

The Effect of Varied Monomer Composition on Adhesive Performance and Peeling Master Curves for Acrylic Pressure-Sensitive Adhesives

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ABSTRACT: A group of pressure-sensitive adhesives were prepared with constant glass transition temperature, using emulsion polymerization. The monomers chosen were butyl acrylate, 2-ethylhexyl acrylate, and methyl methacrylate, along with a small amount of acrylic acid. The proportion of acrylic acid monomer was held constant for each polymer preparation but acrylic ester monomer levels were varied. The glass transition temperatures of the acrylate copolymers were measured by using differential scanning calorimetry. Drying and weighing the tetrahydrofuran-insoluble polymer fractions were used to determine the polymer gel fractions. Films of constant coating thickness were applied to poly(ethylene terephthalate) film and adhesive properties (tack and shear) were examined. Peel was exam-

ined through the construction of master curves derived from peel tests conducted over a range of temperatures and peel rates. As the 2-ethylhexyl acrylate content increased, the latex gel fractions were found to increase. With increasing EHA and gel fraction, peel shear was found to increase. When peel force master curves were compared, divergence in peel master curves occurred as peel rates increased where polymers with higher butyl acrylate contents reached greater peel stress values. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2909–2917, 2004

Key words: acrylate; adhesives; cohesion; glass transition; gels

INTRODUCTION

Acrylic pressure-sensitive adhesives (PSAs) obtained by emulsion polymerization currently hold the biggest share of the PSA market. Their success is attributable, in part, to the replacement of flammable and environmentally unfriendly solvents with water. Other advantages of acrylic dispersions are their high solids, their ease of application, and the fact that they may be formulated, in many instances, without the need for addition of tackifiers.

Polymers of acrylic and methacrylic esters that yield low glass-transition temperatures (T_g 's) and high molecular weights are the basis of acrylic PSAs. Commercially, the main monomers used for their preparation are butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA). However, to raise the room-temperature performance of these soft acrylic homopolymers, it is necessary to raise their T_g 's.¹ Raising the polymer T_g can be accomplished by copolymerizing with one or

more high- T_g monomers such as methyl methacrylate (MMA; $T_g = 105^\circ\text{C}$), acrylic acid (AA, $T_g = 106^\circ\text{C}$), or any of a number of hardening monomers.

In early studies, Mao and Reegen² noted that for acrylic monomers copolymerized with MMA the peel strength increased as the number of carbon atoms in the side chain of the comonomers increased. Druschke showed that probe tack increased for acrylic homopolymers as T_g decreased.³ Mao and Reegen also noted the increase in peel strength of acrylic PSAs by the copolymerization of small levels of carboxylic acid. Aubrey and Ginosatis⁴ studied the effect of carboxylic acid level on the peeling force–rate relation by including the use of peel master-curve construction. By comparing the peel master-curves, Aubrey and Ginosatis were able to demonstrate that the inclusion of carboxylic acid groups had a larger effect on the bulk polymer viscoelastic response than the interfacial one. More recently, Ahn and Shull⁵ suggested that the increase in the peel adhesion attributed by Aubrey and Ginosatis to the bulk polymer effect of acrylic acid might have been due to the significant T_g differences between the poly(butyl acrylate) homopolymer and poly(butyl acrylate)–poly(acrylic acid) random copolymer. Aubrey and Sherriff⁶ showed the effect of varying adhesive T_g on adhesive performance via displacement of the horizontal axis of the peel master-curve

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towards lower peeling rates with increasing adhesive T_g .

In addition to emulsion copolymer composition, the way the emulsion copolymerization is carried out can have a profound effect on the resultant polymer properties.⁷ To reduce the occurrence of copolymer heterogeneity (different polymer phases present within the copolymer) that can accompany batch polymerizations of monomers of differing reactivity ratios and water solubilities, a semibatch emulsion polymerization can be adopted. Rather than using the batch polymerization method of adding all the reactants to the reaction vessel at the start of the polymerization, during a semibatch polymerization, monomer is introduced in a controlled way, often as a preemulsified mixture of monomer, water, and surfactant. Semibatch polymerizations proceeding under starved monomer feed conditions, with monomer feeds of uniform composition, have been demonstrated to yield polymers of uniform composition.⁸

The manufacture of water-borne acrylic PSA by the emulsion polymerization process can lead to the formation of microgels inside latex particles.^{9,10,11} Recent studies of emulsion polymerized poly(butyl acrylate-co-acrylic acid)^{10,12} and poly(2-ethylhexyl acrylate-co-acrylic acid)¹⁰ random copolymers have linked adhesive performance to the level of gel formed. Tobing and Klein¹⁰ found that as gel content decreased loop tack and peel increased. They also found a strong correlation between shear holding power and gel content. Zosel¹² acknowledged that the gel structures found in acrylic emulsion polymers contribute to their good PSA performance.

