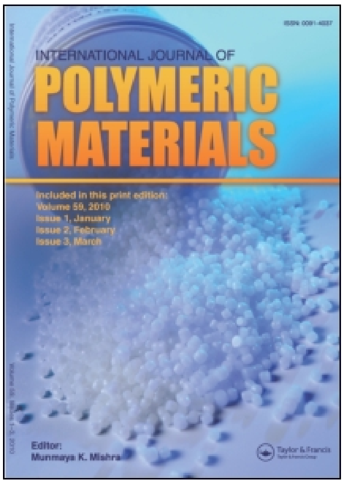

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On the Adhesive Properties of Vinyl-Acrylic Latex Particles Functionalized with Acrylic Acid

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On the Adhesive Properties of Vinyl-Acrylic Latex Particles Functionalized with Acrylic Acid

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A series of pressure-sensitive adhesives, based on vinyl acetate (VA) and butyl acrylate (BuA) and functionalized with small amounts of acrylic acid (AA), were synthesized by semicontinuous emulsion polymerization. This technique allowed preparing latex particles with high monodispersity and pre-defined particle size. The influence of the VA/BuA ratio on the tack, peel, and shear strength of the coatings was investigated. To explain the dependence of adhesive properties (shear, peel, and tack) on particle composition, a Monte Carlo simulation based on a simple model was used to understand the film formation process. The simulation showed that dense adlayers were formed from dispersions containing a relative high content of BuA. Experimental

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testing showed that films with a low VA/BuA ratio (30/70) exhibited moderate values of shear resistance due to well-structured layers formation, with improved tack and peel properties. A positive influence of functionalization on the adhesive properties was observed at low AA content (1% w.) in coatings enriched in BuA, as a result of surface particle saturation with charged groups.

Keywords: pressure-sensitive adhesives, vinyl acetate, butyl acrylate, acrylic acid, Monte Carlo simulation

INTRODUCTION

Environmental considerations continue to be a major force behind technical innovation, as exemplified by the search for technically viable adhesives with low or no organic solvent content [1]. Likewise, a more stringent legislation has led to the substitution of solvent-based adhesives with waterborne dispersions of polymers [2–3]. These materials comprise water-reducible dispersions, resins synthesized in solvent and then reduced in water and latexes. The latter are defined as an aqueous dispersion of polymer particles stabilized with a surfactant [4]. However, many organic solvents or additives are added to waterborne coatings to get better film drying and properties. For example, small amounts of plasticizers (mainly phthalates) are often added to acrylic or vinyl emulsions used as pressure-sensitive adhesives (PSAs) to accelerate particle coalescence and improve the film forming process. After the polymeric film is formed, phthalate may diffuse from polymer to air [5–6] causing environmental pollution, so it is necessary to control the properties of polymer films by other ways; it is well known that the glass transition temperature may be modified by adjusting the copolymer composition, for example. In addition, the quality of the film may also be improved by changing the average particle size and particle size distribution of latexes.

Latexes with a predefined particle size and narrow particle size distribution are often obtained by semicontinuous emulsion polymerization [7]. In this process, a reactor containing water along with small amounts of surfactant, initiator, and monomer (the seed) is fed from two stirring tanks; one with a pre-emulsion (monomer dispersed in water by means of a surfactant) and the other with an initiator solution. The main reactor operates under starved feed conditions; this means that reagents are introduced into the reactor at a feed rate that is lower than the polymerization rate (determined previously in a batch reactor with the same conditions of composition and temperature). The monodispersity, average particle size, and particle size distribution may be adjusted by means of the concentration of the seed synthesized in the main reactor before the pre-emulsion addition.

The adhesive film features (and with them, the adhesion properties) strongly depend on the composition of the polymer particles. A great number of PSAs are synthesized from a combination of monomers, whose polymers have a low and a high glass-transition temperature [8–9]. These copolymers have attracted a growing interest because of their main adhesive properties (peel, shear, and tack) [10–11]. However, the dependence of the adhesive properties of waterborne coatings on the particle composition is not straight and the film formation mechanism is also involved [12]. Functionalization during the synthesis of copolymer particles with a polar co-monomer, such as acrylic or methacrylic acid, allows an improvement of both shear and peel properties [13]. The polar groups in the polymer chains increase the adhesion to the substrate, and in large amounts, they contribute to enhance the material rigidity [14] due to their high Tg [15].

