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# Behavior and Adhesion Performance of Acrylic PSAs using Semi-IPN Structure and UV/UV Stepwise Curing

### Gyu-Seong Shim<sup>a</sup>, Ji-Soo Kim<sup>a</sup>, Hyun-Joong Kim<sup>a,b,1,\*</sup>

<sup>a</sup> Laboratory of Adhesion and Bio-Composites, Program in Environmental Materials Science, College of Agriculture and Life Sciences, Republic of Korea <sup>b</sup> Research Institute of Agriculture and Life Sciences, College of Agriculture and Life Sciences, Seoul National University, Seoul 08826, Republic of Korea

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#### Introduction

Pressure-sensitive adhesives (PSAs) are viscoelastic and can adhere to adherends based on pressure and contact time [1,2]. Owing to these characteristics, PSAs can be used for label papers and protective films [3]. In addition, studies on the applicability of PAS to flexible electronic devices are actively being conducted [4]. We hope your application can be applied in flexible electronics. Generally, the physical properties of acrylic PSAs can be altered based on the mechanical and chemical properties. For example, the degree of crosslinking [5] or the crosslinking curing system [6] can be adjusted, which accounts for its extensive use in industrial applications.

Pre-polymers are formed when UV radiation is applied while the monomers and photoinitiators are blended. PSAs can also be manufactured by the addition of additives and crosslinking agents. UV-curable PSAs have numerous advantages. For example, PSAs are solvent free and low volatile organic compounds (VOCs), which make them suitable for the coating and adhesive production industries [7–10]. In addition, acrylic resin has certain advantages affecting the polymer processing property [11] and the thermal curing of the smart device restricts the temperature to one that

E-mail address: hjokim@snu.ac.kr (H.-J. Kim).

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ABSTRACT

Pressure-sensitive adhesives (PSAs) and UV-curable acrylic systems are widely utilized. In particular, PSAs have currently attracted significant attention because of their utility and applicability for manufacturing re-useable modules for smart devices. In this study, adhesion properties, UV-curing behavior, viscoelastic properties, and gel fraction were investigated. The UV/UV step curing process was utilized to overcome limitations, such as re-work or gap filling. The difference in physical properties between primary curing and secondary curing was confirmed. In addition, by adjusting the content of the crosslinking agent, the experiment based on controlling the structure of the semi-interpenetrating polymer network was conducted. We determined that physical properties varied with the crosslinking agent content. The degree of crosslinking and the crosslinking density increased for 0.5–1 phr. © 2020 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights

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does not damage the module [12]. Therefore, in order to prevent damage to the module, UV-curable PSA with a relatively low heat generation is preferred.

Semi-interpenetrating polymer networks (Semi-IPNs) are a mixture of liner and crosslinked polymers. The physical properties of semi-IPN structures are based on non-covalent interactions [13]. In addition, the semi-IPN structure is formed by the characteristics of pre-polymer PSAs. Fig. 1. shows the semi-IPN structure of the PSA. When the pre-polymer is polymerized, it exists in the form depicted in Fig. 1a. However, prior to manipulating the properties and synthesizing the PSA coated film, the pre-polymer is blended to resemble the configuration depicted in Fig. 1b. UV/UV step-curing was implemented using black light (BL; prolonged curing using a low-pressure light source) and a UV conveyor belt (rapid curing using a high-pressure light source) [14].

We verified the possibility of step curing in a previous study. In this study, we polymerized pre-polymers and blended multifunctional monomers. Before step curing, the pre-polymer resembles structure A (Fig. 2a). Structure B (Fig. 2b) is added during advanced blending. When the step curing proceeds, the result is the semi-IPN with physical property control. In particular, step curing was introduced to validate the possibility of rework characteristics. We confirmed the change in physical properties based on the semi-IPN structure, whose composition was dependent on the amount of crosslinking agent. Probe tack and peel strength were measured to investigate the adhesion properties, whereas Photo-DSC was used to confirm the UV-curing

<sup>\*</sup> Corresponding author. Tel.: +82 2 880 4784; fax: +82 2 873 2318.

<sup>&</sup>lt;sup>1</sup> www.adhesion.kr.

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Fig. 1. Schematic of Semi-IPN PSA (a) pre-polymer and (b) Blending pre-polymer, additive and crosslinking agent.



Fig. 2. Schematic of Semi-IPN PSA (a) structure A and (b) structure B.

behavior. Dynamic mechanical analysis (DMA) was used to determine the  $T_{\rm g}$  and storage modulus. The gel fraction was measured to confirm the degree of crosslinking.

