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Tailoring rheological properties of uncrosslinked water-borne pressure-sensitive adhesives by means of polymer maximum volume fraction

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ABSTRACT

Pressure-sensitive adhesives (PSAs) based on butyl acrylate (BA), 2-ethylhexyl acrylate (2-EHA), methyl methacrylate (MMA), vinyl acetate (VAc), and acrylic acid (AA) were prepared via semicontinuous emulsion polymerization, the obtained latexes having nanometer particles, narrow monomodal particle size distribution, and concentrations close to maximum packing fraction. The rheological behavior of liquid adhesives was described using the generalized Maxwell model and the observed differences are a consequence of different particle surface polarity. As the copolymers polarity increases by incorporation of VAc, the amount of surfactant deposited onto the particles decreases, which leads to lower viscosities and higher values for critical volume fraction of polymer. The viscoelastic properties of solid adhesives were investigated by Dynamic Mechanical Analysis. Copolymers of MMA have higher glass transition temperatures than what would be expected theoretically, indicating a higher cohesive strength for these copolymers. Moreover, MMA copolymers have lower molecular masses between entanglements than those containing VAc. All these viscoelastic characteristics are in very good agreement with the adhesive performance characteristics observed.

1. Introduction

Pressure-sensitive adhesives (PSAs) are materials that combine elastic and viscous characteristics which enable them to flow even in a dry state under lightly applied mechanical pressure. These unique characteristics make them very easy to handle as no mixing or curing process is required.

Available as hot melt, solvent or water-borne versions, acrylic PSAs are the only ones that can be obtained directly from synthesis as permanently tacky and used without further formulation. The lack of cohesion of the more tacky acrylic homopolymers, such as poly(butyl acrylate) or poly(2-ethylhexyl acrylate) has been overcome by copolymerization with more polar or cross-linkable comonomers [1–7].

In the case of aqueous dispersions the final properties of latexes are influenced not only by the polymer structure [8–11], but also by interactions between particles and the aqueous phase, by the particles size and size distribution [12,13], these last two parameters controlling macroscopic viscosity and rheological behavior. At the same time, many studies have focused on the effects exerted by copolymer composition [9,10,14], a presence of a particular crosslinker [15] or an initially preformed acrylic resin [16] upon PSA performance. On the other hand, a bi- or multimodal particle size distribution is required to obtain high solid content latexes [17–20], while for a monomodal distribution, concentrations higher than 50% are almost impossible to attain. Colloidal properties can be controlled by emulsion polymerization techniques [21,22], types of initiator [23] and/or surfactants [24,25] used.

In a previous work [24] we have shown that the rheological and adhesive properties of acrylic water-borne PSAs depend on the nature of surfactants, which influence the volume fraction of particles at maximum packing. Thus, as the surface charge induced by the ionic surfactant onto the particles decreases, the critical particle volume fraction increases. In this way, even at relatively high concentration of latexes (approximately 42%), the polymer particles do not incommode each other and a Newtonian behavior is exhibited.

In this paper acrylic water-based PSAs were prepared by emulsion polymerization. The monomers employed, ratio between monomers, surfactant, and the entire synthesis procedure were selected such as the final water-borne dispersions will have

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nanometer particles with narrow monomodal size distribution and concentrations close to the maximum packaging fraction of polymer particles. Different soft and hard monomers were used and the rheological properties of the aqueous dispersions and of the solid copolymers were investigated and related to adhesive performance.

2. Experimental

2.1. Materials

Butyl acrylate (99%, Sigma-Aldrich, Germany), BA, methyl methacrylate (99%, Sigma-Aldrich, Germany), MMA, 2-ethylhexyl acrylate (> 98%, Fluka, Buchs, Germany), 2-EHA, vinyl acetate (> 99%, Merck-Schuchardt, Germany), VAc, and acrylic acid (≥ 99%, Fluka, Buchs, Germany), AA, were used as monomers. Sodium dodecyl sulfate (≥ 99%, Fluka, Buchs, Germany), SDS, was used as surfactant and potassium persulfate (+99%, Sigma-Aldrich, Germany), KPS as initiator. Sodium bicarbonate (98%, Reactivul, Romania) was added as buffer. All ingredients were used as received. PTFE membrane filter, pore size 5 μm and 37 mm diameter, was purchased from Sigma-Aldrich.

