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Kinetic and characterization of UV-curable silicone urethane methacrylate in semi-IPN-structured acrylic PSAs

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To improve the thermal stability of general acrylic pressure-sensitive adhesives (PSAs), polydimethylsiloxane (PDMS) was used and UV curing was employed. Silicone urethane methacrylate (SiUMA) was synthesized and introduced into acrylic PSAs for a semi-interpenetrating polymer network structure. The structure of the SiUMA was investigated through C NMR, H NMR, and FT-IR. The kinetics and behaviors of SiUMA (S1) were found by adding photoinitiators (PI) of 0.5, 1.0, 5.0, and 10 phr in a binder, which were examined using the photo-DSC (pDSC). After setting PI as 5.0 phr in a binder and UV intensity as 1000 mJ/cm², the SiUMA, which was prepared by a radical polymerization, was added to acrylic PSA to 20, 40, 60, and 80% composition, and its kinetics and behaviors were analyzed by pDSC. Finally, the peel strength was checked to evaluate adhesion performance of the acrylic PSAs. The reaction rate was increased with increasing amounts of S1 and PI. Peel strength was dropped sharply with increasing crosslinking density.

Keywords: acrylic PSA; semi-IPN; silicone; urethane acrylate; photo-DSC

1. Introduction

UV or EV polymerization provides an excellent method for the rapid conversion of multifunctional acrylate monomers into crosslinked polymer networks at room temperature. This photo-technology is applied mainly in coating and printing industries that deal with thin film applications.[1] UV curing or polymerization has many advantages such as solvent-free formulation, low energy consumption, and ambient temperature operation. Acrylates are highly reactive, rapidly transforming from a liquid resin to a solid polymer upon exposure to light. This characteristic makes them very good materials for different applications.[2,3]

Polydimethylsiloxanes (PDMSs) has well-known, unique characteristics such as very high thermal and chemical resistances, high flexibility and hydrophobicity, and stability against different types of radiation. Polysiloxanes with different organofunctional substituents have been used as starting compounds in the preparation of polymeric materials.[4,5] PDMSs containing acrylic and methacrylic ester groups, linked to the siloxane chain as pendant units through aliphatic ether moieties, have been researched.[6,7] Until now, silicone acrylates have been studied and developed for coating materials but not for adhesive materials. If silicone urethane methacrylate (SiUMA) can be induced in acrylic Pressure-sensitive adhesives (PSAs), various products based on the characteristics of PDMS can be made.

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PSAs are semi-solid phase materials which show good viscoelastic properties and adhesion strength on solid substrates upon the application of light contact pressure for a short time. In general, PSAs need to exhibit various physical properties according to the characteristics of the product in various industries, including medical, electronic, construction, and automobile industries.[8] These properties are controlled by the molecular weight, structures, and side chains.

An interpenetrating polymer network (IPN) consists of an intimate combination of two or more polymer networks. However, this network is not a chemical linkage between distinct networks. The network can be synthesized by crosslinking polymerization of two multifunctional monomers or telechelic oligomers, which are polymerized by different mechanisms, e.g. radical and cationic polymerization.[9] Homogeneous IPNs can be synthesized by UV-curing technology.[10] Moreover, high polymerization rates can be easily reached at room temperature under high light intensities.[11] IPNs are solvent-free and thus environmental friendly.[11,12] Reaction rates are affected by catalyst concentration, viscosity, reaction sequence, and concentrations. Morphology, phase separation, and composition are determined by reaction kinetics and chemical compatibility. Thus, understanding the reaction kinetics is important in engineering final material properties.[13]

In this study, the structure of SiUMA was characterized by FT-IR. The UV-curing behaviors of SiUMA in acrylic PSAs were studied by photo-DSC (pDSC). The physical properties of the PSAs were investigated with a texture analyzer. The UV reactivity and physical properties of the cured films, with different concentrations of the photoinitiators (PI), were also studied.

2. Experimental

2.1. Materials

2-Ethylhexylacrylate (2-EHA) and acrylic acid (AA) were purchased from Samchun Pure Chemical Co., Ltd. (Republic of Korea). 2,2-Azobisisobutyronitrile (AIBN) from Daejung Chemicals & Metals Co. (Republic of Korea) was used as the initiator for synthesizing acrylic PSAs. Polydimethylsiloxane (PDMS, Shin-Etsu co., Ltd, Japan) and dicyclohexylmethane-4,4'-diisocyanate (H12MDI, Bayer Material Science, Germany) were dried in 100 °C for 12 h prior to use, and 2-hydroxyethylmethacrylate (2-HEMA, Samchun Pure Chemical Co. Ltd, Republic of Korea) was used without pretreatment. Hydroxy dimethyl acetophenone (Micure HP-8, Miwon specialty chemical Co., Ltd, Republic of Korea) was used as the photo-initiator for the UV-polymerization of the acrylic PSAs. Dibutyltin dilaurate was added as a catalyst for rapid urethane reaction.

