

Original Article

Curing behavior and impact of crosslinking agent variation in stepwise UV/UV cured acrylic pressure-sensitive adhesives



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ABSTRACT

Pressure-sensitive adhesives (PSAs) are used in various industries, and have been widely applied in smart devices. In this study, the adhesion properties, viscoelastic properties, and gel fraction of PSAs were investigated after primary and secondary curing to understand their UV-curing behavior. In addition, the impact of concentration of crosslinking agent on the crosslinking density and the degree of crosslinking was investigated. In general, as more crosslinking agent was added, the hardness increased, but this result can be explained by the difference between "crosslinking density" and "degree of crosslinking" at the highest concentration of crosslinking agent actually led to a decrease in "degree of crosslinking". © 2021 The Authors. Published by Elsevier B.V. This is an open access article under the CC

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1. Introduction

Pressure-sensitive adhesives (PSAs) can be applied to various surfaces at a constant temperature [1,2]. Acrylic PSAs have various industrial applications because of their excellent temperature resistance, optical transparency, and adhesion properties [3]; further, the transparency of acrylic PSAs facilitate their application in smart devices [4]. In addition, crosslinking systems can control their properties relatively easily [5,6]. Further, processing smart devices at high temperatures can cause damage to the device; therefore, UV-type PSAs that generate relatively less heat are often used for such applications [7]. UV-reactive PSA blends multi-functional groups to control reactivity [8,9]. For example, mixtures of monomers and photo initiators can be used in the form of a UV-reactive syrup that has the advantages of being solvent-free and containing low amounts of volatile organic compounds (VOCs), thereby facilitating stable industrial applications [10–12]. The characteristics of UV curing systems based on free radicals

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have previously been analyzed via Raman analysis and Fourier-transform infrared spectroscopy (FTIR) [13].

A general aim when designing PSAs is to minimize the presence of residual monomers, which can cause defects [14]. Therefore, crosslinking systems are used to remove residual monomers and improve physical properties. Crosslinking density is an important factor in such systems as it is the most useful way of controlling the properties of the system, and can be changed by altering the amount of crosslinking agent used. Gel fraction is often used as a measure of crosslinking density because the molecular weights of crosslinked PSAs are difficult to measure [15], so conversion is confirmed by the presence of C=C double bonds [16]. In this model, the term crosslinking density is used to indicate how much crosslinking has occurred. However, it should be noted that the crosslinking density can still be low even if conversion or the gel fraction reaches 100%, as shown in Fig. 1, where Fig. 1(a) shows a system with a high crosslinking density, and (b) shows a system with a low crosslinking density. Therefore, the terms "crosslinking density" and "degree of crosslinking" should be used in different contexts. For example, the degree of crosslinking will be 100% in both Fig. 1(a) and (b) when determined using gel fraction measurement via dissolution in a good solvent or FT-IR conversion. However, the crosslinking densities of Fig. 1(a) and (b) will be significantly different. In this study, crosslinking density was measured and conversion was calculated using photo-differential scanning calorimetry (photo-DSC), allowing the curing behavior to be checked intuitively.

UV/UV stepwise curing was implemented using black light (BL; long-time curing using a low-pressure light source) and a UV conveyor belt (fast curing using a high-pressure light source) [17]. Stepwise curing is a method of secondary curing that involves leaving a curing margin during primary curing [18]. This method can allow characteristics to be altered by only forming weak bonds during primary curing, rather than direct formation of the end products. This enables the recycling of expensive materials during lamination in smart devices [19]; however, there is a disadvantage of difficult recycling when modules are glued together, implying that when a defect occurs, the entire unit is unusable. In this study, changes in the physical properties of a PSA were monitored as the amount of crosslinking agent in a stepwise curing system was altered. To control the reactivity, lauryl methacrylate was used. Prior to stepwise curing, the pre-polymer was polymerized, and an additive and crosslinking agent were blended to produce an adhesive film. Changes in adhesion properties were also monitored as crosslinking agent content was varied. In addition, the curing properties during stepwise curing were confirmed through photo-DSC, and gel fraction was used to identify unreacted monomers. At the same time, the change in the crosslinking density was confirmed, and dynamic mechanical analysis (DMA) was employed to determine the glass transition temperature (T_g).

