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WATER-BORNE PRESSURE-SENSITIVE ADHESIVES: EFFECTS OF ACRYLIC ACID AND PARTICLE STRUCTURE

John Garrett, Peter A. Lovell *, Alison J. Shea and Roger D. Viney

Polymer Science and Technology Group, Manchester Materials Science Centre,
University of Manchester & UMIST, Grosvenor Street, Manchester, M1 7HS,
United Kingdom

Abstract: Two types of core-shell pressure-sensitive adhesive latexes have been prepared by semi-continuous emulsion polymerization: (a) *soft-soft* latexes with a poly(n-butyl acrylate) core and a poly[(n-butyl acrylate)-*co*-(acrylic acid)] (PBA/AA) shell; and (b) *rigid-soft* latexes with a poly[(methyl methacrylate)-*co*-(allyl methacrylate)] (PMMA/ALMA) core and a PBA/AA shell. Three series of *soft-soft* latexes were prepared in which: (i) the acrylic acid level in the PBA/AA shell was fixed at 5 mol% and the volume percentage (vol%) of the PBA/AA shell was varied; (ii) the vol% of the PBA/AA shell was varied, but with the acrylic acid level in the shell also being varied such that the total acrylic acid level was constant at 5 mol%; and (iii) the PBA/AA shell was fixed at 20 wt% of the total polymer and the acrylic acid level was varied from 0 to 49 mol%. In the *rigid-soft* latexes, the acrylic acid level in the PBA/AA shell was fixed at 5 mol% and the vol% of the PBA/AA shell was varied. The latexes were adjusted to pH 5.5 using aqueous ammonia solution before being used to form adhesive bonds between Melinex and glass, for measurement of shear resistance, and between Melinex and steel for measurement of peel adhesion. The pressure-sensitive adhesive properties of the latex coatings are interpreted in terms of the effects of the changes in latex particle acrylic acid content and particle structure on the interfacial and bulk properties of the adhesive materials.

1 Introduction

Growing environmental pressures, and the advent of increasingly stringent legislation concerning solvent emissions, have forced the coatings industry to seek the replacement of solvent-borne adhesives by all-solids coatings and/or water-borne coatings. These pressures have been particularly strong in Europe and North America [e.g., 1]. Hence, although water-borne coatings have existed for several decades, interest in them is growing substantially. As most of the conventional solvent-borne coatings are based on water-insoluble polymers, aqueous dispersions are required. Emulsion polymerization is a particularly convenient means of preparing hydrophobic polymers in a form suitable for formulation into water-borne coatings, the principal coating types prepared in this way being paints and adhesives [2]. There has, therefore, been renewed commercial interest in coating materials prepared by emulsion polymerization.

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* to whom correspondence should be addressed

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The impact of this increase of interest in water-borne coatings on the adhesives market is most evident for pressure-sensitive adhesives and contact adhesives, since these types of adhesive have traditionally been dominated by solvent-borne systems. In contrast, adhesives for use with wood and board have for many years been based on poly(vinyl acetate) latexes and so have not been so markedly affected.

Pressure-sensitive adhesives (PSAs) [3] are based on polymers with low glass transition temperatures (typically in the range -40 to -50 °C). In most cases, they are copolymers prepared using either n-butyl acrylate or 2-ethylhexyl acrylate as the principal monomer. The adhesive coatings are usually applied to one of the substrates (the backing) to be bonded, allowed to dry and then protected by applying a release paper to the open adhesive surface. The most common backings are paper labels and tapes. When required, the release paper is removed and the backing bonded to a surface by applying light pressure.

This paper presents an overview of some studies into the preparation and properties of water-borne acrylic PSAs, with emphasis on effects of the way in which acrylic acid is used in the emulsion polymerizations and effects of particle structure.

2 Experimental

2.1 Materials

Potassium persulfate (Aldrich, > 99%), Aerosol MA-80 (Cyanamid & Cytec) and t-dodecylmercaptan (Fluka & Aldrich) were used as supplied. Deionized water was used throughout the work. n-Butyl acrylate, methyl methacrylate and allyl methacrylate [polymerization-grade monomers] were used either as supplied or after removal of inhibitor by washing the monomer several times with dilute sodium hydroxide solution and then several times with water before drying over anhydrous calcium chloride. The inhibitor was removed from acrylic acid (Aldrich, > 99%) just prior to use by passage through a column of silica gel.

