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Effect of propyleneimine external cross-linker on the properties of acrylate latex pressure sensitive adhesives

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ABSTRACT

Acrylate pressure sensitive adhesive (PSA) latexes were synthesized via a starved monomer seeded semi-batch emulsion polymerization process with butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA) and 2-hydroxyethyl acrylate (HEA). These PSA polymers were then cross-linked with trifunctional propyleneimine external cross-linker (SAC-100) to study the cross-linking reaction between carboxylic group of the polymer chain and cross-linking agent. It was found that cross-linking provided a significant influence on the film formation process based on the result of SEM analysis. In addition, with the increase of SAC-100 content, the gel content of the polymer increased significantly, while molecular weight between cross-link points (M_c) and the sol molecular weight (M_w, M_n) of the polymer decreased remarkably. The TGA result showed that the addition of the external cross-linker can enhance the thermal stability of the latex film. Moreover, for the cross-linked adhesive film, the shear strength was improved greatly while at the sacrifice of loop tack and peel strength, when compared with the uncross-linked counterparts. Besides, dynamic mechanical analysis (DMA) was also used to evaluate the viscoelastic properties of the acrylate emulsion PSA film.

1. Introduction

Pressure sensitive adhesives (PSAs) are viscoelastic materials with permanent stickiness, and can adhere strongly to solid surfaces upon application of slight contact pressure under a relatively short contact time [1]. The adhesion properties of the PSA are characterized by three basic applicative properties: tack (the property that enables an adhesive to form a bond of measurable strength with a surface of another material upon brief contact under light pressure), peel strength (the force required to remove a standard PSA strip from a specified test surface under a standard test angle (90° or 180°) under standard conditions), and shear strength (the length of time it takes for a standard strip of PSA to fall from a test panel after application of a load) [2].

Acrylic ester monomers are widely used to synthesize pressure sensitive adhesives (PSAs) through solution or emulsion polymerization. Their saturated nature makes them transparent, colorless, and resistant to yellowing from sunlight or oxidation [3]. However, as these synthesized acrylic PSAs consist of linear molecules that are held together by physical cross-linking, van der Waals forces, or hydrogen bonding, they have insufficient thermo-mechanical stability. On the other hand, the environmental disadvantage and high cost have promoted the replacement of many solvent-borne acrylic PSAs with emulsion counterparts. Nevertheless, the solvent-borne acrylic PSAs have been preferred over the emulsion PSAs in high performance applications which require a high shear holding power together with high peel and tack. It is known that solvent-borne acrylic PSA films have a much higher shear-holding power than that of their emulsion counterparts [4]. This is mainly due to the continuous network morphology formed by the chain entanglements in the solvent-borne adhesive when the solvent has evaporated [5]. In contrast, microgels were produced during the process of emulsion polymerization and retain their discrete morphology in the adhesive film [4]. This morphology decreases the shear resistance of the emulsion adhesive because of the poor interconnections between the microgels and the linear polymers in the film.

Cross-linking is one of the key techniques controlling the balance between cohesive and adhesive strength of the PSA polymer. Typical cross-linking methods are based on the chemical reaction that takes place between the cross-linking agents and the main chain of the PSA copolymers [6]. With the aid of cross-linking agents, an increase in cohesion may be accomplished during the drying stage of the PSA film. As expected, the adhesion properties of the PSA film, such as tack and peel adhesion, decrease with the increment in cross-linker concentration (Fig. 1). The cross-linking of PSAs based on acrylates has been discussed in many industrial papers [7–10]. The physico-chemical and mechanical properties of cross-linked PSAs are determined to a large extent by the type and

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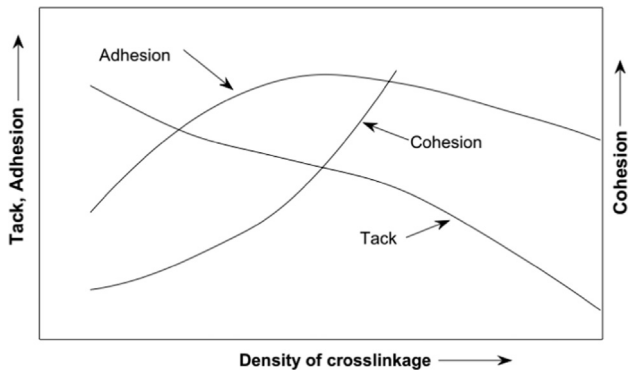


Fig. 1. General effects of cross-linking to the PSA performances [13].

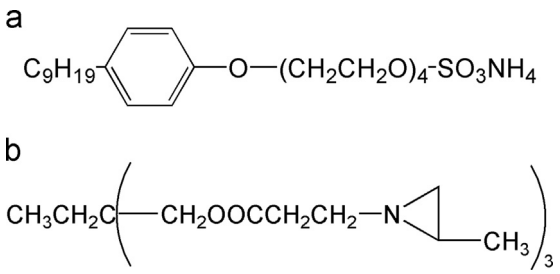
amount of cross-linking agents added to the copolymer. For example, Tobing and Klein [11] synthesized acrylic emulsion PSAs with different functional groups, using isobutoxy methyl acrylamide (IBMA) and AA comonomers. Their research showed that cross-linking reactions between reactive groups in the adhesive film at an elevated temperature resulted in high shear resistance without significant loss in peel and tack properties. Czech [12] discussed the influence of some kinds of cross-linking agents (internal and external cross-linkers) and their contents on the important properties of acrylic based PSA dispersions such as tack, adhesion and cohesion.