2.2. Methods

2.2.1. Synthesis of basic acrylic PSAs

An acrylic PSA was synthesized from 2-EHA and AA in ethyl acetate solvent with about 50% solid contents. The polymerization was performed in a 500 ml, four-necked, round-bottom flask equipped with a thermo-coupler, a condenser, a dropping funnel, and a mechanical stirrer. The resin with 0.05 wt.% of AIBN was heated up to 80 °C for about an hour, and afterward, the mixture was kept at 80 °C for 3 h until the completion of solvent polymerization and more 0.05 wt.% of AIBN was added three times.

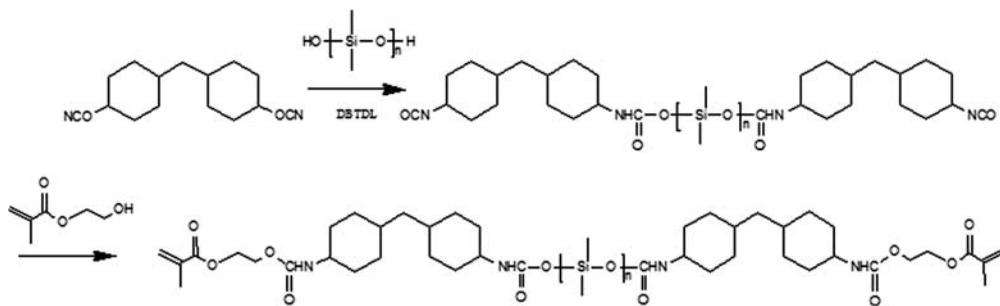


Figure 1. Synthesis of SiUMA.

2.2.2. Synthesis of SiUMA

The SiUMA was synthesized by adding an equimolar amount of PDMS with 0.1wt.% dibutyl tin dilaurate dropwise to H₁₂MDI (i.e. NCO:OH=2:1) under nitrogen gas. The reaction was maintained at room temperature for two hours. An equimolar amount of HEMA with 0.5 wt.% of hydroquinone as a thermal polymerization inhibitor was added dropwise to the PDMS–H₁₂MDI adduct. Five hours later, the absorption peak of NCO group disappeared almost completely. The temperature was kept below 60 °C to remove non-reactive sites. At this time, the absorption peak of the NCO group at 2250 cm⁻¹ disappeared completely (Figure 1).

3. Results and discussion

3.1. Curing kinetics and behaviors of SiUMA in acrylic PSAs

3.1.1. FT-IR

Figure 2(a) shows the FTIR spectrum of HMDI. The bands at 2248 cm⁻¹ were due to the NCO group. The disappearance of the band indicated the completion of the reaction in

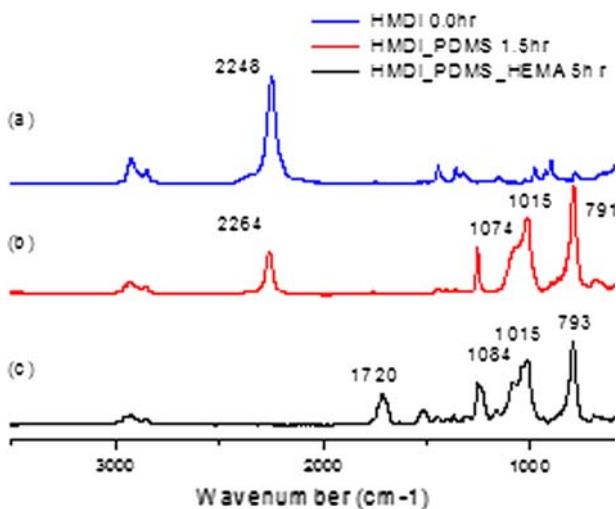


Figure 2. FTIR spectra of (a) HMDI, (b) addition of PDMS, and (c) addition of HEMA.

(a)–(c). Figure 2(b) shows the characteristic bands of PDMS: the bands at 1015 and 1074 cm^{-1} indicated Si–O–Si stretching vibration; the band at 791 cm^{-1} indicated to S–CH₃ stretching vibration; the band at 2248 cm^{-1} indicated the isocyanate group, which meant urethane reaction. Figure 2(c) is associated with the band of the acrylic double bond at 810 and 1638 cm^{-1} , which shows very weak intensity, so the band at 1720 cm^{-1} (C=O) stretching vibration indirectly shows that HEMA was induced in SiUMA.

