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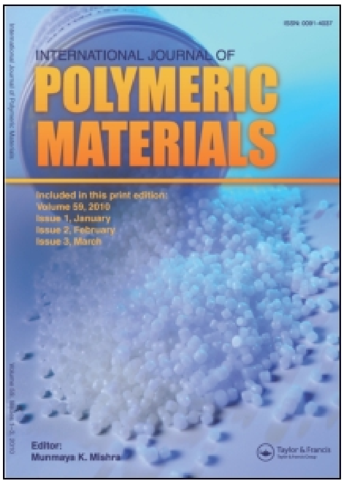

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Pressure-Sensitive Adhesives Based on Nanostructured Latex Particles

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Pressure-Sensitive Adhesives Based on Nanostructured Latex Particles

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Conceivably, when a polymer with two opposite properties is required, two different monomers may chemically be combined by a simple copolymerization reaction. One of the commonest techniques is to synthesize copolymers by an emulsion polymerization. The homogeneous particles obtained by this method simply show a balance between the individual properties of the homopolymers. In contrast, two-stage emulsion polymerization affords simultaneously an improvement of both opposing properties (synergy). In order to study the influence of particle structure on adhesion properties, a series of nanostructured particles based on a copolymer of vinyl acetate and butylacrylate P(VA-co-BuA) and polybutylacrylate (PBuA) were synthesized by semicontinuous emulsion polymerization. The particle size and P(VA-co-BuA)/P(BuA) ratio were varied. The obtained dispersions were characterized by quasi-elastic light scattering. The adhesion properties (tack, peel, and shear strength) of the particles were evaluated according to industrial methods. It was found that improved values of peel and tack were obtained when a P(VA-co-BuA) rigid core was enveloped with a thin shell made of PBuA. A strong influence of the particle size and PBuA content on the adhesion properties was detected. The best performance was found at large particle sizes and thick shells.

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Keywords: pressure-sensitive adhesives (PSAs), vinyl acetate (VA), butyl acrylate (BuA), core-shell particles

INTRODUCTION

The restrictive environmental regulations concerning volatile organic compounds (VOCs) have made solvent-borne pressure-sensitive adhesives (PSAs) unattractive [1–2]. In addition, the high cost of solvent-borne PSAs coupled with the requirements of solvent recovery considerably increases the product cost [3]. These environmental and economic disadvantages have stimulated the development of new water-borne PSAs [4], which can be conveniently prepared by emulsion polymerization [5–8]. The final product of such kinds of polymerization is an aqueous dispersion of spherical particles named latex.

Emulsion polymerization may also be employed for combining the opposite properties of two different polymers by simple copolymerization of their monomers. The homogeneous particles prepared by this way show an average between the individual properties of the homopolymers. In contrast, a more sophisticated technique, called two-stage emulsion polymerization, allows obtaining simultaneously an improvement of both opposite properties [9]. This process consists of the polymerization in a semicontinuous reactor of particles made of a first polymer. Subsequently, the particles are used as reactive sites for the polymerization of a second monomer. The composite particles prepared by this technique may exhibit a great number of morphologies such as homogeneous interpenetrated, moonlike, raspberry, sandwich, and so on [9] (see Figure 1). However, the morphology that has found the greatest number of industrial applications is that called core-shell. Core-shell particles made of a rigid core enveloped by a sticky soft shell have been used recently as high-performance PSAs.

A study of the adhesion properties of composite particles based on a copolymer of vinyl acetate and butylacrylate and polybutylacrylate is presented in this work. A semicontinuous process for obtaining highly monodisperse particles with a pre-defined size was first developed. Three rigid cores of poly(vinyl acetate-co-butyl acrylate), P(VA-co-BuA), of different diameters were synthesized by this way. Afterward, the cores were enveloped by different amounts of polybutylacrylate (PBuA). The average particle diameters were measured by Quasi-Elastic Light Scattering (QELS). The adhesive properties (tack, peel, and shear) were evaluated and reported as a function of the P(VA-co-BuA)/PBuA ratio and particle size.

