
209	2	3	0.11	5	0.085271	0.082687	0.020015	adhesive
210	1	1	0.35	12.56	0.68155			adhesive
210	1	2	0.24	12.56	0.467349			adhesive
210	1	3	0.22	12.56	0.428403			adhesive
210	2	1	0.23	12.56	0.447876			adhesive
210	2	2	0.28	12.56	0.54524			adhesive
210	2	3	0.28	12.56	0.54524	0.519276	0.093524	adhesive
211	1	1	0.12	5	0.093023			adhesive
211	1	2	0.09	5	0.069767			adhesive
211	1	3	0.12	5	0.093023			adhesive
211	2	1	0.1	5	0.077519			adhesive
211	2	2	0.09	5	0.069767			adhesive
211	2	3	0.08	5	0.062016	0.077519	0.012971	adhesive
212	1	1	0.38	12.56	0.739969			adhesive
212	1	2	0.33	12.56	0.642605			adhesive
212	1	3	0.35	12.56	0.68155			adhesive
212	2	1	0.44	12.56	0.856806			adhesive
212	2	2	0.36	12.56	0.701023			adhesive
212	2	3	0.4	12.56	0.778915	0.733478	0.076582	adhesive
213	1	1	0.23	12.56	0.447876			adhesive
213	1	2	0.26	12.56	0.506295			adhesive
213	1	3	0.28	12.56	0.54524			adhesive
213	2	1	0.18	12.56	0.350512			adhesive
213	2	2	0.24	12.56	0.467349			adhesive
213	2	3	0.23	12.56	0.447876	0.460858	0.06594	adhesive
214	1	1	0.21	12.56	0.40893			adhesive
214	1	2	0.3	12.56	0.584186			adhesive
214	1	3	0.19	12.56	0.369984			adhesive
214	2	1	0.189	12.56	0.368037			adhesive
214	2	2	0.18	12.56	0.350512			adhesive
214	2	3	0.26	12.56	0.506295	0.431324	0.093581	adhesive
215	1	1	0.18	12.56	0.350512			adhesive
215	1	2	0.22	12.56	0.428403			adhesive
215	1	3	0.26	12.56	0.506295			adhesive
215	2	1	0.2	12.56	0.389457			adhesive
215	2	2	0.24	12.56	0.467349			adhesive
215	2	3	0.23	12.56	0.447876	0.431649	0.055648	adhesive

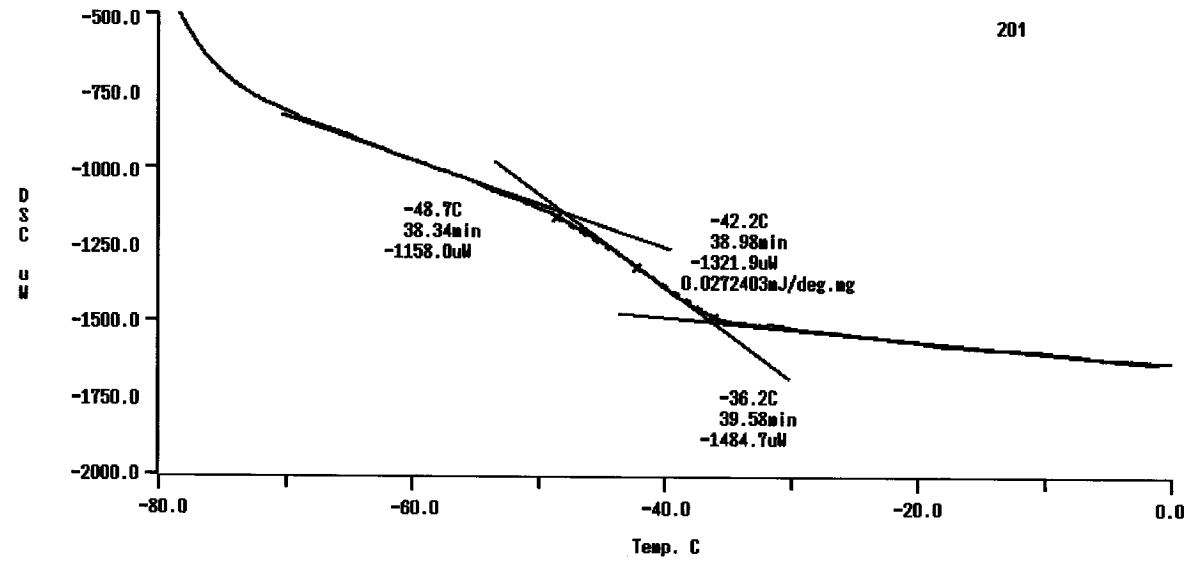


Figure 32 Glass transition temperature determination for Run 201 (Chapter 5)

