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Preparation and adhesion performance of transparent acrylic pressure sensitive adhesives: effects of substituent structure of acrylate monomer

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ABSTRACT

Three different acrylate monomers containing a cyclohexyl moiety were designed and synthesized to prepare transparent acrylic pressure sensitive adhesives (PSAs) comprised of semi-interpenetrated structured polymer networks. The effects of substituent structure in the acrylate monomer on the adhesion performance of the acrylic PSA were investigated. The prepared UV-curable acrylic PSA syrups were characterized and the optical properties of their acrylic PSA film were also examined. The acrylic PSAs exhibited high transparency in the visible wavelength region. Adhesion performance was evaluated using the peel strength, cohesion strength, and probe tack tests. The adhesion properties of the acrylic PSAs depended on the substituent structure in the acrylate monomer.

1. Introduction

Pressure-sensitive adhesives (PSAs) are usually viscoelastic materials that can stick firmly to solid substrates with the application of a light pulling force and a short contact time [1–6]. The first PSA was a blend of natural rubber and a rosin ester tackifier made from a toluene and heptane solution [7]. Since then, PSAs have expanded to various applications such as printing, electrical insulation and automobile parts, the performance demands for PSAs have diversified and various types of PSA have been developed [8–14].

In recent years, due to increasing social and political awareness, UV-processing has rapidly expanded in PSA industries due to its unique advantages such as solventless processing, low cost energy, new properties and the high quality of chemical crosslinking bonding [15–18]. Acryl-based polymers have been well established among solventless UV-curable PSAs for a long time due to their excellent physical properties and their aging stability. The selection of suitable acrylate monomers for adhesives is dictated by the intended application of the PSAs and the desired end-product properties [19,20]. Generally, PSAs used for optical applications consist of three major acrylate monomers such as soft monomers for tack and flexibility in the adhesives, hard monomers for cohesion strength, and functional monomers for adhesion strength. The product of copolymerization is a polymer with a higher T_g, which depends on the type and also on the amount of added comonomer.

In this study, our interest was in determining how much the chemical structure of the alicyclic substituent on the acrylate monomer affects the adhesion performance of acrylic PSAs. We designed three different monomers containing a cyclohexyl moiety that fulfilled the hard segment role in the PSAs. Then, transparent acrylic PSAs containing the newly designed acrylate monomers were prepared by UV irradiation with a standard acrylic PSA formulation. By changing the substituent structure of the acrylate monomers, we examined the adhesive performance and viscoelastic properties as well as the optical properties of the acrylic PSAs.

2. Experimental section

2.1. Materials

2-Ethylhexyl acrylate (2-EHA; Junsei), 2-hydroxyethyl acrylate (2-HEA; Junsei) and cyclohexyl acrylate (CHA; TCI) were used without further purification as comonomers. 1,4-cyclohexane dimethanol (Aldrich), 1-bromohexane (Aldrich), acryloyl chloride (Chemax), 1,6-hexanediol (Junsei), (bromomethyl)cyclohexane (TCI) were used as starting materials. 1-Hydroxycyclohexyl phenyl ketone (PI, Irgacure 184; Ciba Specialty Chemicals) and 1-dodecanethiol (DT; Aldrich) were used as photoinitiator and chain transfer agent, respectively. 1,6-Hexanediol diacrylate

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Table 1
Formulations of UV-photopolymerization for the acrylic PSA syrups.

Sample ID	Momomer[a] [mol%]	2-EHA [mol%]	2-HEA [mol%]	PI/CTA[b] [wt%]	DT [wt%]	UV irradiation time [s]
CHA-PSA	50	25	25	0.05/0.01	0.02	70
NCA-PSA	50	25	25	0.05/0.01	0.02	360
CNA-PSA	50	25	25	0.05/0.01	0.02	130

[a] CHA or NCA or CAN.
[b] Photoinitiator/chain transfer agent.

(HDDA; Aldrich) was used as crosslinker. Light release liner, heavy release liner and PET film (ROL751, ROH751, U48; Toray Advanced Materials Korea Inc.) were used. All other chemicals and solvents were an analytical grade and used without further purification.

2.2. Synthesis of acrylate monomers

(*4*-((*hexyloxy*)*methyl*)*cyclohexyl*)*methanol* (1): 1,4-Cyclohexane dimethanol (24 g, 166.4 mmol) was dissolved in acetonitrile (250 ml) and added KOH (13.94 g, 249.0 mmol). After the solution was stirred for 30 min at 60 °C, 1-bromohexane (13.7 g, 83.0 mmol) dissolved in acetonitrile (100 mL) was added dropwise. The reaction was allowed to proceed for 24 h at 100 °C. The mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The mixture was extracted with dichloromethane (DCM). The organic layers were rinsed with brine and dried over $MgSO_4$. The crude product was purified by silica column chromatography eluting with a mixture of ethyl acetate/hexane (3:7, v/v) to give a colorless oil (14.02 g, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.88 (t, 3H), 1.41 (m, 18H), 1.83 (m, 1H), 3.39 (m, 4H), 3.54 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 71.3, 68.8, 66.4, 40.8, 38.4, 35.5, 31.8, 29.8, 29.6, 29.1, 26.0, 25.5, 22.8, 14.2.

