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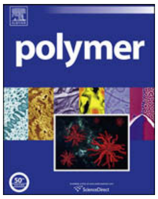

Control of adhesive properties through structured particle design of water-borne pressure-sensitive adhesives

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ABSTRACT

The concept of using structured particles and the mechanism of film formation from latexes to produce pressure-sensitive adhesive (PSA) films with controlled sub-micron and nanometre scale morphology has been investigated with the objective of enhancing adhesive performance. Structured particle acrylate-based latexes were synthesised by seeded semi-continuous emulsion polymerisation procedures. Aliquots removed at intervals during the polymerisations were analysed for conversion and *z*-average particle diameter; the results confirm that the particles grew without secondary nucleation or coagulation. Three-layer particles were studied first and comprised a core whose composition was the same for all particles, an interlayer between core and shell which was crosslinked during synthesis (using 1,6-hexanediol diacrylate, HDDA) and a shell which contained diacetone acrylamide (DAAM) repeat units that provided for interfacial crosslinking between particles during film formation by reaction with post-added adipic acid dihydrazide (ADH). The three-layer latexes produced adhesive films with high shear resistance when ADH was added, but peel adhesion was generally low and further reduced by increasing either the thickness or HDDA concentration of the interlayer. Thus two-layer latexes with shell layers containing DAAM but no pre-crosslinked interlayer were the main focus of the study. The effects of core:shell ratio and amount of DAAM on adhesive performance were optimum with a core:shell ratio of 80:20 and 2 wt% DAAM in the shell copolymer, for which interfacial crosslinking using the stoichiometric amount of ADH led to a marked increase in shear resistance with only a slight reduction in peel adhesion. Increasing the level of *n*-dodecylmercaptan (DDM) chain transfer agent used in synthesis of the core increases peel adhesion and reduces shear resistance in the absence of ADH, but high shear resistance can be recovered through interfacial crosslinking with ADH. Adhesive performance can be optimised by using a high DDM level in the core and a low DDM level in the shell, a combination that enables both high peel adhesion and shear resistance to be achieved with the addition of ADH. The results from this study define guiding principles for development of commercial water-borne PSAs that can compete with solvent-borne PSAs in high-performance applications.

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1. Introduction

Pressure-sensitive adhesives (PSAs) are viscoelastic materials which adhere to substrates on the application of slight pressure over short periods of time. The largest proportion of the PSA market is now held by water-borne acrylic systems based on latexes prepared by emulsion polymerisation [1]. The monomers typically used to produce the commercial PSA latexes are *n*-butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA) which produce high molar mass, permanently tacky polymers (*i.e.*, with a very low glass transition temperature, T_g) [2]. Carboxylic acid containing monomers, such as methacrylic acid (MAA) and acrylic acid (AA), are included at low levels because, after neutralisation, the acid groups enhance latex colloidal stability, facilitate stronger bonds to polar substrates and provide physical crosslinking via ion clustering. Such water-borne PSA latex systems have gained market share at the expense of flammable, environmentally unfriendly solvent-borne acrylic PSAs not only because they replace solvents with water but also because the latexes can achieve much higher solid contents at low viscosity which brings further benefits in formulation, transport and coating.

There are, however, some PSA applications for which current water-borne PSAs cannot match the performance of, and thus replace, solvent-borne acrylic PSAs. Such applications typically require high cohesive strength whilst retaining high peel and tack performance and/or bonding to low energy surfaces, such as

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polyethylene and polypropylene. The latter substrates are inherently difficult for water-borne PSAs because latexes are, by nature, hydrophilic and do not easily wet such hydrophobic surfaces and also because, even though the acrylic polymer may be highly hydrophobic, the latex particle surfaces are hydrophilic due to functional groups and ionic charges derived from surfactant, initiator and functional comonomers. The challenge of enhancing the adhesive performance of water-borne PSAs such that they can compete with solvent-borne PSAs in high-performance applications was central to the 'NsHAPe Project' (see Acknowledgements), some of the results from which are presented in this paper.

The objective of the work reported herein was to establish whether the mechanism of film formation from latexes, which leads to retention of particle structure/morphology in the adhesive films [3,4], can be used to advantage to achieve both sub-micron and nanometre scale control of adhesive film morphology (inaccessible using solvent-borne adhesives) combined with manipulation of fundamental parameters known to modify adhesive performance in order to enhance the performance of water-borne PSAs. This approach had been tried before [5,6], but the lack of control of polymer architecture led to application properties which were inferior to the homogeneous systems. Through careful design and synthesis of latexes with structured particles that facilitate simultaneous control of film morphology and the properties of the phases in the film, it has been possible to relate chemical and particle design parameters to adhesive performance and, thereby, define principles for enhancing the performance of water-borne PSAs.

2. Experimental

2.1. Materials

Styrene (Merck, 99%), *n*-butyl acrylate (BA) (Alfa Aesar, 98%), ethyl acrylate (EA) (Aldrich, 99%) and 2-ethylhexyl acrylate (EHA) (Aldrich, 98%) were washed three times with aqueous sodium hydroxide solution (0.5 M) to remove the phenolic inhibitor, then washed three times with water and dried over calcium chloride. Acrylic acid (AA) (Aldrich, 99%) and methacrylic acid (MAA) (Aldrich, 99%) were treated immediately before use to remove most of the inhibitor by standing over silica gel for 30 min. Water was deionised using an ElgaStat Option 3 water purifier. Ammonium persulfate (BDH, AR) sodium carbonate (BDH, AR), methanol (BDH, GPR), tetrahydrofuran (BDH, GPR), hexadecane (Aldrich, 99%), 1,6-hexanediol diacrylate (HDDA) (Aldrich, tech., 80%), hydroquinone (Aldrich, 99%), *n*-dodecylmercaptan (DDM) (Aldrich), *tert*-butyl hydroperoxide (Aldrich, 70 wt% in water), hydroxymethanesulfinic acid monosodium salt dihydrate (Aldrich), diacetone acrylamide (DAAM) (Aldrich, 99%), adipic acid dihydrazide (ADH) (Sigma, 98%), Servoxyl VLA2170 (Elementis Specialities), Sipomer β-CEA (Rhodia), Rhodacal DS4 (Rhodia, 23% active), Rhodapex AB/20 (Rhodia, 29% active) and Dowfax 2A1 (Dow Chemical, 45% active) were used as received.

The acrylate/styrene copolymer seed latex used in the emulsion polymerisations was supplied by Cytec Surface Specialties SA (Drogenbos, Belgium) at 34 wt% solids (33 wt% polymer) and with a volume-average particle diameter of 46 nm determined by hydrodynamic chromatography.

2.2. Emulsion polymerisations

Reactions were performed under a flowing nitrogen atmosphere with mechanical stirring in flanged vessels contained in a water bath thermostated at 80 °C, which corresponded to a temperature of 78–79 °C in the reaction vessel. Example polymerisations are described below for the three types of latex preparation carried out, namely core particle latex, multi-layer particle latex grown from a pre-made core latex, and direct 'one-pot' synthesis of multi-layer particle latex. Details of the standard core and shell monomer compositions are given in Table 1.

2.2.1. Example 1: preparation of core particle latexes (CL1–CL5)

Note that core particle latexes CL1–CL5 were repeat preparations carried out using identical formulations, procedures and conditions, which were as follows. Sodium carbonate (3.60 g) was dissolved in water (600 g) in the reaction vessel and the solution stirred for 30 min while flushing with nitrogen and heating to the reaction temperature. A solution of ammonium persulfate (0.88 g) in water (10.60 g) was added and stirring continued for 5 min before adding seed latex (38.180 g), followed by water (60 g) which was used to ensure complete transfer of the seed latex. The reaction mixture was stirred for a further 5 min before beginning addition of: (i) a solution of ammonium persulfate (1.77 g) in water (18.88 g) over a period of 120 min using an Infors HT Predicor syringe pump; and (ii) a monomer emulsion (1096.006 g; prepared from 530.19 g EHA, 120.50 g EA, 80.327 g BA, 40.164 g styrene, 20.073 g AA, 12.055 g Sipomer β-CEA, 0.243 g DDM, 263.79 g water, 13.955 g Rhodapex AB/20 (4.047 g active), 3.045 g Dowfax 2A1 (1.370 g active) and 11.664 g Rhodacal DS4 (2.683 g active)) over a period of 120 min using a Watson-Marlow Model 505S peristaltic pump. When the additions of the initiator solution and monomer emulsion were complete, the reaction mixture was stirred for a further 60 min at 80 °C and then cooled to 60 °C. A 7 wt% aqueous solution of *tert*-butyl hydroperoxide (3.50 g) was then added, followed by addition of a 5 wt% aqueous solution of hydroxymethanesulfinic acid monosodium salt dihydrate (8.80 g) over a period of 30 min. Finally, the reaction mixture was heated at 60 °C for a further 30 min before cooling the latex to room temperature.

2.2.2. Example 2: preparation of a three-layer particle latex from a core latex (D3L5)

Core latex CL2 (420.01 g) was charged to the reaction vessel and stirred for 30 min while flushing with nitrogen and heating to the reaction temperature. Part (15.00 g) of the first monomer emulsion (prepared from 66.672 g EHA, 15.156 g EA, 10.097 g BA, 5.049 g styrene, 2.019 g MAA, 11.009 g HDDA, 0.0330 g DDM, 36.10 g water, 1.900 g Rhodapex AB/20 (0.551 g active), 0.409 g Dowfax 2A1 (0.184 g active) and 1.582 g Rhodacal DS4 (0.364 g active)) was added, followed by stirring for a further 30 min. A solution of ammonium persulfate (0.40 g) in water (4.80 g) was then added and stirring continued for 5 min before beginning addition of: (i) a solution of ammonium persulfate (0.80 g) in water (8.53 g) over a period of 150 min using an Infors HT Predicor syringe pump; and (ii) the remainder of the first monomer emulsion (135.026 g) over a period of 75 min using a Watson-Marlow Model 505S peristaltic pump. Immediately on completing addition of the first monomer emulsion, addition of a second monomer emulsion (150.036 g, prepared from 66.679 g EHA, 15.157 g EA, 10.098 g BA, 5.049 g

Table 1
Standard comonomer feed compositions.

Monomer	Core/wt%	Shell/wt%
EHA	66	66
EA	15	15
BA	10	10
Styrene	5	5
AA	2.5	–
β-CEA	1.5	–
MAA	–	2
DAAM	–	2

styrene, 2.020 g MAA, 11.00 g DAAM, 0.0330 g DDM, 36.109 g water, 1.900 g Rhodapex AB/20 (0.551 g active), 0.409 g Dowfax 2A1 (0.184 g active) and 1.582 g Rhodacal DS4 (0.364 g active)) was begun and proceeded over a period of 75 min so that the addition finished at the same time as addition of the initiator solution. When these additions were complete, the reaction mixture was stirred at 80 °C for a further 60 min before cooling to 60 °C. A 7 wt% aqueous solution of *tert*-butyl hydroperoxide (1.60 g) was then added, followed by addition of a 5 wt% aqueous solution of hydroxymethanesulfinic acid monosodium salt dihydrate (4.0 g) over a period of 30 min. Heating at 60 °C was continued for a further 30 min before cooling to room temperature and filtering the latex through a 53 μm sieve to remove any dispersed coagulum.

For latex preparations where the mass ratio of the two monomer emulsions was not 1:1, the addition times for the monomer emulsions were adjusted so that the rate of addition was approximately constant throughout and the total addition time was 150 min. In cases where this method was used for preparation of two-layer latexes, a single monomer emulsion was used which was added over a total period of 150 min. In cases where the total mass of the outer two layers was less than 55% of the total polymer, there were three consecutive monomer additions, beginning with addition of further core monomer emulsion (see Section 2.2.1), followed directly by addition of appropriate quantities of the first and second monomer emulsions, the total period for the three feeds again being 150 min.