The development of water-based dispersions of VA/BuA copolymers, along with the assessment of their adhesion properties (peel, shear, and tack) through different industrial tests, are discussed in this work. The copolymers were functionalized with different percentages of acrylic acid to study the influence of the content of polar groups on adhesion. The film formation process of the VA/BuA dispersions was simulated by the Monte Carlo (MC) method and qualitatively compared with the experimental results.

EXPERIMENTAL

Materials

Technical grade monomers (Celanese) vinyl acetate (VA), n-butyl acrylate (BuA), and acrylic acid (AA) were used as received. These chemicals contain hydroquinone monomethyl ether at 50, 15, and 250 ppm, respectively. The emulsifier system consisted of the non-ionic aromatic surfactant ABEX-26-S (Rhodia, Mexico). The initiator was ammonium persulphate ($NH_4S_2O_8$, Aldrich) of analytical grade, which was employed without further purification. Tert-dodecanethiol (Aldrich) was used as transfer agent. Distilled water was employed throughout the experimental work.

Synthesis of the Vinyl Acrylic Emulsions

A series of copolymers, with different *VA/BuA* ratios (0/100, 10/90, 20/80, 50/50, 80/20, 90/10, and 100/0 w./w.) and functionalized with 3% w. of AA were prepared. The list of the latex components is given

TABLE 1 Formulation of Vinyl-Acrylic Emulsions Synthesized by Semicontinuous Emulsion Polymerization at 80°C

Main Reactor	
Initiator aqueous solution (9.6% w.)	14.6 g
Distilled water	290.0 g
Feeding Tank 1 (pre-emulsion)	
Monomers	660.0 g
Transfer agent	0.6 g
Surfactant aqueous solution (12% w.)	170.0 g
Feeding Tank 2	
Initiator aqueous solution (0.7% w.)	50.0 g

in Table 1. The emulsion polymerizations were carried out in a semicontinuous reactor composed of a glass vessel (1 L) and two feeding tanks. The ancillary equipment consisted of a reflux condenser, a stirrer (two-blade propeller type), an inlet for inert gas (e.g., nitrogen), a thermocouple, and an inlet for the feeding pump. The agitation speed was fixed at 250 rpm.

The temperature in the main reactor was fixed at 80 ± 1°C. The pre-emulsion and initiator solution were fed into the reactor over a time period of 3 h, this way starved feed conditions were assured. At the end of the monomer addition, the temperature was raised from 80 to 90°C for ca. 1 h to complete the polymerization reaction. An additional series of vinyl-acrylic particles (VA/BuA: 10/90 w./w.), functionalized with 0, 1 and 3% of acrylic acid, were prepared following the previously mentioned polymerization method.

Characterization of the Vinyl Acrylic Emulsions

The solid content in latexes was measured gravimetrically by taking a few grams of the sample from the reactor and drying it under reduced pressure at 80°C. The z average particle diameter and particle size distribution of latexes were measured by quasi-elastic light scattering (QELS) with a Coulter LS-230 nanosizer. This information was employed to determine the average diameters of latex particles, Dp_n, Dp_w, and Dp_z, as well as the polydispersity index, I [16]. The viscosity of the vinyl-acrylic dispersions was determined at 22°C with a Brookfield RVF viscometer. The pH of the latex was measured with a Micronal B-474 potentiometer.

The copolymers were precipitated from the aqueous dispersion by adding some drops of a solution at 3% w./w. HCl, washed with distilled water, dissolved in chloroform and finally precipitated again with CH_3OH. The glass transition temperatures of the acrylic adhesives were determined with a Perkin Elmer DSC-7 calorimeter with an intracooler device working at a heating rate of 20°C/min.

Preparation and Testing of Adhesive Tapes

The adhesive bonds were prepared and tested following a series of standardized industrial control methods [17–21]. The acrylic latexes were coated onto six PET tapes (Dupont Mylar® type 200 A, 2 mm thick) using a K-22 bar and dried in two steps; the first at room temperature for 15–20 min in a fume hood and the second at 130°C for 3 min. The film obtained was within 20–22 g/m^2. A release liner, silicone-coated James River Sticknot SN462, was used to handle the sample and avoid sticking. The tack, peel, and shear resistance were assessed at a constant temperature (20 ± 1°C) in an environment with a relative humidity of $50 \pm 5\%$.