3.1.2. *pDSC*

The reactions were carried out with PI concentrations of 0.5, 1.0, 5.0, and 10 phr in a binder at room temperature. Through this experiment, the amount of required UV intensity was determined. Figure 3 shows the values of the enthalpies measured in isothermal curing conditions at room temperature for 300s with benzophenone as the PI for different contents. Over PI concentration of 5 phr in a binder, no significant differences were observed. So, PI concentration of about 5 phr in a binder was considered properly and UV intensity of 1000 mJ/cm^2 was sufficient.

S1 reactions were studied by the blends of acrylic PSA (80%), S1 (20%), and PI of different amounts. These reactions were carried out with PI concentrations of 0.5, 1.0, 5.0, and 10 phr in a binder at room temperature as shown in Figure 4. The UV intensity was kept constant at 1000 mJ/cm^2 . All of the reactions were increased significantly with increasing amount of PI but decreased dramatically over PI concentration of 5 phr in a binder. Because of the high rate of recombination of the radicals, UV light of the initiator was more absorbed in the top layers and the PI became somewhat incompatible with the rigid polymers.[14] The reaction rate was slow due to dilution for other monomers.[15]

The reaction rate was increased significantly with increasing amount of S1. Figure 5 shows that with increasing S1 fraction, the enthalpy increased significantly. And not only the acceleration but also deceleration was seen sharply with increasing S1 mass fraction. These results mean that the S1 fraction influenced both the acceleration and the deceleration because the propagation mobility of S1 was reduced due to the acrylic PSAs (acrylate gel).[13]

Theoretical enthalpy could be obtained from the integral graph for PI concentrations of 0.2, 0.4, 0.6, and 0.8 based on pure S1 from Figure 6. Each reaction increased about 20%

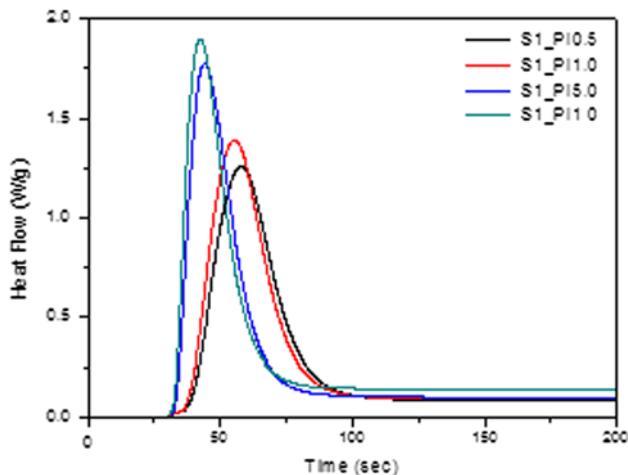


Figure 3. Heat flow profiles of S1 reaction.

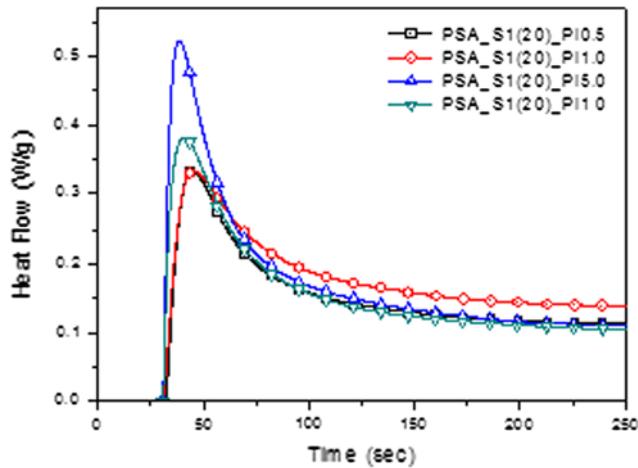


Figure 4. Isothermal curing at room temperature with different amounts of PI contents.

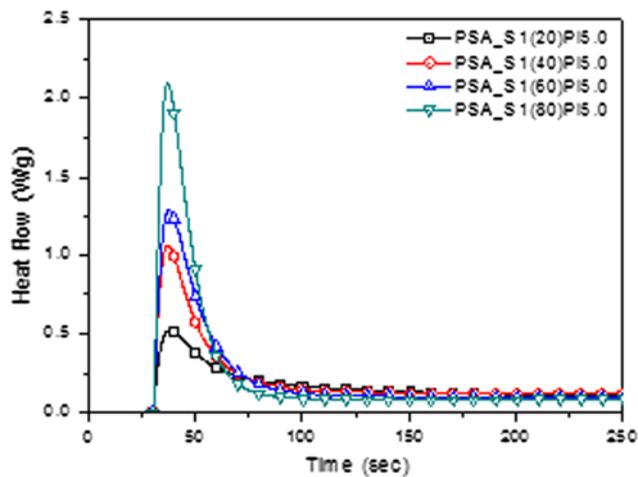


Figure 5. Different mass fraction of S1 with acrylic PSAs.

more than theoretical values. This means that the space allows S1 to move in acrylic PSAs, and easy to match each other for complete reaction. Also, acrylic PSAs consist of the 50 wt. % of solvents, which provided the mobility of S1.