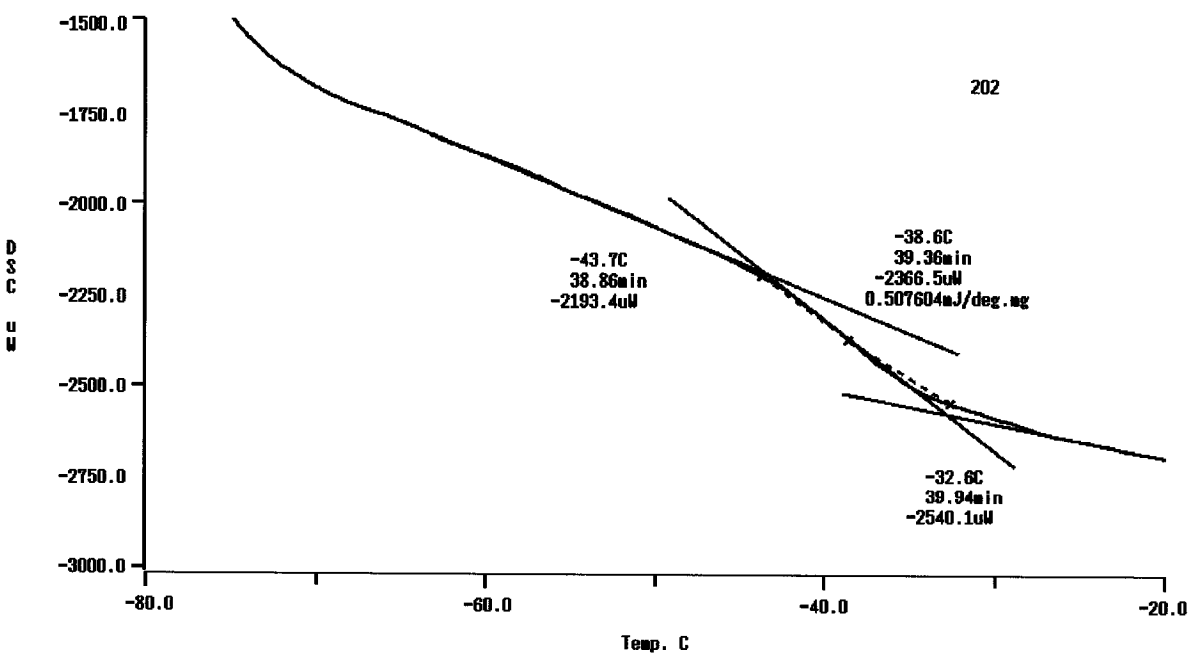


Figure 33 Glass transition temperature determination for Run 202 (Chapter 5)

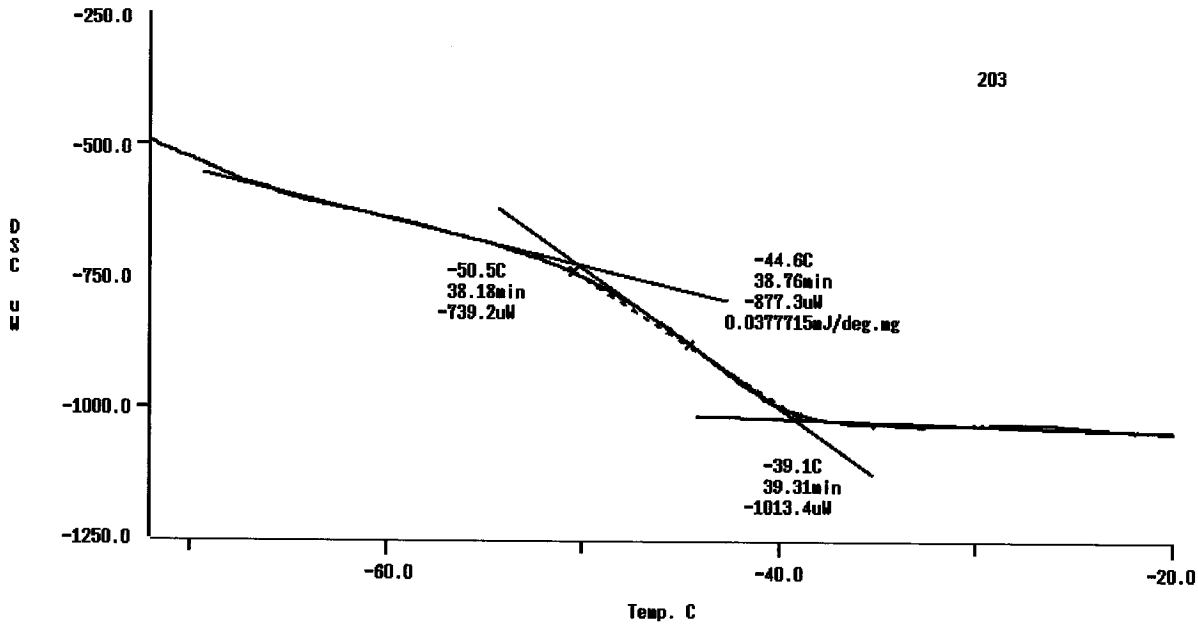


Figure 34 Glass transition temperature determination for Run 203 (Chapter 5)