Multifunctional propyleneimines have proved to be versatile and highly effective external cross-linking agents or curing agents for acrylic PSAs (which contain acrylic acid in the polymer chain) and other adhesive types containing carboxylic groups [8]. In the present study, a series of emulsion acrylic pressure sensitive adhesives have been synthesized and cross-linked with trifunctional propyleneimine external cross-linker (SAC-100) at contents of 0.0–0.8 wt%. The effects of curing agent contents on the gel content, molecular weight between cross-links (M_c), soluble molecular weight (M_w, M_n) and its distribution (M_w/M_n) and adhesive properties of the PSA copolymers were investigated. In addition, IR, TGA, SEM and DMA were used to characterize the latex film before and after cross-linking.

2. Experimental

2.1. Materials

Butyl Acrylate (BA; technical grade, Shanghai Huayi Acrylic, China), Methyl Methacrylate (MMA; Reagent grade, Shanghai Lingfeng Chemical, China), Acrylic Acid (AA; reagent grade, Shanghai Lingfeng Chemical, China), 2-Hydroxy ethyl Acrylate (HEA, technical grade, Shanghai Huayi Acrylic, China), Ammonium persulfate (APS; technical grade, Shanghai Aijian Modern Reagent Factory, China) and Sodium Bicarbonate ($NaHCO_3$; reagent grade, Shanghai Lingfeng Chemical, China) were used as the initiator and the buffer agent. All these materials were used without further purification. The emulsifier used in this work was CO-458 (58–60 wt%), which was supplied by Shanghai Honesty Fine Chemical (China), and it was used as received. Distilled deionized water (DI-H_2O) was used throughout the study. Ammonia (25 wt% in H_2O) was obtained from Nanjing Chemical Reagent Co. All solvents used in the polymer characterization such as tetrahydrofuran (THF, HPLC grade, Shanghai Lingfeng Chemical) and toluene (reagent grade, Nanjing Chemical Reagent Co.), were also used as supplied by the manufacturer. PTFE porous membranes with pore size of 0.22 μm for use in gel content and M_c measurements, were purchased from Science, China. Trimethylolpropane-tris-(N-methylaziridinyl)-propionate was used as the propyleneimine external cross-linking agent obtained from Shanghai UN Chemical, China, and the product model was SAC-100. The molecular structures of CO-458 and SAC-100 are shown in Scheme 1.



Scheme 1. The molecular structures of (a) CO-458 and (b) SAC-100.

2.2. Preparation of pre-emulsion and initiator solution

The 75 g DI-H_2O and 6.0 g surfactant were added to a 1 L four-neck round-bottom flask and were stirred rapidly to make the emulsifier dissolved sufficiently, then the monomer mixture, which contains 258.93 g BA, 14.07 g MMA, along with 3 g AA and 6 g HEA, was slowly added into the water–emulsifier mixture through a constant pressure funnel over 20 min. After that, the pre-emulsion was stirred for further 30 min.

Then, the initiator stock solution was prepared by adding 1.05 g APS into 75 g DI-H_2O and continuously stirred to become homogeneous solution.

2.3. Polymerization procedure

The latex was prepared by the monomer seeded semi-batch emulsion polymerization process, which was carried out in a 1 L four-neck round-bottom flask equipped with an electromotive stirrer, thermometer, two separated addition funnel, and reflux condenser. The theoretical solid content in the formulation was 50 wt%. The stirring speed was maintained at 230 rpm throughout the experiments. First, a homogeneous aqueous solution containing 150 g DI-H_2O, 0.3 g CO-458, and 0.6 g $NaHCO_3$ was charged into the reactor. When the temperature reached 70 °C, an initiator solution containing 0.45 g APS and 15 g water and a monomer mixture containing 17.07 g BA and 0.93 g MMA were charged into the reactor to form the seed latex. The temperature was then raised to 83 ± 2 °C and the seed polymerization was continued for an additional 30 min. Subsequently, the pre-emulsion and initiator stock solutions were added slowly to the reactor using two separate constant pressure funnels. The feeding times for the pre-emulsion and the initiator solution were 3.5 and 4.0 h, respectively. After the feed was completed, the reaction was allowed to proceed for an additional 1 h to increase monomer conversion. The latex was then cooled to room temperature and ammonia was added to adjust the pH to 7–8.

2.4. Characterization

2.4.1. IR spectrographic analysis

Infrared (IR) spectra of the latex films were recorded with a Bruker VERTEX80 IR spectrometer (Germany) in the range 4000–400 cm^{-1}.

2.4.2. Gel content and M_c determination

The gel content of the acrylic PSA polymers was measured via the solvent-extraction method. Three samples (around 0.2 g) of the dried latex film were weighed and sealed in the PTFE coated membrane pouch. Then the membrane pouch was put in a Soxhlet extractor with tetrahydrofuran (THF), refluxing for 24 h. After the extraction process, the membrane pouch was removed and first dried in a fume hood for 3 h and then in a vacuum oven at 70 °C