2.2.3. Example 3: direct preparation of a two-layer 'core–shell' particle latex (D2L16)

Sodium carbonate (1.60 g) was dissolved in water (330.30 g) in the reaction vessel and the solution stirred for 30 min while flushing with nitrogen and heating to the reaction temperature. A solution of ammonium persulfate (0.80 g) in water (9.60 g) was added and stirring continued for 5 min before adding seed latex (16.967 g), followed by water (40 g) which was used to ensure complete transfer of the seed latex. The reaction mixture was stirred for a further 5 min before beginning addition of: (i) a solution of ammonium persulfate (1.92 g) in water (20.48 g) over a period of 360 min using an Infors HT Predicor syringe pump; and (ii) a first monomer emulsion (866.133 g; prepared from 418.70 g EHA, 95.164 g EA, 63.436 g BA, 31.718 g styrene, 15.864 g AA, 9.518 g Sipomer β-CEA, 1.2689 g DDM, 208.00 g water, 10.943 g Rhodapex AB/20 (3.173 g active), 2.379 g Dowfax 2A1 (1.071 g active) and 9.142 g Rhodacal DS4 (2.103 g active)) over a period of 240 min using a using a Watson-Marlow Model 505S peristaltic pump. On completing addition of the first monomer emulsion, the reaction mixture was stirred for a further 60 min at 80 °C before beginning addition of the second monomer emulsion (218.20 g; prepared from 105.60 g EHA, 24.018 g EA, 16.00 g BA, 8.00 g styrene, 3.20 g MAA, 3.20 g DAAM, 0.0588 g DDM, 52.464 g water, 2.759 g Rhodapex AB/20 (0.800 g active), 0.600 g Dowfax 2A1 (0.270 g active) and 2.305 g Rhodacal DS4 (0.530 g active)) over a period of 60 min so that this addition finished at the same time as the initiator addition. On completion of these additions, the reaction mixture was stirred at 80 °C for a further 60 min before cooling to 60 °C. A 7 wt% aqueous solution of *tert*-butyl hydroperoxide (3.2 g) was then added, followed by addition of a 5 wt% aqueous solution of hydroxymethanesulfinic acid monosodium salt dihydrate (8.0 g) over a period of 30 min. Heating at 60 °C was continued for a further 30 min before cooling to room temperature and filtering the latex through a 53 μm sieve to remove any dispersed coagulum.

Some latex preparations were carried out by starting the feed of the second monomer emulsion immediately on completing addition of the first monomer emulsion (*i.e.*, without the 60 min period between the additions described above for preparation of latex D2L16). In these cases the amount of ammonium persulfate solution was reduced such that the same rate of initiator solution addition was used.

2.3. Characterisation

Aliquots (*ca.* 3 g) of latex were removed at intervals during each of the emulsion polymerisations for analysis. Each sample was quenched by adding to a known amount of 2 wt% aqueous hydroquinone solution in a vial which was then cooled in ice/water.

Conversions were determined from measurements of latex solid contents. For this purpose, accurately weighed portions (~2 g) of the quenched samples were placed in aluminium foil dishes and dried at 80 °C to constant weight.

The level of residual monomer in each latex was measured using gas chromatography (GC). In each case, a sample of the final latex (~10 g, accurately weighed) was dissolved in tetrahydrofuran (60.0 g) and methanol (60.0 g) then added to precipitate the dissolved polymer. Hexadecane (~50 mg, accurately weighed) was added as an internal standard. The mixture was allowed to stand overnight and the resulting liquid phase was filtered through a 0.2 μm PTFE filter. Samples of the resulting solution (1 μl) were injected onto a Hewlett–Packard HP-Wax (0.25 μm film) capillary column (30 m × 0.25 mm) installed in a Perkin–Elmer AutoSystem gas chromatograph fitted with a flame ionisation detector, employing helium as carrier gas with a back pressure of 1.5 psi and a split ratio of ~10. The temperature programme used was as follows: hold at 35 °C for 5 min, then heat at 10 $^\circ\mathrm{C\,min^{-1}}$ to 165 °C and hold until all components elute. Standard solutions containing known amounts of each of the monomers and hexadecane were used to obtain relative response factors from which the chromatograms of latex samples could be analysed to determine the total residual monomer as a mass percentage of the latex.

Latex samples were analysed by photon correlation spectroscopy (PCS) to determine *z*-average particle diameter (d_z) using a Brookhaven BI-9000AT correlator with a Brookhaven BI-200SM goniometer set to a scattering angle of 90° and a Spectra Physics 20 mW HeNe laser (632.8 nm wavelength). Samples were diluted with filtered (0.2 μm) deionised water to give a count rate of ~100 kcounts $\mathrm{s^{-1}}$ at the detector and, after temperature equilibration, were subjected to 20 successive analyses of 1 min each. The vat temperature was held at ~25 °C (controlled to ±0.1 °C) and the exact vat temperature input when analysing the data using Brookhaven Particle Sizing Software v3.72 to obtain individual values of d_z for each of the 20 measurements, the average of which was used to obtain the reported value of d_z (the standard deviation of which was typically ~2 nm).

2.4. Measurement of latex polymer gel fractions

The latex polymer gel fraction was determined for selected latexes using the following procedure. A sample of latex (25 g) was poured into a ~50 cm length of 25 mm diameter Visking tubing (MWCO 12 000–14 000), which was then sealed. The tubing was immersed in a large excess of deionised water and left to dialyse for 7–10 days, changing the reservoir of water for a fresh quantity of deionised water at least once per day. The dialysed latex sample was then subjected to freeze–thaw cycling to induce coagulation. The supernatant was decanted off and the polymer washed with deionised water and dried to constant mass in an oven at 50 °C under vacuum. The gel was separated from soluble polymer by exhaustive Soxhlet extraction for 48 h using glass-fibre thimbles with tetrahydrofuran as solvent, followed by drying the residual gel to constant mass at 50 °C under vacuum.

2.5. Adhesive testing

All latexes were formulated by adjusting the pH to 7 (from typically 4.0 to 4.5 as prepared) by addition of 25 wt% aqueous ammonium hydroxide with mechanical stirring, followed by addition of Servoxyl VLA2170 (a wetting agent) at 0.75 g per 100 g of latex and stirring for 90 min to ensure complete mixing.

Crosslinking of DAAM functional groups during film formation was achieved by mixing the appropriate amount of a 1 or 10 wt% aqueous solution of ADH to the formulated latex by mechanical stirring for 15 min prior to coating. The amount of ADH required for stoichiometric (1:2) reaction of ADH with DAAM repeat units (designated 100% ADH) was calculated for each latex according to the following principles: (i) copolymer composition was assumed to be equal to the overall composition of the total particle (*e.g.*, 2 wt% DAAM in the shell phase of an 80:20 core:shell particle is equivalent to ~0.4 wt% DAAM in the total particle); and (ii) known non-polymeric solids (from salts and surfactants) were subtracted from the measured solid content of the final latex to give the latex polymer content which was then adjusted to take account of the solids (NH_4OH and Servoxyl) added during formulation.

Pressure-sensitive adhesive films were prepared by transfer coating as follows. The fully formulated latex was drawn once across the surface of a 400 × 250 mm sheet of Kraft release paper (supplied by UPM Raflatac Oy, Tampere, Finland) using an Elcometer 56 μm spiral bar coater. The films were then dried for 3 min in a fan-assisted oven set at 110 °C. After allowing the coating to cool to room temperature, the corona-treated side of 60 μm thick oriented polypropylene (OPP) film (supplied by UPM Raflatac Oy, Tampere, Finland) was applied to the adhesive film on the Kraft release paper. The resulting sheets were cut into strips with dimensions of 300 mm (approximate) × 25 mm (exact) with the long axis parallel to the film-drawing direction. Accurate measurement of the dimensions and mass of each strip enabled calculation of the adhesive film thickness based on measured values of mass per unit area for the OPP film and Kraft release paper and assuming the overall polymer density to be 1 g cm^{-3} (which is reasonable given that the density for the homopolymer of the principal monomer 2-ethylhexyl acrylate is [7] 0.99 g cm^{-3}). Samples used for testing had adhesive film thicknesses of 18–21 μm.

Adhesive testing was carried out in accordance with FINAT standards under conditions of controlled temperature (23 ± 1 °C) and relative humidity (50 ± 5%). FINAT Test Method 1 (180° peel adhesion) was performed on bonds to both stainless steel (SS) and high-density polyethylene (HDPE) 20 min and 24 h after bonding, and Test Method 8 (shear resistance) on bonds to SS after 10 min bonding [8]. Values of peel adhesion are reported in the FINAT standard dimensions of N $(25\ mm)^{-1}$. Shear resistance tests were usually terminated for samples that had not failed after 10 000 min because this value greatly exceeds most industrial requirements; such values of shear resistance are reported as >10 000 min. For both peel adhesion and shear resistance measurements, average values are reported from, typically, four measurements for each sample/substrate combination.

2.6. Atomic force microscopy of pressure-sensitive adhesive films

The morphologies of selected pressure-sensitive adhesive films were analysed by atomic force microscopy (AFM) at the University of Surrey using procedures established previously [9].

3. Results and discussion

As stated in Section 1, an important objective of this work was to investigate how advantage could be taken of the ability to control the morphology of adhesive films, from sub-micron to nanometre scale dimensions, made possible by the nature of film formation from water-borne pressure-sensitive adhesives (PSAs). By designing latexes with appropriately structured particles, it is possible to compartmentalise and locate phases within the particles (and hence in the resulting adhesive films) effectively forming what can be called a soft–soft nanocomposite [10]. The strategy pursued was to have structured particles with cores comprising a soft (*i.e.*, low T_g) branched or lightly crosslinked copolymer designed to dissipate energy by viscous flow during debonding to impart high adhesion, and a soft copolymer shell that can be more highly crosslinked to provide a matrix of higher cohesive strength that percolates throughout the adhesive film to provide shear resistance (see Fig. 1). In designing the structured particles the aim was to produce adhesive films with a highly viscoelastic character in which energy can be dissipated by deformation of the discrete core copolymer phases during the debonding process [11,12] and to investigate whether, through careful balancing of the proportions and properties of the phases, this strategy could be used to enhance both peel adhesion and shear resistance.

Previous studies on the effect of AA level in acrylic PSAs have shown that even low levels increase the modulus of the PSA significantly, particularly at very low frequency and in elongation [13–17]. Inclusion of AA as a comonomer is, therefore, necessary in order to increase cohesion and prevent flow of the PSA and to increase adhesion to high energy surfaces. Effects of AA and particle structure on adhesive performance of core–shell latexes have been studied for both rigid and soft cores with a soft pressure-sensitive adhesive shell copolymer [18]; effects of blending particles of different sizes also have been investigated [19]. Of most relevance to the present study are the results for the soft–soft core–shell latexes (with a polyBA core and a copolyBA/AA shell) [18]; shear resistance was shown to increase with the level of AA, whereas peel adhesion reduced on increasing the proportion of the copolyBA/AA shell. High levels of AA (32–49 mol% in shell layer) were found to be detrimental to both peel adhesion and shear resistance. The present work builds on these observations, but employs copolymer compositions more akin to those used commercially in order to achieve a higher baseline adhesive performance.

The high cohesive strength of solvent-borne PSAs often is achieved by homogeneous crosslinking during drying of the adhesive coating, something that is difficult to replicate using water-borne PSAs. Even in the absence of crosslinking agents, acrylate-based water-borne PSAs are lightly crosslinked due to intermolecular chain transfer to polymer followed by coupling of the propagating long-chain branches during acrylate emulsion polymerisations. Thus, crosslinked films formed from water-borne PSAs can have a microgel morphology which is not sufficiently uniform for attaining high cohesive strength [20–22], though they can be made more uniform by grafting of the ‘free’ polymer chains to the

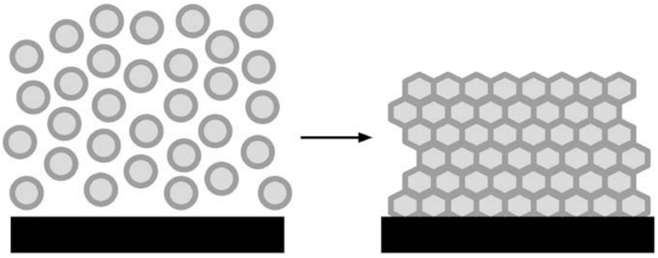


Fig. 1. Schematic diagram showing formation of a honeycomb-like film morphology from a core–shell particle latex in which the particle structure is preserved such that the shells create a continuous percolating phase in which the individual particle cores are embedded as discrete phases.

microgel chains, *e.g.*, by introducing isobutoxymethyl acrylamide repeat units and heat [23]. Interestingly, blends of a high gel-content latex with a gel-free latex of otherwise similar polymer composition gave synergistic effects in increasing shear resistance [24]. In the present work the intention was to achieve a distinct *contrast* in the degree of crosslinking within the different phases of the structured particles and, in particular, to have higher degrees of crosslinking in the outer phases so that in the adhesive films the continuous matrix would provide a molecular mesh that resists flow, thereby enhancing the creep resistance required to resist a shear stress over long periods of time.

The ability to create crosslinks across the interfaces between particles during film formation under ambient conditions has been utilised in both paint and adhesive systems by employing a wide range of functional monomers and crosslinking agents [25,26]. Crosslinking via the coupling reaction between the active carbonyl groups present in diacetone acrylamide (DAAM) repeat units and a hydrazine (most commonly adipic acid dihydrazide, ADH) has been studied extensively (see Scheme 1) and shown to be particularly effective [27–30]. Furthermore, since ADH is water soluble and added to the latex after its preparation (or at any time up to just before a film is cast), most of the ADH is in the aqueous phase and the crosslinking reaction occurs predominantly near the particle surfaces, giving rise to interfacial crosslinking between particles during film formation. Hence, in the present work, DAAM repeat units have been incorporated in the shell phases of the structured particles so that the DAAM–ADH crosslinking chemistry could be used to achieve the desired interfacial crosslinking between particles in the structured adhesive films.

