

IMPROVING THE ADHESIVE PERFORMANCES FOR WATER-BASED PRESSURE-SENSITIVE ADHESIVES

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Emulsion copolymers based on acrylic and vinylic comonomers were prepared by two-stage seeded emulsion copolymerization and evaluated as pressure-sensitive adhesives. The obtained copolymers were characterised by their non-volatile content, viscosity, rheological behaviour and adhesive properties. The influence of composition on adhesive performances on different substrates (stainless steel, plasticized polyvinylchloride, and polyethylene) was investigated. Butyl acrylate offers an increase of peel and shear strength by comparison with ethyl acrylate. Using of monomers with hydroxyl groups is not indicated unless they offer sites for a further cross-linking.

1. Introduction

Pressure-sensitive adhesives (PSAs) are a class of materials that adhere on substrate on contact or on application of a slight pressure in a very short time without heating or curing. The bonds formed are strong enough to use for temporary adhesion. Thus, removable tapes and labels can be pasted and removed many times, and the adhesive is not left on the adherend in a large majority of cases. Because PSAs are very convenient, as describe above, they are often used in many fields, such as cellophane tape and labels, packaging, printing, medical, electrical, and automobile industries.

Traditional PSAs were solutions of rubbers and resins in solvents, and these dominated the market until well after the World War II. From that time, as an increasing array of elastomers became available, as the price of solvents soared, and as environmental opposition to use of solvents increased, water-based and hot-melt types made substantial inroads into the solvent-based market. In water-based systems, acrylic polymers come to be used more and more as they can produce aggressive tack from a single component. The tack is believed to stem from the viscoelasticity of polymers, allowing them to conform to the substrate to be adhered and “wet” it even in the dry state. It follows that a fundamental requirement for tack is a glass transition temperature (T_g) substantially below the application temperature to allow the necessary degree of flow [1].

Esters of acrylic acid may be used to form soft and tacky polymers with low T_g . The suitable monomers commonly reported in patent literature are alkyl acrylates and methacrylates of 4-12 carbon atoms, e.g. 2-ethylhexyl acrylate (2-EHA), that gives a polymer with a T_g of -70°C . To control the adhesive properties of PSAs, the acrylic esters are almost always copolymerized with other monomers giving generally polymers with higher T_g and/or proper functionality. An example of such a secondary monomer is acrylic acid (AA) having a polymer T_g of 106°C and carboxyl groups to provide cross-linking sites

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as well as a suspected improvement in adsorption properties [2]. Composition plays an important role in practical adhesive bonding characteristics of PSAs.

The influence of composition on the adhesive performances and rheological behaviour of some carefully selected acrylo-vinyllic dispersions prepared by two-stage seeded emulsion polymerization is presented into the present paper.

2. Experimental

2.1. Materials

The following chemical substances were used: ethyl acrylate (99%, Merck-Schuchardt, München, Germany), butyl acrylate (99%, Merck-Schuchardt), 2-ethylhexyl acrylate (~95%, Fluka AG, Buchs, Germany), acrylic acid ($\geq 99\%$, Fluka AG), hydroxyethyl methacrylate (~98%, Fluka AG), vinyl acetate ($>99\%$, Merck-Schuchardt) as monomers; sodium dodecyl sulfate as emulsifier, potassium persulfate (99%, Fluka, Madrid, Spain) as initiator, sodium carbonate (99.8%, Reactivul, Romania). All products were used without further purification.

2.2. Polymerizations

Seed latexes were prepared by batch copolymerization in a glass reactor with a water jacket for temperature control. The sudden increase of temperature due to the exothermicity of reaction was controlled using ice. The recipes are given in Table 1. The monomers and the other chemicals, excepting the initiator, were charged together with water.

Table 1. Recipes for seed latexes

Ingredients	Latex S1	Latex S2
2-ethylhexyl acrylate	8.08	8.08
Butyl acrylate (BA)	-	4.04
Ethyl acrylate (EA)	4.04	-
Vinyl acetate (VAc)	7.30	7.30
Surfactant	2.90	2.90
Initiator	0.07	0.07
Buffer	0.08	0.08
Water	77.53	77.53

The polymerization was performed at $80 \pm 1^\circ\text{C}$ for 5 h. In this stage the entire amount of emulsifier was added. The addition of initiator (as aqueous solution) started after the system reached the reaction temperature. The initiator was 0.36 wt % referred to the monomers added in this stage. The seed latexes were used without further treatment in the second polymerization stage.