#### Experimental

#### Materials

All monomers were used without purification. The monomers were: 2-Ethylhexyl acrylate (2-EHA), acrylic acid (AA), 2-hydroxyethyl acrylate (2-HEA), and methyl methacrylate (MMA) produced by Samchun Pure Chemical Co., Ltd. (Republic of Korea). Isobornyl acrylate (IBA) was produced by Sigma-Aldrich (USA). Hydroxydimethyl acetophenone (HA, Micure HP-8, Miwon Specialty Chemical, Republic of Korea) was used as the initiator. HA absorbs in both wavelengths and initiates an initiation reaction in the absorbed wavelengths (265–280 and 320–335 nm). The composition of the PSA is summarized in Table 1.

Pre-polymer synthesis

The pre-polymer was synthesized from a mixture of 2-EHA, AA, IBA, MMA, 2-HEA, and HA (0.3 wt%) by bulk radical polymerization, which was performed in a 500-mL four-necked flask equipped with a mechanical stirrer,  $N_2$  inlet, thermometer, and a light-emitting diode UV lamp. The temperature at the start of the reaction was maintained at 23 °C and a constant stirring speed of 100 rpm was used. The experiment was performed using a 500-mL reaction tool in a reaction zone and a 200-g arrangement. The monomer mixture was exposed to UV light (20 mW/cm<sup>2</sup>, main wavelength: 365 nm). The reaction proceeded until the temperature improved to 15 °C, after which, air was blown for 30 minutes to facilitate termination [12].

#### Adhesive film preparation

UV curable pre-polymers are prepared by blending crosslinking agents and additives. Ethoxylated trimethylolpropane triacrylate (EO6TMPTA, Sigma-Aldrich) is a commonly used crosslinking

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#### Table 1

Composition of acrylic pre-polymer.

\_\_\_\_\_Composition (%)

PSAs		Composition (%)
Reactive Monomer(pre-polymer)	2-EHA (2-ethylhexyl acrylate)	64
	AA (Acrylic acid)	3
	IBA (Isobornyl acrylate)	19
	MMA (Methyl methacrylate)	4
	2-HEA (2-hydroxyethyl acrylate)	10
Photo initiator	Hydroxydimethyl acetophenone	0.3



Fig. 3. Schematic of lauyl acrylate monomer.

agent [15]. EO6TMPTA was used to evaluate the delay in primary UV curing and to determine the uncured marginal portion of the pre-polymer [14]. Lauryl acrylate (LA; Fig. 3) was used to delay the UV curing reaction by promoting a reaction with the chain transfer agent [16]. In order to confirm the change in physical properties based on the LA content, the experiment was conducted by varying the amount of crosslinking agent to 0.0, 0.1, 0.3, 0.5, 0.7, and 1.0 phr, respectively.

#### Step curing

The corona-treated polyethylene terephthalate films (SKC Co. Ltd., Republic of Korea) were coated with a thickness of 100  $\mu$ m. The curing method performed was that of stepwise-curing. We utilized a BL curing machine equipped with a low-pressure mercury UV lamp (20 mW, main wavelength: 365 nm) for primary curing. The conveyor-type UV-curing machine with medium-pressure mercury UV lamps (154 mW/cm<sup>2</sup>, main wavelength: 365 nm) was used for secondary curing [14,17].

#### Photo-DSC

The UV-curing behavior of adhesives was evaluated by photo-DSC (DSC Q200, TA Instruments, USA) using a spot-cure light source (OmniCure S2000, Excelitas Technologies Corp., Waltham, MA, USA). The UV lamp used a 100 W mercury vapor bulb. The UV light level of the UV accessory equipped with a 90% UV filter was determined as 10% [18]. The sample weight was 2-3 mg. All measurements were performed at 25 °C.

#### Adhesion properties

#### Peel strength

Peel strength (180° peel strength test) was measured based on the ASTM D3330 Standard Test Method (TA-XT2i texture analyzer, Micro Stable Systems, UK). The crosshead speed was measured at 300 mm/min at 25°C. The adhesive area (25 mm) was left for 24 hours at 23°C. A total of five samples were measured and averaged with units of N/25 mm. SUS304 was used as the base material. Primary curing was performed in the film state, whereas secondary curing was conducted after attachment to SUS304. The sample was chosen by selecting the method that was applied in the particular industry.

