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Construction and adhesion performance of biomass tetrahydro-geraniol-based sustainable/transparent pressure sensitive adhesives

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ABSTRACT

Using the tetrahydro-geraniol acrylate (TGA) synthesized from biomass tetrahydro-geraniol, UV-cured transparent acrylic pressure sensitive adhesives (PSAs) composed of semi-interpenetrating networks were successfully fabricated. The utility for optically clear adhesive on adhesion performances according to various concentrations of TGA in the acrylic PSAs were investigated. After characterizing the photo-polymerized PSA syrups, the optical properties for the acrylic PSA films were examined using UV–vis spectroscopy, a color-difference meter, and a haze meter. The acrylic PSAs exhibited high transparency and stable weather-ability under reliability testing (85/85 test). With increasing TGA concentration in the acrylic PSAs, adhesion properties such as the 180° peel strength, shear holding power, and probe tack had decreased.

Introduction

Until now, fossil fuels have been the primary source of synthetic chemicals used to produce man-made organic products such as plastics, adhesives, coatings, and foams due to their convenience, versatility, and relatively low cost. However, potential shortages of fossil fuels have greatly increased the need to replace petroleum-based chemicals with renewable resources [1]. A need had also arisen for general materials required in pressure sensitive adhesives (PSAs) to be replaced with eco-friendly materials because they are non-recyclable, non-compostable, and complete their life cycles as toxic waste [2,3]. Indeed, the manufacturing process based on UV light to produce PSAs is an environmentally friendly process because of its reduced volatile organic compounds (VOCs) emissions, faster curing time, versatility, excellent energy efficiency, and pretty low cost. Thus, these UV-curable PSAs are being broadly used in applications in various industrial areas such as flat-display industries.

Previous many efforts for utilizing biomass related materials in PSAs production included the utilitarian applications of triglycerides, fat-based polyols, fatty acids, and animal vegetable-based polyols, as well as lactones and lactides [4,5]. Unfortunately, these materials are usually not applied to UV-induced free radical polymerization to produce acrylate-type PSA syrups and need to be chemically converted to introduce desired functional groups. Acrylic copolymers containing some sugar-derived moieties have been polymerized using alkyl polyglycosides with maleic anhydride through conventional free radical polymerization [6]. Another research groups have designed a special macromonomers based on biomass for waterborne resin coating materials prepared by mini-emulsion polymerization. Moreover, acrylated methyl oleate has been copolymerized with commercial petro-based acrylate monomers such as 2-ethylhexyl acrylate and methyl methacrylate [7–9]. These copolymers demonstrated comparable tack, static shear, and elasticity compared to commercial available PSAs [9].

In our laboratory, we designed and synthesized various reactive acrylate monomers pending several biomass-based derivatives [10–12] to replace the petroleum-based acrylate monomers and for preparation of UV-curable acrylic PSAs syrups. The monomers were produced for application in electronic devices equipped with a touchscreen or touch panel switch as an input device. An adhesive film is used to attach the transparent conductive film to the touchscreen to reduce the weight of the device and prevent breakage; this film requires various physical properties such as high contrast, clarity, high refractive index, and good reliability [13].

In this study, we also designed and synthesized a reactive acrylate monomer pending tetrahydro-geraniol by simple

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substitution reaction to replace petroleum-based acrylate monomer. The derivative was photo-polymerized with 2-hydoxyethyl acrylate and isobornyl acrylate to prepare a UV-curable acrylic PSA syrup. By changing the content of the tetrahydro-geraniol-based acrylate monomer while fixing the mole ratio for the 2-hydroxyethyl acrylate and isobornyl acrylate in the PSAs, we were able to investigate the adhesive performance, viscoelastic properties, optical properties, and reliability of the transparent acrylic PSAs.

Experimental

Materials

Isobornyl acrylate (IBOA) and 2-hydroxyethyl acrylate (2-HEA) were purchased from TCI, Japan. 3,7-Dimethyl-1-octanol(tetrahydro-geraniol; TCI, Japan) and acryloyl chloride (Chemax, Korea) are obtained. 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba Specialty Chemicals, Switzerland), 1-dodecanethiol (Aldrich Chemicals, USA) and 1,6-hexanediol diacrylate (Samchun Chemical, Korea) were used as the photoinitiator, chain transfer agent and difunctional monomer, respectively. Light release liner, heavy release liner and PET film were used as ROL751, ROH751 and U48, respectively from Toray Advanced Materials Korea Inc.

Synthesis of 3,7-dimethyloctyl acrylate(tetrahydro-geraniol acrylate: TGA)

To a stirred a solution of 3,7-dimethyl-1-octanol (20.0 g, 126.4 mmol) and triethylamine (16.6 g, 164.3 mmol) in dried dichloromethane (200 mL), acryloyl chloride (14.9 g, 164.3 mmol) was added dropwise in the ice bath (0 °C) and then stirred the solution at 25 °C for 12 h. The reaction mixture was quenched with distilled H_2O (25 mL) and extracted into dichloromethane (3 × 150 mL). The combined organic layers were washed with brine again, dried with $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2) to afford the desired acrylate (19.3 g, 72%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.39 (dd, 1H), 6.11 (dd, 1H), 5.81 (dd, 1H), 4.19 (m, 2H), 1.75–1.09 (m, 10H), 0.91 (t, 3H), 0.87 (d, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.46, 130.50, 128.83, 63.30, 39.33, 37.27, 35.64, 30.01, 28.09, 24.74, 22.82, 22.73, 19.68; APCI/MS *m/z* 235.2 $[M+Na]^+$ (calcd. *m/z* 235.17).