2. Materials and methods

2.1. Materials

2-Ethylhexyl acrylate (2-EHA), acrylic acid (AA), 2hydroxyethyl acrylate (2-HEA), and methyl methacrylate (MMA) manufactured by Samchun Pure Chemical Co., Ltd. (Republic of Korea) were used for the pre-polymer preparation. All monomers were used without further purification. Hydroxydimethyl acetophenone (HA, Micure HP-8, Miwon Specialty Chemical, Republic of Korea) was used as photoinitiator for the polymerization [17]. The composition of the PSA is summarized in Table 1.

2.2. Synthesis of the pre-polymer

The pre-polymer was prepared using bulk radical polymerization. The reaction was performed in a 500 mL four-necked



Fig. 1 - Schematic of typical polymer structures with (a) high crosslinking density and (b) low crosslinking density.

Table 1 – Raw materials used to prepare the pre-polymer.		
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

flask equipped with a mechanical stirrer set to 100 rpm and a system of purging N₂ gas. The flask was charged with 200 ml of monomer, and the reaction was initiated with a UV light-emitting diode lamp (20 mW/cm², 365 nm). The reaction temperature was 23 °C, and the chemical process was terminated by increasing the temperature by 15 °C and air blowing for 30 min.

2.3. Gel permeation chromatography

UV curable pre-polymers were blended with a crosslinking agent-ethoxylated trimethylolpropane triacrylate (EO6TMPTA, Sigma—Aldrich) and an additive - lauryl methacrylate (LMA, 2phr) [20]. Both EO6TMPTA and LMA slow the rate of curing. For this reason, the degree of curing in the stepwise curing system was adjustable by varying the crosslinking agent contents to 0.0, 0.1, 0.3, 0.5, 0.7, and 1.0 phr.

2.4. Preparation of cured acrylic PSA: stepwise curing

PSA films were molded through bar coating method on corona-treated polyethylene terephthalate films (SKC Co. Ltd., Republic of Korea) to give a thickness of 100 μ m. Primary curing used low UV light intensity (20 mW/cm², main wavelength of 365 nm), while secondary curing used medium-intensity UV curing conveyor (154 mW/cm², main wavelength of 365 nm) [17,18]. The UV irradiation dose was fixed at 3000 mJ/cm² (in primary curing). In secondary curing, all specimens were irradiated with 2500 mJ/cm².

2.5. Photo-differential scanning calorimetry (Photo-DSC)

The UV-curing behavior of the adhesive was monitored via photo-DSC (DSC Q200, TA Instruments, USA) using a spot-cure light source (OmniCure S2000, Excelitas Technologies Corp., Waltham, MA, USA) and a 90% UV filter. All measurements were performed at 23 °C. The curing margin was measured in the films after both primary and secondary curing. All experimental specimens had weights of 1.0–1.5 mg to reduce errors [12,16].

2.6. Adhesive properties

2.6.1. Peel strength

Peel strength was measured according to ASTM D3330, involving a 180° peel strength test. A texture analyzer (TA-

XT2i texture analyzer, Micro Stable Systems, UK) was employed, with a crosshead speed of 300 mm/min at 25 $^{\circ}$ C. The adhesive area of the specimens used for measurements was fixed at multiplied by peeled length, and samples were left at 23 $^{\circ}$ C for 24 h prior to testing. The measured data were expressed in N/25 mm units. Steel use stainless (SUS304) was used as the attached substrate. The primary curing specimens were cured in the film state and then attached to the substrate, while the secondary curing samples were cured after being attached to the substrate [21].

2.6.2. Probe tack testing

Probe tack testing measures the maximum debonding force (ASTM D3330). The probe used was a 5 mm diameter stainless steel cylinder. The speed of approaching to the specimen was 0.5 mm/s, and the contact force was 100 g/cm². After maintaining contact for 1 s, the debonding speed was 0.5 mm/s [21].

2.7. Viscoelastic properties

Viscoelastic properties were investigated by operating a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA) in film tension mode on specimens of 11–13 mm (length) x 12 mm (with) x 1 mm (thickness). The strain rate was 0.1%, the frequency was 1 Hz, the heating rate was 5 °C/min, and the temperature range was -40 to 60 °C [1,17].