The peel test is often used to measure the force required to peel away a test strip bonded to a rigid surface where bonding was achieved by using a pressure-sensitive adhesive. The construction of peeling master-curves (where curves prepared by measuring peeling force as a function of peeling rate at various temperatures are superpositioned) allows the prediction of peel behavior over a very wide range of peeling rates.¹³ Also, as the peeling rate is varied, distinct modes of peeling are clearly visible. The peeling mode can pass from cohesive failure through adhesive failure to low peel force failure with complete adhesive transfer and these failure modes may be correlated with the adhesive's different viscoelastic states as the peeling rate is varied.^{14,15}

The objective of the present study was to examine the effect of varying the relative levels of emulsion copolymerized EHA, MMA, and BA on the adhesive performance of the resultant polymers through construction and analysis of the peel master-curves and the measurement of loop tack and shear holding power. Loop tack is an adhesive performance indicator often used within industry to gain a measure of the capability of a PSA to adhere immediately to a sub-

strate under light pressure.³ Shear holding power is also an important industry test, often used by label laminate producers as an indicator of adhesive cuttability and die cuttability.¹⁶ To isolate as far as possible the effect of the varying the ester acrylic monomer combinations, the emulsion polymers were prepared in an identical manner by using a starved-feed, semibatch technique. In addition, the emulsion polymer recipes utilized for the preparation of the test PSA polymers used a fixed carboxylic acid level and were designed to yield polymers with a fixed T_g .

EXPERIMENTAL

Materials

All the reagents were used as supplied. The BA, MMA, and AA monomers were all technical grades obtained from Orica Australia Ltd. Technical grade EHA was obtained from Mitsubishi Rayon Co (Tokyo, Japan). The initiator used was technical grade ammonium persulfate obtained from Hoechst Australia Ltd. Deionized water was used throughout the polymer preparations. Technical grade ammonia solution (ammonia, 25%) from Orica Australia Ltd. (Ascot Vale, Australia) was used diluted 1 : 1 with water to partially neutralize each polymer latex. Latices were protected from biological attack via the addition of Acticide SPX as supplied from Thor Australia Ltd (Seaford, Australia). The polymerization surfactant used was a mixture of ethoxylated anionic and nonionic surfactants from Rhodia HPCII (Archerfield, Australia). Its activity in H₂O is 35 wt %. The surfactant system employed will be referred to as surfactant A and its composition cannot be revealed for proprietary reasons.

Preparation of acrylic PSAs containing varied monomer compositions with constant T_g and acrylic acid level

The neat emulsion acrylic PSAs used in this study were based on EHA-BA-MMA-AA copolymers prepared by using a starved feed, semibatch emulsion polymerization technique. For all polymer preparations in this study, the AA level was held constant at 4.0 wt % of total monomer. For each PSA composition, the monomer concentrations of BA, EHA, and MMA were adjusted to yield a theoretical polymer T_g of -42°C. The monomer concentrations were calculated by using the Fox equation for random copolymers.¹⁷ Five polymers of differing monomer concentrations ranging from 75 wt % EHA (based on total monomer) to 0 wt % EHA were prepared.

Preparation of monomer emulsion

Deionized water (523 g), 146 g of surfactant A, 58.2 g AA, and 1398 g in total of a mixture of BA, EHA, and

TABLE I
Acrylate Copolymer Compositions
and Sample Designation

Formulation	Monomer charged per total monomer (%wt)			
	AA	MMA	EHA	BA
AA4M91-1	4.00	5.00	0	91.00
AA4M61-1	4.00	9.66	25.00	61.34
AA4M50-1	4.00	11.44	34.56	50.00
AA4M25-1	4.00	15.39	55.61	25.00
AA4M02-1	4.00	19.02	75.00	1.98

MMA were charged to a 3-L beaker. The monomer mixture was mixed by using a laboratory Silverson mixer until a homogenous, white, and viscous emulsion was achieved. The mixing time required was about 2 min.

Preparation of initiator solution

The initiator solution was prepared by adding 3.64 g of ammonium persulfate into 70.0 g of deionized water. The mixture was then stirred by use of a glass rod. The amount of ammonium persulfate is equivalent to 0.25 wt % of total monomer.

Polymerization procedure

All polymerizations were carried out in a 3-L glass, round-bottomed reaction vessel. The total batch size for all polymerizations was 2800 g and only the mass ratios of monomers were varied as summarized in Table I.