2.2 Latex Preparation and Characterization

The PSAs were prepared as 50% solids latexes by semi-continuous emulsion polymerizations involving three sequential stages, all polymerizations being carried out under a swept nitrogen atmosphere at 75 °C. The first stage involved the formation of seed particles of 110 nm diameter. This was followed by two growth-stages, which took the final particle diameter to 300 nm. In the first of the growth stages the same polymer was formed as was produced in the seed stage; the second growth-stage formed a poly[(n-butyl acrylate)-*co*-(acrylic acid)]. Thus, the particles produced can be considered to be of the core-shell type in which the core is formed from the seed stage plus the first growth-stage and the shell is formed from the second growth-stage. Two types of latexes were prepared in this way: (i) latexes with particles having a poly(n-butyl acrylate) core; and (ii) latexes with particles having a poly[(methyl methacrylate)-*co*-(allyl methacrylate)] core. The formulations used for 2-litre scale preparations are given in Tables 1 and 2. Note that for the growth stages, only the mass ratios of monomers, chain transfer agent and surfactant are given; the sum of the quantities of monomers used in the two growth-stages was 950 g. Mass ratios are given because the relative proportions of the two growth-stage reactant mixtures was changed in order to produce a range of PSAs with different proportions of core and shell.

Table 1. Formulation for preparation of PSA latexes with a poly(n-butyl acrylate) core and a poly[(n-butyl acrylate)-*co*-(acrylic acid)] shell

Formulation Component	Seed Stage (mass / g)	Growth Stages (total monomer = 950 g)	
		Stage 1 (mass ratio)	Stage 2 (mass ratio)
Butyl acrylate	50.00	100.00	97.12[a] → 86.32[b]
Acrylic acid	–	–	2.88[a] → 13.68[b]
Dodecyl mercaptan	–	0.035	0.035
Aerosol MA-80	2.50	1.25	1.25
Deionized water	800.0 50.0	150.0 g	
Potassium persulfate	2.15 0.54	0.64 g	

[a] 95 mol% n-butyl acrylate; 5 mol% acrylic acid
[b] 78 mol% n-butyl acrylate; 22 mol% acrylic acid

Table 2. Formulation for preparation of PSA latexes with a poly[(methyl methacrylate)-*co*-(allyl methacrylate)] core and a poly[(n-butyl acrylate)-*co*-(acrylic acid)] shell

Formulation Component	Seed Stage (mass / g)	Growth Stages (total monomer = 950 g)	
		Stage 1 (mass ratio)	Stage 2 (mass ratio)
Methyl methacrylate	49.37	98.74[a]	–
Allyl methacrylate	0.63	1.26[a]	–
Butyl acrylate	–	–	97.12[b]
Acrylic acid	–	–	2.88[b]
Dodecyl mercaptan	–	–	0.035
Aerosol MA-80	5.00	1.25	1.25
Deionized water	800.0 50.0	150.0 g	
Potassium persulfate	2.15 0.54	0.64 g	

[a] 99 mol% methyl methacrylate; 1 mol% allyl methacrylate
[b] 95 mol% n-butyl acrylate; 5 mol% acrylic acid

The following general procedure was used for preparations on a 2-litre scale. The seed-stage surfactant and part of the deionized water (700 g) were added to a 2-litre flanged reaction vessel which was then equipped with a condenser, nitrogen inlet and mechanical stirrer. A nitrogen atmosphere was established whilst the surfactant solution attained the reaction temperature. The seed-stage monomer was added next and, after the reaction temperature had again stabilized, a solution of potassium persulfate (2.15 g) in deionized water (100 g) was added, thus marking the start time of the reaction. After 55 min reaction a further quantity of potassium persulfate (0.54 g) in deionized water (50 g) was added. A further 5 min was allowed for completion of the seed stage, addition of the first growth-stage reactant mixture then being started. Immediately upon completion of this addition, the second growth-stage feed was started. For both growth stages the reactant mixture was metered at a rate of ~5.3 g min^{-1} using a Watson-Marlow Model 505S peristaltic pump. Solutions comprising potassium persulfate (0.215 g) in deionized water (50.0 g) were added at 115, 175 and 235 min reaction time. Following completion of the addition of the second growth-stage reactant mixture, a further 60 min was allowed before cooling the latex to room temperature and filtering through a 53 µm sieve. Samples were taken at regular intervals during the course of each latex preparation in order to determine overall and instantaneous monomer conversions (gravimetric analysis) and z-average particle diameter, d_z (Malvern Autosizer IIc photon correlation spectrometer).

