Synthesis and Characterization of Water-Borne Adhesives Based on 2-Ethylhexylacrylate-butylacrylate Copolymers Functionalized with Acrylic Acid

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A series of copolymers, based on 2-ethylhexylacrylate (2-EHA) and butylacrylate (BuA), and functionalized with small amounts of acrylic acid (AA) were synthesized by emulsion polymerization techniques and monodisperse latexes were obtained. Their average particle size and particle size distribution were determined by quasi-elastic light scattering and confirmed by transmission electron microscopy. The change in the adhesive properties (peel, shear, and tack) as a function of 2-EHA/BuA ratio was studied. An optimal balance between these three properties was determined at a 2-EHA/BuA ratio 10/90 wt/wt. The influence of the functionalization of these copolymers with AA was also evaluated when the comonomers ratio was kept constant. Good results were found at an AA content of 1 wt%.

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are viscoelastic-elastomeric materials that develop significant adhesion upon contact with a solid

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surface without requiring a chemical reaction [1]. Several general articles have been written addressing the unique properties of these materials [2–3]. These adhesives play an important role in everyday use and their market is still growing as new applications are continually being discovered [4]. Commercial use of PSAs covers a broad range of label, tape, medical, and cosmetic products [5]. These materials are based on polymers with glass transition temperatures between -40 and $-50°$C, and are commonly copolymers of acrylic monomers such as 2-ethylhexylacrylate (2-EHA) or butylacrylate (BuA) [6]. In fact, the performance of an acrylic PSA could be adjusted, changing the selection of monomers at specific ratios [7].

On the other hand, growing environmental pressures and more stringent environmental regulations has made solvent-borne acrylic PSAs less attractive [8–9]. In addition, the high cost of solvent-borne acrylic PSAs coupled with the requirements of solvent recovery considerably increase the product cost [10]. This economic disadvantage has stimulated the development of new water-borne PSAs, based on aqueous polymer emulsions [11]. These dispersions can be conveniently prepared by emulsion polymerization techniques [12–15].

In the present investigation, a series of *2-EHA/BuA* copolymers functionalized with acrylic acid (AA) were prepared by semicontinuous emulsion polymerization. This synthesis process was used in order to obtain latexes with a narrow particle size distribution and pre-defined average particle size. The influence of the *2-EHA/BuA* ratio and AA content on the adhesive properties was studied.

EXPERIMENTAL

Synthesis of the Acrylic Emulsions

The monomers, 2-ethylhexylacrylate (2-EHA), butylacrylate (BuA), and acrylic acid (AA), stabilized with 45 ppm of MEHQ, were purchased from Celanese, Mexico and used as received (the inhibitor agent was eliminated with an excess of initiator, $NH_4S_2O_8$, ammonium persulphate from Aldrich). The emulsions were stabilized with ABEX-26-S, a non-ionic aromatic surfactant furnished by Rhodia. The dispersion medium during the synthesis was distilled and deionized water. An important factor, which plays a substantial role in the performance of the PSAs, is the polymer molecular weight. In order to avoid the formation of polymer chains with too high molecular weight, small amounts of a transfer agent, t-dodecylmercaptan (Aldrich), were introduced into the system. A series of copolymers, with different *2-EHA/BuA* ratios (100/0, 90/10, 80/20, 50/50, 20/80, 10/90, and 0/100 wt/wt) and functionalized with 3 wt% AA were prepared. All syntheses were performed using a semicontinuous

TABLE 1 Composition of Acrylic Emulsions Synthesized by Semicontinuous Emulsion Polymerization

Main reactor	$NH_4S_2O_8$ aqueous solution (9.6 wt%)	14.6 g
	Deionized water	290.0 g
Feed tank 1 (pre-emulsion)	Monomers	660.0 g
	Transfer agent	0.6 g
	Surfactant aqueous solution (12 wt%)	170.0 g
Feed tank 2	$NH_4S_2O_8$ aqueous solution (0.7 wt%)	50.0 g

device, with a main glass reactor and two feed tanks. A general formulation of the acrylic emulsions is shown in Table 1.

An inert atmosphere in the main reactor during polymerization was ensured by a continuous flow of N_2. All the reactions were performed at 80°C. The pre-emulsion and initiator solution were fed into the reactor for a period of three hours, in order to avoid a monomer accumulation (starved feed conditions). Once the addition was completed, the temperature was raised to 90°C for one hour.