The 180° peel adhesion test was used to measure the adhesive strength of the different vinyl-acrylic coatings. Testing was carried out on PET substrate at a crosshead rate of 30.5 cm/min. An 18 N roller allowed the samples to be applied onto a standard substrate.

The shear adhesion test was applied to check the cohesive strength of the adhesives. For this test, the sample was subjected to a standard load so that a constant stress was applied parallel to the sample surface. This property was measured for the time required for the bond to fail. A 90°-tack test was also used to perform the tack measurements. During this evaluation, the tape was removed at a crosshead speed of 30.5 cm/min and the force to remove the tape was recorded. The 180° peel adhesion and tack strength assessments were performed with a Sintech M181730 mechanical tester.

SIMULATION OF THE ADHESIVE FILMS

The Monte Carlo simulation, based on a model that mimics the growth kinetics of colloidal films, was used to depict film formation. The main features of this model are presented here, whereas related details can be found elsewhere [22]. A simulation box prism of side $L_x = L_y = 30\,d$ and length $L_z = 12\,d$ was filled with $N = 3000$ identical particles of unitary diameter $d = 1$. As they are considered hard spheres, their overlapping is not allowed (Figure 1).

The interaction of the colloid particles with the liquid-vapor interface U_{ic} (right-hand wall of Figure 1) was simulated as an effective external field, by using a soft repulsive potential [23]:

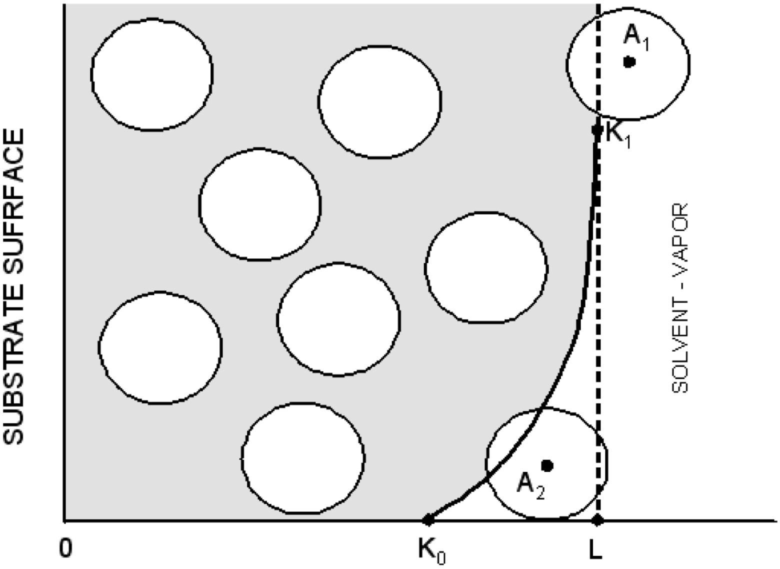

FIGURE 1 Schematic representation of the simulation box. Curve K_0-K_1 indicates the region of the repulsive effective potential due to the vapor–liquid interface, particle A_2 is in the zone of this potential and A_1 is "frozen" (immobilized) because of its location in the vapor phase. The arrow shows the displacement of the solvent–vapor interface during solvent evaporation.

$$U_{ic}(z) = \left(\frac{d}{z}\right)^{n} \tag{1}$$

where z is the normal distance from the center of a polymer particle to the interface; n is a parameter of softness that can be related with the system temperature [22, 24]. The parameter n was kept constant at $n = 8$.

The interaction between polymer particles U_{cc} was simulated with a soft potential in the form

$$U_{cc}(r) = \left(\frac{d}{r}\right)^{n_c} \tag{2}$$

where r is the distance between two polymer particles. The hardness or softness of the polymer particles was achieved by modifying the value of n_c, as this exponent is increased the particle hardness is increased too.

The interaction of polymer particles with the solid substrate (left-hand wall of Figure 1) was modeled through the *attractive* Yukawa potential [23] as follows:

$$U_{wc}(z) = K\exp(Az), \tag{3}$$

Parameters K and A are related to the strength and range of the interaction potential, respectively; they were chosen to be $K = -5$ and $A = -3$.

