Effect of the Composition Profile of 2-Ethyl Hexyl Acrylate/Methyl Methacrylate Latex Particles on Adhesion

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ABSTRACT: The adhesive properties (tack, shear, and peel) of 2-ethyl hexyl acrylate/methyl methacrylate copolymer latex particles of different composition profiles (constant, positive, and negative gradients) but similar molecular weight distributions were studied. The composition profile had a strong effect on tack in the region of low molecular weights (weight-average molecular weight $\leq$ 100,000 g/mol), but this effect was less important for higher molecular weights. No effect of the composition profile on shear or peel was observed for low-molecular-weight latices; nevertheless, for higher molecular weights (400,000 g/mol), resistance to shear strongly increased as heterogeneity increased, and resistance to peel was higher for gradient profiles. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1258–1265, 2001

Key words: copolymer composition profile; pressure sensitive adhesive; adhesive properties; emulsion polymerisation

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are used for many applications (e.g., tape and labels), and the market is still growing as new applications are regularly discovered. Their success results from their convenient and fast handling and their easy removability without damage to the substrate. Environmental regulations[1] have led to the substitution of solvent-based adhesives with waterborne latices and aqueous adhesive emulsions; for example, emulsion acrylic copolymers currently have the biggest share of the PSA market.

The acrylic PSAs are copolymers whose principal monomer has a low glass-transition temperature (T_g) of less than $-40°C$ [monomers such as butyl acrylate ($T_g = -54°C$), iso-octyl acrylate ($T_g = -80°C$), and 2-ethyl hexyl acrylate (2EHA; $T_g = -70°C$) are useful for this purpose], and a high-T_g monomer ($T_g > 30°C$), usually methyl methacrylate (MMA; $T_g = 105°C$), is used as secondary monomer.

These systems have been extensively studied; the effects of blended copolymers, the use of polar monomers, the type of surfactant, functional groups, or crosslinking on the principal adhesive properties (tack, shear, and peel) have been reported in the literature.[2–7] The evolution of these properties as a function of molecular weight has been studied by Satas.[2–3] Satas showed that both tack and resistance to peel first increased with increasing molecular weight until a maximum (different for each property) was reached and

then decreased. He also found that resistance to shear also increased with increasing molecular weight, but it suffered catastrophic failure at a fairly high molecular weight. Delgado[4] reported that the use of polar comonomers such as acrylic and methacrylic acid in the polymerization produces an increase of both shear and peel adhesion. He also showed that the surfactant used in the polymerization may have a significant effect on the quality of the PSA produced. Papon et al.[5] studied the effect of the polymerization process, batch versus starved semibatch, on the tack of emulsion copolymers of 2EHA and MMA of a 50/50 molar composition. They found that the tack strength of the copolymer prepared by a batch process was high and the adhesive tape separated neatly from the substrate. For the more homogeneous copolymer, that is, the one prepared through a starved semibatch process, they found that tack strength was lower but the tack energy was much larger. They speculated that because of the more homogeneous composition of the copolymer, the adhesive separated in a fibrillated manner and this gave a much larger tack energy. Unfortunately, they did not report the molecular weights obtained in each experiment. Lovell[6] studied the effect on shear and peel adhesion of different core–shell morphologies of PSAs formed by BA/AA and MMA/BA/AA copolymers. He found that both properties were strongly influenced by the type and amount of each comonomer present in the copolymer shell. Mayer et al.[7] showed that a correlation could be found between the structure of copolymer latex particles, dynamic mechanical properties in the solid state of the copolymers, and the peel adhesion performance of the adhesive films. Three types of structured BA/MMA/AA latex particles were used in their work; uniform compositions, core–shell particles, being the core of poly(butyl methacrylate) or polystyrene, and composition profiles varied across the particle radii prepared by means of the power-feed strategy. Unfortunately, they did not report the molecular weight of their copolymer latices, and the adhesives film used in the peeling test was prepared with a crosslinking agent.