#### Probe tack

The probe tack was used to measure the maximum debonding force (ASTM D3330) [19]. Probe tack was measured at  $25 \,^{\circ}$ C. The probe used a 5-mm-diameter stainless steel cylinder probe, which approached the sample at a speed of 0.5 mm/s and continued for 1 s after contact. The contact force was maintained at  $100 \,\text{g/cm}^2$ . The debonding speed after contact was 0.5 mm/s.

#### Viscoelastic properties

Viscoelastic properties were measured with a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA) using the film tension mode as the test mode. The dimensions of the specimens used in the measurements were approximately 11–



Fig. 4. Real-time heat flows after (a)prinmary curing and (b) secondary curing.

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13 mm (length), 12 mm (width), and 1 mm (thickness). The test method used the following conditions: strain rate = 0.1%, frequency = 1 Hz, and heating rate =  $5 \degree C/min$ . The temperature was measured from -40 to  $60 \degree C$  [14].

#### Gel fraction

The gel fraction of the crosslinked polymers or network polymers was determined using toluene [20]. After immersing the crosslinked adhesive in toluene for 24 h, the insoluble portion was filtered. The filtered sample was dried in an oven at 80 °C [21]. The gel fraction was calculated as gel fraction (%) =  $(W_1/W_0) \times 100$ , where  $W_0$  is the weight of the original sample, and  $W_1$  is the weight of the dried insoluble residue.

#### **Results and discussion**

#### Curing behavior determined by photo-DSC

Photo-DSC can be used to measure the exothermic reaction and confirm the kinetics of the crosslinking reaction [19]. An

exothermic reaction occurs when the acrylic C=C double bond reacts. In general, when crosslinking proceeds, the double bond of the crosslinking agent reacts, which enables the determination of the degree of crosslinking.

After primary curing, the reaction increased to 0.5 phr, based on the sample without the crosslinking agent, which can be seen in Fig. 4. After 0.7 phr was added, the reaction appears to decrease. The results obtained from the samples involving 1 phr of crosslinking agent were comparable with those containing 0 phr. This phenomenon is expected to retard the reactivity as the crosslinking agent is added. However, impact of the phenomenon was reduced because the reaction began when a high content of crosslinking agent was added. In the secondary curing, it was observed that secondary curing did not occur in samples where  $\geq$ 0.5 phr of the crosslinking agent was added. However, the secondary curing at 0.3 phr demonstrated that there is a reaction site where the reaction rate is delayed. This can also be observed in the area under the exothermic curve.

Fig. 5 depicts the integral for heat flow. The point where the plateau occurs is confirmed as the end of the reaction. At 0.3–0.5 phr, the reaction lasted longer than 200 s, but was terminated at



Fig. 5. Area under the exothermic curve (a) primary curing and (b) secondary curing.



Fig. 6. Conversion profiles: (a) primary curing and (b) secondary curing steps.

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Fig. 7. Schematic diagram of expected structure in crosslinking agent contents variation (a) primary curing and (b) secondary curing steps.

other concentrations. A similar phenomenon occurred in secondary curing. In secondary curing, majority of the reaction site was exhausted. Consequently, the 0.3 phr for secondary curing exhibited a shape similar to that of 0 phr for primary curing.

If the reaction proceeds, the double bond becomes exhausted and crosslinking occurs. Thus, the conversion rate can be calculated according to the response.

The conversion or polymerization rate  $(d\alpha/dt)$  can be defined as:

$$d\alpha/dt = (dH/dt)/\Delta H_{\text{total}} \tag{1}$$

where dH/dt is the measured heat flow, and  $\Delta H_{\text{total}}$  is the total exothermic heat of the reaction. Integration of Eq. (1) allows conversion at time  $t(\alpha_t)$  to be calculated as:

$$\alpha_t = \Delta H_t / \Delta H_{\text{total}} \tag{2}$$

where  $\Delta H_t$  is the cumulative heat of reaction up to curing time *t* [14].

Fig. 6. depicts the conversion profiles. The time (300 s) time taken to achieve 100% conversion of the 0 phr specimen (primary curing) is represented by a red dotted line. In general, when a graph is represented by a straight line, there is no reaction. As a result, the reaction progresses via primary curing. In addition, the 0.7 phr specimen confirmed that the reaction terminated prematurely. In secondary curing, all specimens demonstrated near-linear graph deformation at the time (238 s) of 100% conversion, which is believed to delay the reaction. The reactivity was slow in the first 50 s. After the reaction began, the graph began to curve, which indicated the reactivity.