Deionized water (560 g) was charged to the reaction vessel and heated to 75°C with stirring. A few minutes prior to commencement of the monomer, emulsion and initiator solution feeds, 10.1 g of surfactant A, and 3.50 g of initiator (ammonium persulfate) were added to the reaction vessel. The monomer emulsion and initiator solutions were fed at constant rates into the reaction vessel over 5 h. The initiator solution was fed by using a peristaltic pump into the reaction vessel via silicone tubing and the feed rate was monitored volumetrically as the solution was transferred from a 100-mL measuring cylinder to the reaction vessel. The emulsified monomer mixture was fed to the reaction vessel volumetrically via a graduated feed funnel. The feed funnel was topped up as required from the 3-L beaker in which the emulsified monomer mixture was prepared. Throughout the polymerization process, the reaction vessel was immersed in a temperature-controlled water bath and a water-cooled condenser fitted to the top of the reactor was used to prevent significant water loss. During the first 4.5 h of feeding, the reaction temperature was controlled to 74–76°C. Dur-

ing the final 30 min of feeding and for 1 h following the completion of feeding, the reaction temperature was controlled at 79–81°C. The reaction mixture was then cooled to room temperature and 4.2 g of biocide (Acticide SPX) was added. The latex pH was adjusted to 5.4–5.6 by using aqueous ammonia solution. The emulsion viscosity was adjusted to 200–300 cP by using deionized water.

Polymer characterization

Determination of polymer gel content

The gel content of latex polymer samples was determined gravimetrically. A droplet of latex sample weighing ~ 0.2 g was transferred into a Polytetrafluoroethylene (PTFE) dish by using a pipette and dried in a fan-forced oven at 130°C for 1 h. The resultant dried polymer film was then weighed accurately into a 100-mL screw-capped, glass jar. Tetrahydrofuran (THF; 50 g) was added to the jar and the cap was tightened. The jar was shaken for 1 min, allowed to stand for 24 h, and then shaken for a further 1 min. The process was repeated over 3 days. The polymer solution was filtered through a Buchner funnel by using a previously weighed Whatman No. 1 filter paper. Filtering was assisted via the use of a vacuum pump. The filter paper and THF swollen gel was then allowed to dry under a fume hood for 2 h followed by oven drying at 110°C for 1 h. The gel content was calculated as the (dried weight of gel/initial weight of dried polymer) × 100%. The gel content of each sample was determined three times. The average value is presented as the sample gel content.

Determination of T_g by DSC

The polymer T_g presented in this work was measured by using a Perkin–Elmer DSC7 by heating at a rate of 10°C/min. Polymer samples were prepared by weighing ~ 2 g of latex polymer and drying in a fan-forced oven at 130°C for 45 min. Approximately 10 mg of dried polymer samples were accurately weighed into crimped aluminum DSC sample pans. Immediately prior to measuring each sample T_g , the sample was heated to well above T_g and then cooled rapidly to –70°C to ensure samples had equivalent thermal histories. Transition temperatures were calibrated with a pure indium standard and were obtained by using the half $-\Delta C_p$ method.

Adhesive performance testing

Each PSA latex was coated onto polyester film (Terphane SEM12) by using a motorized laboratory coater (RK Coater) equipped with a wire-wound drawdown bar. The adhesive coated films were dried at 105°C for

4 min before lamination with a solventless silicone-coated release paper (KV75 from Jac Australia). To measure the adhesive coating weight, a 150×50 mm sample of adhesive laminate was obtained by cutting around the edges of a 150×50 mm template. The release backing was removed and the adhesive-coated polyester film was accurately weighed. The adhesive was removed from the test sample by washing with acetone; then the sample was dried at 50°C and reweighed. The coating weight was calculated from the difference in mass and expressed as gram adhesive per square meter film. The adhesive-coated samples were left for at least overnight in a controlled environment ($21\text{--}25^\circ\text{C}$, $45\text{--}55\%$ relative humidity) testing laboratory prior to testing the adhesive properties.

To measure the adhesive static shear resistance, first a 150×20 mm strip of adhesive laminate was prepared and formed into a loop using staples. One end of the adhesive laminate loop was adhered to a glass plate with a 20×20 mm contact area. Rolling a standard 2-kg rubber roller across the bonded area five times formed an adhesive bond. The glass plate was supported at 2° to the vertical and 1.5 kg weight suspended from the loop was prepared in the adhesive test strip. The static shear resistance was the time elapsed between suspending the weight and the failure of the adhesive bond, recorded when the adhesive strip and test weight fell completely from the test plate. An automatic timer recorded the interval. The static shear resistance of each sample was determined three times. The average of these three determinations was recorded as the sample static shear resistance.