To our knowledge, no correlation between the homogeneity of the polymer composition and adhesive performance (tack, shear, and peel) has been reported.

The effect of the copolymer composition profile of 2EHA–MMA latices on tack, peel, and shear was studied. Different composition profiles (constant, positive, and negative gradients) were syn-

thesized with closed-loop control strategies that have already been reported to be reliable to prepare copolymers and terpolymers of the desired composition.[8–11] The molecular weight of these copolymers was controlled in an open-loop fashion to produce latices of similar molecular weight distributions (MWDs) but with clearly different composition profiles. The goal of producing such polymers was to isolate the effect of the copolymer composition on the adhesive properties of the latices.

EXPERIMENTAL

Materials

All the reagents were used as supplied. Technical-grade monomers, 2EHA and MMA (Atochem, France), double deionized water (Milipore, Spain), sodium lauryl sulfate ($C_{12}H_{25}O_4SNa$; Sigma, Spain) as an anionic surfactant, sodium carbonate ($NaHCO_3$; Fluka, Spain) as a buffer, dodecyl mercaptan ($C_{12}H_{26}S$, Fluka, Spain) as a chain-transfer agent (CTA), and potassium peroxodisulfate ($K_2S_2O_8$; Fluka, Spain) as an initiator were used throughout the work.

Composition Profiles

The monomers 2EHA (A; $T_{g2EHA} = -85°C$) and MMA (B; $T_{gMMA} = 105°C$) were polymerized in an 85/15 molar ratio to produce a PSA with high tack and acceptable shear and peel resistances. To study the influence of the polymer particle composition profile on the adhesive properties of the latices, four different profiles of the cumulative copolymer composition of 2EHA as a function of conversion were chosen:

a. $Y_{A,cumul} = 0.85$: an 85/15 homogeneous copolymer of 2EHA/MMA (instantaneous composition: $Y_{A,inst} = 0.85$).

b. $Y_{A,cumul} = 0.75 + 0.1x$: a copolymer with a molar cumulative composition of 2EHA/MMA varying from 75/25 at overall conversion (x) zero to 85/15 at overall conversion one (increasing profile; instantaneous composition: $Y_{A,inst} = 0.75 + 0.2x$). The overall conversion is defined as the ratio between the weight of polymer in the reactor and the total amount of monomer in the formulation.

c. $Y_{A,cumul} = 0.95 - 0.1x$: a copolymer with a

Table I Parameters Used to Obtain the Monomer Profiles

Parameter	Value
$K_{w,d}^A$ [18]	1.35×10^{-3}
$K_{w,d}^B$ [18]	1.695×10^{-2}
$K_{w,p}^A$ [18]	2.08×10^{-3}
$K_{w,p}^B$ [18]	2.325×10^{-2}
k_{pA} (L mol^{-1} s^{-1}) [19]	2.26×10^4
k_{pB} (L mol^{-1} s^{-1}) [20]	8.33×10^2
r_A [21]	0.49
r_B [21]	2.25
$(-\Delta H_A)$(J mol^{-1}) [21]	78.2×10^3
$(-\Delta H_B)$(J mol^{-1}) [21]	55.6×10^3

A = 2-ethyl hexyl acrylate; B = methyl methacrylate.

molar cumulative composition of 2EHA/ MMA varying from 95/5 ($x = 0$) to 85/15 ($x = 1$; decreasing profile; instantaneous composition: $Y_{A,\text{inst}} = 0.95 - 0.2x$).

d. Heterogeneous copolymer with an overall 85/15 molar composition of 2EHA/MMA produced in a batch process.