2.8. Gel fraction

In general, the gel fraction of a polymer network that has been crosslinked is measured by dissolving it in toluene and measuring the gel contents [22]. After immersing the molded film in toluene for 24 h, the undissolved material was filtered off, dried in an oven at 80 °C, and then the gel content was weighed. The gel content expressed as the gel fraction (in %) was calculated according to the relationship (W_1/W_0) × 100, where W_0 is the weight of crosslinked polymer network and W_1 - the weight of the same network after toluene extraction and drying.

3. Results and discussion

3.1. Curing behavior via photo-DSC

The photo-DSC used in this experiment is the result of measurement after the progress of primary and secondary curing. Therefore, the results of Figs. 3–5 can be explained after the(a) primary curing and (b) secondary curing. Each reaction can be seen as a result of confirming the residual margin after the after primary curing, following which the secondary curing finally proceeded. When C=C double bonds react, an amount of energy is released, which can be measured by photo-DSC and finally allows evaluating the degree of crosslinking. Crosslinking density and degree of crosslinking can be seen in different senses. Assuming that the C=C double bond has undergone a and finally allows evaluating, the degree of crosslinking can be said to be 100%. However, just because the degree of crosslinking is 100%, it does not automatically mean that the crosslinking density is high. This is the situation



Fig. 2 – Schematic representations of (a) blending resin structures with (b) Low crosslinking agent contents and (c) High crosslinking agent contents.



Fig. 3 - Real-time heat flows after (a) primary curing and (b) secondary curing.



schematically displayed in Fig. 2, where a PSA is illustrated as a structure of a semi-interpenetrating polymer network (semi-IPN). The semi-IPN structure is formed during primary curing, while in secondary curing, the polymerization process involving monomers or unreacted crosslinking agents react. The main chain is formed as the polymerization progresses. Further, as the polymerization progresses, unreacted monomer, crosslinking agent, and lauryl methacrylate begin to blend, and the process of blending may be schematically illustrated as Fig. 2 (a). However, if a small amount of crosslinking agent of approximately 0.1–0.5 phr is added (Fig. 2 (b)), sufficient crosslinking density is not formed during primary curing. For these reasons, crosslinking density will not improve even if secondary curing advances. However, the



Fig. 5 - Conversion profiles after (a) primary curing and (b) secondary curing.

secondary curing to the degree of crosslinking may be improved because the reaction site may be used up. On the contrary, when the content of crosslinking agent is 0.7–1 phr (Fig. 2 (c)), the crosslinking density is expected to increase during primary curing. Further, it is expected that enough reaction sites will also remain. For these reasons, it is expected that more diverse crosslinked chains can be obtained when the amount of curing agent is small after the initiation of secondary curing.

In a typical crosslinking reaction, the degree of crosslinking should increase as the loading of the crosslinking agent increases [23]. These results can be confirmed in Fig. 3, that shows the photo-DSC thermograms recorded (in isothermal mode) after (a) primary curing and (b) secondary curing. As the measurements took place after the curing steps, the results can be correlated with the amount of unreacted C=C double bonds after primary and secondary curing. At loadings of 0-0.3 phr, a certain degree of reactivity remained after primary curing; however, this was significantly reduced at loadings of 0.5-1 phr. This increase in the degree of crosslinking occurred because the increasing the amount of crosslinking agent allowed the reaction to carry out in primary curing. UV light. These results can be better seen in Fig. 4, which shows the integrated areas of the DSC curves. In general, when such plots are flat, the reaction is completed [2,24]. The termination of this reaction can be seen as an increase in the degree of crosslinking. The conversion rate $(d\alpha/dt)$ was calculated as follows:

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

where dH/dt is the measured heat flow and Δ Htotal is the total exothermic heat of the reaction. Integrating Eq. (1) leads to Eq. (2), giving the conversion of C=C double bonds at time t (α t):

$$\alpha t = \Delta H t / \Delta H_{total}$$
 (2)

where Δ Ht is the cumulative heat of reaction at curing time t [23,25].

The calculated values are shown in Fig. 5 (a), and a gentle curve is exhibited after primary curing. However, in the case of Fig. 5 (b), it shows an approximately straight-line graph, and it may indicate the overall termination of the reaction.