An additional series of acrylic particles functionalized with 1 and 2 wt% acrylic acid were prepared following the previously described method of synthesis.

Characterization of Acrylic Emulsions

The final solid content of the acrylic emulsions was determined by conventional gravimetry technique. The z average diameter and particle size distribution of the prepared latex particles were determined by quasi-elastic light scattering (QELS) technique using a Coulter LS-230 nanosizer. The data of the particle size distribution were employed to calculate the average particle size function (Dp_z) and the polydispersity index I [16]. These functions are defined as:

$$Dp_n = \frac{\sum_i n_i Dp_i}{\sum_i n_i}$$

$$Dp_w = \frac{\sum_i n_i Dp_i^2}{\sum_i n_i Dp_i}$$

$$Dp_z = \frac{\sum_i n_i Dp_i^3}{\sum_i n_i Dp_i^2}$$

$$\text{and } I = Dp_w \Big/ Dp_n$$

where n_i is the number of particles with a size Dp_i.

The latex samples were stained with osmium tetroxide and observed by transmission electron microscopy (TEM) with a JEOL JEM-100 CX microscope. The glass transition temperatures of the acrylic adhesives were determined by scanning differential calorimetry (DSC) with a Perkin Elmer DSC-7 calorimeter.

Preparation and Testing of Adhesive Tapes

The preparation and testing of adhesive bonds were carried out in accordance with standard industrial test procedures [17–20]. The acrylic latexes were coated onto six tapes (DuPont Mylar® type 200 A, 2 mm thick) using a No. 22 K-bar and dried in two steps, first at room temperature for 15–20 min in a fume hood and second at 130°C for 3 min. The coatings then were used to determine peel adhesion, tack, and shear resistance as follows. Adhesive bonds were formed by rolling a standard 4.5 pound roller across the bonded area five times. All adhesive testing was performed at $20 \pm 1°C$ and relative humidity $50 \pm 5\%$.

The 180° peel adhesion was measured, after 20 min contact time, as the force per unit width required to peel a 1 inch wide strip of the coated Mylar from a steel plate at an angle of 180° using a cross-head displacement rate of 12 inches/min, on a Syntech Instrument.

Shear holding power was measured as the time taken to complete failure of an overlap bond (1×1 inch contact area) between the coated Mylar and a stainless steel panel (held parallel to the vertical) under a static shear force applied by suspending a 0.5 kg weight from the coated Mylar after 15 min contact time.

For the loop tack test, a series of strips ($2.5 \, cm \times 15 \, cm$) were die cut from the PSA-coated Mylar film. The strips were folded to form loops where on each ends, $2.5 \times 2.5 \, cm$. Paper was used to cover $2.5 \times 2.5 \, cm$. area. Glass of $2.5 \times 5.0 \, cm$ was mounted on the lower grip of the tensile tester and the loop was mounted on the upper grip. The upper grip holding the loop was brought in contact with the substrate using 30 cm/min downward crosshead speed until the distance between the grip and the substrate reached 5.0 cm making a contact area of $2.5 \times 2.5 \, cm$. After 1 s contact, the upper grip would be brought upward at 30 cm/min crosshead speed until detachment occurred. The maximum force of detachment was recorded as loop tack.

RESULTS AND DISCUSSION

The first series of acrylic emulsions were prepared at different *2-EHA/BuA* wt ratios. All these copolymers were functionalized with

TABLE 2 Main Features of *2-EHA/BuA* Copolymers Prepared by Semicontinuous Emulsion Polymerization (AA Content = 3 wt%)

2-EHA/BuA(wt/wt)	0/100	10/90	20/80	50/50	80/20	90/10	100/0
S.C. (wt%)	57.8	57.04	58.2	61.7	60.8	58.44	60.4
Dp_z (nm)	170	196	210	229	225	217	222
Tg (°C)	−39.2	−40.2	−43.6	−46.3	−48.2	−49.6	−60.8

3% wt AA. The main features of the latexes obtained are given in Table 2.

The QELS characterization of the polymeric dispersions revealed that the polydispersity index, I, was lower than 1.1 in all cases, which means that all particle size distributions may be considered as monodisperse (average particle size determination (Dp_z) and the high monodispersity were confirmed by TEM). A micrograph of one of the synthesized latexes and its particle size distribution obtained by QELS are shown in Figures 1a and b, respectively.