Experimental Setup

The reactions were carried out in a commercial reactor calorimeter (RC1; Mettler-Toledo, Switzerland) equipped with a 1.5-L stainless steel jacketed reactor vessel (HP60; Mettler-Toledo, Switzerland), a fluidfoil impeller (narrow-bladed hydrofoil; Lightnin Mixers, U.K.), platinum resistance thermometers, an electrical calibration heater, and a sampling tube. The RC1 was operated in isothermal mode at a set reactor temperature of 60°C. To minimize heat loss and obtain a stable baseline, we used a separate thermostatically controlled bath to circulate water at 65°C through the reactor stainless steel lid. An external computer was attached to solve online the material and energy balances of the reactor and to monitor and control the reaction. Additional details about the reactor operation can be found elsewhere.[8,9]

Copolymer composition profiles a, b, and c were produced with a closed-loop control strategy[9–11] that tracked the optimal trajectories of monomer in the reactor, which were calculated with the method of de la Cal et al.[12] with the parameters given in Table I. The recipes used for all reactions are given in Table II. The semicontinuous polymerizations, runs 1a, 1b, 2, and 3, were carried out as follows. The reactor was charged with all but 15 g of water and all of the emulsifier, buffer, and CTA. The reactor was heated to 60°C, and a preheated solution of the initiator in 15 g of water was added. Then, the monomers were fed at the required feed rates. We carried out the batch polymerizations (runs 4a and 4b) by charging the reactor with all but 15 g of water and all of the emulsifier, buffer, CTA, and monomers. The reactor was heated to 60°C, and then a preheated solution of initiator in 15 g of water was added.

Polymer Characterization

Samples were withdrawn from the reactor, and polymerization was short-stopped with hydroqui-

Table II Recipes Used for the Different Runs

| Composition Profile (2EHA) | Amount (g) | | | | | |
	Run 1a: Constant	Run 1b: Constant	Run 2: Positive Gradient	Run 3: Negative Gradient	Run 4a: Heterogeneous	Run 4b: Heterogeneous
H$_2$O (g)	785.45+ 15.20[a]	784.95+ 15.65[a]	784.37+ 15.25[a]	786.05+ 13.96[a]	785.09+ 15.10[a]	785.05+ 15.30[a]
SLS (g)	6.01	6.00	6.00	6.01	6.03	6.00
NaHCO$_3$ (g)	2.00	2.00	2.01	2.00	2.02	2.01
CTA (g)	3.99	4.03	4.03	4.00	3.99	0.69
K$_2$S$_2$O$_8$ (g)	2.01	2.01	2.01	2.01	2.00	2.00
2EHA (g)	365.58[b]	365.84[b]	365.64[b]	365.60[b]	365.11	365.03
MMA (g)	35.05[b]	35.20[b]	34.86[b]	35.10[b]	35.10	35.05
Stirrer speed (rpm)	400	400	400	400	400	400

[a] Amount charged into the reactor with the initiator.
[b] Amount fed into the reactor during the reaction.
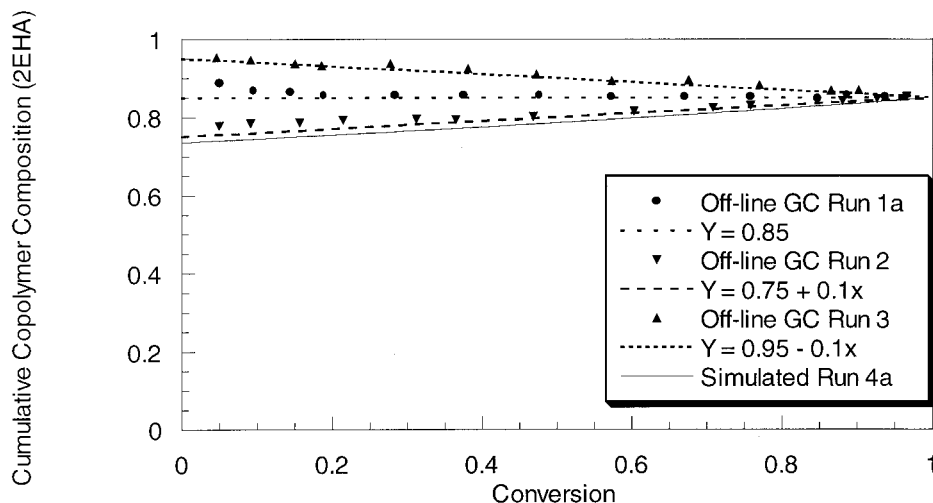
Figure 1 Evolution of the cumulative copolymer composition for runs 1a, 2, 3, and 4a.

none. Conversion was measured by gravimetry, and polymer composition was measured by gas chromatography (by measuring the amounts of unreacted monomer). Particle size was measured along the process with a dynamic light scattering device (Coulter N4-Plus, California, USA).