The rate of movement of the liquid–vapor interface can be ascribed to the rate of film drying. According to the Metropolis algorithm [25], after each particle in the box is moved ν times, the right-hand wall is moved by a step of $l_i = 0.01$ to reduce the film thickness, which increases its density. This artifice emulates both water evaporation and the subsequent increment of solid content during the film formation process. In other words, the number of MC configurations may be related qualitatively with drying time.

This model takes into account the possibility that the particles may reorganize themselves between two consecutive interface displacements (due to Brownian motion and/or capillary forces). In this simulation, the influence of the dispersive medium (i.e., water) is taken into account by the interparticle potential and by the liquid–vapor surface tension, which hinders the latex particles from leaving the system. In consequence, the displacement of the polymer particles to the top of the wet coating is not energetically favored.

In the MC simulation, the particle hardness was modified to simulate the effect of the different *VA*/*BuA* ratios; for instance $n_c = 8$ was related to soft spheres and a high BuA content, $n_c = 30$ to partially rigid spheres for a *VA*/*BuA* 50/50 w./w., and hard spheres related to PVA. In the simulation, the drying rate was kept constant at $\nu = 48$.

RESULTS AND DISCUSSION

As previously stated, a first series of acrylic emulsions were prepared at different *VA*/*BuA* ratios and functionalized with 3% w. of AA. The main features of the obtained latexes are given in Table 2.

The characterization of the polymeric dispersions by QELS revealed that all of the latexes were monodispersed in size, $I < 1.1$. The particles with a higher content of BuA showed a smaller particle diameter and greater stability (i.e., lower percentages of precipitates) due to the relative high hydrophobicity of the BuA structural units in the polymer chains. In the case of the hydrophilic VA, they can form hydrosoluble chains that destabilize the colloids already formed. The VA in the system also produces another effect during particle nucleation;

TABLE 2 Main Features of the VA/BuA Copolymers Prepared by Semicontinuous Emulsion Polymerization (AA content = 3% w.)

VA/BuA (w./w.)	0/100	10/90	20/80	50/50	80/20	90/10	100/0
Solid content (% w.)	57.83	58.85	59.20	58.39	56.40	55.60	52.30
Dp_z (nm)	169	181	193	208	215	362	375
Viscosity (cps)	30	40	100	240	180	220	370
pH	4.29	4.78	4.60	4.02	4.30	4.50	4.05

a small number of water soluble and long oligomer chains are formed, and every chain acts as a precursor so that few seed particles are formed in the main reactor and therefore a large size of particle is obtained.

The experimental glass transition temperatures of the copolymers and those obtained by the Fox equation are reported in Figure 2. The presence of increased amounts of BuA resulted in a continuous decrement of the Tg values. As the Tg decreases the coating rigidity

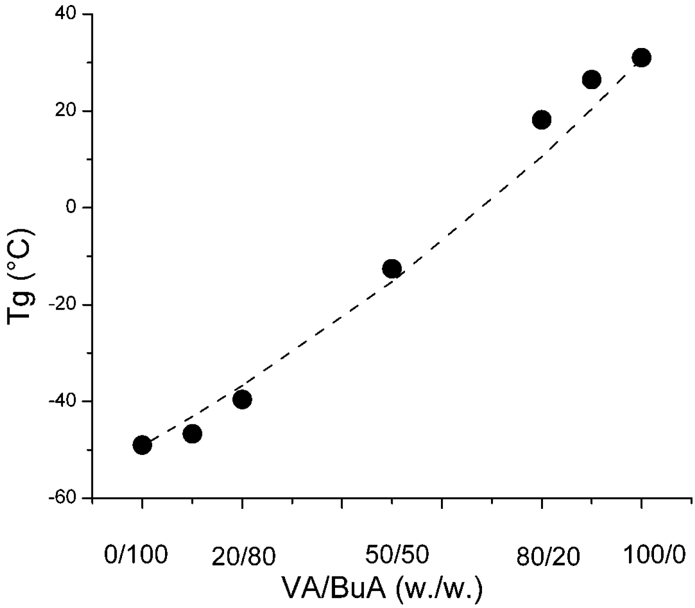

FIGURE 2 Glass transition temperature of latex particles made of VA/BuA copolymers functionalized with 3% w. of AA. The dashed line corresponds to the Fox equation calculations.

was also reduced, which possibly means an improvement in the adhesive properties. The glass transition temperatures determined displayed a good correlation with the values theoretically predicted by the Fox equation.