Preparation of the acrylic PSA syrups and the acrylic PSA films

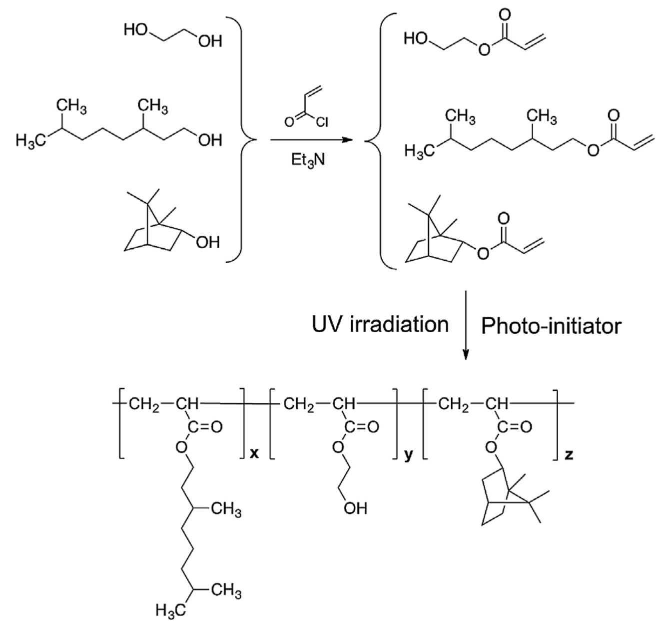
The designed acrylic PSA syrups were polymerized by bulk photo-polymerization according to the previous literature [12]. UV-curable acrylic PSA syrups were composed of synthesized acrylic PSA syrup with photoinitiator (0.5 phr) and difunctional monomer (0.2 phr). The UV-cured acrylic PSA films were fabricated according to reported literature [12].

Instrumental measurements

All instruments and conditions for the characterization of monomers and acrylic PSA syrups, as well as the characteristic measurement of UV-cured acrylic PSA films, are the same instruments and conditions as those used in the previous literature [12]. But mass spectroscopy was conducted with Advion, expression CMS, USA.

Results and discussion

The simple synthetic route for preparing the acrylic PSA syrups is shown in Scheme 1. First, the new monomer was synthesized from the prepared biomass-based derivative, where one hydroxyl group was replaced with an acryloyl group to enable polymerization. The synthesis was carried out in a typical S_N2 substitution reaction. The esterification reaction of one free hydroxyl group in the tetrahydro-geraniol was conducted with the acryloyl chloride in the presence of the base; thus, the acryloyl group is introduced to the tetrahydro-geraniol. The successful synthesis of the acryloyl derivatives of tetrahydro-geraniol was confirmed by the appearance of expected new signals (^{1}H NMR) and exact integral ratios at around 6.11 (dd, $CH_2{=}CHCO-$) and 4.19 ppm (m, O–CH_2CH_3-), respectively, attributed to the vinyl and alkoxy groups and the presence of the definitive number and position of the peaks in the ^{13}C NMR (Figs. S1 and S2, Supporting information); a mass peak (APCI/MS) at *m/z* 235.2 $[M+Na]^+$ further confirmed the structure (Fig. S3, Supporting information).



Scheme 1. Chemical structures of the used monomers and synthesized acrylic PSA copolymer chain.

Using the bulk photo-polymerization technique, the UV-curable acrylic PSA syrups were prepared since this technique can easily control the viscosities of the desired acrylic PSA syrups and can be also operated without organic solvent during fabrication of the PSA film. The compositions of the monomers and additives for the UV-curable acrylic PSA syrups used in this study are presented in Table 1. As shown in Table 1, we selected two conventional monomers, 2-HEA and IBOA, which we copolymerized with the newly synthesized biomass-based acrylate. Although these two conventional monomers can be synthesized through a typical petroleum-based low-cost process, two substituents of the acrylates, ethylene glycol [14] and borneol [15,16], can also be synthesized through a biomass conversion pathway (Scheme 1). Although the acrylic PSAs were derived from biomass-base acrylate with two petroleum-based acrylates, we assumed there was no need to evaluate their optical and adhesion properties because the acrylic PSAs consisted of the same acrylates synthesized from the entire biomass. The characteristics of the prepared UV-curable acrylic PSA syrups such as molecular weight (Mw and Mn), polydispersity index (PDI), and their viscosities are represented in Table 2. Because a high viscous coating syrup obstructs the formation of a smooth coating layer and because a low viscous coating syrup reduces the cohesion strength of the coating syrup [17], the viscosity control of the coating syrup can play an important role in PSA industries. In this study, the