2.3 *Adhesive Testing*

The preparation and testing of adhesive bonds were carried out in accordance with standard industrial test procedures [4]. The PSA latexes (adjusted to pH 5.5 with aq. NH_3) were first coated onto 36 µm Melinex 'S' film using a No.7 K-bar and dried at 105 °C for 4 min. The coatings then were used to determine peel adhesion and shear resistance as follows. Adhesive bonds were formed by applying a rolling a standard 2 kg roller across the bonded area five times. All adhesive testing was performed at 23 °C and 50% relative humidity. Shear resistance was measured as the time taken to complete failure of an overlap bond (20 × 20 mm^2 contact area) between the coated Melinex and a glass plate (held at 2° to the vertical) under a static shear force applied by suspending a 1.5 kg weight from the Melinex after 10 min contact time. Peel adhesion was measured after 1 h contact time as the force per unit width required to peel a 25 mm wide strip of the coated Melinex from a steel plate at an angle of 180° using a cross-head displacement rate of 200 mm min^{-1} on an Instron.

3 Results and Discussion

3.1 *Effects of Acrylic Acid*

Three series of latexes with poly(n-butyl acrylate) cores were prepared. In the first series (termed *layer-AA-fixed*), the acrylic acid level in the second growth-stage mixture was fixed at 5 mol% and the volume percentage (vol%) of the poly[(n-butyl acrylate)-*co*-(acrylic acid)] (PBA/AA) outer layer varied. In the second series (termed *total-AA-fixed*), the vol% of the PBA/AA again was varied, but the acrylic acid level in the second growth-stage mixture was varied such that the total acrylic acid level summed over the first and second growth-stages was constant at 5 mol%. In the third series (termed *AA-layer-level* and not specifically indicated in Table 1), the amount of second growth-stage monomer was fixed at 20 wt% of the total monomer and the acrylic acid level used in this stage varied from 0 to 49 mol%. Recognising that, for each series, the core of the latex particles is more hydrophobic than the shell, and that the reactions were run under monomer-starved conditions, good control of core-shell morphology was expected [5].

3.1.1 Latex preparations

All latex preparations in the *layer-AA-fixed* and *total-AA-fixed* series proceeded under monomer-starved conditions and with good control of particle growth, as evidenced by good agreement between the measured and theoretical particle sizes. Typical variations of percentage conversion and particle size with reaction time are shown in Figure 1.

Six latexes were prepared in the *AA-layer-level* series, respectively comprising 0, 11.4, 21.9, 31.7, 40.8 and 49.3 mol% acrylic acid in the second growth-stage monomer mixture. The latex preparations using the three lower acrylic acid levels proceeded as for the *layer-AA-fixed* and *total-AA-fixed* latex series, with the reactions running under monomer-starved conditions and with good control of particle growth. However, although the three latex preparations at the highest levels of acrylic acid proceeded under monomer starved conditions throughout, particle growth was not controlled during the second growth-stage. For these three latex preparations, the particles grew in a controlled way up to the end of the first growth-stage, as in the other preparations, but the measured particle size exceeded the theoretical value by an increasingly greater amount as the reaction progressed to complete conversion. The final values of d_Z were 407 nm, 614 nm and 944 nm, respectively, for the latexes comprising 31.7, 40.8 and 49.3 mol% acrylic acid in the second growth-stage monomer mixture. Bearing in mind that d_Z represents the hydrodynamic volume of the particles, then such large values of d_Z indicate that the outer PBA/AA layers are highly swollen, the degree of swelling increasing as the level of acrylic acid increased. At such high levels of acrylic acid, the formation of water-soluble polymer by homogeneous polymerization in the aqueous phase is likely, though this clearly did not affect the colloidal stability of the latexes because the coagulum levels for these three latex preparations were 0.12%, 0.14% and 0.16%, respectively, compared to the mean level of 0.18±0.14% taken over all preparations.