Different vinyl-acrylic coatings were prepared from dispersions of *VA/BuA* copolymers functionalized with AA. The adhesive properties as a function of the co-monomer ratio are summarized in Figures 3 and 4. In the case of tack, it was observed that a maximum was attained at a composition of $VA/BuA = 20/80$ w./w. However, a drastic fall in tack with the *VA/BuA* ratio was observed at higher VA contents. This behavior may be explained by considering that the tack, the condition of an adhesive when it feels sticky and sensitive to pressure, depends strongly on the interfacial contact between the PSA coating and the substrate. Consequently, the tack is determined by the structure and properties of the PSA film.

The simulation of the film formation process (Figure 5) of a vinyl-acrylic latex shows that the greater the polymer particle softness the greater the density of the first monolayer located over the substrate.

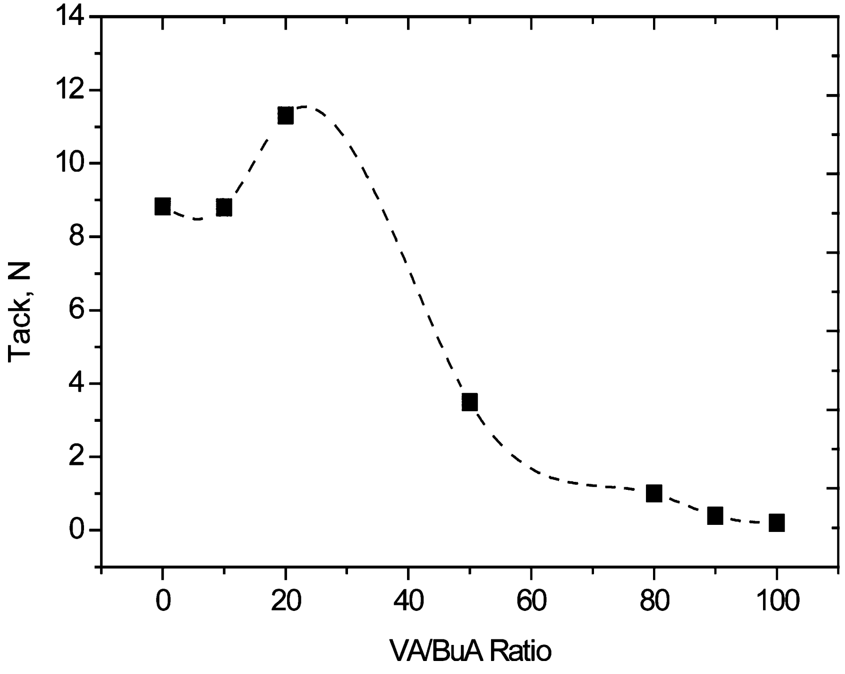

FIGURE 3 Determination of the tack adhesion as a function of the composition of VA/BuA copolymers functionalized with 3% of AA.

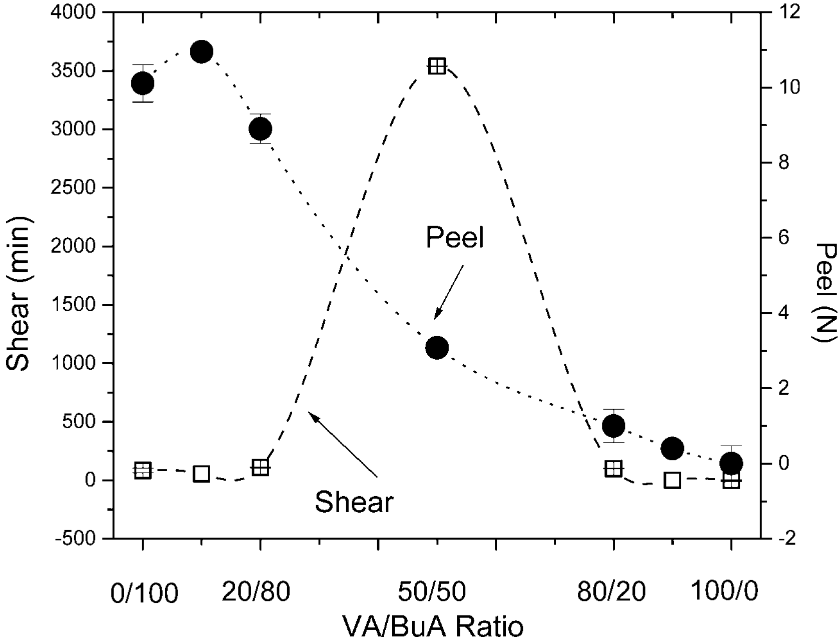

FIGURE 4 Determination of shear resistance and peel adhesion as a function of the composition of VA/BuA copolymers.