In addition to the effects of particle structure and crosslinking, it was also necessary to consider effects of chain transfer agent and comonomer composition because they are known to be significant. Leiza et al. [31] showed that the levels of chain transfer agent and crosslinking agent could be modified independently to control adhesive performance for BA-based, homogeneous particle water-borne PSAs. Acrylic ester comonomer composition levels have an impact on adhesive performance of latexes containing the same levels of carboxylic acid comonomer and approximately constant T_g [1,32]. Latexes made with higher levels of 2-ethylhexyl acrylate (EHA) had higher gel fractions and produced films with higher peel adhesion and shear resistance. Further work showed that both EHA and AA contribute to gel formation, with the higher levels of AA contributing to adhesive performance via hydrogen bonding interactions [33]. These observations correlate with the known higher extents of chain transfer to polymer in free-radical polymerisation of EHA as compared to BA [34].

Thus, through these considerations and by careful design and synthesis of latexes with structured particles, in the present work it has been possible to relate chemical and particle design parameters to adhesive performance and, thereby, define principles for enhancing the performance of commercial water-borne PSAs.

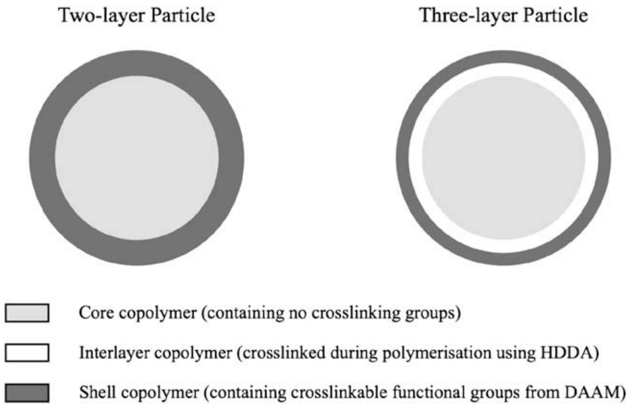


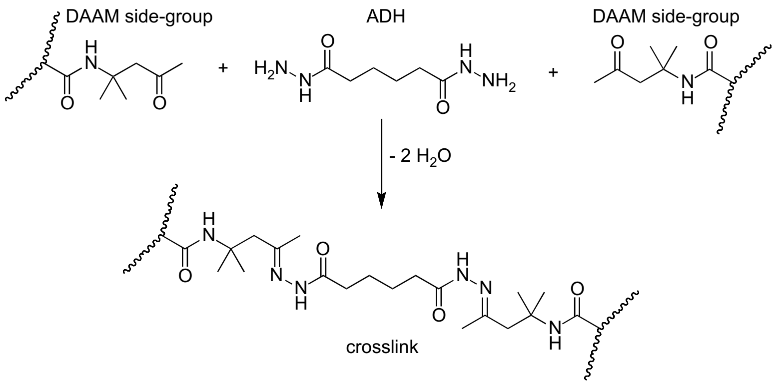
Fig. 2. Schematic diagrams of idealised particle cross-sections for the two classes of latex particle synthesised.

Two general classes of latex comprising two-layer and three-layer particles were synthesised for study, as shown schematically in Fig. 2. The core copolymer composition was the same for all types of particle; the initial seed particles constituted only 0.7 wt% of the final particles and so made no contribution to the final properties other than allowing for consistent control of the final latex particle diameter, which was 247 ± 3 nm averaged over all latexes synthesised. Similarly, the standard shell copolymer composition was the same for the two- and three-layer particles and included DAAM repeat units to provide for interfacial crosslinking by reaction with ADH added during latex formulation. The three-layer particles are distinguished by having an intermediate layer between core and shell which was crosslinked directly during synthesis using hexane-1,6-diol diacrylate (HDDA).

Results from the initial work on three-layer particles showed that the intermediate pre-crosslinked layer had a detrimental effect on adhesive performance, which led to the work being focused on latexes in which this intermediate layer was omitted. Most of the work, therefore, concerned the simpler two-layer particles and, for this reason, the observations on the three-layer particle systems will be considered first.

3.1. *Three-layer particle latexes*

The thinking underlying the investigation of three-layer particles was to provide an adhesive film in which there were two



Scheme 1. Chemistry of crosslinking by reaction of DAAM side-groups with ADH.

crosslinked phases with distinctly different degrees of crosslinking, so that each could contribute to the deformation behaviour in a different region of the stress–strain curve. Thus the aim was that the more highly (pre-) crosslinked interlayer copolymer would be discrete, encapsulating each particle core in the film, whereas the DAAM–ADH interfacial crosslinking introduced between particle shells during film formation would provide a lightly crosslinked continuous phase within the film which should dominate the high-strain deformation behaviour.

3.1.1. *Synthesis of three-layer particle latexes*

All latexes prepared in this work were synthesised using the same batch of seed latex supplied by Cytec Surface Specialties; their analysis of the seed latex by hydrodynamic chromatography gave a volume-average particle diameter of 46 nm and indicated a bimodal particle size distribution with a small amount (~1% by volume) of particles of much larger diameter present as a broad peak centred ~500 nm. Analysis of the seed latex by PCS gave a *z*-average particle diameter of ~100 nm, no doubt due to the contribution from the small amount of larger particles. If the mean final particle diameter of all the three-layer and two-layer particle latexes described in this paper is used to back-calculate the diameter of the original seed latex particles, assuming that particles grew without secondary nucleation or coagulation, this gives a seed latex particle diameter of 47.25 nm which is only marginally different from the quoted volume-average particle diameter and certainly within the experimental error of the particle diameter measurements. Hence, the seed latex *z*-average particle diameter was taken to be 47.25 nm for calculations of total particle number in synthesis of three-layer (and two-layer) particle latexes.

The core of the particles for the three-layer particle latexes was prepared separately in larger batches (see Table 2), typical conversion and particle growth data for which are shown in Fig. 3. The apparent decrease and then increase in total particle number evident in Fig. 3(b) is probably due to the low instantaneous conversion that exists earlier in the reaction; thus, swelling of the particles by unreacted monomer and measurement of the swollen particle diameter lead to an apparent lower particle number. Further confirmation of this interpretation is the observation that, within experimental error, the final particle number is the same as that of the seed latex.

Synthesis of the three-layer particles was completed by using one of the core latex batches to provide seed particles in two-stage semi-batch emulsion polymerisations involving sequential metered addition of the HDDA- and DAAM-containing comonomer mixtures. Monitoring of conversion and particle diameter during both of the particle growth stages indicated that the polymerisations proceeded under monomer-starved conditions with controlled particle growth, as can be seen from the representative data plotted in Fig. 4. Residual monomer levels (determined by GC) in the final latexes were low (≤0.2%), which is important because at high levels, residual monomer may significantly affect T_g and adhesive properties.

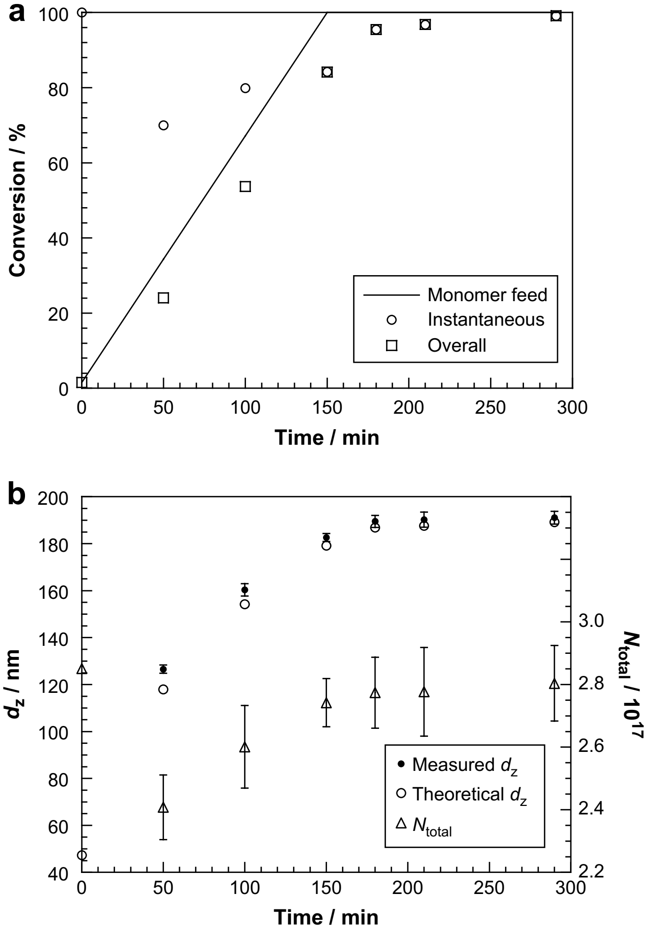


Fig. 3. Plots of (a) conversion and (b) *z*-average particle diameter (d_z) and total particle number in the reaction vessel (N_{total}) for synthesis of the core latex CL3.

Table 2
Characterisation data for core latexes.[a]

Latex code	Theoretical final latex d_z/nm[b]	Final latex	
		d_z/nm[c]	Solids/wt%
CL1	189	192	44.7
CL2	189	189	44.5
CL3	189	191	44.8
CL4	189	185	44.5
CL5	189	187	44.5

[a] All latexes were prepared according to the procedure described in Section 2.2.1 with 1 wt% (active) surfactant to monomer using as surfactant a mixture of Rhodapex AB20/Rhodacal DS4/Dowfax 2A1 in the active weight ratio 50.0/33.1/16.9. The standard core comonomer feed composition given in Table 1 was used with DDM at a level of 0.03 wt% to total monomer. The polymer from the seed latex constituted 0.7 wt% of the final polymer.

[b] Calculated using a seed latex particle diameter of 47.25 nm (see Section 3.1.1).

[c] Measured by PCS with a reproducibility of ±2 nm.

For the initial series of three-layer latexes, the core comprised 45 wt% of the total polymer; the remaining 55 wt% was divided between the HDDA-containing pre-crosslinked interlayer and the DAAM-containing shell. For a particle of diameter 250 nm, this corresponds to a core diameter of ~190 nm diameter and a total interlayer plus shell thickness of ~30 nm. Two mass ratios of interlayer to shell were used, namely 1:1 and approximately 1:2. For the DAAM-containing shell, two levels of DAAM (2 wt% and 10 wt%) were used. Similarly, the HDDA-containing interlayer comprised either 10 wt% or 20 wt% of HDDA. Thus a total of eight latexes (coded D3L1-D3L8) were prepared, details of which are given in Table 3. As can be seen from the data in Tables 2 and 3, *z*-average particle diameter (d_z, measured by PCS) for the five batches of core latex varied from 185 to 192 nm and d_z for the final three-layer latexes D3L1–D3L8 ranged from 241 to 251 nm in accord with values predicted from the core particle d_z, thus confirming that the polymerisations were controlled and reproducible.

3.1.2. *Effects of particle design on adhesive performance for three-layer particle latexes*

Prior to casting films for adhesive testing, latexes were formulated as described in Section 2.5, which included addition of the

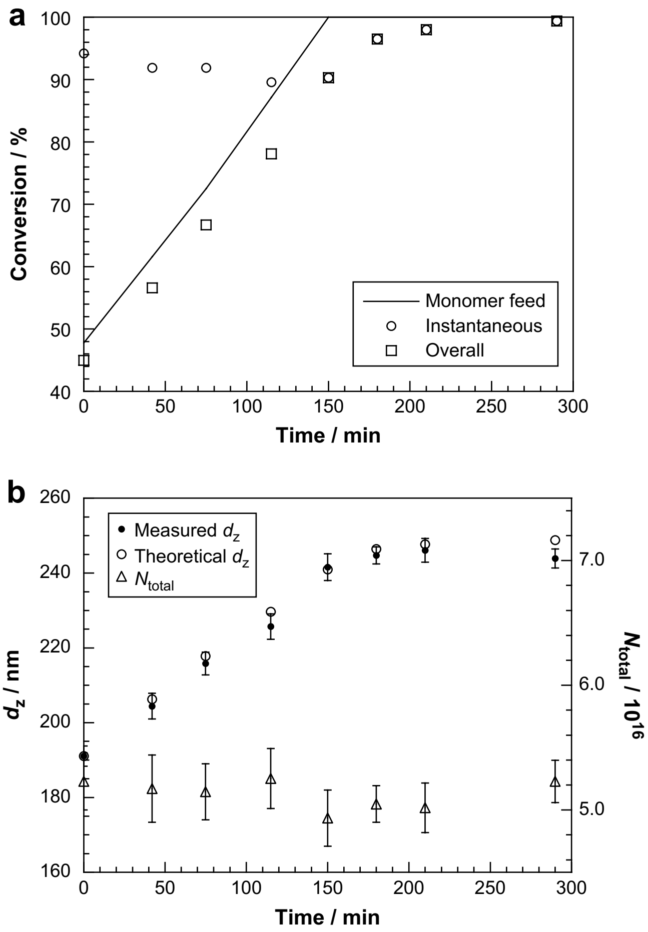


Fig. 4. Plots of (a) conversion and (b) *z*-average particle diameter (d_z) and total particle number in the reaction vessel (N_{total}) for synthesis of the three-layer particle latex D3L7 from core latex CL3.

stoichiometric amount of ADH (designated as 100% ADH) required for complete reaction with the DAAM repeat units present in the latex. The films cast from these formulated latexes were tested for 180° peel adhesion on both stainless steel (SS) and high-density polyethylene (HDPE) and for shear resistance on SS. Tables 4–6 give the results from peel adhesion testing.