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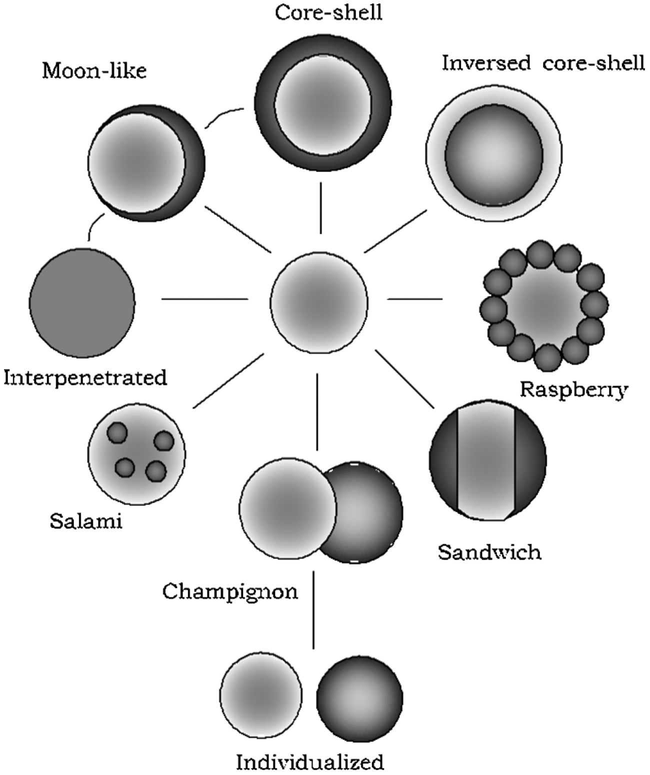

FIGURE 1 Morphologies of nanostructured latex particles of two polymers.

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MATERIALS AND METHODS

Materials

Technical grade vinyl acetate and n-butyl acrylate monomers (Celanese) were used as received. These chemicals were stabilized with hydroquinone monomethyl ether (50 and 15 ppm, respectively). The emulsifier system consisted of a non-ionic aromatic surfactant ABEX-26-S (Rhodia). The initiator was sodium persulphate ($NH_4S_2O_8$, Aldrich) of analytical grade, which was employed without further purification. Distilled water was employed throughout the experimental work.

Synthesis of Monodisperse Latex Particles

A first series of homogeneous polymer particles of different average particle size were prepared by semicontinuous emulsion polymerization in order to study the influence of the amount of surfactant contained in the main reactor on the final particle size. A general formulation is given in Figure 2. The monomer ratio employed in the reactions were VA (85% w.) and BuA (15% w.). The emulsion polymerizations were carried out in a semicontinuous reactor composed of a glass container of 1 L of capacity, maintained at 72 ± 1°C with a water bath, and two feeding tanks. The reactor was equipped with a reflux condenser, a stirrer (two-blade propeller), and a thermocouple. The agitation speed was mantained at 250 rpm. All reactions were made in an inert atmosphere using nitrogen. At the onset of the polymerization, the monomer and initiator in the main reactor were were left to react during 15 min, in order to form seed particles. These minuscule particles will act as reaction sites during the polymerization. Afterward, the pre-emulsion and initiator solution were added into the main reactor over a time period of three h; this way starved feed conditions were assured along the polymerization.

At the end of the monomer addition, the temperature was raised from 72 to 85°C for 1 h to complete the polymerization reaction.