2.2. Emulsion polymerization

Copolymers of BA/VAc/AA, (PBVA), 2-EHA/VAc/AA, (PEVA), BA/MMA/AA, (PBMA), and 2-EHA/MMA/AA, (PEMA) were prepared via emulsion polymerization, using the ingredients indicated in Table 1. The ratio between monomers was always 80/17/3.

The latexes were prepared in a four-necked 250 mL glass reactor, equipped with mechanical stirrer, reflux condenser, water jacket for temperature control and argon gas inlet. The initial charge of the reactor, which contains water, monomers, surfactant, initiator and buffer as indicated in Table 1, was vigorously stirred in order to obtain a fine emulsion of monomers in water. The water bath temperature was increased and then maintained at 70 ± 0.1 °C during the entire reaction period. Three feeds were performed: 0.037 M SDS water solution, with an approximately feed rate of 0.2 mL/min, 0.014 M KPS water solution with a feed rate of 0.08 mL/min, and the monomers mixture was added with a rate of about 0.4 mL/min. After all the reagents were fed into reactor, the polymerization reaction was continued for another hour.

The experiments were duplicated in order to check reproducibility. Differences between latexes concentrations and average particle size were less that 1%.

2.3. Solid content

At the end of the reaction samples of about 1 mL were extracted and left to dry at 60 °C under vacuum. Latex concentration was calculated as the ratio between sample weight after water evaporation and initial sample weight.

2.4. Dynamic light scattering

Particle size and particle size distributions were determined by dynamic light scattering (DLS) with ZetaSizer ZS from Malvern. The latexes were diluted up to 0.05%. The average size was calculated as average number diameter:

$$\overline{D}_n = \sum n_i d_i \tag{1}$$

where n_i represents the number fraction of particles having d_i diameter.

Table 1
Recipes of the prepared latexes.

Reagents	PBMA/PBVA		PEMA/PEVA	
	Initial	Added	Initial	Added
BA	7.88	31.52	–	–
2-EHA	–	–	7.88	31.52
MMA/VAc	1.67	6.69	1.67	6.69
AA	0.30	1.18	0.30	1.18
SDS	0.20	0.79	0.20	0.79
KPS	0.12	0.37	0.12	0.37
$NaHCO_3$	0.05	–	0.05	–
H_2O	19.69	29.54	19.69	29.54

2.5. Polymer density

Samples of about 3 mL latex were left to dry at room temperature until a constant weight was attained. Density was measured at 25 ± 0.1 °C using a pycnometer. The final values were obtained as the average of three measurements. Volume fraction of polymer, ϕ, was calculated as the ratio between latex concentration and polymer density.

2.6. Gel content

Samples of about 0.06 g of dry copolymer were placed in a sealed PTFE membrane (pore size 5 μm) and immersed in THF according to the method described by Tobing and Klein [26] and left to swell under gentle shaking at room temperature for 24 h. Then the samples were dried at ca. 60 °C under vacuum and the gel fraction was calculated as the ratio between the mass of dried samples after removing soluble components and the mass of the initial, unswollen polymer.

2.7. Rheological characterization

Both rotational viscometry and oscillatory tests were performed in order to investigate the rheological behavior of copolymers in dispersed systems. Using a Haake VT550 viscotester, shear rates were increased linearly from 0 to 1000 s^{-1}, while shear stress and apparent viscosity were recorded. For dynamic (oscillatory) measurements a Micro Fourier Transform Rheometer MRF 2100, GBC Scientific, Australia, was used. The rheometer applies a complex displacement signal known as “pseudorandom noise”. Thus, the sample located between the upper and below plates of the rheometer undergoes a squeeze flow under action of nearly random displacement (exerted by the upper plate) with a broadband frequency. If the amplitude of such a complex signal is small enough, the sample can be studied within its linear viscoelasticity region. In fact, a pseudorandom displacement signal can be considered as an input signal consisting of a large number of superimposed sinusoids, each of them being associated to a certain frequency. The force signal transmitted through the viscoelastic sample would have a similar content of sinusoids (shifted with the loss angle), so that it is facile to obtain both storage and loss modulus at a large number of discrete frequencies by Fourier transform simultaneously applied to the displacement and force signals [27]. Thus, the following working regime was applied for all samples: squeezing flow, frequency range 0.5–120 s^{-1}, 240 discrete frequencies simultaneously analyzed in that range by a step of 0.5 s^{-1}, 30 spectra consequently acquired every tested sample, gap between the upper and bottom plates of the rheometer 0.3 mm and displacement amplitude 0.03 μm (to fall into linear viscoelastic domain).