For the measurement of loop tack, adhesive test strips measuring 150×25 mm were prepared from the adhesive laminates with known coating weights. Loops were formed from the test strips with the release backing outer-most. The release backing was removed to expose the adhesive and a 50×25 mm paper was used to cover a 25×25 mm area at each end of the test strip, thus enabling the loop to be handled. The loop was clamped into the upper grip of a tensile test instrument (Hounsfield 10KM Tensile Test Instrument). A 100×25 mm stainless steel substrate was mounted in the lower grip of the tensile test instrument. The upper grip holding the test loop was brought into contact with the stainless steel test substrate at a rate of 300 mm/min until the distance between the upper grip and the test panel measured 25 mm. After reaching the required separation distance, the motion of the upper grip was immediately reversed. The maximum force recorded during the 300 mm/min separation of the adhesive test loop from the test substrate was recorded as loop tack. The loop tack of each sample was determined five times. The average of these five determinations was recorded as the sample loop tack.

Peel master-curves were constructed via the measurement of 180° peel force, P , at six discrete rates ranging from 10 to 500 mm/min at each of 10 temperatures ranging from 238 to 338 K. Peel tests were conducted on a Hounsfield 10KM Tensile Test Instrument in a temperature-controlled test chamber where the temperature was controlled to $\pm 1^\circ\text{C}$. As described by Aubrey,¹⁴ curves of reduced peel force, $P_r = 298P/T$, against \log (peeling rate), R , were superimposed experimentally to yield a master-curve at 298 K. Measurements of 180° peel force were conducted by using test strips that had been adhered 24 h previously to mirror-finish stainless steel test panels. The test strips measured 180×25 mm and were cut from previously prepared test laminates with known coat weights. The test strips were bonded to the test panels by rolling a standard 2-kg rubber roller over the test strips five times. In the 24 h preceding the 180° peel force measurement, the bonded joints were stored in the controlled environment testing laboratory. At each of the 10 test temperatures, each bonded test strip was used to measure the peel force in duplicate at each of the six different peel rates. Each bonded joint was subjected to the test temperature within the temperature-controlled test chamber for at least 10 min before commencing the peel force measurements.

RESULTS AND DISCUSSION

T_g of acrylic PSAs

Table I shows the monomer levels used for the preparation of each emulsion polymer. The success of the approach used to maintain an equivalent polymer T_g for each emulsion polymer where the soft monomer compositions were varied from entirely BA to predominantly EHA, whereas increasing the level of MMA according to those dictated by the Fox equation (as measured by DSC) is borne out in the closeness of T_g values reported in Table II. PSA performance, as measured by peel, tack, and shear holding power, was widely demonstrated as strongly dependent upon such fundamental polymer parameters as T_g .^{18,19} Eliminating T_g as a variable in the properties of the polymers used for the present study was considered important to assist in examining the effects of the change in relative levels acrylic ester monomers on adhesive performance.

Effect of varied monomer content on gel fraction

The polymerization conditions used to prepare the latices for this study led to polymer containing a significant level of gel (Table II). The formation of gel during emulsion polymerization in the absence of crosslinking agents can occur via intermolecular chain transfer to polymer.¹⁰ The slow addition of monomers

TABLE II
Properties of the Acrylate Copolymers

Property	Polymer formulation				
	AA4M91-1	AA4M61-1	AA4M50-1	AA4M25-1	AA4M02-1
Viscosity (cP)	246	248	244	246	254
pH	5.4	5.5	5.5	5.5	5.4
Solids (%)	50.0	48.7	47.4	46.1	44.1
T_g by DSC (°C)	-39.7	-40.3	-41.0	-41.3	-40.4
Gel fraction (%)	45.6	60.2	61.9	63.3	61.7
Test laminate coating weight (g/m ²)	35.9	34.3	33.3	37.4	37.3
Average tack (N/25 mm)	12.4	12.6	11.9	11.9	12.9
Average shear (min)	397	2159	2753	3247	4884

during the preparation of the emulsions used in this study will have resulted in low monomer concentrations relative to the polymer concentrations. Such conditions favor chain transfer to polymer, leading to the formation of highly branched polymer structures²⁰ and microgels inside latex particles.⁹

Figure 1 shows the increase in gel content as the polymer weight fraction of EHA increases. The gel content reached a plateau maximum of around 62 wt % of polymer at a polymer weight fraction of around 35 wt % EHA. The level of gel recorded in the work presented in this study represents the polymer fraction that cannot be dissolved in THF. The measured gel, or apparent gel, may be a mixture of high molecular weight material of many different structural forms. However, the origin of the apparent gel will have been the high molecular weight material that was principally generated via intermolecular transfer to polymer leading to long-chain polymer branching, propagation to terminal double bonds, and through termination by combination.²¹ Intramolecular transfer to polymer yields short-chain polymer branching and is not considered to directly contribute to gel formation.¹⁰