The results obtained from the *2-EHA/BuA* study of copolymers coated onto Mylar are given in Figures 2 and 3. It can be seen that first there is a decrease in loop tack with the 2-EHA content until it reaches a minimum (at 2-EHA content of 50 wt%). An increase in tack is observed with BuA contents higher than 50 wt% (see Figure 4).

Peel strength curve revealed an opposite dependence on the system composition as presented in Figure 5. Indeed, the polymers rich in 2-EHA showed high values of peel strength, with a maximum for the composition with a 2-EHA/BuA ratio = 50/50 wt/wt (the materials with a large 2-EHA content showed relatively high peel values, with a minimum of the function at a 2-EHA/BuA ratio = 90/10 wt/wt). On the other hand, a continuous diminution of the shear strength with the 2-EHA content was found. In fact, a transition from a debonding mechanism to a decohesion mechanism was observed at a 2-EHA/BuA ratio = 50/50 wt/wt. This change of the separation mode may be explained in terms of the film forming process. Indeed, the introduction in the polymer chains of a greater number of BuA structural units makes the polymer more rigid, with a loss of tack and an increment of peel. However, the interdiffusion of the chains at the particle–particle interface is also more difficult, because of the decrease of the mobility. At BuA contents great 50%wt, the interfacial adhesion between the particles decreases and the film shows a considerable number of defects, which promotes the development of fractures and the material decohesion. This decohesion produces also a complete loss of shear strength.
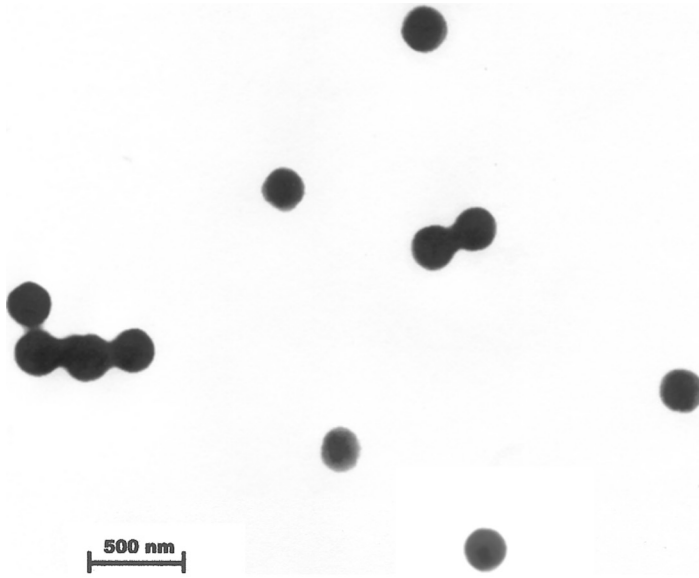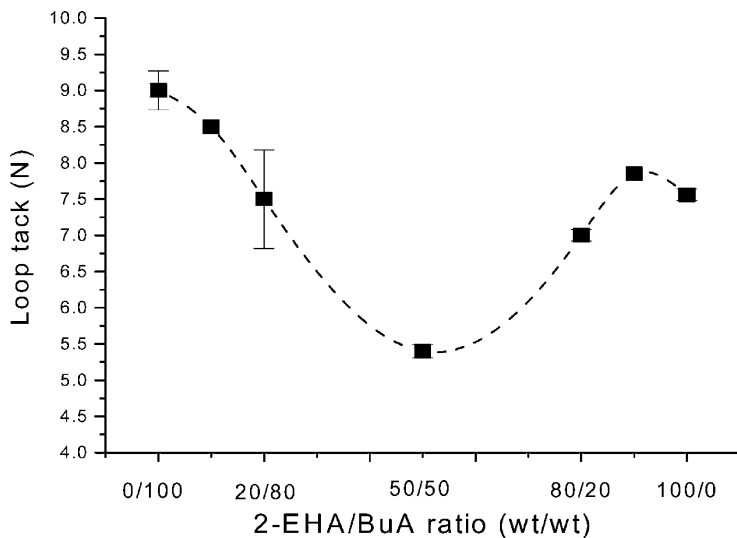
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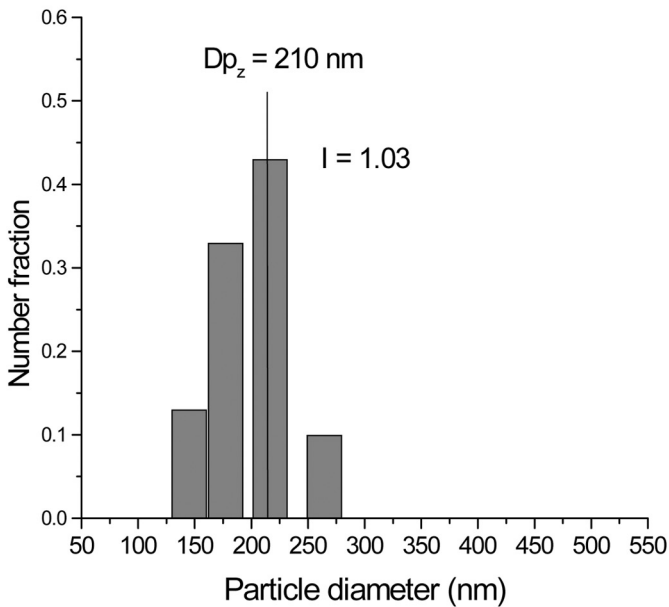
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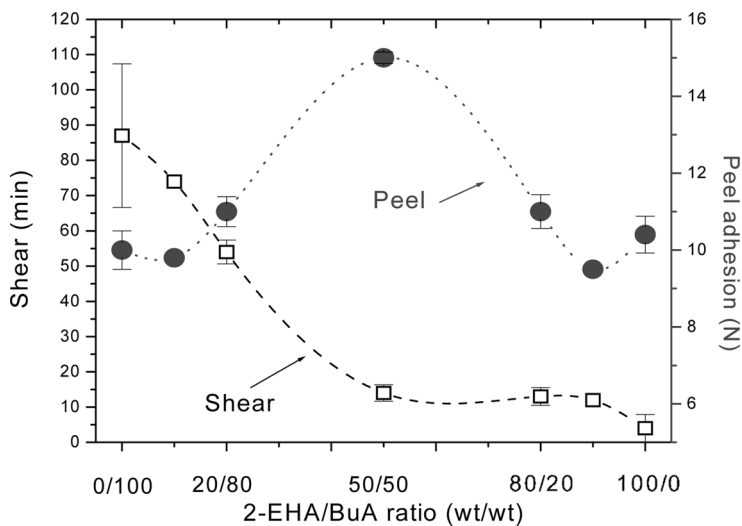**FIGURE 1** a. Transmission Electron Micrograph, b. Particle Size Distribution from QELS measurements of latex particles with a composition 2-EHA/BuA: 50/50 wt/wt and functionalized with 3 wt% of AA.