(*4*-((*hexyloxy*)*methyl*)*cyclohexyl*)*methyl acrylate* (2): (4-((Hexyloxy)methyl)cyclohexyl)methanol (3 g, 13.1 mmol) dissolved in DCM (22 mL) was cooled down to 0 °C and triethylamine (1.3 g, 12.8 mmol) and 4-(dimethylamino)pyridine (0.06 g, 0.49 mmol) were added. Acryloyl chloride (1.2 g, 13.2 mmol) dissolved in DCM (8 mL) was added dropwise. The solution was stirred at room temperature for 6 h. After workup with DCM, the crude product was purified by silica gel column chromatography eluting with a mixture of ethyl acetate/hexane (1:9, v/v) to give colorless oil (3.1 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.89 (t, 3H), 1.32 (m, 16H), 1.83 (m, 2H), 3.31 (m, 4H), 4.04 (d, 2H), 5.82 (dd, 1H), 6.12 (m, 1H), 6.40 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.5, 130.6, 128.8, 71.4, 69.7, 67.5, 38.2, 35.6, 31.8, 29.8, 29.4, 29.2 , 26.0, 25.7, 25.7, 22.8, 14.2; ESIMS *m/z*: 282.4 $[M]^+$ (calcd. *m/z*: 282.22)

6-(*cyclohexylmethoxy*)*hexanol* (3): 1,6-Hexanediol (10 g, 84.6 mmol) was dissolved in acetonitrile (70 ml). KOH (7.12 g, 126.9 mmol) was added and the solution was stirred for 30 min at 60 °C. (Bromomethyl) cyclohexane (7.49 g, 42.3 mmol) dissolved in acetonitrile (50 ml) was added dropwise. Under nitrogen atmosphere, the reaction was allowed to proceed for 24 h at 100 °C. After removing solvent, the organic layer was extracted with DCM. The organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified by silica column chromatography eluting with a mixture of ethyl acetate/hexane (3:7, v/v) to give a colorless oil (2.5 g, 28%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.42 (m, 20H), 3.19 (d, 2H), 3.39 (t, 2H), 3.64 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 77.0, 71.1, 63.1, 38.2, 32.9, 30.3, 30.3, 29.8, 26.8, 26.1, 26.0, 26.0, 25.7.

6-(*cyclohexylmethoxy*)*hexyl acrylate* (4): 6-(Cyclohexylmethoxy) hexan-1-ol (2 g, 9.3 mmol) in THF (13 mL) was stirred at 0 °C. Triethylamine (0.94 g, 9.3 mmol) and 4-(dimethylamino)pyridine (0.04 g, 0.33 mmol) were added. Acryloyl chloride (1.01 g, 11.2 mmol) was dissolved in THF (7 ml) and added dropwise. The solution was stirred at room temperature for 6 h. After the reaction, the organic layer was extracted with DCM. The organic layers were rinsed with brine and dried over $MgSO_4$. The crude product was purified by silica column chromatography eluting with a mixture of ethyl acetate/hexane (1:9, v/v) to give colorless oil (1.7 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.39 (m, 19H), 3.19 (d, 2H), 3.84 (t, 2H), 4.15 (t, 2H), 5.81 (dd, 1H), 6.11 (s, 1H), 6.39 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.5, 130.6, 128.8, 77.0, 71.0, 64.7, 38.2, 30.3, 30.3, 29.8, 28.7, 26.8, 26.0, 26.0, 25.9, 25.8; ESIMS *m/z*: 268.4 $[M]^+$ (calcd. *m/z*: 268.20).

2.3. Synthesis of acrylic PSA syrups

Acrylic PSA syrups were synthesized by bulk polymerization under UV irradiation (Scheme 2). The formulations of acrylic PSA syrups are depicted in Table 1. Three monomers were placed into a 300 ml flask equipped with a mechanical stirrer. The mixture was degassed with bubbling of nitrogen gas for 30 min and then subsequently exposed to UV black light lamp (18 W, Philips Co., Holland) at room temperature under a nitrogen atmosphere. The UV irradiation time was variable to make the viscosity of PSA syrup similar. After removal of the UV radiation, oxygen gas was injected into the mixture for 30 min to allow termination of the radical reaction. The obtained syrup comprised polymeric long chains and unreacted monomers.

2.4. Preparation of acrylic PSA film

UV-curable acrylic PSA syrups were prepared by blending of the synthesized acrylic PSA syrup with photoinitiator (0.5 phr) and difunctional acrylate monomer (0.2 phr). The UV-curable acrylic PSA syrups were coated onto a heavy release liner (75 μm, Toray Advanced Materials Korea, Korea) using a bar-coater (100 μm thickness), and covered with another light release liner. These UV-curable PSA films were cured using UV curing equipment with a 36 W black light lamp for 8 min under a nitrogen atmosphere. The UV intensity of the lamp was approximately 20 mW/cm^2.

2.5. Measurements

2.5.1. Characteristics of monomers and acrylic PSA syrups

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS 400 FT NMR spectrometer using $CDCl_3$, as the solvent. Mass spectra were obtained on an Agiliant 6100 Series Single Quadrupole LC/MS mass spectrometer. The viscosity of the prepared acrylic PSA syrup was measured using a DV2T LVT10 (Brookfield Engineering, USA) viscometer equipped with a small sample adapter. The molecular weight and polydispersity (PDI) were examined by Gel Permeation Chromatography (Agilent Technologies Co., Agilent 1260 GPC system) equipped with PL gel 5 μm MIXED-C and RI detector. THF was used as an eluent solvent at a flow rate of 1 mL/min. Photo-DSC experiments were conducted using a DSC Q2000 (TA Instruments, USA) equipped with a photocalorimetric accessory (Omnicure S2000), which used light from a 200 W high-pressure mercury lamp. Measurements were carried out at 30 °C. Thermogravimetric analysis (TGA) was carried out using TGA Q50 (TA