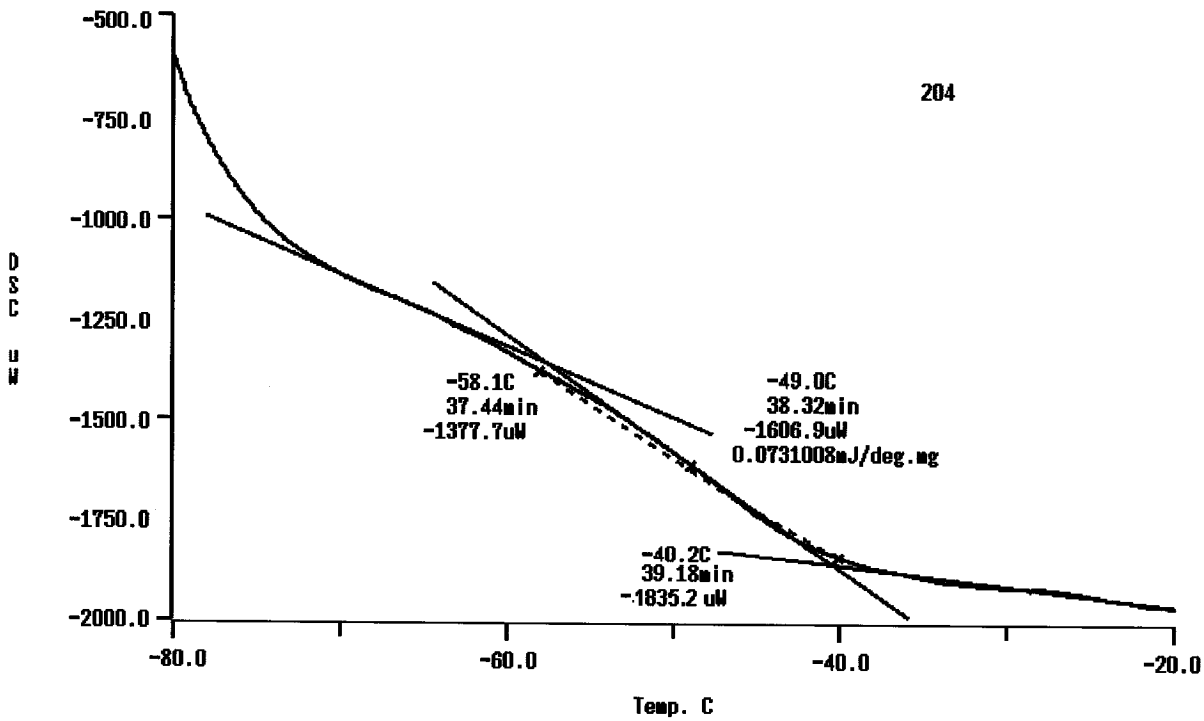


Figure 35 Glass transition temperature determination for Run 204 (Chapter 5)

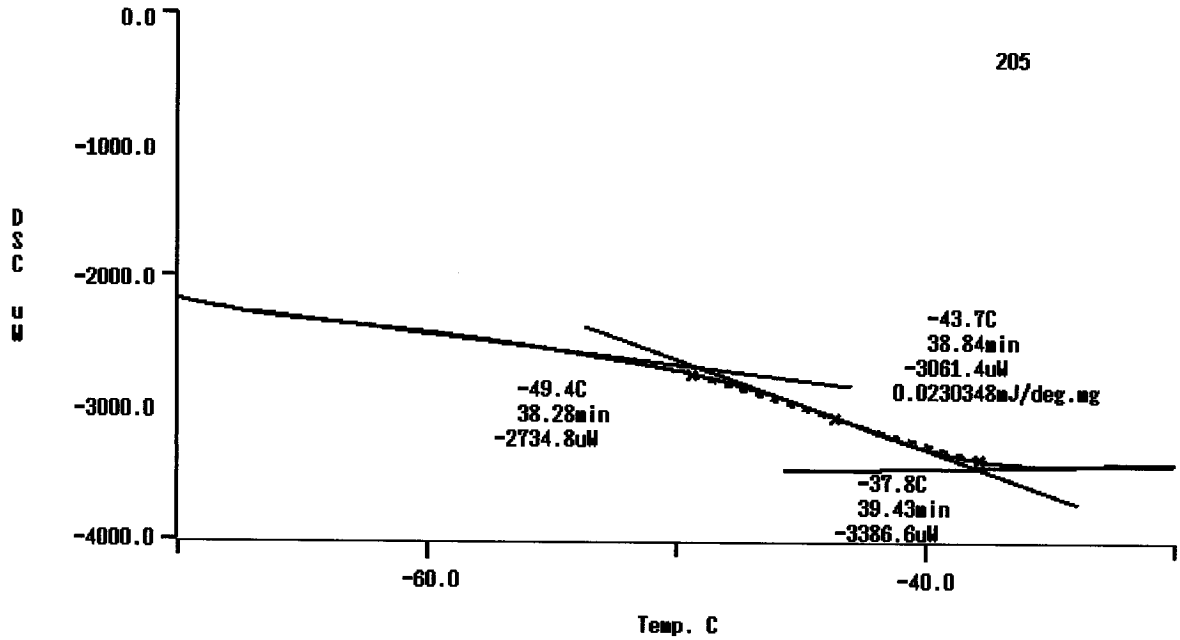


Figure 36 Glass transition temperature determination for Run 205 (Chapter 5)