FIGURE 2 Loop tack as a function of the composition of 2-EHA/BuA copolymers functionalized with 3 wt% AA.

FIGURE 3 Shear and Peel adhesion as a function of the composition of 2-EHA/BuA copolymers.

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TABLE 3 Main Features of *2-EHA/BuA* Copolymers Functionalized with Different AA Contents (*2-EHA/BuA* ratio = 10/90 wt/wt)

| AA (wt%)	0	1	2	3
S.C. (wt%)	60.10	61.69	58.90	57.04
Dp_z (nm)	280	239	230	196
Tg (°C)	−55.2	−52.7	−49.6	−40.2

In consequence, the analysis of all this data indicates that an adhesive with a 2-EHA/BuA = 10/90 wt/wt composition presents a good balance between tack, shear, and peel.

It is well known that the performance of PSAs based on acrylic polymers can be sensibly improved by adding certain amounts of AA. In order to study the influence of the particle functionalization with AA on the adhesion properties, a series of particles with a constant monomer ratio 2-EHA/BuA: 10/90 wt/wt and small functionalizations were prepared. A slight decrease of average particle size with the percentage of AA was observed (see Table 3). It may be explained in terms of shrinking of the functionalized chains in the particle, due to a charge reaccommodation on the particle surface. The polydispersity index of the samples was always near I = 1 (monodisperse systems). All latexes exhibited high colloidal stability and high values of solid content.

The assessment of the acrylic materials functionalized with small amounts of AA revealed a tendency for tack reduction with the slight functionalization.

On the other hand, a clearer change of the shear strength with the functionalization was observed when this property was evaluated; a continuous increment of the shear strength was obtained when small amounts of AA were introduced into the polymer chains. However, the same functionalization produced an opposite change in the case of the peel. The fall of this property was not so great at an AA content of 1% w, but a more drastic loss of peel strength was detected at functionalizations with AA of 2 and 3% w. Consequently, good values of tack and shear without a sensible fall of peel strength may be obtained in BuA-2-EHA copolymers with a slight functionalization with AA of 1% w.