Recent work by Heatley et al.²² showed that chain transfer to polymer during the free-radical polymerization of EHA is more extensive than for equivalent free-radical polymerizations of BA. They were, however, unable to draw conclusions regarding the relative levels of short and long chain branching. Work by Britton et al.²³ showed that the introduction of MMA into acrylate copolymerizations to reduce the levels of branching and measurement of gel contents of emulsion polymers reported by Araujo et al.²⁴ revealed that copolymerized MMA serves to lower gel contents. A similar effect was demonstrated with the copolymerization BA and styrene, where a lowering of chain branching levels was observed with increasing styrene levels, which resulted in a dramatic lowering of polymer gel fraction.²⁵ These findings suggest that altering the incidence of chain transfer to polymer during emulsion polymerization can act to alter the level of gel formation. Specifically, it is suggested that the data presented in Figure 1 show that increasing the level of copolymerized EHA in the polymerization recipe used here results in higher gel contents through higher levels of intermolecular chain transfer to polymer as a result of an overall increase in the tendency

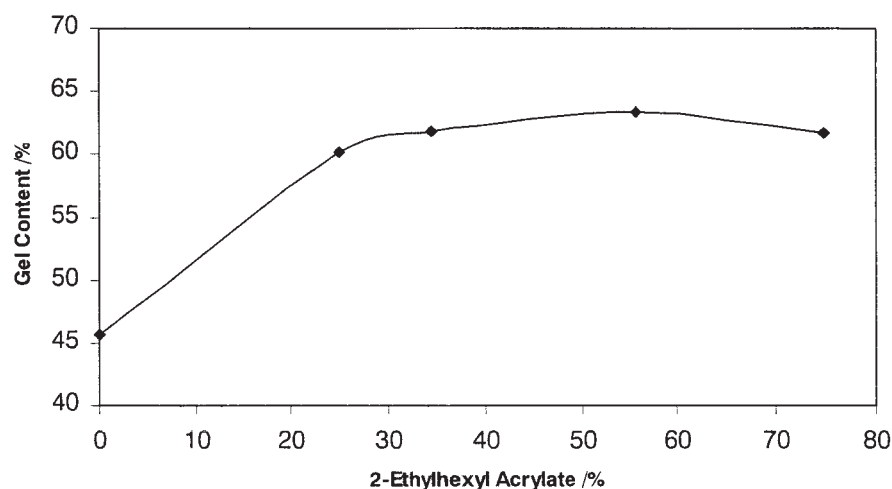


Figure 1 Gel content after THF extraction for AA4M-1 copolymers.

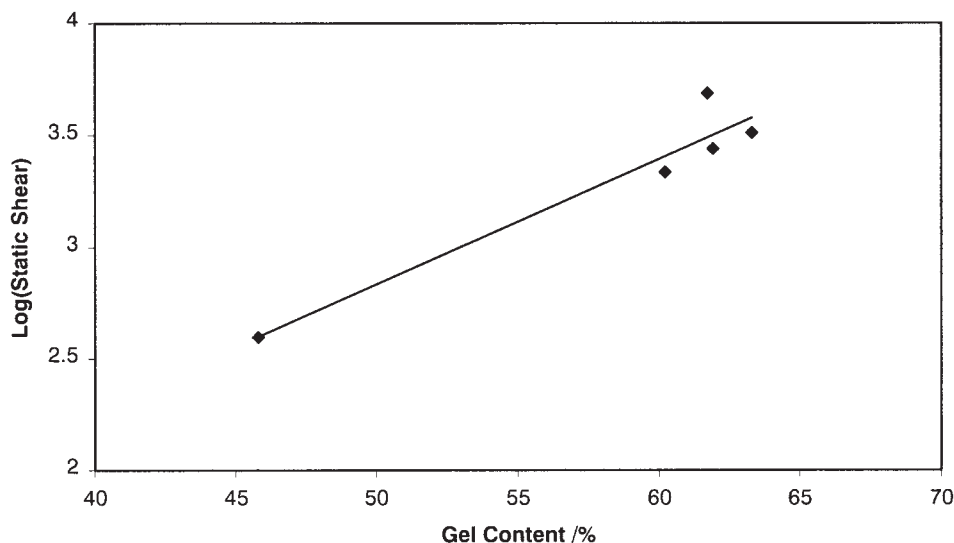


Figure 2 Log shear versus % gel for AA4M-1 copolymers.

for chain transfer to polymer. It is suggested that Figure 1 also reflects the competing influence of MMA where the increasing level of copolymerized MMA serves to moderate the tendency for chain branching and gel formation as a result of the increasing EHA level.