Table 4 compares the peel adhesion of pairs of latexes in which the level of DAAM in the shell copolymer is either 2 wt% or 10 wt%, but which otherwise have identical compositions. In all cases a marked reduction in peel adhesion can be seen at the higher level of DAAM. It should, of course, be noted that in the formulation of the latexes with shells comprising 10 wt% DAAM, the amount of ADH added was increased fivefold to match the increase in DAAM level. Thus the higher level of interfacial crosslinking is detrimental to peel performance.

Similarly, Table 5 compares pairs of latexes containing either 10 wt% or 20 wt% HDDA in the pre-crosslinked interlayer, but which otherwise have identical compositions. An increase in HDDA concentration (and therefore in the level of crosslinking within the interlayer) gave rise to a reduction in peel adhesion. The reduction was not as large as that observed when increasing the level of DAAM in the shell (Table 4), but the HDDA level was only increased twofold compared to the fivefold increase of DAAM level.

Table 6 compares peel adhesion results for pairs of latexes in which the levels of HDDA and DAAM in their respective layers are the same, but the relative proportions of the two layers are different. The effects are small and in some cases the peel adhesion is very small, making any differences statistically insignificant. There is, however, some evidence that increasing the proportion of the DAAM-containing shell relative to the HDDA-containing interlayer results in a reduction in peel performance. This observation is in accord with the conclusions from the results presented in Table 4, as discussed above.

The highest-performing latex of the series D3L1–D3L8 was D3L1 and so films from this latex were tested both with and without addition of ADH prior to film formation in order to investigate the effects of shell/interfacial crosslinking (see Table 7). The results show that addition of the stoichiometric amount (100%) of ADH has the effect of reducing peel adhesion for both SS and HDPE, though the effect is most clearly evident when HDPE is the substrate.

For the three-layer particle latexes D3L1–D3L8, shear resistance on SS is relatively high, even in the absence of ADH (*e.g.*, 2399 min after 24 h without ADH for D3L1), due to the high proportion of gel in the polymer (typically 70–80%, as prepared) arising from three contributions: (i) the relatively low level of chain transfer agent (0.03 wt%) used in synthesis of the core (which gives rise to ~10%

Table 3
Composition and characterisation data for three-layer particle latexes comprising an HDDA pre-crosslinked interlayer and a DAAM-containing shell.[a]

Latex code	Core latex		Theoretical final latex d_z/nm[e]	Core	Interlayer[b]		Shell[c]		Final latex		
	Code	d_z/nm[d]		wt% of total polymer	wt% of total polymer	HDDA/wt% in layer	wt% of total polymer	DAAM/wt% in layer	d_z/nm[d]	Solids/wt%	Mon./wt/%[f]
D3L1	CL1	192	250	45.2	27.4	10	27.4	2	241	55.8	0.21
D3L2	CL1	192	250	45.2	17.9	10	36.9	2	248	55.9	0.14
D3L3	CL2	189	247	44.7	28.0	20	27.3	2	247	55.4	0.15
D3L4	CL2	189	247	45.0	18.0	20	37.0	2	246	55.4	0.13
D3L5	CL2	189	247	45.0	27.5	10	27.5	10	249	55.8	0.17
D3L6	CL2	189	247	45.0	18.0	10	37.0	10	247	55.7	0.14
D3L7	CL3	191	249	45.0	27.5	20	27.5	10	244	55.5	0.17
D3L8	CL3	191	249	45.0	18.0	20	37.0	10	245	56.5	0.15
D3L9	CL3	191	249	80.0	10.0	10	10.0	2	251	54.7	0.11
D3L10	CL3	191	249	90.0	5.0	10	5.0	2	243	54.4	0.21

[a] All latexes were prepared according to the procedure described in Section 2.2.2 with 1 wt% (active) surfactant to monomer using as surfactant a mixture of Rhodapex AB20/Rhodacal DS4/Dowfax 2A1 in the active weight ratio 50.0/33.1/16.9. The previously prepared core latex constituted 45 wt% of the final polymer.

[b] The comonomer feed composition was based on the standard shell comonomer feed composition given in Table 1 with HDDA replacing the defined proportion (10 or 20 wt%) of the total monomer and the remaining monomer comprising EHA/EA/BA/Sty/MAA in the same weight ratio as in the standard shell comonomer feed composition (*i.e.*, 66/15/10/5/2). DDM was used at 0.03 wt% to total monomer.

[c] The standard shell comonomer feed composition given in Table 1 was used with DDM at 0.03 wt% to total monomer. For latex preparations in which DAAM was used at 10 wt%, the remaining monomer comprised EHA/EA/BA/Sty/MAA in the same ratio as for the standard comonomer feed composition (*i.e.*, 66/15/10/5/2).

[d] Measured by PCS with a reproducibility of ±2 nm.

[e] Calculated from the core latex d_z measured by PCS.

[f] Total residual monomer in the latex measured by GC.

Table 4
Effect of shell layer DAAM level on 180° peel adhesion for three-layer particle latexes.[a]

Latex code	Interlayer			Shell			Peel adhesion/N (25 mm)$^{-1}$			
	wt% of total polymer	HDDA/wt% in layer	HDDA/wt% of total polymer	wt% of total polymer	DAAM/wt% in layer	DAAM/wt% of total polymer	On stainless steel		On HDPE	
							20 min	24 h	20 min	24 h
D3L1	27.4	10	2.74	27.4	2	0.55	2.5	5.1	1.3	1.7
D3L5	27.5	10	2.75	27.5	10	2.75	1.1	1.5	0.3	0.6
D3L3	28.0	20	5.60	27.3	2	0.54	1.5	3.2	0.8	1.4
D3L7	27.5	20	5.50	27.5	10	2.75	0.5	0.8	0.2	0.5
D3L2	17.9	10	1.79	36.9	2	0.74	1.9	3.3	1.2	1.3
D3L6	18.0	10	1.80	37	10	3.70	0.8	1.2	0.2	0.5

[a] All results are for coatings from latexes formulated with 100% ADH added.

gel in the particle core due to intermolecular chain transfer to polymer; see Discussion of the results for the two-layer particle latexes in Section 3.2.4); (ii) use of HDDA crosslinking in the interlayer, which is expected to have a very high gel fraction; and (iii) immobilising of a high proportion of the shell copolymer via grafting to the interlayer copolymer through reaction of residual pendant acrylate C=C double bonds from HDDA with monomer from the shell-growth addition. When ADH is added to these latexes, additional crosslinking takes place during film formation leading to further increases in shear resistance to values that are above 10 000 min, a level of performance that is greatly in excess of most practical requirements.

Overall, therefore, the results indicate strongly that lower amounts of both HDDA and DAAM could be beneficial for adhesive properties. Hence two further latexes were prepared in which each of the three layers had composition as in D3L1, but the relative proportions of the core, interlayer and shell were changed from 45.0/27.5/27.5 (D3L1) to 80.0/10.0/10.0 (D3L9) and 90.0/5.0/5.0 (D3L10). It is interesting to compare the results from these latexes with one of the initial two-layer particle latexes, D2L1 (see later discussion), since this contained no HDDA or DAAM and had a core:shell ratio of 45:55. The shell comonomer feed in this case contained MAA (2.04 wt%), which differs slightly from the core which contained AA (2.5 wt%) and Sipomer β-CEA (1.5 wt%), *i.e.*, the standard core composition. However, the core and shell comonomer compositions were otherwise equivalent and so D2L1 can be considered as approximating to an all-core latex. The peel adhesion results for films from this latex are, therefore, included with those from the other three latexes in Fig. 5, which shows the change in peel adhesion (both with and without ADH) as a function of the total proportion of interlayer plus shell. In each case, the peel adhesion reduces as the total proportion of crosslinked layers increases. Table 8 gives the shear resistance data for these adhesive films and shows that when the total proportion of crosslinked layers is 20 wt% and 55 wt%, addition of ADH increases the shear resistance from ∼2000–3000 min to greater than 10 000 min, providing good evidence for a significant level of interfacial crosslinking between particles. However, for latex D3L10 comprising 10 wt% total of crosslinked layers, the shear resistance is lower, as is that for the latex D2L1 containing no HDDA or DAAM; furthermore, for latexes D3L10 and D2L1, only small increases in shear resistance are observed on addition of ADH. These results suggest that the DAAM-containing shell needs to be above a certain thickness and/or to have a certain level of DAAM in order for the crosslinking to be effective in raising the shear resistance. In the case of latex D3L10, the DAAM-containing shell comprises only 5 wt% of the total polymer and is theoretically only ∼2 nm thick, so is not expected to form a shell, but more likely simply mixes with the interlayer copolymer phase near the particle surface. In the case of latex D2L1 (with no DAAM in the shell), it is not clear why there should be an increase in shear resistance on addition of ADH, albeit small relative to D3L1, D3L9 and other two-layer particle latexes (discussed in the following section). Possibly the ADH, remaining unreacted in this case, is able to form strong hydrogen bonds with carboxylic acid groups on the particle surfaces and thus increase cohesive strength.

The results presented in Fig. 5 imply that the interlayer and shell can be considered as a single (albeit non-uniform) phase, and that the main parameter controlling adhesive behaviour is the total amount of crosslinking. Increasing the total amount of crosslinking in the interlayer plus shell leads to significant improvements in shear resistance but reductions in peel adhesion on both SS and HDPE, which can be understood in terms of the anticipated changes in linear viscoelastic properties induced by the crosslinking. As the level of crosslinking increases, the shear modulus becomes too high and the viscoelastic energy dissipation is too low to maintain peel adhesion, and instead favours propagation of cracks at the interface [35,36].

3.2. Two-layer particle latexes

The incorporation of a pre-crosslinked interlayer in the three-layer particles had a significant detrimental effect on peel adhesion.

Table 5
Effect of interlayer HDDA level on 180° peel adhesion for three-layer particle latexes.[a]

Latex code	Interlayer			Shell			Peel adhesion/N (25 mm)$^{-1}$			
	wt% of total polymer	HDDA/wt% in layer	HDDA/wt% of total polymer	wt% of total polymer	DAAM/wt% in layer	DAAM/wt% of total polymer	On stainless steel		On HDPE	
							20 min	24 h	20 min	24 h
D3L1	27.4	10	2.75	27.4	2	0.55	2.5	5.1	1.3	1.7
D3L3	28.0	20	5.60	27.3	2	0.54	1.5	3.2	0.8	1.4
D3L2	17.9	10	1.79	36.9	2	0.74	1.9	3.3	1.2	1.3
D3L4	18.0	20	3.60	37	2	0.74	1.9	2.2	1.0	1.1
D3L5	27.5	10	2.75	27.5	10	2.75	1.1	1.5	0.3	0.6
D3L7	27.5	20	5.50	27.5	10	2.75	0.5	0.8	0.2	0.5

[a] All results are for coatings from latexes formulated with 100% ADH added.