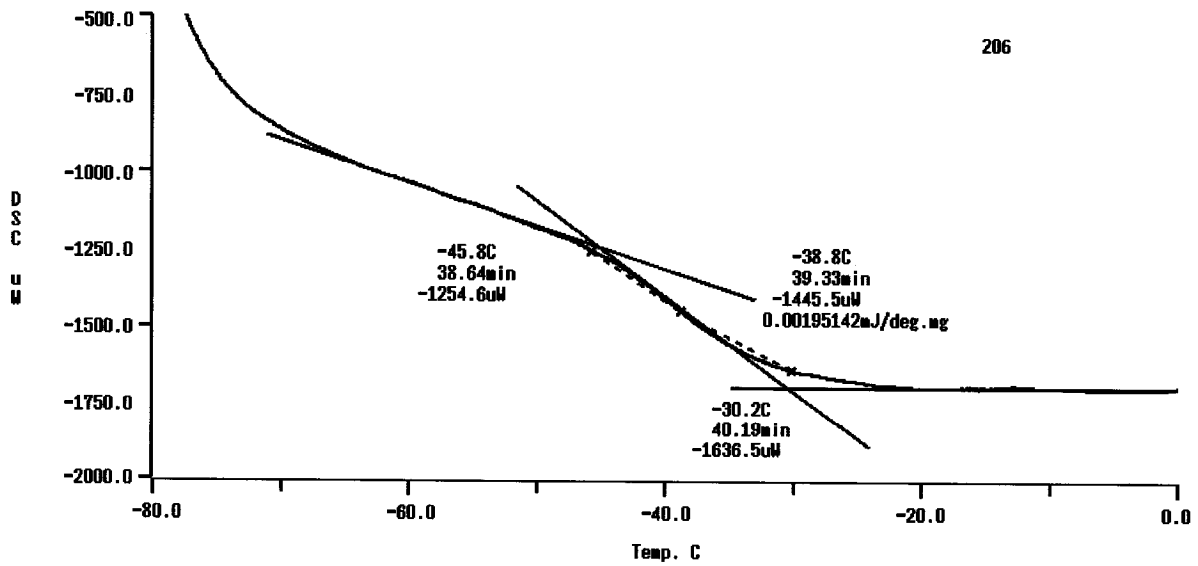


Figure 37 Glass transition temperature determination for Run 206 (Chapter 5)

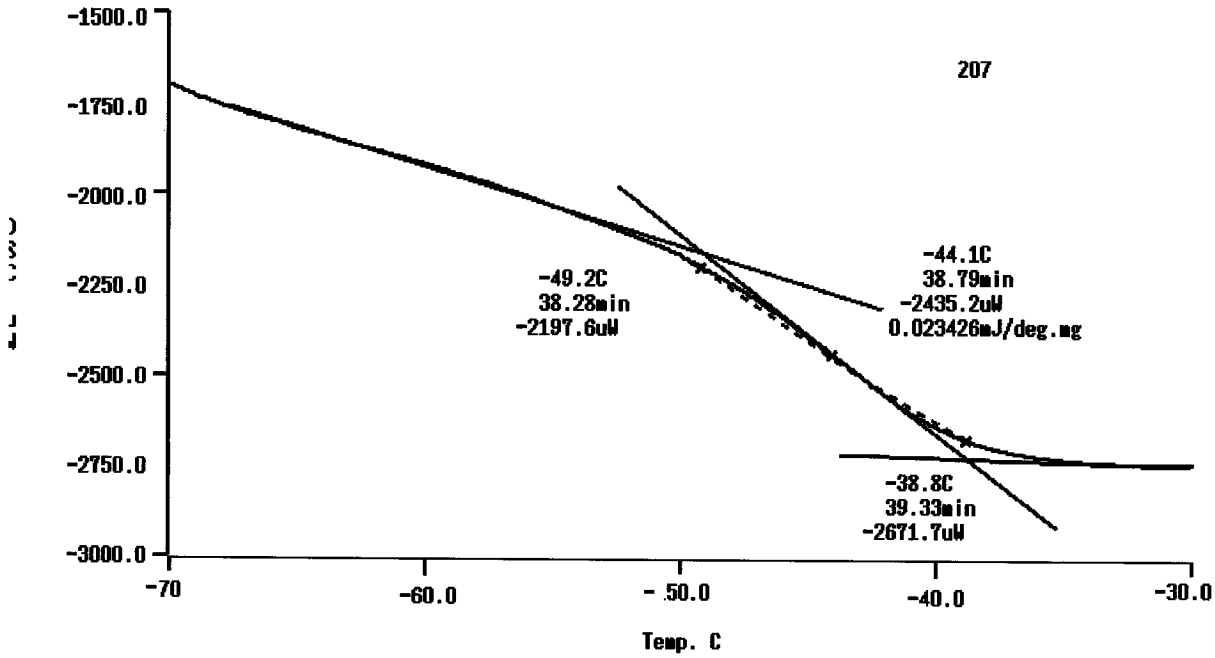


Figure 38 Glass transition temperature determination for Run 207 (Chapter 5)