Effect of gel fraction on adhesive performance

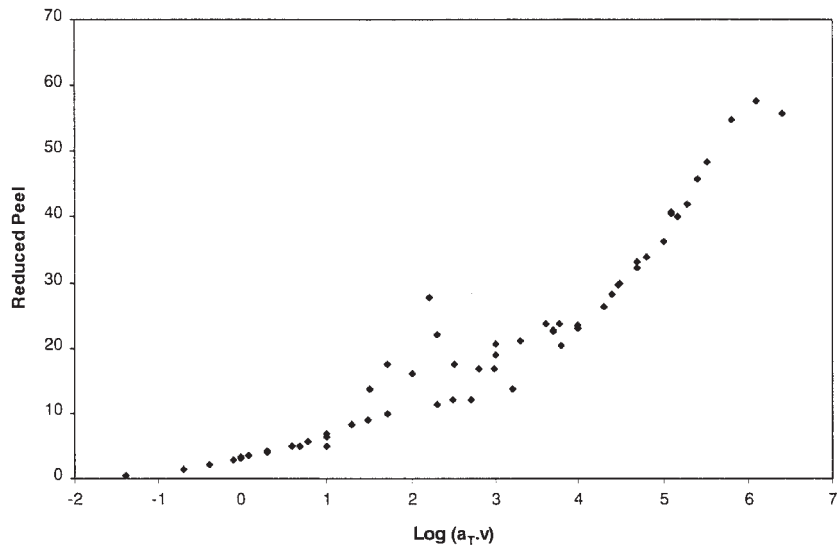
In a recent study by Tobing and Klein⁹ where gel content of BA-AA copolymers and EHA-AA copolymers were prepared by both solution and emulsion polymerization methods, they were also able to show that static shear values fell dramatically as gel content was decreased. As shown in Figure 2, our study shows that, for acrylate copolymers with equivalent levels of AA and very similar T_g 's, log (static shear) is proportional to the gel content. The expected increasing rigidity of the polymer network, and therefore decreased polymer mobility, as gel fraction increases, in addition to the EHA content, is attributed to the measured increase in shear holding power or shear resistance.

Data presented in Table II indicate that a correlation between loop tack value and gel content was not observed for the polymer series examined. Pressure-sensitive tack can be considered as a two-step process consisting of bond formation and bond separation. It is widely acknowledged that bond formation is governed by viscous flow, whereas viscous energy dissipation during debonding significantly contributes to bond separation. In the polymer systems investigated by Tobing and Klein,⁹ they found that tack levels decreased with increasing gel content. They suggested that higher sol fractions allowed increased intimate contact with the substrate during the bonding step and increased vis-

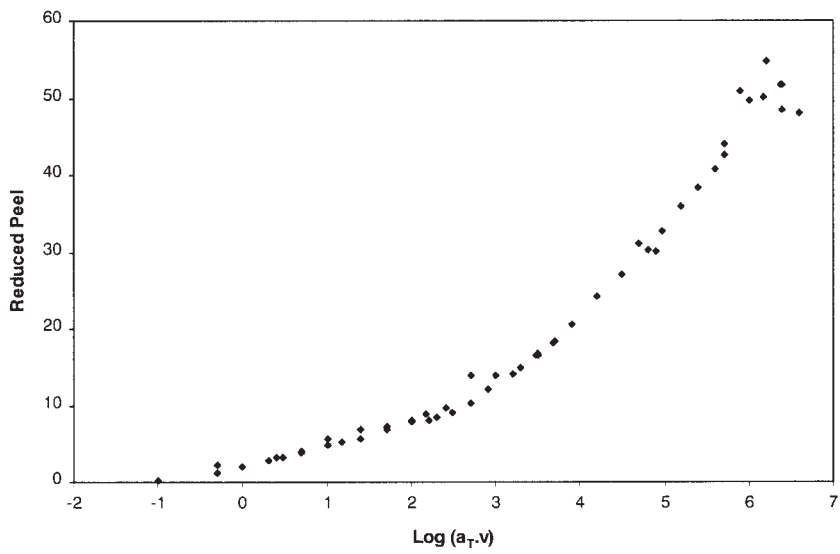
coelastic energy dissipation during the debonding step. Our polymer series returned a range of gel contents from 45.6 to 63.3 wt % compared with much higher ranges in gel (32–77 wt % for EHA/AA emulsion copolymers) presented in the work by Tobing and Klein.⁹ The smaller range of gel contents displayed by our polymers may not be sufficient to display any dependence of tack on gel content. It is interesting to note that, however, for the polymer series investigated, the two polymers with the highest measured levels of gel returned the lowest tack values.