Table 6
Effects of the levels of interlayer HDDA and shell layer DAAM on 180° peel adhesion for three-layer particle latexes.[a]

Latex code	Interlayer			Shell			Peel adhesion/N (25 mm)$^{-1}$			
	wt% of total polymer	HDDA/wt% in layer	HDDA/wt% of total polymer	wt% of total polymer	DAAM/wt% in layer	DAAM/wt% of total polymer	On stainless steel		On HDPE	
							20 min	24 h	20 min	24 h
D3L1	27.4	10	2.75	27.4	2	0.55	2.5	5.1	1.3	1.7
D3L2	17.9	10	1.79	36.9	2	0.74	1.9	3.3	1.2	1.3
D3L3	28.0	20	5.60	27.3	2	0.54	1.5	3.2	0.8	1.4
D3L4	18.0	20	3.60	37.0	2	0.74	1.9	2.2	1.0	1.1
D3L5	27.5	10	2.75	27.5	10	2.75	1.1	1.5	0.3	0.6
D3L6	18.0	10	1.80	37.0	10	3.70	0.8	1.2	0.2	0.5
D3L7	27.5	20	5.50	27.5	10	2.75	0.5	0.8	0.2	0.5
D3L8	18.0	20	3.60	37.0	10	3.70	0.3	[b]	0.2	[b]

[a] All results are for coatings from latexes formulated with 100% ADH added.
[b] Very low value of peel adhesion that could not be measured reliably.

In contrast, crosslinking of the DAAM-containing shell in these particles using ADH had led to substantial improvements in the cohesive strength of the films (as evidenced by shear resistance data), though with a concomitant reduction in peel adhesion. These results indicated that by controlling the extent of crosslinking through the level of DAAM or the amount of ADH used, an improvement in the balance of adhesive performance would be possible. Hence, further work focused solely on simpler two-layer particles with a DAAM-containing shell.

3.2.1. *Synthesis of two-layer particle latexes*

Characterisation and synthesis parameters for all the two-layer particle latexes are summarised in Table 9. Some of the two-layer latexes were synthesised in the same way as the three-layer particle latexes, namely by preparation first of a core latex, which was isolated and then used to provide seed particles for growth of the shell layer. Controlled growth of particle size was achieved for all these latexes, as can be seen by comparison of theoretical with measured values of the final d_z calculated from the diameter of the core latex. (Figs. 3 and 4 are also typical of synthesis data for these two-layer particle latex preparations.) Other latexes were synthesised by preparation of the core *in situ* and addition of the shell layer directly without isolation of the core latex (*i.e.*, the direct 'one-pot' method). Controlled growth was again seen and all the final latexes had d_z within the range from 242 to 253 nm, in accordance with the target; typical conversion and particle growth data for these preparations are plotted in Fig. 6 (as for Fig. 3(b), the apparent slight reduction and then increase in total particle number to its original value, within experimental error, is thought to be due to swelling of the particles by unreacted monomer in the earlier part of the reaction). Only latex D2L18 had a moderately high residual monomer level (0.65%), which is due to the lower rate of copolymerisation resulting from use of a much higher level of styrene in formation of the shell layer for this latex; nevertheless, the residual monomer level was not high enough to compromise comparison of its adhesive performance with other latexes (see Section 3.2.5).

Table 7
Effect of ADH on 180° peel adhesion for the three-layer particle latex D3L1.

%ADH added[a]	Peel adhesion/N (25 mm)$^{-1}$			
	On stainless Steel		On HDPE	
	20 min	24 h	20 min	24 h
0	2.5	5.7	2.1	2.2
100	2.5	5.1	1.3	1.7

[a] % of the stoichiometric amount for 1:2 reaction of ADH:DAAM.

The adhesive performance of most of the two-layer particle latexes (for which DAAM is mostly present at a level of 2 wt% in the shell layer) is given in Table 10 for films formed in the absence and presence of ADH. Latexes D2L3 and D2L4 have identical formulations, but were prepared by the first (indirect) and second (direct 'one-pot') methods, respectively. As can be seen from Table 10, the values for peel adhesion on HDPE and of shear resistance are almost identical for films cast from these latexes. Latex D2L3 does give a film with a slightly higher peel adhesion than D2L4 on SS, but the difference is within experimental error. Thus the method used for synthesis of the latex had no significant effect on adhesive performance. Reproducibility of latex synthesis was evaluated by synthesis of latexes D2L2 and D2L9 which are syntheses of the same latex carried out on different dates with different batches of initial core latex. The synthesis data for these latexes show small differences that are within normal experimental error, but there are some differences in adhesive performance. The largest difference is in the peel adhesion on SS (18.5 and 13.1 N (25 mm)$^{-1}$ for D2L2 and D2L9, respectively), but this is mainly a consequence of a change in mode of failure from cohesive to adhesive and the result for D2L9 is just in the region where a changeover in failure mode occurs (see later discussion). Shear resistance results for the two latexes are

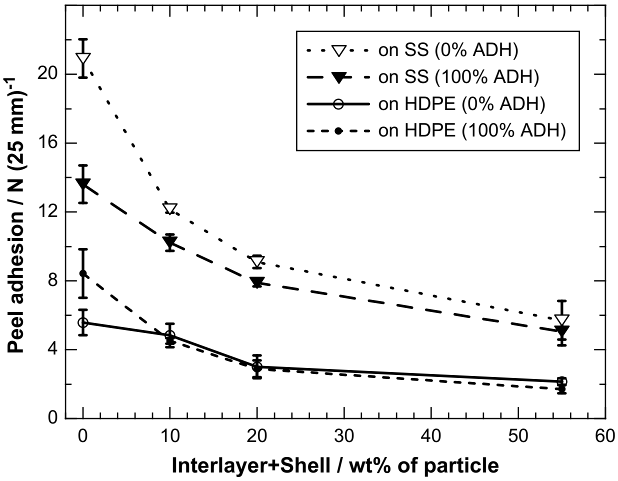


Fig. 5. Effect of the total proportion of interlayer plus shell on the 180° peel adhesion (at 24 h) for films produced from the three-layer particle latexes D3L1, D3L9 and D3L10. The values at 0% interlayer plus shell are for the two-layer particle latex D2L1 which has no DAAM in the shell. Note that some error bars are similar to the size of the data points and so are not easily visible. (SS = stainless steel; HDPE = high-density polyethylene.)

Table 8
Effect of core phase on shear resistance for three-layer particle latexes.

Latex code	Core phase/wt% of total polymer	Shear resistance on stainless steel/min	
		0% ADH	100% ADH[b]
D3L1	45	2399	>10 000
D3L9	80	2758	>10 000
D3L10	90	1704	1944
D2L1	100[a]	932	2050[c]

[a] The results are for the two-layer particle latex D2L1, which has a shell layer that contains no DAAM and so is an essentially 100% core phase, though it does have a slightly different composition with respect to the carboxylic acid monomers used in synthesis of the core and shell layers (see Table 9).

[b] % of the stoichiometric amount for 1:2 reaction of ADH:DAAM.

[c] Equivalent amount of ADH added to that required for a 45:55 latex with 2 wt% DAAM in the shell.

acceptably close when experimental errors are taken into account (887 ± 135 min for D2L2 and 620 ± 186 min for D2L9 for 0% ADH).

AFM images of the surface morphologies of films formed from the latexes provide further validation of the structuring of the latex particles. To illustrate this point and demonstrate that the particle structuring does indeed produce film morphologies in accord with the schematic diagram shown in Fig. 1, representative AFM images (from latexes D2L9 and D2L18) are shown in Figs. 7 and 8. The height images show the surface topography, whereas the phase images reflect differences in the local material stiffness and viscoelasticity (the image becoming brighter as the local material becomes stiffer and less dissipative). Fig. 7(a) and (b) shows, respectively, the morphology of the D2L9 latex film surface without addition of ADH and with addition of 20% ADH prior to film formation. In both cases, the differences in local material stiffness represented in the phase image provide the greatest contrast, which is enhanced very slightly by the low level crosslinking resulting from inclusion of ADH. Similarly, Fig. 8(a) and (b) shows, respectively, the morphology of the D2L18 latex film surface without addition of ADH and with addition of 100% ADH prior to film formation. In this case, the morphology is evident from both the topographic and phase images and the enhancement in contrast with crosslinking is much greater due to the higher degree of crosslinking in the interconnecting phase arising from the much greater concentration of DAAM in the (much thinner) outer phase of the D2L18 latex particles compared to latex D2L9 and from use of the full stoichiometric amount of ADH.

3.2.2. *Effects of interfacial crosslinking and core:shell ratio on adhesive performance for two-layer particle latexes*

Latexes D2L1–D2L10 were synthesised using the chain transfer agent *n*-dodecylmercaptan (DDM) at a level of 0.03 wt% to monomer in the core phase, but with some variations in DDM content in the comonomer feed for the shell layer. The addition of 100% ADH to latex D2L2 produces films which exhibit a significant decrease in peel adhesion on both SS and HDPE; the larger decrease observed on SS is related to the change in mode of failure from cohesive to adhesive failure (the preferred mode for most applications so that deposits are not left on the substrate). The cohesive strength of the films is clearly enhanced by the crosslinking that results from

Table 9
Composition and characterisation data for two-layer particle latexes comprising a DAAM-containing shell.[a]

Latex code	Core latex		Theoretical final latex d_z/nm[d]	Core[b]		Shell[b]				Final latex		
	Code	d_z/nm[c]		wt% of total polymer	DDM/wt%[e]	wt% of total polymer	DAAM/wt% in layer	DDM/wt%[e]	Other monomers/wt% in layer	d_z/nm[c]	Solids/wt%	Mon./wt/%[f]
D2L1	CL1	192	250	45	0.03	55	0	0.032	–	244	55.6	0.18
D2L2	CL1	192	250	45	0.03	55	2	0.037	–	248	55.7	0.18
D2L3	CL4	185	242	45	0.03	55	2	0.03	–	248	54.2	0.16
D2L4[g]	–	–	247	45	0.03	55	2	0.03	–	251	55.2	0.09
D2L5[g]	–	–	247	70	0.03	30	2	0.03	–	243	54.3	0.12
D2L6[g]	–	–	247	80	0.03	20	2	0.03	–	249	54.8	0.12
D2L7[g]	–	–	247	90	0.03	10	2	0.03	–	248	54.7	0.12
D2L8[g]	–	–	247	80	0.03	20	5.5	0.03	5.5% MAA[h]	246	55.2	0.21
D2L9	CL4	185	242	45	0.03	55	2	0.037	–	245	54.9	0.16
D2L10	CL4	185	242	45	0.03	55	2	0.06	–	252	54.6	0.19
D2L11	CL5	187	244	45	0.1	55	2	0.037	–	242	54.7	0.22
D2L12	–	–	247	80	0.1	20	2	0.037	–	245	53.9	0.38
D2L13	–	–	247	80	0.1	20	5.5	0.037	2% MAA[h]	251	54.3	0.18
D2L14	–	–	247	80	0.15	20	2	0.037	–	253	54.1	0.32
D2L15	–	–	247	80	0.15	20	2	0.01	–	247	54.0	0.28
D2L16	–	–	247	80	0.2	20	2	0.037	–	249	54.9	0.12
D2L17	–	–	247	80	0.2	20	2	0.01	–	246	54.3	0.26
D2L18	–	–	247	80	0.1	20	2	0.037	4% BA, 11% Sty[i]	248	54.2	0.65
D2L19	–	–	247	80	0.1	20	2	0.037	96% EHA[j]	244	54.2	0.28
D2L20	–	–	247	80	0.1	20	2	0.037	96% IDA[j]	251	54.7	0.13

[a] For latexes prepared using the procedure described in Section 2.2.2, the previously prepared core latex used is identified in the table and constituted 45 wt% of the final polymer. All other latexes were prepared according to the procedure described in Section 2.2.3. For both types of latex preparation, a surfactant mixture of Rhodapex AB20/Rhodacal DS4/Dowfax 2A1 in the active weight ratio 50.0/33.1/16.9 was used at 1 wt% (active) surfactant to monomer. Regardless of the method of latex synthesis, the polymer from the initial seed latex constituted 0.7 wt% of the final polymer.

[b] The comonomer feed compositions for growth of the core and shell phases were as defined in Table 1 except where indicated under *other monomers* for the shell phase.

[c] Measured by PCS with a reproducibility of ±2 nm.

[d] Calculated from the particle diameter of the core or seed latex (as appropriate).

[e] Wt% DDM to total monomer in the growth stage.

[f] Total residual monomer in the latex measured by GC.

[g] Latexes prepared using the procedure described in Section 2.2.3 but in which feeding of the shell-growth monomer emulsion was started immediately on completing addition of the core-growth monomer emulsion.

[h] DAAM and the monomers listed under *other monomers* were used at the levels indicated; the remaining monomer comprised EHA/EA/BA/Sty in the same weight ratio as in the standard shell comonomer feed composition (*i.e.*, 66/15/10/5).

[i] The BA/Sty ratio was changed to that indicated so that the EHA/EA/BA/Sty/MAA/DAAM shell comonomer feed composition was 66/15/4/11/2/2.

[j] The remaining monomer comprised 2 wt% MAA and 2 wt% DAAM.