MWD was measured with size exclusion chromatography (Waters, Spain). The dried sample was dissolved in tetrahydrofuran (THF; 99%; Fluka) and injected into a setup of three columns in series, Styragel HR 2, 4, and 6 (Waters), packed with fully porous and highly crosslinked styrene–divinylbenzene copolymer particles of 10^2, 10^3, and 10^6 Å pore sizes, respectively. The final samples were extracted under reflux conditions in THF, and the insoluble amount of the polymer was considered to be gel.

T_g of the final latex was determined by dynamical mechanical thermal analysis (MK1 Polymer Laboratories, Rheometric, USA). The instrument was run under shear mode at a frequency of 1 Hz, the T_g calculated by the peak-loss modulus.

Preparation of the Latices

Latices with similar molecular weights and different copolymer composition profiles (but the same overall composition) were prepared. Two levels of molecular weights [weight-average molecular weight (M_w) ≈ 100,000 and 400,000 g/mol] were considered. Four different copolymer composition profiles were prepared. Runs 1a and 1b were aimed at producing homogeneous copolymers of an 85/15 molar composition of 2EHA/MMA with different molecular weights. The same

recipe was used in these reactions (Table II), but different monomer feeding times were employed (95 min for run 1a and 120 min for run 1b). Figure 1 shows that a homogeneous 85/15 copolymer was indeed obtained in run 1a. A similarly homogeneous copolymer was produced in run 1b (not shown). Table III shows that the M_w obtained in run 1b was higher than that of run 1a. The reason for this difference is that a longer feeding time was used in run 1b, which had two consequences. First, the process proceeded under more starved conditions that promoted chain transfer to polymer, that is, higher molecular weights. Second, a lower average concentration of CTA was present in run 1b because $C_{12}H_{26}S$ is rather reactive and the longer the process time is, the lower its concentration is. In addition, the chain transfer to polymer and the varying CTA concentration yielded to an MWD broader than that of run 1a (Fig. 2).

In run 2, a copolymer with an instantaneous composition of 2EHA/MMA varying from 75/25 to 95/5 and a relatively low molecular weight was sought. Therefore, the monomers were fed in a short period of time (90 min). Figure 1 shows that the desired copolymer composition profile was achieved. Table III shows that a low molecular weight was obtained.

In run 3, a copolymer with an instantaneous composition of 2EHA/MMA varying from 95/5 to 75/25 molar ratios and a relatively high molecular weight was obtained (Figs. 1 and 2 and Table III).

In run 4a, a batch copolymer with the same overall composition of 2EHA (0.85) was produced.

Table III   Characteristics of the Copolymers Tested

|	Run					
	1a	1b	2	3	4a	4b
Composition profile (2EHA)	Constant, 0.85	Constant, 0.85	Increasing, $0.75 + 0.1x$	Decreasing, $0.95 - 0.1x$	Heterogeneous	Heterogeneous
M_w (g/mol)	98,500[a]	404,300[b]	98,800[a]	360,500[b]	72,200[a]	414,900[b]
Solids content (%)	30.2	31.8	31.7	30.7	30.8	32.0
T_g (°C)	−19	−12	−13.5	−14	−21.5	−11
Gel fraction (%)	0	0	0	0	0	0
Average tack (cm)	1.3	5.8	1.8	7.0	2.4	7.9
Standard deviation (cm)	0.2	1.2	0.3	1.8	0.4	1.5
Average shear (s)	30	173	28	300	26	607
Standard deviation (s)	8	70	6	137	6	236
Average peel (Newton/100 mm)	4.2	15.0	5.5	25.3	4	15.3
Standard deviation (Newton/100 mm)	0.6	0.8	0.5	0.9	0.4	1.2
Final particle diameter (nm)	68.6	63.9	68.8	62.4	97.9	88.6

[a] Copolymers with a similar MWD.
[b] Copolymers with another similar MWD.