3.1.2 Adhesive properties

The adhesive testing results for the *layer-AA-fixed* series of PSA latexes are shown in Figure 2. The shear resistance increases at a progressively increasing rate as the vol% of the PBA/AA outer layer increases, whilst the peel adhesion shows a steady decrease. The shear resistance test depends to a large extent on the bulk properties of the adhesive material, increasing as the material becomes stiffer provided that both substrates are wetted by the adhesive. Thus the increase in shear resistance may be interpreted in terms of the increasing proportion of the PBA/AA layer leading to a material that is increasingly stiffer due to hydrogen-bonding and ionic interactions arising from the partially-neutralized acrylic acid repeat units. Peel adhesion is a much more complex property that is affected by many factors, which include wetting of the substrate surfaces, interactions with the substrate and the mechanical properties of the adhesive. The adhesive bond failed at the steel surface for all the latexes containing acrylic acid, whereas the all-poly(n-butyl acrylate) latex (i.e., 0 vol% PBA/AA) failed at the Melinex surface with the adhesive completely transferring to the steel plate. This implies that a small amount of PBA/AA substantially improves adhesion to the polar Melinex and reduces the adhesion to steel. Further increases in the amount of PBA/AA clearly reduce the peel strength of the bond to the Melinex, possibly as a consequence of the increase in stiffness of the adhesive.

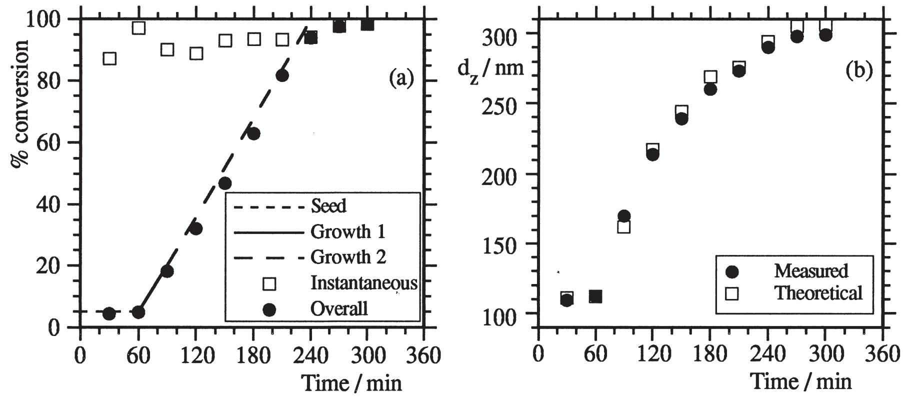

Figure 1. Preparation of the PSA latex from the *AA-total-fixed* series with a poly(n-butyl acrylate) core diameter of 175 nm (25 vol% of particle). (a) Variation of the overall and instantaneous percentage conversions with reaction time. The lines are the monomer feed profiles for each stage in the polymerization. (b) Variation of measured and theoretical z-average particle diameter, d_Z, with reaction time. The theoretical values of d_Z were calculated from the measured value of d_Z at the end of the seed stage and the overall percentage conversion, assuming that the particles grew spherically without secondary nucleation and were not swollen by unreacted monomer.

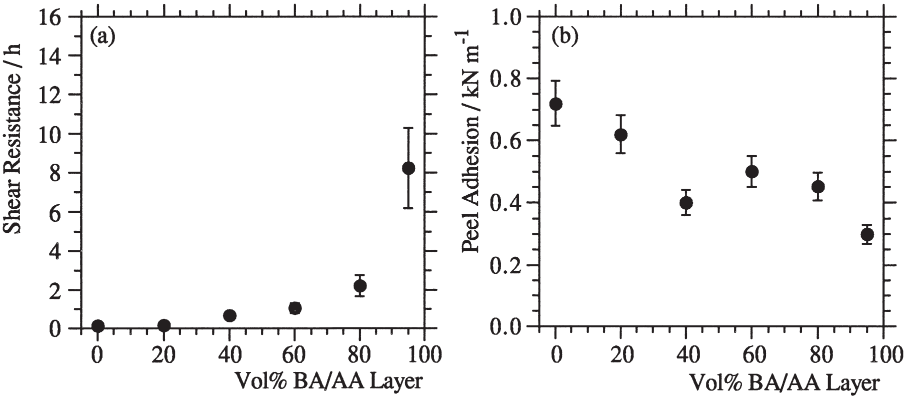

Figure 2. The effects on adhesive properties of the proportion (volume % of particle) of the poly[(n-butyl acrylate)-*co*-(acrylic acid)] layer for the *layer-AA-fixed* series of PSA latexes: (a) shear resistance and (b) peel adhesion.