Effect of monomer composition on adhesive performance

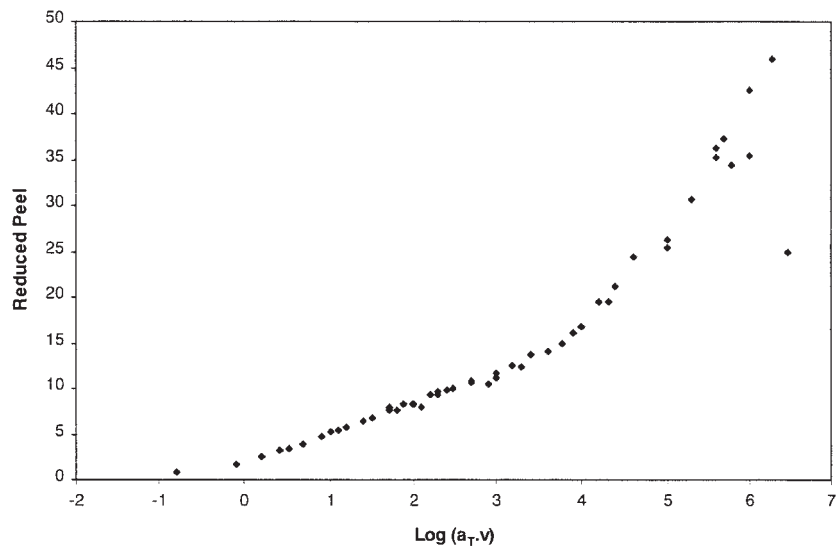
The average shear (Table II) is shown to increase proportionally to EHA concentration. While BA concentration decreases and MMA concentration increases through this series of shear results, EHA is the lowest T_g or softest monomer. The T_g is constant, although gel content increases are almost constant across EHA concentrations. The tack is constant through all compositions. This implies that tack is determined by the T_g or softness of the copolymers and the constant polar acrylic acid concentration. The physical distinction between tack and shear is that tack is the instantaneous adhesion, whereas shear results from flow of the adhesive after the initial constant. The flow of adhesive, or wetting of the substrate, must be dominated by the EHA content. The higher shear with EHA may receive a contribution from entanglements due to the ethylhexyl side groups. Increased wetting and entanglements provide different mechanisms that directly relate to T_g or chemical crosslinks that were used to explain higher shear. The dramatic increase in shear with EHA content shows how the monomer



(a)

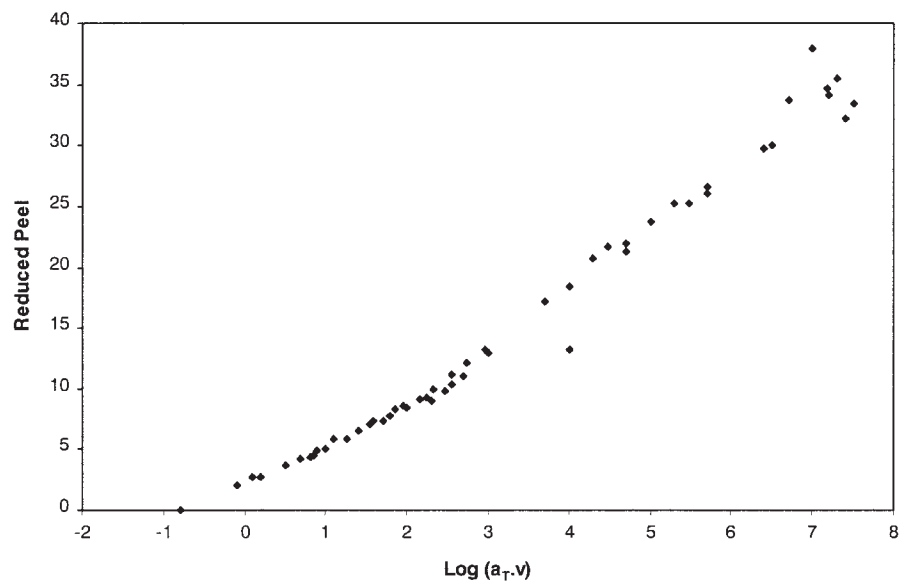


(b)

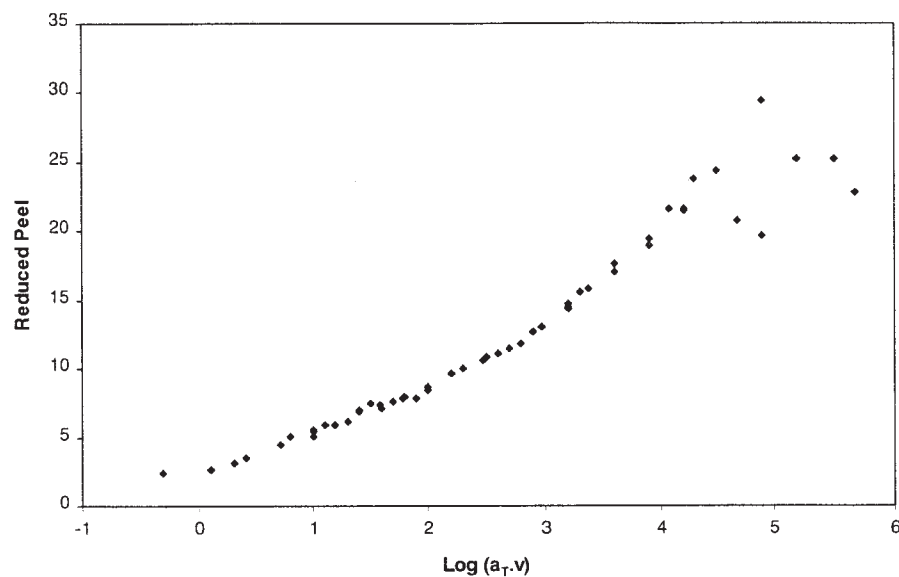


(c)