3.2. Adhesion properties

Peel strength and probe tack tests are the most commonly used methods of measuring the adhesive properties of acrylic PSAs. These adhesive properties are greatly affected by crosslinking. Fig. 6 shows the peel strength and probe tack results; it can be seen that the adhesive strength corresponding to primary curing, except in the system without any crosslinker, was highest at a crosslinking agent loading of 0.3 phr, with a continuous decrease in adhesive strength up to 1 phr. When a tri-functional monomer is used as a crosslinking agent, the peel strength and probe tack have an inflection point that initially increases and thereafter decreases. As can be seen in Fig. 6, at 0.3 phr, the peel strength is at the highest point during the increasing trend. However, the probe tack can be expected to have an inflection point between 0.3 and 0.5 phr. However, the reason why the high tack of 0.1 phr was observed during the secondary curing in the probe tack, although a higher value was expected, was because of a large amount of uncured portion in the primary curing that was cured within sufficient time. These results show that the hardness increased as the crosslinking agent loading was



Fig. 6 – Peel strength and probe tack results as a functions of crosslinking agent loading.





Fig. 7 – Temperature-dependent tan δ of cross-linked acrylic PSAs prepared using different exposure energies: (a) primary and (b) secondary curing and (c) Temperatures of maximum tan δ extracted from parts (a) and (b).

increased, or as the crosslinking density decreased. These results were also confirmed through an examination of the mechanical properties using DMA.

3.3. Viscoelastic properties (DMA)

When a large amount of crosslinking agent is added, hardness generally increases, while T_g decreases. Fig. 7(a) and (b) show the tan(δ) results obtained using DMA after primary and secondary curing; it can be seen that the peak shifted to the left

after primary curing in all specimens to which crosslinking agent was added. Fig. 7(c) shows the temperatures at which the peak values of $\tan(\delta)$ were attained for different crosslinking loadings, and shows that the maximum temperature decreased as the crosslinking agent loading increased, representing a decrease in T_g. This result can be explained by the difference between "crosslinking density" and "degree of crosslinking". Fig. 8 (a) and (b) shows that the size of each unit of the crosslinked polymer is different, but if all the reaction sites are exhausted, the "degree of crosslinking" can be



Fig. 8 – The schematic of curing process (a) low crosslinking agent contents variation and (b) low crosslinking agent contents variation.



Fig. 9 – Gel fractions of cross-linked acrylic PSAs prepared at different curing agent contents.

explained as 100%. However, the "crosslinking density" will be checked differently. If the reaction proceeds in a situation where the mixture of low crosslinking agent contents (Fig. 8(a)) cannot react simultaneously, a large crosslinked polymer will result; similarly, in a mixture containing high crosslinking agent contents (Fig. 8(b)), a relatively small crosslinked polymer will result. Due to this phenomenon, it is expected that a decrease in T_g occurs because the "crosslinking density" of the specimen containing 0.5–1phr of crosslinking agent is low. This is expected because multiple crosslinked polymers of relatively small size can increase the fluidity rather than one large crosslinked polymer.

The method of measuring gel fraction used indirectly checks the degree of crosslinking by investigating the insoluble portion of a material [26]. Fig. 9 shows the gel fraction results, where it can be seen that the degree of crosslinking was over 90% even at a crosslinking agent loading of 0.1 phr. Additionally, no difference between primary and secondary curing could be observed for the crosslinking agent loadings of 0.7 phr or higher. This proves that most crosslinking had occurred after primary curing. In addition, the high gel content is indicative of very small amounts of linear molecules (including monomer molecules) remaining un-crosslinked in the studied systems.

4. Conclusions

PSA films cured using a stepwise system showed decreased curing margins as the crosslinking agent loading increased. When the loading was above 0.7 phr, most crosslinking occurred during primary curing, as confirmed by gel fraction and photo-DSC results. Despite this, the hardness of the system tended to decrease, showing that the degree of crosslinking increased but the crosslinking density decreased. In other words, as the crosslinking agent loading was increased, smaller crosslinked polymer domains were formed, resulting in greater softness, as confirmed by the adhesive strength measurements and decreased T_g . Unlike the previous studies, the difference in physical properties after secondary curing was relatively small since the reactivity was increased due to the use of methacrylate. This study confirmed that the "crosslinking density" can be controlled by the effect of low light intensity and excessive crosslinking agent content of primary curing. However, the variation does not appear to have occurred to a large extent. Therefore, in order to control the "crosslinking density" in further research, in-depth studies are being conducted that makes changes to the light sources used for primary and secondary curing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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