This monolayer density can be translated into a larger number of contact sites between the latex particles and the substrate when the copolymer is soft, for example, low VA content. Therefore, the high pressure sensitivity of the coatings with a low Tg copolymer is not only a consequence of the elastomeric features of the material but also it is the result of the formation of a dense monolayer of polymer particles with a low defect content. When the polymer particles become more rigid, the monolayer at the interface is formed with a reduced number of particles and the substrate–polymer contact is weaker. In the snapshots shown in Figure 5, it can be clearly observed that as the particles grow softer a denser and more structured monolayer is formed. The effect of a low Tg along with a dense monolayer formation may explain the improvement of the tack adhesion exhibited by the latexes with a relative high BuA (Figure 3).

An assessment of the PSAs revealed a contrasting behavior between the peel adhesion and shear resistance with polymer composition; the tack property behaved similarly to peel adhesion with polymer composition (Figure 3). The peel adhesion reached a maximum (Figure 4) at

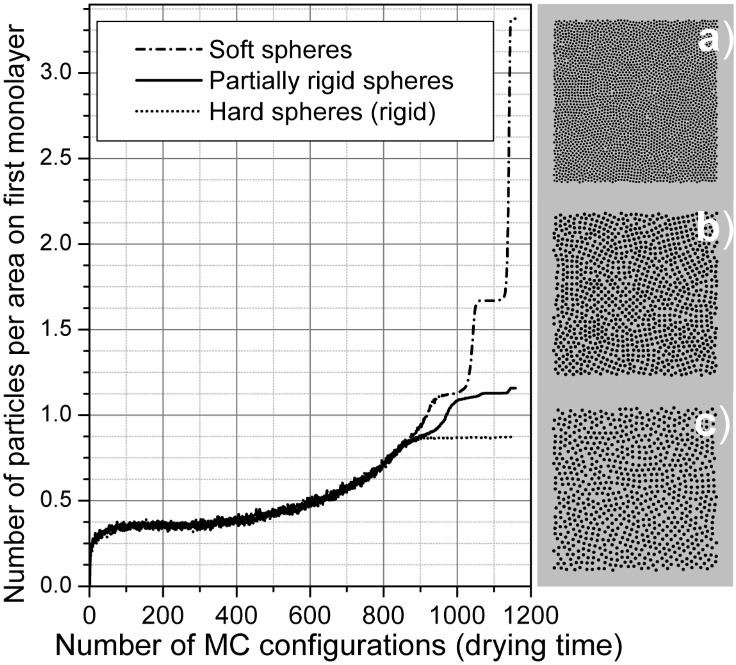

FIGURE 5 The adlayer particle density located over the substrate as a function of drying time (number of MC configurations). Snapshots of the monolayer for (a) soft particles (PBuA), (b) partially rigid particles (BuA/VA copolymers), and (c) hard particles (PVA).

a composition of $VA/BuA = 10/90$ w./w., followed by a considerable loss of adhesion at greater VA values. In contrast, the only good values of shear resistance were found at intermediate compositions of BuA (40–60% w.). A debonding mechanism of the testing tapes was observed at this intermediate composition and a decohesion mechanism in the other cases.

From the density profiles of polymer films determined by the MC simulations (Figure 6), it can be observed that well-ordered layers were achieved with partially soft particles. In the case of rigid particles the structure of the film may become poorly structured, as seen by the broad density distribution observed. It is interesting to note that, with the same number of particles in the simulation box (solid content), the structure of the film can be modified just by changing the particle softness. For soft spheres only one layer is obtained due to better packing; for partially rigid spheres two layers are formed