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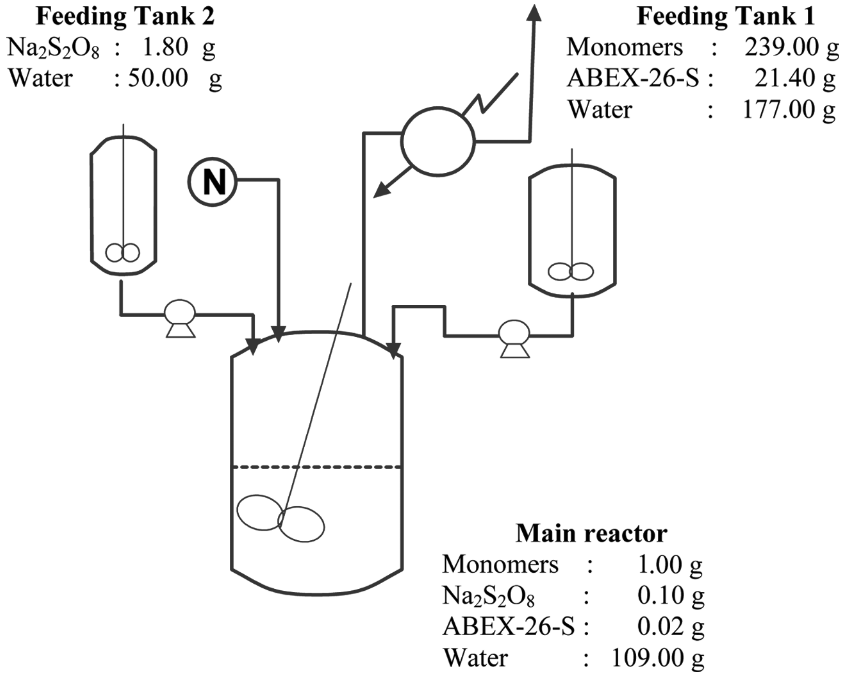

FIGURE 2 Scheme of semicontinuous reactor and general formulation for emulsion polymerization.

Composite latex particles were prepared by two-step emulsion polymerization in accord to the formulation mentioned earlier, employing pure BuA as monomer. The temperature and feeding rate were the same as those of the synthesis of homogeneous particles.

Characterization of the Vinyl Acrylic Emulsions

The solid content was measured gravimetrically. The 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 z average diameter of latex particles, Dp_z, as well as the polydispersity index, I [10].

Preparation and Testing of Adhesive Tapes

The adhesive tapes were prepared and assessed following a series of standard and industrial control methods [11–19]. Six PET tapes (Dupont Mylar® type 200 A, 2 mm thick) were coated with the dispersions using a K-22 bar and dried first at room temperature for 15–20 min in a fume hood and then at 130°C for 3 min. The coating obtained was within 20–22 g/m^2. A release liner (silicone coated James River Sticknot SN462) allowed to handle the sample and avoid sticking. The peel, shear, and tack properties were assessed with a mechanical tester Sintech M181730 at constant temperature (20 ± 1°C) and relative humidity of 50 ± 5%.

The adhesive strength of the adhesives was evaluated with a 180° peel adhesion test, performed at a crosshead rate of 30.5 cm/min. An 18 N roller was used to apply the polymer samples onto the PET standard substrate.

A 90°-tack test was used to measure the tack measurements. The tape removing was performed at a crosshead speed of 30.5 cm/min.

The shear adhesion test allowed measuring the cohesive strength of the different nanostructured coatings. For this test, the sample was subjected to a standard load so that a constant stress was applied parallel to the sample surface. The shear adhesion test was evaluated from the time required for the bond to fail.

RESULTS AND DISSCUSION

Synthesis of Homogeneous Latex Particles

A series of P(V-co-BuA) latex particles were synthesized by semicontinuous emulsion polymerization. All the dispersions were stable

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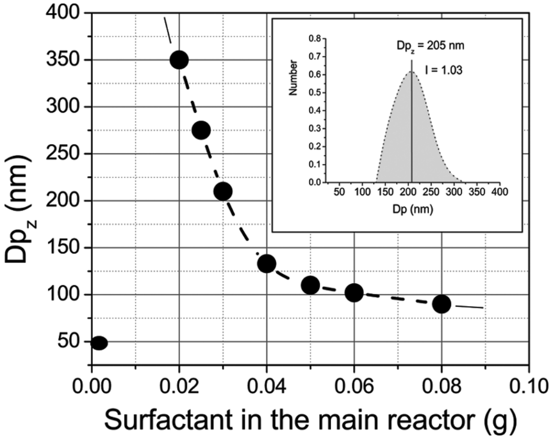

FIGURE 3 Average particle size of poly(vinyl acetate-co-butyl acrylate) particles prepared by semicontinuous emulsion polymerization as a function of the surfactant content in the main reactor. Insert: Example of particle size distribution measured by QELS.