Figure 3 (a) Peel master-curve for AA4M91-1 copolymer. (b) Peel master-curve for AA4M61-1 copolymer. (c) Peel master-curve for AA4M50-1 copolymer. (d) Peel master-curve for AA4M25-1 copolymer. (e) Peel master-curve for AA4M02-1 copolymer.



(d)



(e)

Figure 3 (Continued from the previous page)

structure is important in controlling the adhesion but not the tack.

Peel master curves for acrylic PSAs

The peel master-curves are shown in Figure 4(a–e). During the initial part of the curves (the section of the curves corresponding to testing conducted at the highest temperatures), the debonding mechanism displayed by each polymer was that of adhesive transfer. In all cases, a debonding mechanism transition to adhesive failure mode took place at reduce peel rates of at or below $\log(a_T v) \approx 2$ except for the low gel adhe-

sive without EHA AA4M91-1, which showed a debonding mechanism transition from adhesive transfer to cohesive failure at $\log(a_T v) \approx 1$. Curve AA4M91-1 showed cohesive failure mode between $\log(a_T v) \approx 1$ and $\log(a_T v) \approx 2$, whereupon a debonding mechanism transition from cohesive to adhesive failure at $\log(a_T v) \approx 2$ took place. The cohesive-to-adhesive failure mode transition of AA4M91-1 is evidenced in the peel master-curve by the rapid fall in reduced adhesion value over a small reduced rate range just above $\log(a_T v) \approx 2$.

All the polymers demonstrate adhesive failure mode above $\log(a_T v) \approx 2$. As the peel rate increases,

the peel stress increases during the adhesive failure region where the adhesive layer is deformed. At higher peel rates, the data become more scattered as the unstable slip-stick region is approached. At the highest peel rates and lowest temperatures [the highest values of $\log(a_T v)$], the polymers begin to enter the rigid adhesive failure region (glassy response), with a decrease in peel stress at the highest rates and failure mode reverting to adhesive transfer indicating the onset of this region.

In an apparent contradiction of earlier work by Mao and Reegen,² the polymers show increasing peel adhesion values [particularly at higher $\log(a_T v)$ levels] with increasing copolymerized levels of BA. In addition, only the polymer with the highest copolymerized level of BA showed a cohesive failure to adhesive failure mode transition as $\log(a_T v)$ was increased. It should be noted with the current results, however, that with decreasing levels of copolymerized BA (or increasing levels of copolymerized EHA) that the level of gel tends to increase, although not to the same extent as the increase in shear. EHA is the softer monomer in the current work, whereas BA was the softer monomer in Mao and Reegen. As previously stated, gel can be regarded as crosslinked polymer obtained through intermolecular chain transfer to polymer rather than via the introduction of specific crosslinking agents. Increasing crosslink density narrows the mesh width of the entanglement network resulting in a loss of mobility between chains and a raising of the modulus of elasticity above the glass transition zone.^{3,26} As a result of this decreasing polymer mobility, transitions from cohesive failure-to-adhesive failure occur at progressively lower peel rates and higher temperatures.²⁷ In the case of the peeling master curve for AA4M91-1, a cohesive failure mode transition to adhesive failure mode is visible. However, for polymers with an increasing level of copolymerized EHA and increasing levels of gel, the cohesive to adhesive failure mode transition disappears. With increasing rates of peel, polymers with increasing gel levels show lower peel values as a result of the increasing polymer rigidity.

CONCLUSION

PSA with constant T_g were prepared from acrylate monomers (BA, EHA, MMA, AA) by using emulsion polymerization. In addition to comonomer content, gel content was a variable quantity. Gel content increased with EHA content until a plateau was reached. The increasing shear stress was dominated by EHA content, and gel content was important, although data were grouped about a high stress-gel content cluster. Loop tack strength was independent of EHA composition and gel content. The T_g and

acrylic acid content was the determinant of tack. Peel tests under variable temperatures were used to prepare peel master curves. The master curves revealed cohesive failure, flexible adhesive failure, and unstable, slip-stick failure regions. The peel stress was more sensitive to monomer content than gel content. Low BA or high EHA content provided the highest peel stress.

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