These results may be explained considering that a greater hydrophilicity of the particles is obtained when the number of acrylic acid groups that are introduced into the polymer particles is increased. This parameter favors the permanence of the latex particles in the water and makes more difficult the formation of cohesive films [21]. Indeed, a greater number of defects is obtained and there is a diminution of the tack and peel strength. However, the increment of the
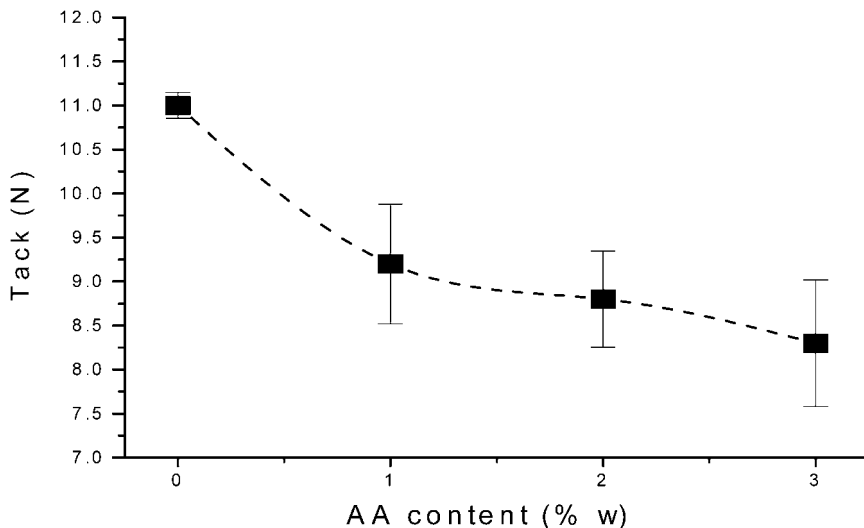
FIGURE 4 Tack of functionalized particles as a function of the [AA], 2-EHA/BuA: 10/90 wt/wt copolymers.
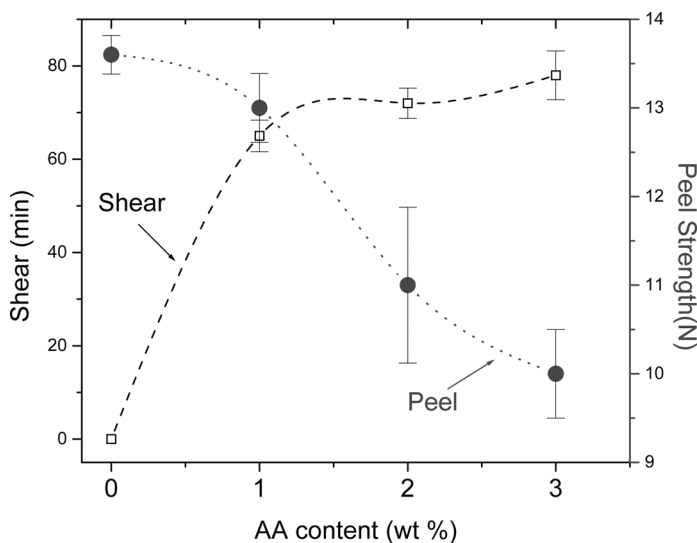
FIGURE 5 Shear and peel strengths of functionalized latex particles as a function of [AA], (2-EHA/BuA: 10/90 wt/wt) copolymers.

number of polar groups tied to the chains which constitute the particles, make the material more rigid and the shear strength is increased.

CONCLUSIONS

A series of water-borne adhesives based on 2-ethylhexylacrylate-butylacrylate copolymers functionalized with acrylic acid were prepared by semicontinuous emulsion polymerization. The QELS characterization of the obtained dispersions showed that they were monodispersed. The measurements of the tack, peel, and shear properties as a function of the EHA/BuA ratio in the particles revealed an optimal balance between the adhesion properties at a BuA content of 90 wt%. However, it was observed that the tack and shear could be improved without a drastic prop in peel strength when the functionalization of the particles with AA was done at 1 wt%. All these results must be interpreted not only in terms of the chemical composition of the polymer chains, but also considering the film formation mechanisms, which depends strongly on the hydrophilicity and particle size.

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