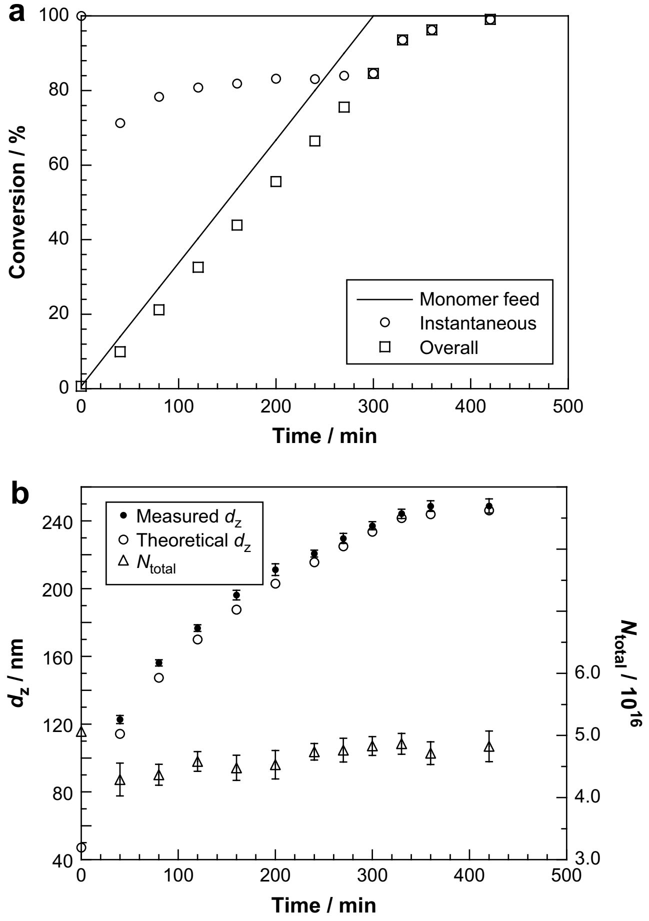


Fig. 6. Plots of (a) conversion and (b) z-average particle diameter (d_z) and total particle number in the reaction vessel (N_{total}) for direct synthesis of the two-layer particle latex D2L6.

addition of ADH, but at the expense of adhesion; this also is evident from the increase in shear resistance to >10 000 min. This confirms the observations described above for the three-layer latex D3L1. Latex D2L1 (in which DAAM was omitted from the shell) shows peel adhesion on both SS and HDPE that is comparable to latex D2L2 in the absence of ADH. The significance of adding ADH in this case is different for the different surfaces. (For comparison, the amount of ADH added to latex D2L1 was the same as the calculated amount for 100% ADH with latex D2L2.) On SS, the mode of failure changes from cohesive to adhesive and the peel adhesion reduces to (a still relatively high) value of 13.6 N $(25\text{ mm})^{-1}$, whereas on HDPE there is a significant increase in peel adhesion to 8.4 N $(25\text{ mm})^{-1}$. Addition of ADH to films formed from latex D2L1 also leads to an increase in shear resistance, which shows that ADH has the effect of increasing the cohesive strength of the films, even in the absence of DAAM. As indicated earlier, this is thought to arise from H-bonding interactions with carboxylic acid groups from the other functional monomers used in the latex syntheses.

The level of crosslinking achieved using 100% ADH in films from latex D2L2 (comprising 55 wt% shell copolymer) leads to substantial improvements in the cohesive strength of the resultant films. Hence, a series of latexes (D2L4, D2L5, D2L6 and D2L7) were synthesised in which the proportion of shell was reduced whilst keeping the level of DAAM in the shell constant at 2 wt%, thereby reducing the overall DAAM content in the particles. Variation in these latexes of the core:shell ratio (45:55, 70:30, 80:20 and 90:10, respectively) meant that, assuming an overall particle diameter of 250 nm, the theoretical thickness of the shell layer would be 29, 14, 9 and 4 nm, respectively. Taking these thicknesses into account and recognising the similarity in the compositions of the core and shell copolymers, for the 80:20 and 90:10 (and possibly the 70:30) core:shell ratios, it is unlikely that the particles have a well-defined core–shell structure [37]; it is more likely that there will be mixing of shell copolymer with the underlying core copolymer, but an overall structuring of the particles with DAAM groups increasingly concentrated near the surface of the particle can be expected as the

Table 10
Adhesive performance of films cast from two-layer particle latexes.[a]

Latex code	Shell/wt% of particle	DDM/wt% in		DAAM/wt% in		Peel adhesion (24 h)/N $(25\text{ mm})^{-1}$						Shear resistance/min on stainless steel		
		Core	Shell	Shell	Particle	On stainless steel[b]			On HDPE[b]			0% ADH	20% ADH[c]	100% ADH[c]
						0% ADH	20% ADH[c]	100% ADH[c]	0% ADH	20% ADH[c]	100% ADH[c]			
D2L1	55	0.030	0.030	0	0	20.9^{ct}	[d]	13.6	5.6	[d]	8.4	932	[d]	2050[e]
D2L2	55	0.030	0.037	2.0	1.1	18.5^{ct}	14.8	6.0	6.4	7.2	2.8	887	12 059	>10 000
D2L3	55	0.030	0.030	2.0	1.1	11.9	[d]	[d]	4.3	[d]	[d]	1571	[d]	[d]
D2L4	55	0.030	0.030	2.0	1.1	10.0	[d]	4.2	4.2	[d]	2.4	1694	[d]	>10 000
D2L5	30	0.030	0.030	2.0	0.6	11.5	[d]	5.2	4.5	[d]	4.0	1593	[d]	>10 000
D2L6	20	0.030	0.030	2.0	0.4	11.2	[d]	9.0	5.4	[d]	5.0	2001	[d]	>10 000
D2L7	10	0.030	0.030	2.0	0.2	10.5	[d]	10.2	5.0	[d]	4.2	120	[d]	2022
D2L8	20	0.030	0.030	5.5[f]	1.1	9.3	[d]	4.5	4.0	[d]	1.6	1114	[d]	>10 000
D2L9	55	0.030	0.037	2.0	1.1	13.1^{ct}	11.0	[d]	4.9	4.7	[d]	620	>10 000	>10 000
D2L10	55	0.030	0.060	2.0	1.1	13.5^{ct}	[d]	[d]	4.9	[d]	[d]	331	[d]	[d]
D2L11	55	0.100	0.037	2.0	1.1	20.3^{ct}	9.9	[d]	6.1	4.3	[d]	112	5150	[d]
D2L12	20	0.100	0.037	2.0	0.4	23.6^{ct}	[d]	12.0	7.1	[d]	6.0	42	[d]	5013
D2L13	20	0.100	0.037	5.5[f]	1.1	21.2^{ct}	[d]	[d]	7.4	[d]	[d]	36	[d]	[d]
D2L14	20	0.150	0.037	2.0	0.4	16.2^{ct}	[d]	19.6^{ct}	15.8^{ct}	[d]	7.6	15	[d]	1487
D2L15	20	0.150	0.010	2.0	0.4	18.5^{ct}	[d]	12.8	17.8^{ct}	[d]	8.6	22	[d]	1443
D2L16	20	0.200	0.037	2.0	0.4	13.2^{ct}	[d]	10.3	12.1^{ct}	[d]	5.6	31	[d]	258
D2L17	20	0.200	0.010	2.0	0.4	14.6^{ct}	[d]	13.2	13.5^{ct}	[d]	8.6	12	[d]	1051

[a] See Table 9 for latex particle compositions and characterisation data.

[b] The mode of failure in peel testing was 100% adhesive unless the peel adhesion value is denoted with 'ct' which indicates that the failure was cohesive.

[c] % of the stoichiometric amount for 1:2 reaction of ADH:DAAM.

[d] Not tested at this level of ADH.

[e] Equivalent amount of ADH added to that required for a 45:55 latex with 2 wt% DAAM in the shell.

[f] The shell also comprises 5.5 wt% MAA in order to replicate the total DAAM and MAA contents of D2L4.

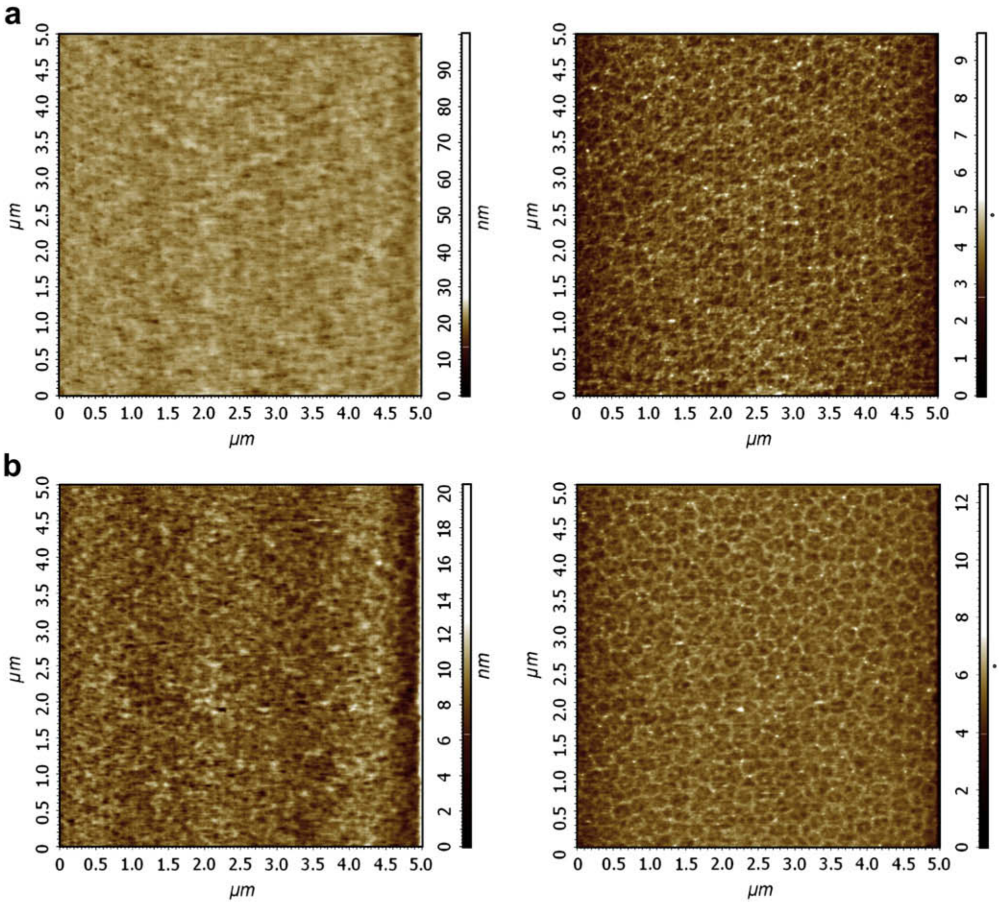


Fig. 7. AFM height (left) and phase (right) images of 5 × 5 μm areas of the surface of pressure-sensitive adhesive films formed from latex D2L9 (a) without addition of ADH and (b) with addition of 20% ADH prior to film formation.

core:shell ratio increases. For the series D2L4–D2L7, the best peel performance on both SS and HDPE was obtained in the absence of ADH for films from the 80:20 core–shell latex (D2L6, with an overall DAAM content of 0.4 wt%). Films cast from this latex with the addition of 100% ADH exhibited the smallest decrease in peel adhesion on HDPE, whilst achieving very high shear resistance (>10 000 min). Indeed the high cohesive strength achieved using these latexes is unaffected by the lower levels of DAAM–ADH crosslinking until the shell proportion of the particles is reduced to 10 wt% (D2L7), in which case use of 100% ADH only raises the shear resistance to 2022 min.

In view of the good balance of adhesive performance achieved with D2L6, a further 80:20 core:shell latex (D2L8) was synthesised in which both the levels of DAAM and MAA in the shell layer were increased to 5.5 wt%, which makes the total amounts of these monomers equivalent to those present in the 45:55 core:shell latex (D2L4). In the absence of ADH, the higher concentrations of DAAM and MAA in the shell lead to reductions in peel adhesion to SS and HDPE of 1.9 N $(25\ \mathrm{mm})^{-1}$ and 1.4 N $(25\ \mathrm{mm})^{-1}$, respectively (*cf.* data for D2L6). Addition of 100% ADH leads to a reduction in peel adhesion, but in this case the values are similar to those for latex D2L4. Thus there appears to be no advantage in increasing the DAAM content of the shell above 2 wt%. Another pair of 80:20 core:shell latexes (D2L12 and D2L13) with the same amounts of shell DAAM as D2L7 and D2L8 (2 wt% and 5.5 wt%, respectively), but higher core DDM content, were also investigated. In this case there was no clear effect of the increase in level of DAAM: for the latex with the higher level of DAAM in the absence of ADH, peel adhesion on SS was marginally lower, whereas on HDPE it was marginally higher.