The second-stage polymerization was carried out in the same reactor using this time two separate feeds: one with neat monomers, the second with an aqueous solution of initiator. After the feeding period (5 h), the systems were left to react further for another hour. The recipes for this stage are given in Table 2.

Table 2. Recipes for pressure-sensitive adhesives

Ingredients	Adhesives			
	A1	A2	A3	A4
2-ethylhexyl acrylate	18.00	18.00	18.00	18.00
Butyl acrylate	-	9.80	-	9.80
Ethyl acrylate	9.80	-	9.80	-
Vinyl acetate	17.22	17.22	17.22	17.22
Acrylic acid	1.63	1.63	-	-
Hydroxyethyl methacrylate	-	-	1.63	1.63
Latex S1	37.00	-	37.00	-
Latex S2	-	37.00	-	37.00
Initiator	0.52	0.52	0.52	0.52
Buffer	0.51	0.51	0.51	0.51
Water	15.32	15.32	15.32	15.32

The ratio between soft monomers (2-EHA, BA and EA) and hard monomers (VAc, AA and HEMA) was 3/2 based on a previous paper [3], as we intended to obtain copolymers with T_g ranging between -50 and -30°C . Assuming that the copolymers were statistical, T_g was calculated with the relation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \dots \quad (1)$$

where w_i is the weight fraction of comonomer i and T_{gi} represents the T_g of the homopolymer given by monomer i . The dispersions were used as they resulted from reactor.

2.3. Surface tension

The surface tensions were determined at 25°C by the du Nouy method using a torsion balance.

2.4. Rheological behavior

A type VT 550 Haake viscometer equipped with MV1, MV2, and MV-DIN sensors was used to generate rheograms and to determine the viscosity at zero shearing rate. All the measurements were made at $25 \pm 0.1^{\circ}\text{C}$. Viscosities at zero shearing rate were obtained by linearization of rheograms by logarithmation and extrapolation.

2.5. Adhesives performances

PSA sheets for mechanical tests were prepared by coating the dispersions on polyester film of 0.4 mm thickness and left to air-dry at room temperature for 48 h. Dried PSA sheets were pressed onto adherends using a 2 kg roller passing over twice. Stainless steel, polyethylene and plasticized polyvinylchloride (PVC) were used as substrates. The samples were seasoned at room temperature for 7 days before measurements. The 180° peel strength

and dynamic shear strength were performed using a dynamometer able to apply the force with a constant rate at room temperature. For plasticized PVC/plasticized PVC bonds the PSAs were coated on both surfaces. Static shear strength was evaluated only for polyethylene by applying a fixed load (500 g) on an overlap bond 12 mm by 12 mm.

3. Results and discussions

Seeded emulsion polymerization received during the last decade a great deal of attention [4,5]. We chose this technique in order to control the locus of the functional groups in the latex particles. It was felt that by adding AA and hydroxyethyl methacrylate (HEMA) during the second-stage of polymerization, the functional groups could be concentrated at the surface of the latex particles.

3.1. Physical properties

The prepared dispersions contain 55% comonomers, 2 wt % surfactant based on the monomer amount and 1 wt % initiator based on the monomer amount. The differences in physical properties, listed in Table 3, are relatively small.

Table 3. Physical properties of the prepared adhesives

Characteristics	Adhesives			
	A1	A2	A3	A4
Concentration, %	54.88	54.60	53.08	55.44
Surface tension, mN/m	39.45	38.00	40.14	43.21
Viscosity at zero shearing rate, mPas	1233.60	1362.00	965.35	1075.00
pH	4.5	4.5	4.5	4.5
T _g (calculated using relation (1)), °C	-35.9	-42.6	-36.8	-43.4

Interesting differences appear in rheological behaviour. The rheograms are presented in Fig. 1 for all the adhesives and all of them have a pseudoplastic behaviour as can be observed.

In spite of the small differences in concentrations (up to 2.32%), the differences in viscosities at zero shearing rate are pretty large, the maximum difference exceeding 41% (see Table 3). Replacing of EA by BA produces an increase of viscosity. This can be explained by the increased length of side chain, which it is expected to increase also the flexibility and the tack of copolymer. When AA is replaced by HEMA the viscosity at zero shearing rate diminished.

3.2. Mechanical properties

The peel and shear strength of the prepared water-based dispersions on different substrates are shown in Table 4.