This phenomenon can be explained by Fig. 7, which can be divided into three types based on experimental data. If the crosslinking agent is 0 phr, a linear polymer is produced in primary

curing. Secondary curing also produces linear polymers. Therefore, the polymer is a form of polymer blending rather than a semi-IPN structure. Reaction sites increase when 0.1–0.5 phr crosslinking agent is added, which is shown to increase reactivity. However, due to the small amount of crosslinking agent, crosslinking will occur and the crosslinking agent and monomers will bind as shown in the Fig. 7. The reaction is expected to proceed simultaneously, rather than in the main chain. Therefore, it is highly responsive but is relatively soft. An identical result is observed with the modulus.



Fig. 8. Gel fractions of cross-linked acrylic PSAs prepared at different curing agent contents.

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Fig. 9. Temperature dependence of PSA storage modulus determined for different exposure energies results for (a) primary and (b) secondary curing.



Fig. 10. Temperature-dependent tan  $\delta$  of cross-linked acrylic PSAs prepared using different exposure energies: (a) primary and (b) secondary curing and (c) Temperatures of maximum tan  $\delta$  extracted from parts (a) and (b).

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Fig. 11. Temperature-dependent tan  $\delta$  of cross-linked acrylic PSAs prepared using different exposure energies: (a) primary and (b) secondary curing.

In addition, for 0.7–1 phr specimens, even if the reaction proceeds simultaneously, the amount of crosslinking agent will increase; thus, the crosslinking density and modulus will increase. The modulus and crosslinking density is illustrated in Fig. 7.

#### Gel fraction measurements

Residual monomers that are not crosslinked can cause defects. Therefore, the degree of crosslinking must be measured. An indirect way to determine the degree of crosslinking is to calculate the insoluble portion [22], which was confirmed by measuring the gel fraction. Fig. 8 shows the results of the gel fraction. After primary curing, there was already a 90% gel fraction and majority of the crosslinking was complete. Since there was a semi-IPN structure, there was approximately 10% loss. The reason for this is that crosslinking occurs but the crosslinking density is low. In other words, as shown in Fig. 7, the degree of crosslinking is high, but the crosslinking density of each specimen is expected to be different.

#### Viscoelastic properties

Fig. 9 illustrates the storage modulus versus the temperature. The storage modulus is usually low. The graphs overlap at the secondary curing time more than at the primary curing time. In other words, after secondary curing, the polymers have similar storage moduli and properties. Fig. 10 is the tan  $\delta$  result. In polymers, tan  $\delta$  represents  $T_g$ , which can be inferred as the



Fig. 12. Peel strength and probe tack as functions of Crosslinking agent contents.

crosslinking density. There was an increase in the  $T_g$  in secondary curing compared with that in primary curing, which indicates that secondary curing occurred. As seen in Fig. 7, the crosslinking density of the main chain decreases slightly at 0.1–0.5 phr, and the crosslinking density increases at 0.7–1 phr. Additionally, Fig. 11 shows that the greater the amount of crosslinking agent added, the smaller the linear region is. At 0.1–0.5 phr, the amount of crosslinking agent is insufficient to achieve complete crosslinking, so there are many linear regions;  $T_g$  decreases although curing occurs. However, at 0.7–1 phr,  $T_g$  increases again because crosslinking is feasible under this condition.

#### Adhesion properties

Fig. 12 shows the adhesion results. At 0 phr, there is no crosslinking; hence, the adhesion and tack appear to be high. However, after a minimal hardening, the adhesion decreases. The 0.3 phr showed the highest value of the adhesive force in the crosslinking state. As the crosslinking agent was added, the adhesive force decreased. This phenomenon indicates that hardening progressed continuously. In addition, as secondary curing proceeds, the adhesion increases to a small extent. Similar trends show that the tack is slightly reduced, which demonstrates that progressing from primary curing to secondary curing is significant.

#### Conclusions

In the process of UV/UV step curing, the physical properties were tested depend on the amount of crosslinking agent. By polymerizing the acrylic pre-polymer, it is possible to control the physical properties. For the 0.1–0.3 phr, the degree of crosslinking was high, but the crosslinking density was low. When the crosslinking agent content was increased to 0.5–1 phr, the degree of crosslinking and crosslinking density also increased. In the case of the crosslinking polymer, molecular weight analysis is relatively difficult but can be inferred from physical and chemical data. However, the quantitative determination confirmed was erroneous. Therefore, in order to compensate for this inaccuracy, additional research is required to investigate the variation in crosslinking agents and additives and to confirm the change in behavior based on the change in the composition of the PSA pre-polymer.

#### **Declarations of interest**

None

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