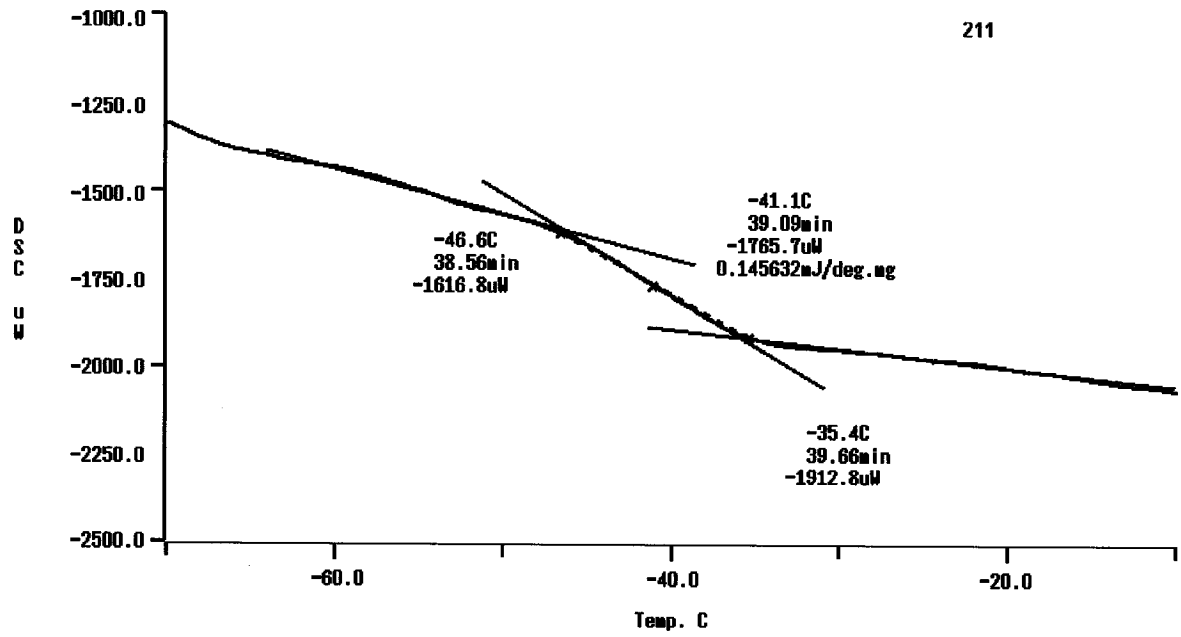


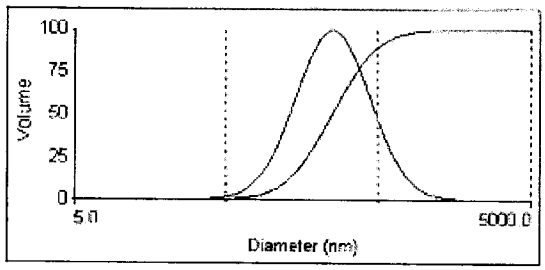
Figure 39 Glass transition temperature determination for Run 211 (Chapter 5)

Brookhaven Instruments Corp
90Plus Particle Sizing Software Ver 2.25

Date: Mar 6, 2004
Time: 09:30:19
Batch: 0

Sample I.D. **r208-7-1 (Combined)**
Operator I.D. **RJ**
Notes

Elapsed Time	00:02:30
Median Diam.	249.8 nm
Mean Diam.	291.2 nm
Polydispersity	0.378
GSD	1.762



Lognormal Size Distribution

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
100.6	26	5	217.2	97	40	362.7	80	75
122.9	44	10	233.0	95	45	396.1	70	80
140.9	58	15	249.8	100	50	443.2	58	85
156.8	70	20	267.9	95	55	507.8	44	90
172.1	80	25	287.4	97	60	620.7	26	95
187.0	87	30	313.8	92	65			
201.9	93	35	333.9	87	70			

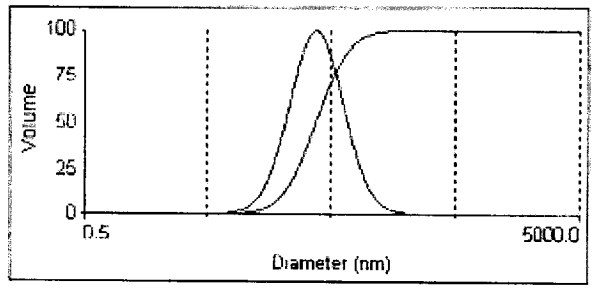
Figure 40 An example of particle size determination Run 208 (Chapter 5)

