



Importance of film morphology on the performance of thermo-responsive waterborne pressure sensitive adhesives

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ABSTRACT

Temperature responsive pressure sensitive adhesives (PSAs) are of interests in many applications due to the possibility of removing strong adhesives by moderate heating. In this work, semicrystalline poly(octadecyl acrylate) obtained by miniemulsion polymerization is used as a key component of the thermal responsiveness. Comparison of the adhesive performance of crystalline hard core-soft shell PSAs with other PSAs of the same overall composition and similar molar mass distributions but prepared by blending soft and hard latexes shows that the arrangement of the phases in the film play a key role in performance of the PSAs. Good adhesive performance and thermal responsiveness is only achieved when the crystalline domains are dispersed in a continuous soft phase containing entangled nanogels. Interestingly, this morphology is achieved with blends, but not with core-shell dispersions. The reasons for this difference are investigated.

1. Introduction

Pressure sensitive adhesives (PSAs) are a special type of adhesives that firmly adhere into a wide range of surfaces by the application of a light pressure (1–10 Pa) for a short contact time (1–5 s) [1,2]. Waterborne (meth)acrylic PSAs have the fastest growth in commercial application because of the low environment impact, balanced end-product properties, compatibility with additives and processability, competitive cost and oxidative ultraviolet resistance [3]. Other advantages of (meth)acrylic PSAs dispersions are their high solids, their ease application, and the fact that they may be formulated, in many instances, without the need for addition of tackifiers [4].

The major challenge in the production of PSAs is to meet the conflicting properties that are required for application (tack, peel strength and shear resistance). As the pure (meth)acrylic formulations present some intrinsic limitations as low cohesive strength [5], attempts to achieve this goal by using polymer-polymer and polymer-inorganic hybrids have been reported. Thus, polyurethane has been incorporated into the (meth)acrylic PSAs to improve cohesive strength [6–12]. Core-shell particles that upon water evaporation yield a percolating cross-linked structure that contains a less crosslinked polymer have reported to increase the adhesive energy on polyethylene [13]. Several types of nanoparticles (clays, carbon nanotubes and graphene, polymers, molybdenum disulfide, silica) [14–22] have also been used to improve the

performance of the PSAs.

Polymer nanoparticles are particularly interesting because in addition of improving the PSA performance, they can have temperature triggered functionality. Thus, the tackiness of the PSAs containing poly(methyl methacrylate) nanoparticles was switched by infrared sintering [18] and PSAs containing semicrystalline domains that strongly adhered to substrates could be easily and abruptly removed by moderate heating [22].

In most of the cases intimate contact between the different phases is preferred as it provides better properties [19,21,22]. This is often achieved by synthesizing composite particles, i.e., particles that contain all the components.

However, Agirre et al. reported an interesting case in which blends allowed the unusual simultaneous increase of both the peel strength and the shear resistance, whereas core-shell particles of the same overall composition exhibited the classical decrease of the peel resistance as shear resistance increased [22]. Although it may be of importance for the design of optimized adhesives, no attempts to understand the fundamental reasons for these findings were reported.

This work is an attempt to understand the fundamental differences between hard core-soft shell PSAs and those prepared by blending hard and soft latexes. A semicrystalline poly(octadecyl acrylate) (also known as poly(stearyl acrylate)) that can provide thermal-responsiveness to the PSA was used as a hard phase and a copolymer containing 2-

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ethylhexyl acrylate (2EHA), methyl methacrylate (MMA) and methacrylic acid (MAA) as soft phase. The adhesive performance of the core-shell and blends was compared showing that the blends had better adhesive properties. A deep characterization of the adhesives was carried out finding that the arrangement of the nanogels in the adhesive film is the most likely reason for the different behavior. In addition, it was observed that these adhesives were temperature responsive.

2. Experimental section

2.1. Materials

Technical grade monomers, methyl methacrylate (MMA, BASF), 2-ethylhexyl acrylate (2EHA, BASF) and methacrylic acid (MAA, BASF), and styryl acrylate (SA, Aldrich) were used without purification. Potassium persulfate (KPS, Fluka) as water soluble radical initiator, sodium bicarbonate (NaHCO_3 , BASF) to control the miniemulsion viscosity by reducing the electrostatic interactions among droplets and Disponil® FES 32 (Fatty alcohol ether sulfate + 4 ethylene oxide, sodium salt) (BASF) as anionic surfactant were used as received. Deionized water was used as polymerization media.