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and their solid content was near 40% w. The average particle size (Dp_z) of the latexes measured by QELS is reported in Figure 3. Decreasing of particle diameter as surfactant content increases in the main reactor is a common behavior because more surfactant is added to the system, more micelles are formed allowing more particles to nucleate, resulting in smaller size. It was also found that a minimum particle size, $Dp_z = 50\,nm$ was reached when no surfactant and no monomer were introduced into the main reactor before the pre-emulsion addition (non-seeded polymerization). In this case, the nucleation of the polymer particles is similar to that of the greater amount of surfactant employed in this study, that is, large amounts of surfactant produce a lot of micelles in which the polymerization takes place.

The QELS characterization revealed also that the polydispersity index of all the latexes was lower than 1.10 (high monodispersity). The insert in Figure 1 shows a typical particle size distribution measured by light scattering.

Synthesis of Two Stages Particles

Three P(VA-co-BuA) cores ($Dp_z = 50$, 205, and 280 nm) were enveloped with different thicknesses of PBuA. By this way three series of composite particles, with different compositions (P(VA-co-BuA)/PBuA: 100/25, 100/50, 100/75, and 100/100 w./w.) were synthesized. QELS

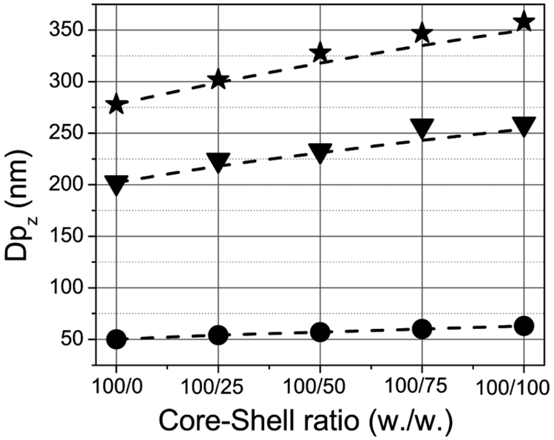

FIGURE 4 Growth of composite latex particles as a function of the poly (VA-co-BuA)/PBuA ratio. Three copolymer cores ($Dp_z = 50$, 205, and 280 nm) were employed as polymerization site for BuA.

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measurements allowed determining the particle growth as a function of the PBuA content, as shown in Figure 4. All the latex particles were highly monodisperse in size, which confirms that there was no formation of new polymer particles because of a secondary nucleation. This also constitutes evidence that the reactor really operates under starved feed conditions.

Adhesive Properties

The objective in preparing the composite latex series was to investigate the influence of the polymer composition and particle size on the adhesive performance of vinyl-acrylic PSAs. The adhesive results for these materials are summarized in Figures 5–7. It is apparent that there is a strong influence of the particle size on the adhesive behavior of PSAs.

The tack is the ability of adhesive agents to form bonds instantaneously, so the interfacial area is very important in this parameter. Small composite particles showed a continuous augmentation of the tack when the BuA content was increased. This could be attributed to the great interfacial area of the smaller particles, even at high values of PBuA added. A similar, but not so pronounced behavior, was observed when the tack adhesion was measured for different composite ratios: the greater the PBuA content, the greater the tack adhesion. Particles with $Dp_z = 280$ nm have minor interfacial area,

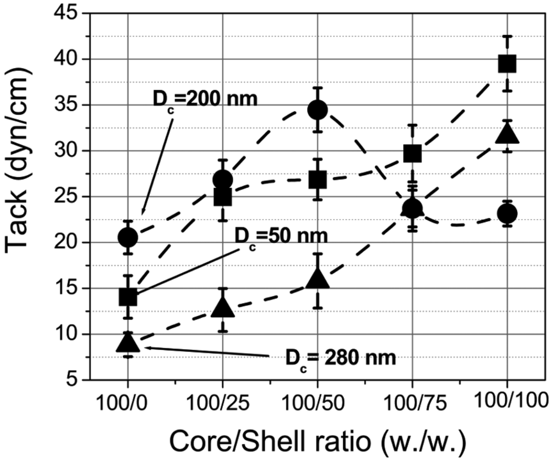

FIGURE 5 Tack as a function of the P(VA-co-BuA)/PBuA ratio for three different core diameters.