Effects of the levels of ADH and chain transfer agent were then investigated for 80:20 core:shell latexes which contained 2 wt% DAAM in the shell, since this particle structure and composition had shown the best balance of adhesive performance with significantly enhanced cohesive strength and only a small reduction in peel adhesion when using 100% ADH.

3.2.3. Effects of the level of ADH and aging on adhesive performance for two-layer particle latexes

Controlling the level of ADH used for crosslinking provides another means of investigating the effects of extent of crosslinking. Fig. 9 presents results from a study of the extent of crosslinking activation using different levels of ADH, in this case for the 80:20 core:shell latex D2L12. For this latex higher levels of chain transfer agent were used in formation of the core and shell (the effects of chain transfer agent level will be discussed in Section 3.2.4). The DAAM present in this latex amounts to only 0.4 wt% of the total monomer, which is reflected in the fact that 100% ADH is required to achieve a substantial increase in shear resistance. The large decrease in 20 min SS peel adhesion observed on increasing the level of ADH from 20% to 40% is accompanied by a change in mode of failure from cohesive to adhesive. The 24 h peel adhesion, however, maintains a cohesive failure mode on SS until the full stoichiometric amount of ADH is added, when it switches to an adhesive failure mode. Fig. 10 presents a plot of peel adhesion against % ADH added for latex D2L2 (a 45:55 core:shell latex),

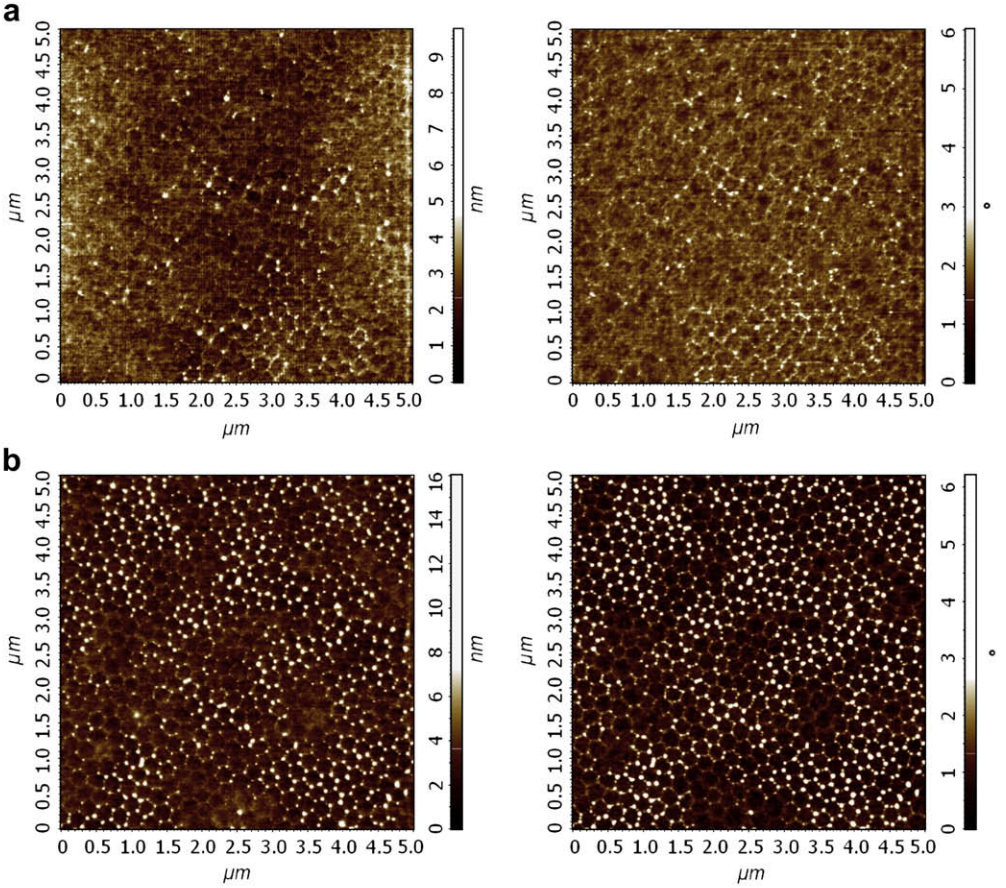


Fig. 8. AFM height (left) and phase (right) images of 5 × 5 μm areas of the surface of pressure-sensitive adhesive films formed from latex D2L18 (a) without addition of ADH and (b) with addition of 100% ADH prior to film formation.

showing that use of 100% ADH leads to a substantial reduction in peel adhesion. However, addition of ADH up to 20% of the stoichiometric level has little negative impact on peel adhesion whilst still markedly improving the shear resistance. For comparison, thick films (1–2 mm) were cast from the equivalent latex D2L9 (a repeat synthesis of D2L2) and analysed for gel fraction; at 20% ADH the gel content was 33% and at 100% ADH it was 59%. Recognising that the latex polymer as prepared (*i.e.*, in the absence of ADH) comprises only 8% gel (see Section 3.2.4), these observations correlate well with the proportion of ADH added. Nevertheless, since the presence of DAAM itself has been shown to have a detrimental effect on peel adhesion, latexes in which excess DAAM is present (compared to the amount of ADH needed for enhancing the cohesive strength of the adhesive films) will not be optimum.

The effects of independently aging for one month prior to adhesive testing both the formulated latex containing 10% ADH and the cast films were studied for latex D2L2. Casting the films from the formulated latex one month after addition of ADH causes no significant change in adhesive performance. However, aging the coated films for one month prior to testing results in a change in the balance of adhesive performance. The peel adhesion after 24 h on HDPE was reduced from 6.7 to 5.8 N (25 mm)$^{-1}$, whilst the shear resistance increased from 2484 to 3549 min. The effect of aging films on adhesive performance also was investigated for the 80:20 core:shell latex D2L15. In this case, aging the films for up to five months prior to testing produced no significant change in peel adhesion, though there was a small reduction in shear performance after five months' aging. These results suggest that for latexes with

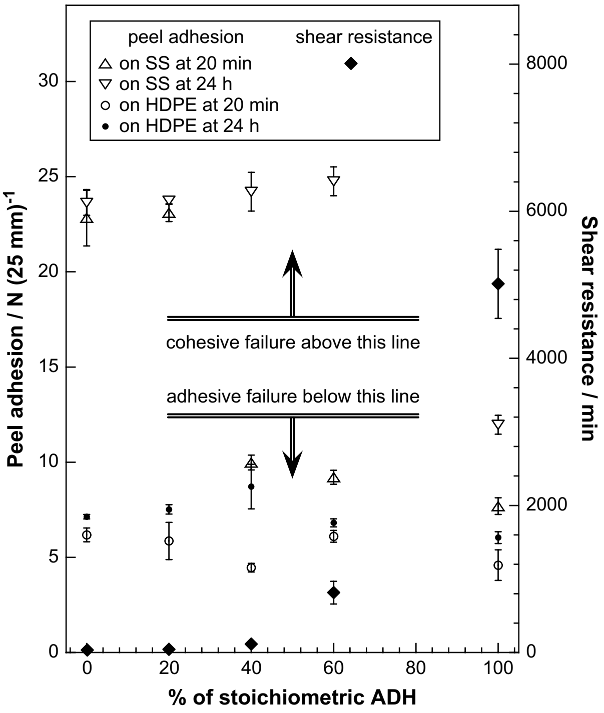


Fig. 9. Effect of % ADH on the 180° peel adhesion and shear resistance of films produced from the two-layer particle latex D2L12. (SS = stainless steel; HDPE = high-density polyethylene.)

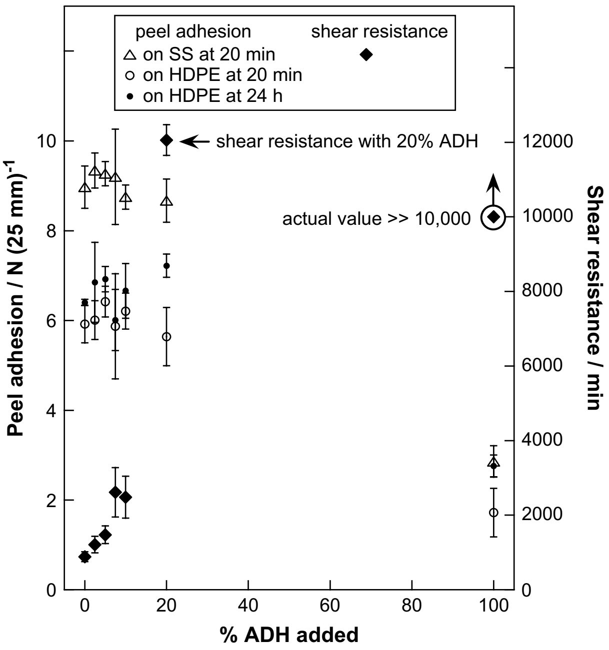


Fig. 10. Effect of % ADH on the 180° peel adhesion and shear resistance of films produced from the two-layer particle latex D2L2. (SS = stainless steel; HDPE = high-density polyethylene).

a thicker DAAM-containing shell (such as D2L2, which theoretically has a shell approximately 28 nm thick), a greater proportion of DAAM repeat units are buried sufficiently deeply within the particle that crosslinking is limited by diffusion of ADH into the particle, giving rise to slow further crosslinking after film formation. In comparison, for latexes with a thin DAAM-containing shell (such as D2L15, which theoretically has a shell approximately 10 nm thick), the DAAM repeat units are much more readily accessible and react quickly with the ADH.

3.2.4. Effects of chain transfer agent on adhesive performance for two-layer particle latexes

Chain transfer agents have a significant effect on the proportion of gel and on the sol fraction molar mass of the latex polymer, both of which are well known to influence adhesive properties. The effects arise from chain transfer to chain transfer agent, which competes with other processes for termination of chain growth and so limits the extent of coupling of propagating long-chain branches, (*i.e.*, the extent of crosslinking arising from intermolecular chain transfer to polymer). Thus, if other synthesis parameters and comonomer compositions are kept constant, increasing the level of chain transfer agent will tend to reduce the underlying level of crosslinked copolymer (*i.e.*, gel fraction) in the core and shell phases, as prepared. The performance of films cast from latexes in which the levels of DDM chain transfer agent used in synthesis of the core and shell was varied are given in Table 10.

The gel fractions of selected latexes were measured to assess the effects of DDM level. The 45:55 core:shell latex D2L2 employed DDM at levels of 0.030 and 0.037 wt% to monomer for synthesis of the core and shell copolymers, respectively, and had an overall polymer gel content of 8%. The 80:20 core:shell latex D2L6 employed DDM at 0.030 wt% to monomer for synthesis of both the core and shell copolymers and had an overall polymer gel content of 9%. Thus at 0.030–0.037 wt% DDM to monomer, a significant, but not high, level of crosslinking arises from intermolecular chain transfer to polymer. For 80:20 core:shell latexes prepared using DDM at levels ≥0.1 wt% to monomer in the core (D2L12, D2L15, D2L16 and D2L18 were analysed), the latex polymer had no measurable level of gel showing that, for such latexes, formation of gel in the shell is not significant even for shell-growth monomer DDM levels ≤0.037 wt%, perhaps due to some carry-over of unreacted DDM from the core growth at these high levels of DDM. Interestingly, in the absence of added ADH, the shear resistance of films formed from latexes D2L12, D2L15, D2L16 and D2L18 is very low (42, 22, 31 and 29 min, respectively) compared to those formed from latexes D2L2 (887 min) and D2L6 (2001 min). Thus, even a relatively small proportion of gel has a significant effect on shear resistance. As will be seen in the following discussion, the latexes of greatest interest are those produced with higher levels of DDM in synthesis of the core, which have no measurable gel content as prepared, but give films with high values of peel adhesion and low shear resistance, the value of which can be increased to acceptable levels without serious loss of peel adhesion by activating the crosslinking of DAAM repeat units through addition of ADH prior to film formation.

Comparison of latexes D2L9 and D2L11 shows that increasing the level of DDM in the monomer feed for the core from 0.03 to 0.10 wt%, even for a 45:55 core:shell latex (D2L11), produces films with significantly improved 24 h peel adhesion on both SS and HDPE in the absence of ADH. The results also suggest that the peel adhesion of films cast from latex D2L11 (with the higher level of DDM in the core) are more adversely affected by the addition of 100% ADH. These observations suggested that it would be beneficial to investigate 80:20 core:shell latexes synthesised using high levels of DDM for the core (≥0.1 wt% DDM to monomer). The indications were that this would improve peel adhesion in the absence of ADH and that the thinner shell would minimise the contribution of interfacial crosslinking to reduction in overall peel performance upon addition of ADH. Hence, six latexes (D2L12-D2L17) were synthesised with a core:shell ratio of 80:20 and ≥0.1 wt% DDM in the core.