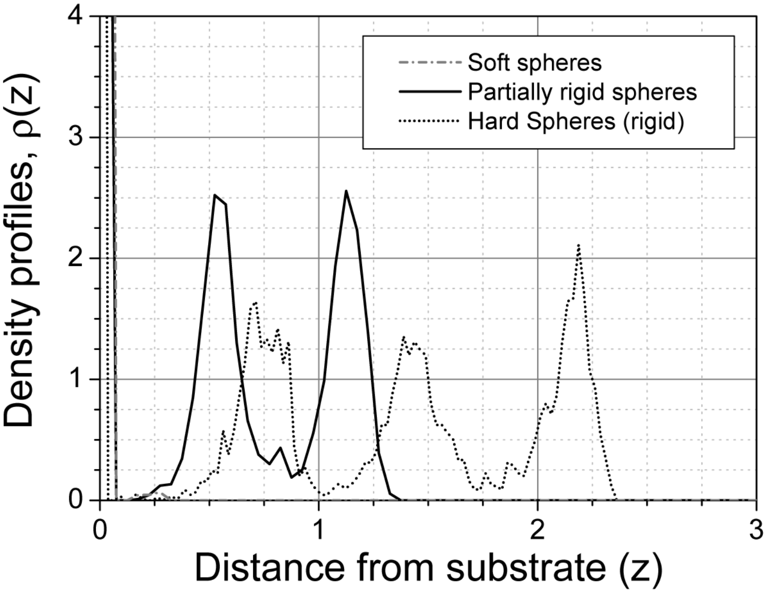

FIGURE 6 Density profiles of final films at different particle softness. Soft spheres form only one high density layer over the substrate.

because not all particles can be introduced into the adlayer (monolayer formed directly on the substrate). These layers are highly structured when compared with the case of rigid particles. In the case of hard-spheres (rigid polymer particles) three layers are formed, the film then becomes thicker than before, so these layers have a poor structure and relatively low adhesive properties.

The maximum value of shear is obtained with partially rigid spheres because the film can dissipate the shear stress in the highly structured layers formed. In the case of the peel failure, it is the result of a debonding mechanism and depends especially on the number of particle–substrate contacts, which in turns is a function of the final adlayer density that can be observed in Figures 5 and 6.

The content of AA was varied from 0 to 3% w. in a second series of vinyl-acrylic latex. In this case, the VA/BuA ratio was of 10/90 w./w. It was observed that there was a considerable reduction of the average particle size with functionalization (Table 3), due to the saturation of particle surface with charged groups. This shrinking effect has also been observed in three-dimensional polymer networks [26–27]. The QELS measurements revealed that all of the latexes were monodispersed in size. The characterization of the VA/BuA copolymers

TABLE 3 Main Features of the VA/BuA Copolymers Functionalized with Different AA Contents (VA/BuA ratio = 10/90 w./w.)

AA (% w.)	0	1	2	3
S. C. (% w.)	60.1	59.74	59.2	58.85
Dp_z (nm)	262	226	211	181
Tg (°C)	−40.45	−37.05	−36.87	−32.69

showed an increase of the Tg with the number of AA groups in the macromolecular chains, as expected.

The effect of functionalization with polar groups (AA) on the tack, peel, and shear strength of the vinyl-acrylic coatings was also studied (Figures 7 and 8). When the tack of the coated tapes was measured, a continuous decrease with the number of AA groups was found (Figure 7). However, the functionalization produced an opposite behavior of the shear strength; there was a continuous improvement of this property when the content of AA was increased in the latex particles.

A transition from debonding to decohesion was observed in the coatings tapes when peel adhesion was evaluated. Figure 8 displays two