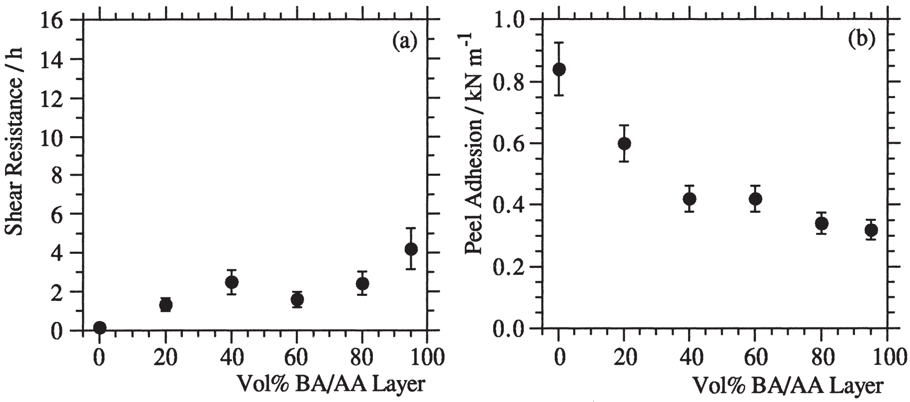

Figure 3. The effects on adhesive properties of the proportion (volume % of particle) of the poly[(n-butyl acrylate)-*co*-(acrylic acid)] layer for the *total-AA-fixed* series of PSA latexes: (a) shear resistance and (b) peel adhesion.

The *total-AA-fixed* series of PSA latexes show only a slight variation of shear resistance with vol% PBA/AA outer layer, but have higher values of shear resistance at lower vol% PBA/AA than the equivalent *layer-AA-fixed* latexes (cf. Figures 3a and 2a). This may be interpreted in terms of the total amount of acrylic acid controlling the stiffness of the adhesive polymer. The peel adhesion results for the PSA latex series are virtually identical (cf. Figures 3b and 2b), implying that peel adhesion is controlled by the vol% of PBA/AA outer layer and not by the total amount of acrylic acid. In comparing the results from these two series of PSA latexes, a point worthy of note is that they were prepared one year apart by different people and that the latexes corresponding to 0 and 95 vol% PBA/AA from each series were equivalent, having been prepared using the same formulations and procedure. The preparations proceeded identically in terms of conversion and particle size data, and so these latexes provide an insight into the reproducibility of the adhesive performance. The shear resistance data at 0 vol% PBA/AA are identical, but the values for the 95 vol% PBA/AA latexes are significantly different, with values of 4.2 h and 8.2 h. This is typical of shear resistance data, the higher the value the greater the error and uncertainty. In contrast, peel adhesion data are much more reproducible, as confirmed by the data for the two sets of latexes at 0 and 95 vol% PBA/AA, which agree within experimental error.

The adhesive testing results for the *AA-layer-level* PSA latex series are shown in Figure 4. Increasing the level of acrylic acid in the second growth-stage from 0 to 21.9 mol% serves to increase the shear resistance, but reduce the peel adhesion. Further increasing the mol% acrylic acid causes reductions in both shear resistance and peel adhesion, the latter decreasing almost to zero (0.01 kN m^{-1}) at 49.3 mol% acrylic acid.

3.2 Rigid Core - Soft Shell PSA Latexes

The *rigid-soft* series of core-shell PSA latexes were prepared with a poly[(methyl methacrylate)-*co*-(allyl methacrylate)] (PMMA/ALMA) core, comprising 1 mol% allyl methacrylate, and a PBA/AA shell comprising 5 mol% acrylic acid. Thus, the outer layers of the particles in these latexes should be identical to those in the *layer-AA-fixed* PSA latexes at the same vol% PBA/AA, the latter series effectively being soft core – soft shell systems.