Brookhaven Instruments Corp.
90Plus Particle Sizing Software Ver. 2.25

Date: Mar 5, 2004
Time: 09:06:30
Batch: 0

Sample I.D. **r209-7-1 (Combined)**
Operator I.D. **RJ**
Notes

Elapsed Time	00:02:30
Median Diam.	38.4 nm
Mean Diam.	43.3 nm
Polydispersity	0.296
GSD	1.664



Lognormal Size Distribution

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
17.0	26	5	33.9	97	40	53.5	80	75
20.4	44	10	36.1	99	45	58.1	70	80
23.0	58	15	38.4	100	50	64.0	58	85
25.3	70	20	40.8	99	55	72.2	44	90
27.5	80	25	43.5	97	60	86.4	26	95
29.6	87	30	47.0	92	66			
31.7	93	35	49.7	87	70			

Figure 41 An example of particle size determination Run 209-Replicate 1 (Chapter 5)

SAMPLE CALCULATIONS AND SUPPORT DOCUMENTATION FOR CHAPTER 6

Copolymer BA/VAc_50/50 : C1

Mixture for sonication

Compound	Weight (g)	Wt. Fr.	phm
Water	600.0800	0.5819	150.0125
SDS	0.6600	0.0006	0.1650
Triton	10.7500	0.0104	2.6874
		0.0000	0.0000
BA	200.0100	0.1940	50.0000
VAc	200.0100	0.1940	50.0000
ODA	7.6783	0.0074	1.9195
CTA	12.0100	0.0116	3.0023
Total	**1031.198**	1	

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	6.47	0.064506
Water	93.83	0.935494
Total	100.3	

Initiator loaded

3.4 g		phm
Initiator (g)	0.219322	0.098793
Water (g)	3.180678	

Reactor loading

Container before	831.17
Container after	258.88
Amount loaded	**572.29**

Figure 42 Recipe Miniemulsion C1 (Chapter 6)

Copolymer BA/VAc_95/5 : C2

26-Jun-02

Mixtures for sonication

Compound	Weight (g)	Wt. Fr.	phm
Water	601.15	0.58233	150.2537
SDS	0.65	0.00063	0.162463
Triton	10.75	0.010413	2.686895
BA	380.08	0.368181	94.99863
VAc	20.01	0.019384	5.001375
ODA	7.6777	0.007437	1.918993
CTA	12	0.011624	2.999325
Total	**1032.318**	1	

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	6.52	0.065187
Water	93.5	0.934813
Total	100.02	

Initiator loaded

3.2 g		phm
Initiator (g)	0.208598	0.0991
Water (g)	2.991402	

Reactor loading

Container before	849.82
Container after	306.76
Amount loaded	**543.06**

Figure 43 Recipe Miniemulsion C2 (Chapter 6)

Copolymer BA/VAc_85/15 : C3

Mixtures for sonication

Compound	Weight (g)	Wt. Fr.	phm
Water	600.11	0.5820	150.0237
SDS	0.65	0.0006	0.1625
Triton	10.75	0.0104	2.6874
		0.0000	0.0000
BA	340	0.3297	84.9979
VAc	60.01	0.0582	15.0021
ODA	7.6707	0.0074	1.9176
CTA	12	0.0116	2.9999
Total	1031.191	1	

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	6.47	0.0639
Water	94.83	0.9361
Total	101.3	1

Initiator loaded

3.6 g		phm
Initiator (g)	0.229931	0.099069
Water (g)	3.370069	

Reactor loading

Container before	864.26
Container after	265.95
Amount loaded	**598.31**

Figure 44 Recipe Minieulsion C3 (Chapter 6)

Copolymer BA/VAc_65/35 : C4

Mixtures for sonication

Compound	Weight (g)	Wt. Fr.	phm
Water	600.23	0.581909	150.0575
SDS	0.67	0.00065	0.1675
Triton	10.74	0.010412	2.685
		0	0
BA	260	0.252064	65
VAc	140	0.135727	35
ODA	7.6741	0.00744	1.918525
CTA	12.17	0.011799	3.0425
Total	1031.484	1	

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	6.42	0.0642
Water	93.58	0.9358
Total	100	1

Initiator loaded

3.2 g		phm
Initiator (g)	0.20544	0.0994
Water (g)	2.99456	

Reactor loading

Container before	883.03
Container after	350.2
Amount loaded	**532.83**

Figure 45 Recipe Minieulsion C4 (Chapter 6)

Minimix BA/VAc 50/50: M1

2-Jul-02

Mixtures for sonication

BA mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600.11	0.5819	150.0050
SDS	0.65	0.0006	0.1625
Triton	10.75	0.0104	2.6871
BA	400.06	0.3879	100.0000
VAc	0	0.0000	0.0000
ODA	7.6719	0.0074	1.9177
CTA	12	0.0116	2.9996
Total	**1031.242**	1	