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so the tack is always lower than that of small particles. However, a completely different behavior was observed for intermediate diameters. Indeed, in the case of composite particles obtained from 200 nm cores, an increase of the tack was observed until it reaches a maximum at a PBuA content of 50% related to the original core. However, larger amounts of BuA polymerized on the particles produced a

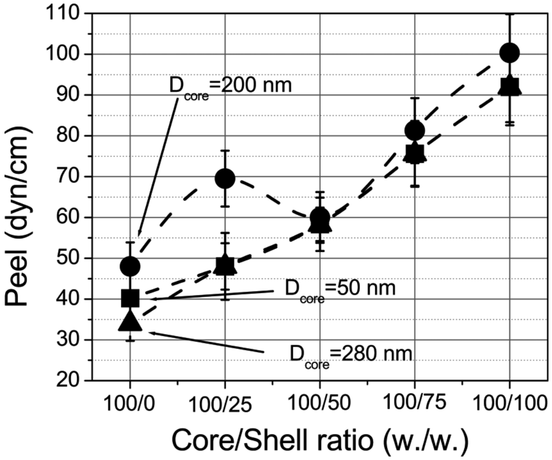

FIGURE 6 Peel adhesion as a function of the P(VA-co-BuA)/PBuA ratio for three different core diameters.

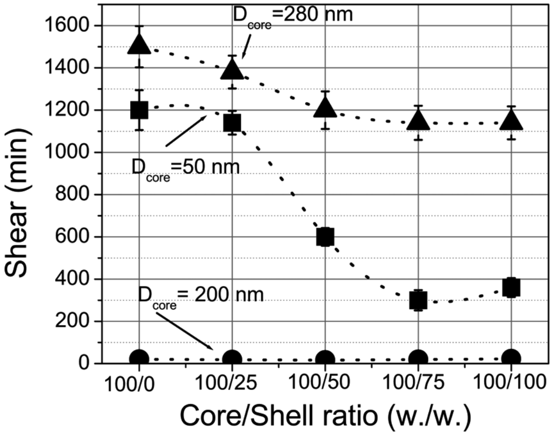

FIGURE 7 Shear resistance as a function of the P(VA-co-BuA)/PBuA ratio for three different core diameters.

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drastic fall of the pressure sensitivity until it feel back to the tack value of the unmodified vinyl-acrylic core.

The measurements of peel adhesion showed a similar dependence of the functional property on the particle composition. In general, it was observed that the larger the PBuA content, the greater the peel adhesion. In this case, it is very difficult to establish a trend, because at high PBuA the experimental error blurrs the results.

The most drastic dependence of the application property on the particle size was detected in the case of shear resistance. Particles with an intermediate size exhibited a complete loss of shear resistance. In contrast, small particles showed a decrease of shear when the soft polymer content was augmented. A similar behavior was detected for large size particles, but with higher values of the adhesion property. This behavior may be attributed to the viscoelastic properties of PBuA. The adhesive film can be considered as copolymer particles P(VA-co-BuA) embedded in a matrix of PBuA. Increasing the PBuA amount increases the volume of the matrix, so small particles cannot dissipate the stress at the interface of the composite particles. On the other hand, big particles are closer to one another, therefore the stress is distributed by the interface of the particles.

CONCLUSIONS

A process to synthesize taylor-made latex particles based on VA and BuA by semicontinuous emulsion polymerization was developed. The final particle diameter can be adjusted by the initial surfactant content of the aqueous dispersion of monomer in the principal reactor. The high monodispersity of the dispersed particles obtained from QELS data allowed confirming that the reactor operates under monomer starved conditions during the polymerization.

This process was adapted for preparing nanostructured latex particles by two-stage emulsion polymerization. The first stage consisted of a rigid core made of P(VA-co-PBuA). Once prepared, the vinyl-acrylic cores were enveloped with a shell of PBuA in order to increase the pressure sensitivity of the rigid core. A series of PSAs were prepared from cores of three different diameters.

A strong influence of the particle diameter on the three adhesive properties was clearly observed. In spite of a good performance of the intermediate size particles coated with small amounts of PBuA, the best combination of tack, peel, and shear was detected with large size particles enriched with great amounts of PBuA. This complex behavior may be the consequence of the interfacial area of particles and the viscoelastic properties of the PBuA matrix.

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