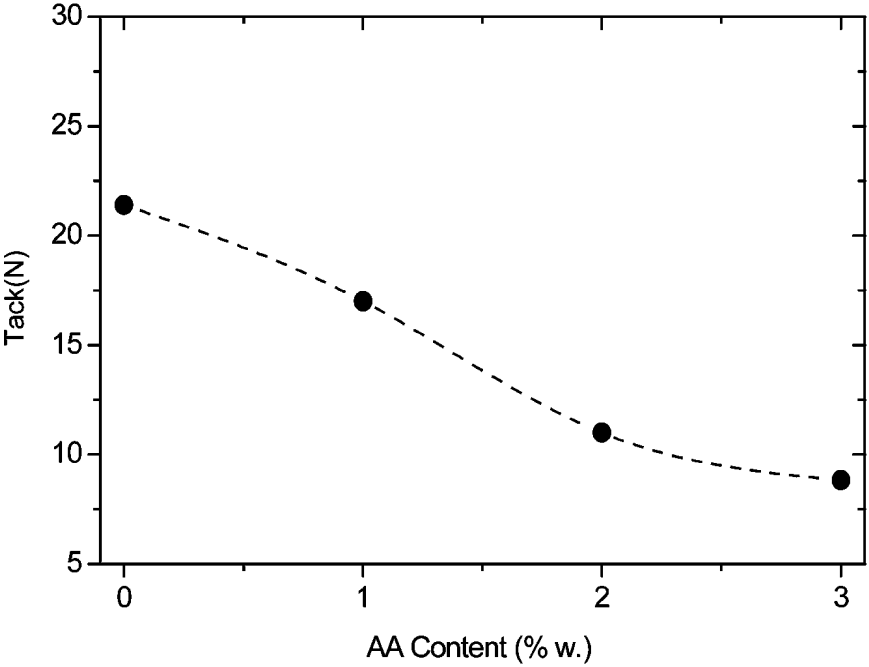

FIGURE 7 Tack assessment of functionalized particles as a function of the AA content, VA/BuA 10/90 w./w.

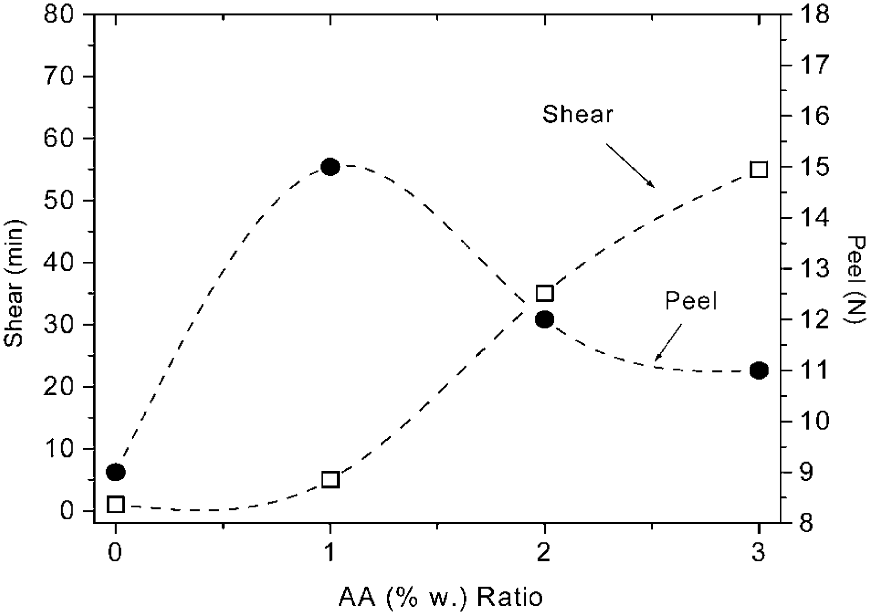

FIGURE 8 Shear and peel assessment of functionalized latex particles as a function of the [AA], (VA/BuA: 10/90 w./w.).

well-defined zones: in the first an increase of peel adhesion is observed and a maximum is then reached; this failure was characterized by a debonding mechanism. In the second, a decrease in peeling is displayed as this failure obeys a typical decohesion mechanism.

CONCLUSIONS

Coatings of latex particles with a pre-defined diameter were synthesized by emulsion polymerization of *VA*/*BuA* in the presence of AA. This procedure may lead to latexes with a balance between the tack and peel conferred by the BuA and the shear resistance provided by the VA.

The coatings rich in BuA (i.e., 70–80%) formed dense structured monolayers, so that these coatings exhibited higher values of tack and peel adhesion than those rich in VA. A slight functionalization of the latex particles (90% BuA) with AA (1% w.) improved the peel and shear strength, an effect attributable to surface particle saturation with charged groups. The films formed at intermediate *BuA*/*VA* ratios displayed the highest shear resistance, but moderate tack and peel adhesion, probably because of the improved film structured monolayer but higher rigidity provided by the VA.

The Monte Carlo simulation describes the film forming process, which qualitatively explains the adhesive properties of the latex particle coatings. The proper selection of the parameters of the simulated model may suggest the experimental conditions to obtain latex dispersions with a suitable copolymer composition with useful adhesive properties.

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