VAc mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600.22	0.5819	150.0550
SDS	0.66	0.0006	0.1650
Triton	10.73	0.0104	2.6825
BA			
VAc	400	0.3878	100.0000
ODA	7.6669	0.0074	1.9167
CTA	12.12	0.0118	3.0300
Total	**1031.397**	1	

PreLoading

	Weight (g)	wt. fr.
BA mini	350.01	0.49985
VAc mini	350.22	0.50015
	700.23	

Reactor loading

Container before	955.33
Container after	373.96
Amount loaded	**581.37**

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	7.5	0.0741326
Water	93.67	0.9258674
Total	101.17	

Initiator loaded

3 g

Initiator (g)	0.2224
Water (g)	2.7776

Time	Empty	L+dish	Dry	Solids	Conversion
1	1.263	2.5096	1.5102	0.1983	0.4351
3	1.2662	2.4202	1.499	0.2017	0.4440
10	1.2722	2.946	1.6632	0.2336	0.5266
60	1.2564	3.1444	1.7932	0.2843	0.6580
180	1.2575	3.4422	2.0279	0.3526	0.8350
300	1.2686	4.2905	2.4296	0.3842	0.9168
451	1.2704	3.5941	2.216	0.4069	0.9757

Amounts loaded

	BA mini	VAc mini	Ini feed	Total	Wt. Fr.	phm
Water	169.1074	169.2145	2.777602	341.0995	0.5837	151.2617
SDS	0.1832	0.1861		0.3692	0.0006	0.1637
Triton	3.0293	3.0250		6.0543	0.0104	2.6848
BA	112.7345			112.7345	0.1929	49.9925
VAc	0.0000	112.7683		112.7683	0.1930	50.0075
ODA	2.1619	2.1615		4.3234	0.0074	1.9172
APS				0.2224	0.0004	0.0986
CTA	3.3815	3.4169		6.7984	0.0116	3.0148
Total	**290.5978**	**290.7722**		584.3700	1.0000	

Figure 46 Recipe Miniemulsion M1 (Chapter 6)

Minimix BA/VAc 95/5: M2

Mixtures for sonication

BA mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600	0.5818	149.9438
SDS	0.65	0.0006	0.1624
Triton	10.75	0.0104	2.6865
		0.0000	0.0000
BA	400.15	0.3880	100.0000
VAc	0	0.0000	0.0000
ODA	7.6719	0.0074	1.9173
CTA	12	0.0116	2.9989
Total	1031.2219	1	

VAc mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600.22	0.5819	150.0550
SDS	0.66	0.0006	0.1650
Triton	10.73	0.0104	2.6825
		0.0000	0.0000
BA	0	0.0000	0.0000
VAc	400	0.3878	100.0000
ODA	7.6669	0.0074	1.9167
CTA	12.12	0.0118	3.0300
Total	1031.397	1	

Time	Empty	L+dish	Dry	Solids	Conversion
2	1.2546	3.8009	2.1438	0.3492	0.8268
4	1.266	3.4371	2.0448	0.3587	0.8514
10	1.267	3.2858	2.0105	0.3683	0.8762
40	1.2622	3.924	2.3042	0.3915	0.9363
60	1.2626	4.1944	2.438	0.4009	0.9608
180	1.2582	3.4552	2.1556	0.4085	0.9804
252	1.2637	4.8706	2.7488	0.4117	0.9889

PreLoading

	Weight (g)	wt. fr.
BA mini	617.6	0.9500
VAc mini	32.5	0.0500
Total	650.1	

Reactor loading

		BA mini (g)	VAc mini g)
Container before	906.42	549.6935	28.92655
Container after	327.8		
Amount loaded	578.62		

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	6.47	0.0639
Water	94.83	0.9361
Total	101.3	

Initiator loaded

3.5 g

Initiator (g)	0.2235
Water (g)	3.2765

Amounts loaded

	BA mini	VAc mini	Ini feed	Total	Wt.Fr.	phm
Water	319.8304	16.8338	3.2765	339.9406	0.5840	151.4087
Sds	0.3465	0.0185		0.3650	0.0006	0.1626
Triton	5.7303	0.3009		6.0312	0.0104	2.6863
BA	213.3002	0.0000		213.3002	0.3664	95.0034
VAc	0.0000	11.2184		11.2184	0.0193	4.9966
ODA	4.0895	0.2150		4.3045	0.0074	1.9172
APS				0.2235	0.0004	0.0996
CTA	6.3966	0.3399		6.7365	0.0116	3.0004
Total	549.6935	28.9265		582.1200	1.0	

Figure 47 Recipe Miniemulsion M2 (Chapter 6)

Minimix BA/VAc 85/15: M3

30-May-02

Mixtures for sonication

BA mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600.11	0.581929	150.005
SDS	0.65	0.00063	0.162476
Triton	10.75	0.010424	2.687097
BA	400.06	0.38794	100
VAc	0	0	0
ODA	7.6719	0.007439	1.917687
CTA	12	0.011636	2.99955
Total	**1031.242**	1	