This type of reaction cannot be controlled because all of the monomers are initially added into the reactor, so the final latex was very heterogeneous in composition. The final latex had a molecular weight of 72,200 g/mol. A second batch experiment, run 4b, was also carried out with a lower amount of CTA to produce a heterogeneous copolymer of higher molecular weight. The latex obtained had a molecular weight of 414,900 g/mol.

The differences between the different composition profiles might seem modest. However, as the fraction of 2EHA in the copolymer is fixed by the T_g required for a PSA, the composition profiles studied in this work represent extreme profiles. More different copolymer composition profiles could be obtained with a lower 2EHA content (e.g., 50%), but in this case, the copolymer would not behave as an efficient PSA.

The properties of the different latices are reported in Table III. The T_g's of the copolymers produced (−11 to −21,5°C) were in the range required for PSAs. The latices produced can be
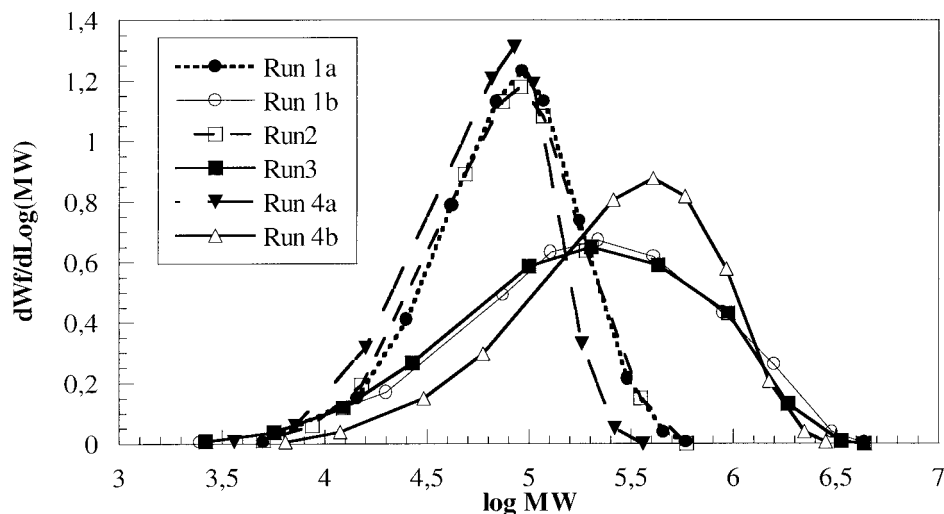
Figure 2   MWDs for runs 1a, 1b, 2, 3, 4a, and 4b.
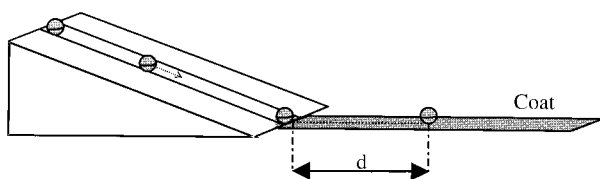
Figure 3 Principle of the rolling-ball tack test.

classified into two different groups according to their MWDs. Latices 1a, 2, and 4a had approximately the same MWD ($M_w \approx 100{,}000$ g/mol), and they differed in their composition profiles: homogeneous (run 1a), homogenous with an increasing profile (run 2), and heterogeneous (run 4a). The remaining latices, 1b, 3, and 4b, also had approximately the same MWDs, but in this case, M_w was about 400,000 g/mol. The differences between these latices came from their composition profiles: homogeneous (run 1b), homogenous with a decreasing composition profile (run 3), and heterogeneous (run 4b).