3.2. Adhesion performance

The crosslinking density is changed according by the concentration of PI as shown in Figure 7. Over 5 phr of PI, the crosslinking density was very high and so the peel strength was low; therefore, no additional PI was needed. Under 40% of S1, the PSA can be controlled to have various properties and some degree of crosslinking.

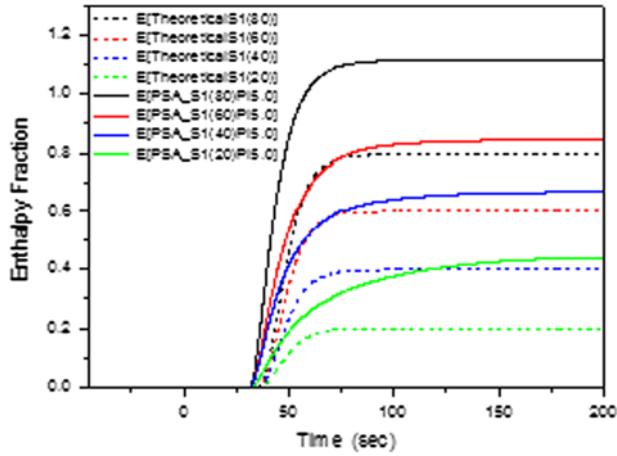


Figure 6. Comparison of theoretical enthalpy fraction with enthalpy mixtures of PSA_S1.

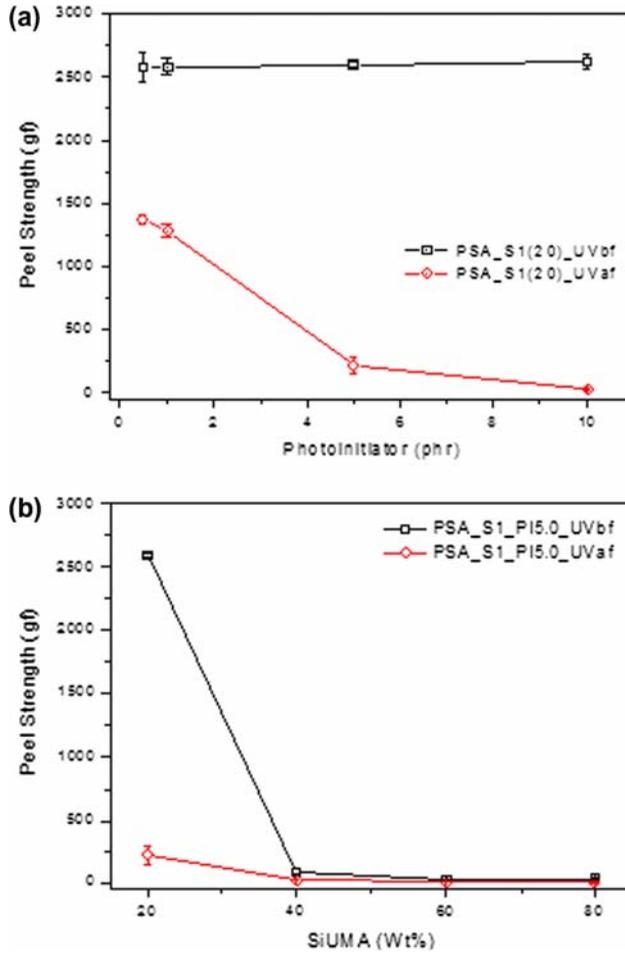


Figure 7. Peel strength with different (a) PI and (b) S1 contents.

4. Conclusion

In this work, the synthesis and characterization of semi-interpenetrating polymer network structured (semi-IPNs) acrylic PSAs from radically initiated S1 were investigated. The structure of the S1 was characterized by FTIR. The disappearance of the band at 2250 cm^{-1} , which was assigned to the isocyanate group, was indicative of the completion of reaction. The reactivity of the semi-IPNs was determined by pDSC measurement. The formation was increased with increasing contents of S1 oligomer in the acrylic PSA. The physical properties of the samples were analyzed.

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