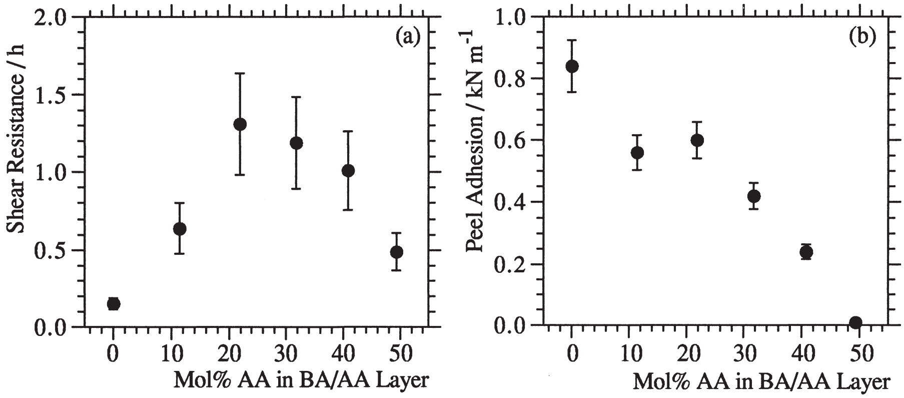

Figure 4. The effects on adhesive properties of the mol% acrylic acid in the second growth-stage feed mixture of n-butyl acrylate and acrylic acid for the *AA-layer-level* series of PSA latexes: (a) shear resistance and (b) peel adhesion.

3.2.1 Latex preparations

Each of the *rigid-soft* PSA latex preparations proceeded under monomer-starved conditions and with good control of particle growth, as is exemplified by Figure 5 which shows representative data for variation of percentage conversion and particle size with reaction time. Since the core of these latex particles is much more hydrophilic than for the poly(n-butyl acrylate)–PBA/AA latexes, allyl methacrylate was used to lightly crosslink the PMMA and provide a kinetic barrier to phase rearrangement during formation of the PBA/AA layer. Together with the operation of monomer-starved conditions, this was expected to ensure controlled core-shell growth of the latex particles [5]. Bearing in mind these factors, the good agreement between measured and theoretical particle sizes provides strong evidence that core-shell growth was achieved.

3.2.2 Adhesive properties

The objective in preparing the *rigid-soft* latex series was to investigate the effect of a rigid core on the adhesive performance of PBA/AA-based latex PSAs. The adhesive results for this series are presented in Figure 6. Comparison with Figure 2 shows that the trends for variation of shear resistance and peel adhesion with vol% PBA/AA are opposite to those for the *layer-AA-fixed* (soft core – soft shell) series. For the *rigid-soft* latexes, shear resistance shows a general trend of reducing as the vol% PBA/AA increases, whilst the peel adhesion increases. When the PBA/AA layer is reduced to 40 vol%, however, both the shear resistance and peel adhesion are effectively zero, i.e., when the PMMA/ALMA core comprises 60 vol% of the latex particle, all useful adhesive performance is lost. At this proportion of PMMA/ALMA core, the PBA/AA layer is only ~24 nm in thickness.

The effects of increasing the size of the PMMA/ALMA core on adhesive properties are consistent with the expected increase in stiffness of the adhesive material. As can be seen from the data in Figure 6a, an extremely large increase in shear resistance was achieved when the PMMA/ALMA core comprised 55 vol% of the latex particles, though inspection of

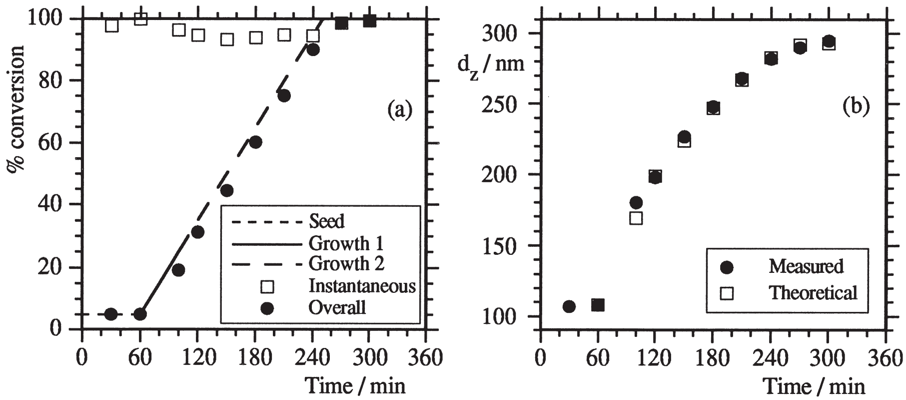

Figure 5. Preparation of the *rigid-soft* PSA latex with a poly[(methyl methacrylate)-*co*-(allyl methacrylate)] core diameter of 180 nm (25 vol% of particle). (a) Variation of the overall and instantaneous percentage conversions with reaction time. The lines are the monomer feed profiles for each stage in the polymerization. (b) Variation of measured and theoretical z-average particle diameter, d_z, with reaction time. Theoretical values of d_z were calculated as described in the caption to Figure 1.