Adhesive Testing

Coat Preparation

The backing used to prepare the adhesive tapes was a biaxially oriented polypropylene film (Poligal®, Spain). The viscosity of the latices was augmented by the addition of 1.5 wt % thickener (the commercial hydroxyethyl cellulose, Rhodia). The latices were applied on the polypropylene film with a 90-μm metallic applicator that produced a thick coat and were dried in an oven heated at 50 ± 1°C for 20 min. The adhesive tape was then cooled for 20 min at room temperature, and after this period, the different tests were carried out at room temperature as explained next.

Rolling-Ball Tack Test

Tack is defined as the property that enables an adhesive to form a bond with the surface of another material on brief contact under light pressure.[2] The rolling-ball tack test is one of several methods used to determine the tack of a pressure-sensitive tape. In this procedure, a 11-mm-diameter stainless steel ball is rolled down an inclined track (angle = 21°30′) to come into contact at the bottom with the horizontal, upward-facing adhesive.[13] The distance, d, that the ball travels along the tape is taken as the measure of tack. Ball rollout distance gives an inverse scale of tack: the greater the distance is, the less tacky the film is.
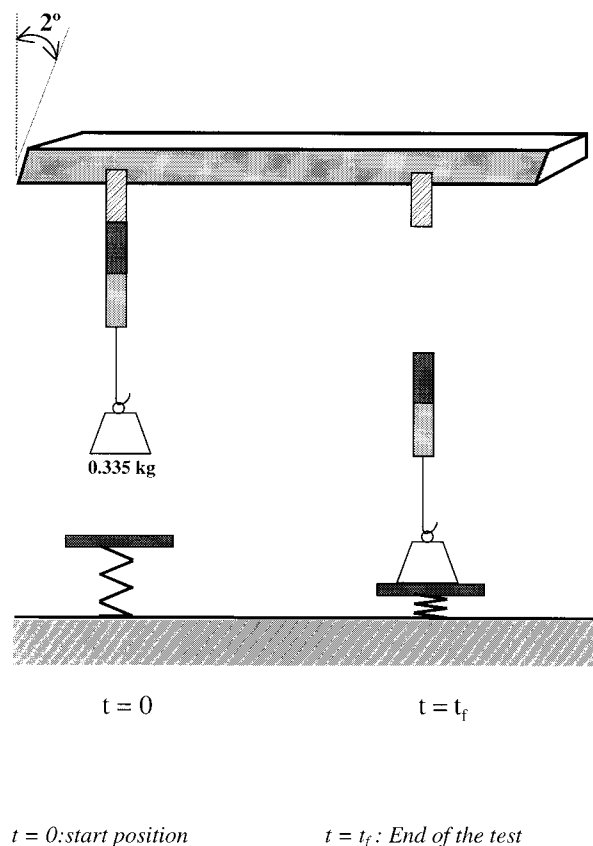
Figure 3 presents a scheme of the setup for this test. Fifteen replicate tests were carried out for each latex.

Shear Test

Holding power is the ability of pressure-sensitive tapes to remain adhered under a load applied parallel to the surface of the tape.[2] The method used in this study consists of holding a mass (335 g in this case) on a standard area of tape (25 × 25 mm) applied to a panel 2° from the vertical.[14] The purpose of the small inclination from the vertical is to ensure that the tape will experience no peeling action, only shear. The time elapsed between the application of the load and the complete separation of the tape from the panel is the measurement of the resistance to shear. The longer this time is, the higher the resistance to shear is. Figure 4 shows a drawing of the setup used for this test. Fifteen replicated tests were carried out for each latex.