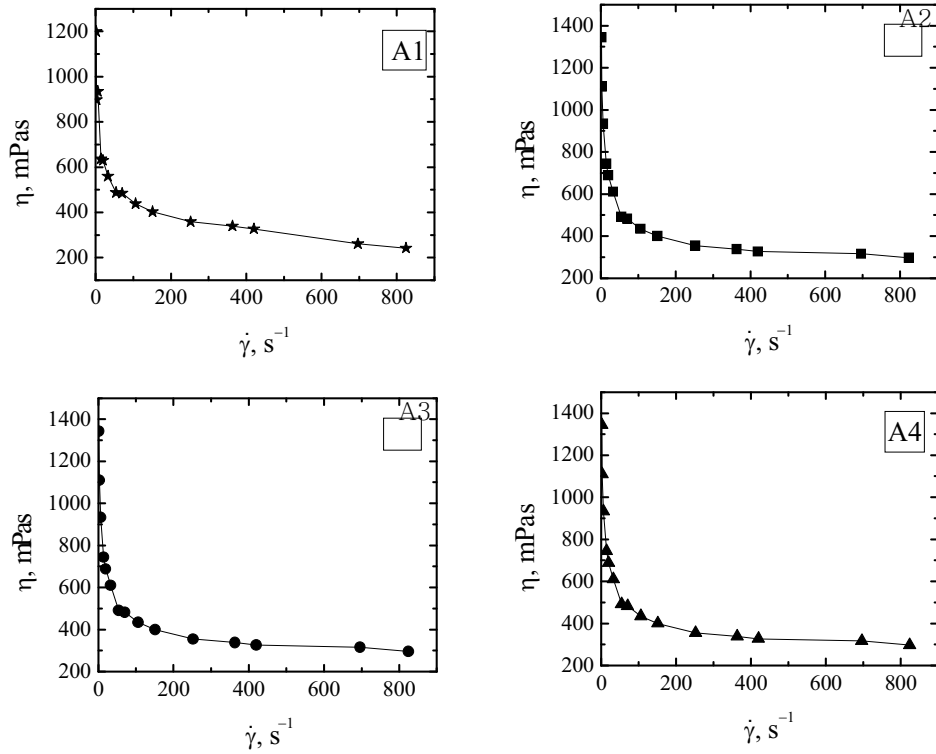


Fig. 1: Rheograms of the prepared dispersions.

Table 4. Mechanical properties of the prepared adhesives

Property	Adhesives			
	A1	A2	A3	A4
Dynamic shear strength, daN/cm ²				
- stainless steel	2.12	3.75	0.90	1.53
- plasticized PVC	5.43	6.29	2.32	3.00
- plasticized PVC/plasticized PVC	7.62	9.45	3.00	3.56
Static shear strength ^a , h				
- polyethylene	13.30	14.00	2.30	4.20
Peel strength at 180°, N/cm				
- stainless steel	3.74	5.21	1.00	1.82
- plasticized PVC	4.95	6.67	2.15	3.45
- polyethylene	1.00	2.00	0.28	0.93

^a12 mm x 12 mm x 500 g

Introduction of functional groups on the latex particle surfaces produces an improving of adhesive performances, especially on polar substrates (see previous paper [3]). The adhesives containing BA have better adhesive performances on all studied substrates. This can be explained by the lower T_g , which increases the ability of the dried film to wet the substrates. Moreover, the higher viscosities of adhesives containing BA offer an increased stability and tackiness.

The functional groups introduced on the particle surfaces were carboxylic and hydroxylic. It can be observed that adhesives containing HEMA show a decreasing both of peel and shear strength on each substrate.

All the adhesives show a better adhesion on PVC, which demonstrate an affinity of acrylic copolymers for this particular substrate. This is supported also by the cohesive nature of the plasticized PVC/plasticized PVC bonds failure.

4. Conclusions

Stable PSAs were prepared by two-stage seeded emulsion copolymerization. This technique was used in order to introduce functional groups on the surface of latex particles. The ratio of monomers was selected in such a way so that the T_g of the resulting copolymers ranged between -50 and -30°C . The obtained dispersions were used without further compounding. They were characterised by their non-volatile content, viscosity, rheological behaviour and adhesive properties.

The influence of different comonomers on adhesive performances was also investigated. Thus, it was founded that BA improves the peel and shear resistance on all the studied substrates compared with EA, while hydroxylic groups decrease the above performances compared with carboxylic groups.

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