2.2. Experimental design

Tables 1 and 2 summarize the experimental design in which the comonomer composition was varied from SA/SC(M)A = 0/100 to SA/SC(M)A = 40/60 wt/wt (SC(M)A = short chain (meth)acrylates). The SA amount in copolymers was limited in order to be able to form tacky films. The SC(M)A compositions were 2EHA/MAA = 99/1 wt% (Table 1) and 2EHA/MMA/MAA = 84/15/1 wt% (Table 2). SA is a water insoluble monomer, and therefore miniemulsion polymerization that does not require monomer transport through the aqueous phase [23,24] was used. 1A is a SA homopolymer synthesized by miniemulsion polymerization [25,26]. The semicrystalline copolymers were prepared by seeded semibatch emulsion polymerization by using Latex 1A as seeds. Thus, the poly(SA) latex was charged into the reactor, and then the pre-emulsion of SC(M)A monomers and the initiator solution were fed separately during 3.5 h under starved conditions (Runs 1D–4D and Runs 1D'–4D'). The reference latexes, 1E and 1E', that were devoid of SA, were synthesized by seeded semibatch emulsion polymerization by using polystyrene seeds (0.1 wt% based on monomer, particle diameter = 31 nm). The SA miniemulsion preparation and the synthesis of the latexes are described in Supporting Information.

Table 1

The summary and characteristic of the PSAs latexes synthesized with SC(M)A: 2EHA/MAA = 99/1 wt%.

	Latex	SA/SC(M)A ^a (wt/wt)	Particle size (nm)	Gel content (%)	Swelling degree	Mw, Soluble part (g/mol)	Đ	T _m (°C)	Xc ^b (%)	T _g ^c (°C)
Series A	Batch miniemulsion									
	1A	100/0	170	79.2 ± 0.2	14.1 ± 0.5	392000	3.3	51	41.8	17.0
Series D	Latex 1A + 3.5 h addition of SC(M)A pre-emulsion and KPS solution									
	4D	40/60	220	71.0 ± 0.1	10.3 ± 0.1	83000	3.3	51	15.9	−62.3
	3D	30/70	236	69.4 ± 0.1	10.2 ± 0.1	86000	2.8	50	11.5	−63.0
	2D	20/80	270	66.3 ± 0.0	10.5 ± 0.2	93000	2.8	50	6.9	−63.0
	1D	10/90	317	66.5 ± 0.0	9.7 ± 0.0	100000	2.8	48	3.4	−65.8
Series E	Seeded emulsion copolymerization									
	1E	0/100	269	63.8 ± 0.1	10.8 ± 0.3	123000	2.7	–	–	−67
Blends	Blending 1A and 1E latexes									
	Blend 4	40/60	–	71.0 ± 1.7	12.5 ± 1.5	184000	3.8	49	17.0	−67.7
	Blend 3	30/70	–	67.5 ± 0.4	12.1 ± 0.4	162000	3.3	49	10.9	−67.2
	Blend 2	20/80	–	67.0 ± 0.5	11.7 ± 1.1	139000	3.4	48	6.6	−67.8
	Blend 1	10/90	–	64.2 ± 0.6	12.3 ± 2.0	129000	3.1	48	3.3	−67.0

^a SC(M)A: 2EHA/MAA = 99/1 wt%.

^b Referred to the whole polymer.

^c For Run 1A, the onset temperature was taken as T_g, whereas for the rest, the inflection point temperature was considered. Poly(SA)(Run 1A) shows weak transitions at low temperature ranges corresponding to the transitions of amorphous part (α and β transitions) [27].

Blending was used to prepare semicrystalline adhesives as well. The amorphous SC(M)A latexes (1E and 1E') were mixed with the poly(SA) Latex 1A to obtain blends with different copolymer composition and crystallinity (Blends 1–4, Table 1; Blends 1'–4', Table 2).

2.3. Characterization

PSAs latexes and films. Monomer droplet and particle sizes of the latexes were measured by hydrodynamic chromatography (HDC); the gel fraction and swelling degree were measured by Soxhlet extraction, using THF as the solvent; the molar mass distribution of the soluble fraction of polymers was determined by size exclusion chromatography (SEC/RI); the molar mass distribution of the whole polymer was determined by asymmetric-flow field-flow fractionation (AF4/MALS/RI); the thermal characterization of the PSAs films was carried out by differential scanning calorimetry (DSC); the morphology of latex particles and adhesive films were studied by means of transmission electron microscopy (TEM) and atomic force microscopy (AFM) respectively; the adhesive property studies were 180° peel, shear resistance, loop and probe tack tests; the mechanical properties of the adhesives were studied in terms of linear viscoelastic (characterized with rheometer) and nonlinear elastic (tensile test) measurements. The detailed description of the characterization methods and adhesive and mechanical tests is provided in Supporting Information.

3. Results and discussions

The volume average particle diameter of the Latex 1A used as seed in Series D and D' and those of the final latexes are given in Tables 1 and 2. It can be seen that the final particle size decreased with increasing SA content. The reason was the increasing number of seed particles used for higher SA contents. The TEM micrograph of latex 2D' is shown in Fig. 1. It can be seen that the semicrystalline particles present a core-shell morphology with the dark poly(SA) domains in the core. Moreover, the small amorphous particles observed in the TEM micrographs show that some secondary nucleation occurred during the second stage of polymerization, most likely by homogeneous nucleation (some of the small amorphous particles are indicated by arrows in the TEM image).

Tables 1 and 2 showed that there were no substantial differences in gel content and crystallinity between the latexes obtained by two stage polymerization (Series D and D') and the blends. The gel fraction and crystallinity values measured for blends agreed well with the average value calculated taking into account the fractions of poly(SA) and poly

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