Peeling Test

Resistance to peel is determined from the force required to peel away a strip of tape from a rigid

$t = 0$: start position $t = t_f$: End of the test

Figure 4 Principle of the shear test.
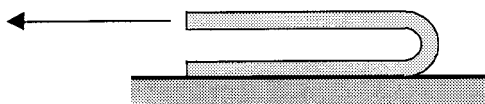
Figure 5 Schematic diagram of the resistance-to-peel test.

surface at a specified angle and speed.[2] Figure 5 presents a scheme of the setup used to measure the resistance to peel of PSA tapes.[15] A 20-m-wide tape is applied to a highly polished steel panel with definite pressure (a 2-kg roller) to make the contact. After 10 min, the free end of the tape is bent back at an angle of 180° and clamped to the upper jaw of an Instron (USA) tensile tester. The upper jaw is then operated at a set speed of 300 mm/min. The values obtained while the first 25 mm of tape is mechanically peeled are disregarded, and the adhesion value considered is the average pull value obtained during peeling of the next 50 mm. It is expressed in Newton/100 mm. Five replicated tests were carried out for each latex.

RESULTS AND DISCUSSION

Tack Test

A comparison of latices 1a, 2, and 4a shows that for low-molecular-weight latices, tackiness increased with homogeneity in copolymer composition. The reasons for this difference are intriguing. Because a water-soluble initiator was used, one would expect to find the polymer chains produced at the end of the process located in the outer shell of the polymer particles. Consequently, particles produced in runs 2 (increasing 2 EHA profile) and 4a (batch process, 2EHA being the less reactive monomer) would have a softer outer shell than particles from run 1a, and the opposite tack behavior would have been observed. Implicit in this reasoning is that no migration of the polymer chains occurred during the particle growth. However, migration of the more hydrophilic polymer (MMA-rich polymer) could easily occur in a soft latex.[16,17] In that case, the more heterogeneous the latex is, the harder the outer shell of the particles is and the lower the tack is, as experimentally observed. High-molecular-weight latices (runs 1b, 3, and 4b) seemed to present the same trend: tackiness increased with homogeneity. A comparison of low- and high-molecular-weight latices show that molecular weight strongly affected tack: the higher the M_w was, the lower the tack was.

Shear Tests

A comparison of latices 1a, 2, and 4a shows that the copolymer composition profile did not affect resistance to shear. One wonders if the low molecular weight of these latices ($\approx$100,000 g/mol) may prevent the observation of any difference in shear. However, a comparison of latices 1b, 3, and 4b shows that for high-molecular-weight polymers, the more heterogeneous the copolymer composition was, the higher the resistance to shear was. Admittedly, no clear explanation of the observed effect can be offered.

Table III also shows that for a given copolymer composition profile, the higher the molecular weight was, the higher the resistance to shear was.

Peeling Tests

Table III shows that for high molecular weights, the latex with a well-defined gradient composition (run 3, decreasing composition) presented a higher resistance to peel. This result can be explained by the fact that the latex with the decreasing profile had the shell polymer with a richer composition of MMA than the other two. This effect was not evident for low-molecular-weight latices. In addition, in the range of molecular weights studied, the resistance to peel increased with M_w.

CONCLUSIONS

The effect of the copolymer composition profile of PSAs made out of 2EHA–MMA latices on tack, resistance to peel, and resistance to shear was studied. Different composition profiles (constant, positive, and negative gradients) were synthesized with a closed-loop control strategy based on calorimetry. In addition, a heterogeneous copolymer composition latex was produced in batch. Latices with two levels of molecular weights (M_w's $\approx$ 100,000 and 400,000 g/mol) were considered. For low-molecular-weight polymers, tackiness tended to increase with homogeneity in the copolymer composition, resistance to shear was not affected by the copolymer composition profile, and resistance to peel seemed to be slightly higher for gradient profiles.

For high-molecular-weight polymers, tack slightly increased with homogeneity in the copolymer composition, resistance to shear strongly increased as heterogeneity increased, and resistance to peel was higher for gradient profiles.

NOMENCLATURE

$K_{j,k}^i$ partition coefficient of monomer i between phases j and k

k_{pi} propagation-rate constant of monomer i ($\text{L mol}^{-1}\text{s}^{-1}$)

r_i reactivity ratio of monomer i

$(-\Delta H_i)$ enthalpy of polymerization of monomer i (J mol^{-1})

Subscripts

w aqueous particle phase
d monomer droplet particle phase
p polymer particle phase

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