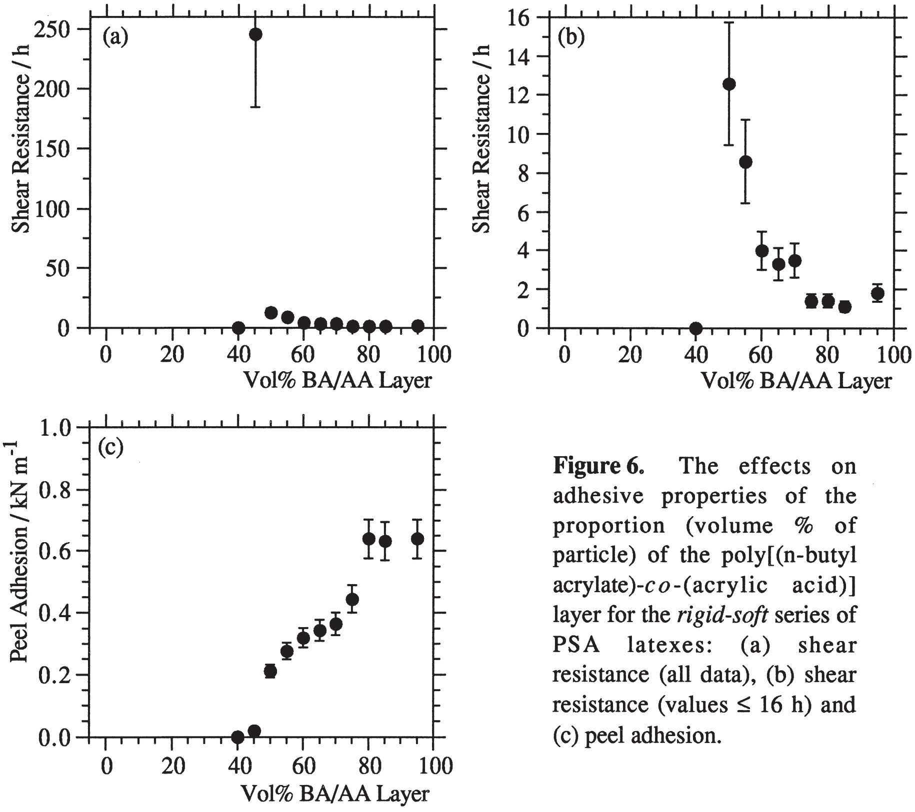

Figure 6. The effects on adhesive properties of the proportion (volume % of particle) of the poly[(n-butyl acrylate)-*co*-(acrylic acid)] layer for the *rigid-soft* series of PSA latexes: (a) shear resistance (all data), (b) shear resistance (values ≤ 16 h) and (c) peel adhesion.

Figure 6c shows that this was achieved with almost complete loss of peel adhesion. At 50 vol% PMMA/ALMA core, the shear resistance is still higher than achieved with the *layer-AA-fixed* series of latexes and the peel adhesion is significant, though not high. The adhesive results for the *rigid-soft* latex series and the *layer-AA-fixed* latex series are most easily compared by considering Figures 2a and 6b, and Figures 2b and 6c, since the corresponding ordinate axes are identical. Close comparison shows that both series of PSA latexes give similar optimum balances of adhesive properties.

4 Conclusions

The results from the investigations of the effects of acrylic acid level and particle structure on the pressure-sensitive adhesive properties of core-shell latexes with a PBA/AA shell lead to three principal conclusions.

(i) For latexes with a poly(n-butyl acrylate) (i.e., soft) core and overall acrylic acid levels up to 5 mol% to n-butyl acrylate, shear resistance is controlled principally by, and increases with, the level of acrylic acid, whereas peel adhesion depends mainly on, and reduces with, the vol% of the PBA/AA shell.

(ii) Both shear resistance and peel adhesion reduce with acrylic acid level when high levels (32–49 mol%) of acrylic acid are used in formation of the PBA/AA shell.

(iii) For latexes with a PMMA/ALMA (i.e., rigid) core, shear resistance and peel adhesion show opposite trends of variation with vol% PBA/AA as compared to the equivalent latexes with a poly(n-butyl acrylate) core. Shear resistance reduces and peel adhesion increases as the vol% PBA/AA increases. By using a rigid core, however, very high values of shear resistance can be achieved, though with almost complete loss of peel adhesion.

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