VAc mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600.22	0.581949	150.055
SDS	0.66	0.00064	0.165
Triton	10.73	0.010403	2.6825
BA	0	0	0
VAc	400	0.387824	100
ODA	7.6669	0.007434	1.916725
CTA	12.12	0.011751	3.03
Total	**1031.397**	1	

Time	Empty	L+dish	Dry	Solids	Conversion
2	1.2663	3.3294	1.9555	0.3341	0.8068
4	1.2724	3.1514	1.9144	0.3417	0.8266
10	1.2621	4.3843	2.3386	0.3448	0.8347
40	1.2748	3.0891	1.953	0.3738	0.9099
60	1.2603	2.7419	1.8263	0.3820	0.9312
180	1.2607	2.5827	1.7831	0.3952	0.9653
300	1.2637	3.3228	2.0979	0.4051	0.9911

PreLoading

	Weight (g)	wt. fr.
BA mini	510.11	0.850027
VAcmini	90	0.149973
	600.11	

Reactor loading

		BA mini (g)	VAc mini (g)
Container before	600.11	507.4409	89.52909
Container after	3.14		
Amount loaded	**596.97**		596.97

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	6.34	0.062568
Water	94.99	0.937432
Total	101.33	

Initiator loaded

3.6 g in 1 min=

Initiator (g)	0.2252
Water (g)	3.3748

Amounts loaded

	BA mini	VAc mini	Ini feed	Total	Wt.Fr.	phm
Water	295.2948	52.1013	3.3748	350.7709	0.5841	151.4698
SDS	0.3198	0.0573		0.3771	0.0006	0.1629
Triton	5.2897	0.9314		6.2211	0.0104	2.6864
	0.0000			0.0000	0.0000	0.0000
BA	196.8566			196.8566	0.3278	85.0066
VAc	0.0000	34.7215		34.7215	0.0578	14.9934
ODA	3.7751	0.6655		4.4406	0.0074	1.9175
APS				0.2252	0.0004	0.0973
CTA	5.9048	1.0521		6.9569	0.0116	3.0041
Total	**507.4409**	**89.52909**		600.57	1	

Figure 48 Recipe Miniemulsion M3 (Chapter 6)

Minimix BA/VAc 65/35: M4

Mixtures for sonication

BA mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600	0.5818	149.9438
SDS	0.65	0.0006	0.1624
Triton	10.75	0.0104	2.6865
BA	400.15	0.3880	100.0000
VAc	0	0.0000	0.0000
ODA	7.6719	0.0074	1.9173
CTA	12	0.0116	2.9989
Total	1031.2219	1	

VAc mini

Compound	Weight (g)	Wt. Fr.	phm
Water	600.22	0.5819	150.0550
SDS	0.66	0.0006	0.1650
Triton	10.73	0.0104	2.6825
BA	0	0.0000	0.0000
VAc	400	0.3878	100.0000
ODA	7.6669	0.0074	1.9167
CTA	12.12	0.0118	3.0300
Total	1031.397	1	

Time	Empty	L+dish	Dry	Solids	Conversion
2	1.2796	2.4468	1.5922	0.2678	0.6267
4	1.267	3.1236	1.7819	0.2773	0.6511
10	1.2602	3.5665	1.9458	0.2973	0.7021
20	1.2721	3.5983	2.0064	0.3157	0.7493
60	1.2688	3.6711	2.1097	0.3500	0.8373
180	1.2735	4.193	2.4415	0.4001	0.9655
240	1.2511	3.7869	2.281	0.4061	0.9811

PreLoading

	Weight (g)	wt. fr.
BA mini	395.06	0.6496843
VAcmini	213.02	0.3503157
	608.08	

Reactor loading

BA mini (g) VAc mini (g)

Container before	859.2	363.0695	195.77045
Container after	300.36		
Amount loaded	558.84		

Initiator feed

Compund	Weight (g)	Wt. Fr.
APS	6.52	0.065187
Water	93.5	0.934813
Total	100.02	1

Initiator loaded

3.2 g

Initiator (g) 0.20859828

Water (g) 2.99140172

Amounts loaded

	BA mini	VAc mini	Ini feed	Total	Wt.Fr.	phm
Water	211.2462	113.9283	2.9914	328.1660	0.5907	151.3625
SDS	0.2289	0.1253		0.3541	0.0006	0.1633
Triton	3.7848	2.0367		5.8215	0.0105	2.6851
	0.0000	0.0000		0.0000	0.0000	0.0000
BA	140.8836	0.0000		140.8836	0.2536	64.9808
VAc	0.0000	75.9244		75.9244	0.1367	35.0192
ODA	2.7011	1.4553		4.1564	0.0075	1.9171
APS				0.2086	0.0004	0.0962
CTA	4.2249	2.3005		6.5254	0.0117	3.0098
Total	358.8446	195.7705		555.51457	1	

Figure 49 Recipe Miniemulsion M4 (Chapter 6)

Appendix B

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