The 80:20 core:shell latex with 0.10 wt% DDM in the core (D2L12) showed greater peel adhesion, in both the absence and presence of 100% ADH, when compared to an 80:20 core:shell latex with 0.03 wt% DDM in the core (latex D2L6 – although this had slightly different shell DDM content, the effect of the differences in the core would reasonably be expected to be dominant). Peel adhesion (24 h) values for films on SS and HDPE, after activation with 100% ADH, are 12.0 and 6.0 N (25 mm)$^{-1}$ respectively. The

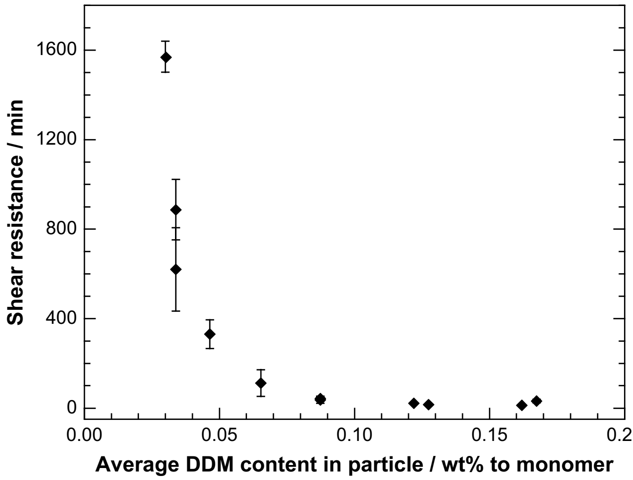


Fig. 11. Effect of the total wt% of DDM chain transfer agent to total monomer on the shear resistance of films formed from two-layer particle latexes using 0% ADH.

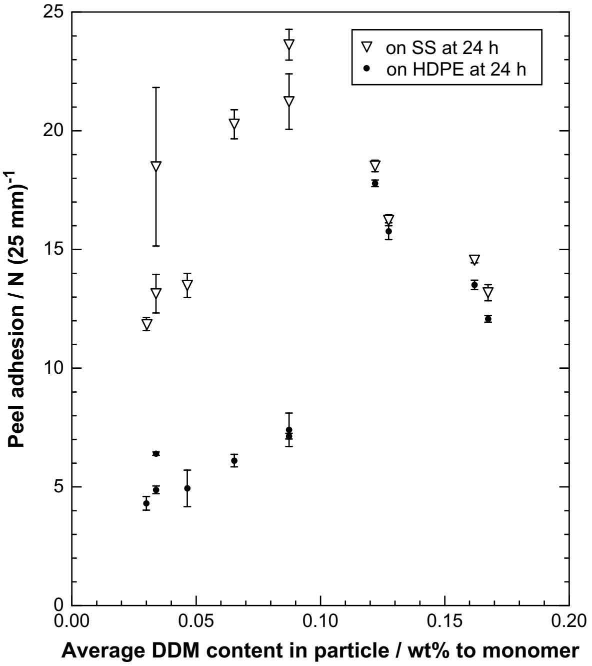


Fig. 12. Effect of the total wt% of DDM chain transfer agent to total monomer on the 180° peel adhesion of films formed from two-layer particle latexes using 0% ADH. (SS = stainless steel; HDPE = high-density polyethylene.) The failure mode on SS was adhesive for DDM<0.06 wt% and cohesive above that level, except for the film at 0.034 wt% DDM which showed mixed failure and, as a consequence, larger scatter in the data. The failure mode on HDPE was adhesive for DDM<0.12 wt% and cohesive above that level with no exceptions.

shear resistance of the films is, however, reduced by increasing the level of DDM in the core. For example, the shear resistance of latex D2L12 is 42 min in the absence of ADH. However, use of 100% ADH again leads to a significant increase in shear resistance, giving a relatively high value of 5013 min. Increasing the level of DDM in the core to 0.15 wt% to monomer (D2L14) and using 100% ADH lead to a further increase in the peel adhesion on HDPE to a value of 7.6 N (25 mm)$^{-1}$. However, the mode of failure remains cohesive on SS, even with the addition of 100% ADH, and the improvement in shear resistance is reduced. Further increasing the DDM level in the core to 0.20 wt% to monomer (D2L16) has a detrimental effect on both peel adhesion and on the effect of DAAM–ADH crosslinking (*e.g.*, the shear resistance is only 258 min with 100% ADH).

The level of DDM used in synthesis of the shell was studied to investigate its effect on peel adhesion and the efficiency of the DAAM–ADH crosslinking reaction. Films cast from a latex (D2L15) containing 0.15 wt% DDM to monomer in core, but with only 0.01 wt% DDM to monomer in shell, showed a good balance of adhesive performance. The mode of failure on both SS and HDPE with 100% ADH was adhesive and the peel adhesion values were high (12.8 and 8.6 N (25 mm)$^{-1}$, respectively). The shear resistance achieved was similar to that for latex D2L14, showing that, in this case, crosslinking was unaffected by the reduction of DDM level in the shell. Reducing the shell DDM level did, however, improve both peel adhesion and shear performance for comparable latexes containing 0.20 wt% DDM to monomer in the core (D2L16 and D2L17). On addition of 100% ADH, high peel adhesion values of 13.2 and 8.6 N (25 mm)$^{-1}$ on SS and HDPE, respectively, were observed for D2L17 together with a significant improvement in shear resistance to 1051 min. The higher molar mass of the shell polymer produced at lower shell DDM levels provides a greater probability for shell-phase network formation in the films.

The cumulative effect of DDM (*i.e.*, core plus shell) on shear resistance of films for the series of core–shell latexes is presented in Fig. 11. The data are for film performance in the absence of ADH. Clearly, a low level of DDM (about 0.03 wt% to monomer) is required to achieve an industrially useful shear resistance time (>1500 min) without activating crosslinking of the DAAM groups with ADH. An equivalent plot showing peel adhesion for the same selection of latexes is presented in Fig. 12. The overall DDM level which gives the best balance of peel performance on both SS and HDPE in the absence of ADH is ~0.1 wt% DDM to monomer, but the change in failure mode from adhesive to cohesive occurs at different levels for SS and HDPE. Cohesive failure on SS is predominant for films containing >0.06 wt% DDM to monomer, whereas high cohesive peel adhesion values are only evident on HDPE when ≥0.12 wt% DDM to monomer is used. The shear resistance results from latexes containing these levels of chain transfer agent were low (typically ≤100 min). However, as already discussed, the shear resistance for these latexes can be increased to ≥1000 min by the use of DAAM–ADH crosslinking whilst, for the most interesting latexes, retaining high levels of peel adhesion.

3.2.5. *Effects of shell copolymer composition on adhesive performance for two-layer particle latexes*

A further series of 80:20 core:shell latexes were synthesised to investigate the effect of shell comonomer composition, particularly with respect to the T_g of the shell copolymer. The peel adhesion and shear resistance data for films cast from these latexes are compared in Table 11 to that obtained for the equivalent latex (D2L12) synthesised using the standard shell comonomer mixture. Core–shell latexes containing a predominantly isodecyl acrylate (IDA) or 2-ethylhexyl acrylate (EHA) shell produced films with considerably reduced peel adhesion compared to D2L12. Marginally increasing the shell copolymer T_g by replacing some BA in the shell comonomer mixture with styrene (latex D2L18) produced films that showed reduced peel adhesion on SS (compared to D2L12) and unchanged performance on HDPE in the absence of ADH; the

Table 11
Effects of shell copolymer composition on adhesive performance of films cast from two-layer particle latexes comprising 20 wt% shell.[a]

Latex code	Comment on the change in shell copolymer composition	Theoretical shell copolymer T_g/°C	Peel adhesion (24 h)/N (25 mm)$^{-1}$				Shear resistance/min	
			On stainless steel[b]		On HDPE[b]		On stainless steel	
			0% ADH	100% ADH[c]	0% ADH	100% ADH[c]	0% ADH	100% ADH[c]
D2L18	Sty increased to 11 wt% by reducing BA to 4 wt%	−31	18.3^{ct}	21.4^{ct}	6.8	9.3	29	2294
D2L12	Standard composition	−38	23.6^{ct}	12.0	7.1	6.0	42	5013
D2L19	EHA replaces EA, BA and Sty	−46	20.0^{ct}	[d]	5.7	[d]	31	[d]
D2L20	IDA replaces EHA, EA, BA and Sty	−51	14.9^{ct}	[d]	$4.6/8.0^{ct}$	[d]	135	[d]

[a] See Table 9 for latex particle compositions and characterisation data.
[b] The mode of failure in peel testing was 100% adhesive unless the peel adhesion value is denoted with ‘ct’ which indicates that the failure was cohesive.
[c] % of the stoichiometric amount for 1:2 reaction of ADH:DAAM.
[d] Not tested at this level of ADH.

addition of 100% ADH gave rise to an increase in 24 h peel adhesion on both SS and HDPE. The latex with an IDA-based shell (latex D2L20) showed a small enhancement in shear resistance compared to the other 80:20 core:shell latexes in the absence of ADH, which is consistent with the ability of IDA to form a significant amount of gel in the shell due to chain transfer to polymer. Latex D2L18 achieves satisfactory shear performance upon addition of 100% ADH. Overall, it appears that the reduction in peel adhesion observed on reducing the T_g of the shell polymer is related not to T_g, but more likely to the ability of the monomers used to change the gel fraction because the extent of chain transfer to polymer (and hence gel fraction) is known to be significantly increased by EHA and IDA [34,38], but reduced by styrene [39].

4. Conclusions

The concept of using structured particles and the mechanism of film formation from latexes to produce PSA films with controlled sub-micron and nanometre scale morphology has been investigated with the objective of enhancing adhesive performance. Initial work focused on latexes comprising three-layer particles in which the core copolymer composition was the same for all particles, the interlayer between core and shell was crosslinked during synthesis (using HDDA) and the shell contained DAAM repeat units (capable of providing interfacial crosslinking by reaction with ADH). In general, the three-layer particle latexes produced adhesive films with high shear resistance when the crosslinking agent ADH was added. However, peel adhesion was generally low and further reduced by increasing either the proportion or the HDDA concentration of the pre-crosslinked interlayer. Results from the three-layer particle latexes also showed that addition of ADH tended to reduce peel adhesion, while providing marked increases in shear resistance. These results suggest that the three-layer systems were over-crosslinked and did not meet the criteria to form viscoelastic fibrils upon debonding, thus giving a low peel adhesion.

Hence, further work focused on simpler two-layer (core–shell) latexes with shell layers containing DAAM (and with no pre-crosslinked interlayer). Studies of the effects of core:shell ratio and amount of DAAM showed that optimum adhesive performance was obtained with a core:shell ratio of 80:20 and 2 wt% DAAM in the shell (0.4 wt% overall). For this latex, addition of the stoichiometric amount of ADH led to a marked increase in shear resistance but only a slight reduction in peel adhesion. Using this particle composition/morphology, the effects of DDM chain transfer agent concentration in synthesis of both the core and the shell phases were studied. Increasing the concentration of DDM in the core led to increased peel performance and reduced shear resistance, but high shear resistance could then be recovered through interfacial crosslinking using ADH. The best adhesive performance was obtained when there was a contrast between DDM concentration in the two regions of the particle, with a high level of DDM in the core and a low level of DDM in the shell. Thus, based on the particle structure targeted through the latex synthesis, an adhesive film with a percolating phase of crosslinked particle shell copolymer encapsulating a much more viscoelastic core copolymer gives the best balance in adhesive performance. Further systematic studies of the effects of particle structure on linear and non-linear viscoelastic properties of these adhesives will be published in subsequent papers.

In summary, the adhesive films formed from latexes which gave optimal performance after crosslinking of DAAM groups through addition of ADH, showed high peel adhesion on both SS and HDPE, as well as industrially useful levels of shear resistance. Even though the structured latex particles are unlikely to have highly defined core–shell morphology due to similarity in the compositions of the phases and, for some particles, the small thicknesses of the outer layers [37], the results demonstrate that the particles were sufficiently well structured to induce the desired effects through control of adhesive film morphology, evidence for which has been obtained by atomic force microscopy. Thus, the concept of using structured particles and the mechanism of film formation from latexes to produce adhesive films with controlled heterogeneity and enhanced adhesive performance [10] has been validated. In particular, the ability to create adhesive films with a percolating soft copolymer phase that has a much higher crosslink density than a similarly soft, but more highly dissipative, discrete phase facilitates enhancement of both peel adhesion and shear resistance. The results from this study, therefore, define guiding principles for development of new commercial water-borne PSAs that can compete with solvent-borne PSAs in high-performance applications.

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