

Acid-free 아크릴계 접착제의 접착 물성 및 경화거동 연구

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Adhesion Performance and Curing Behaviors of Acid-free Acrylic PSAs Using Two Types of Curing Agents

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Abstract: Acrylic pressure-sensitive adhesives are used in many different parts in the world. But acrylic acid in PSAs may occur unexpected results such as corroding adherends or producing by-products when applied within electronic devices. This study employed acrylic PSAs based on 2-ethylhexyl acrylate (2-EHA), 2-hydroxyethyl acrylate (2-HEA) and butyl acrylate (BA) with different coating thickness. There are two types of curing agents. One is methylaziridine derivative (MAZ) and the other is aluminum acetylacetonate (AIACA). This study examined the adhesion performance and curing behaviors using peel strength, probe tack and gel fraction. Also, the viscoelastic properties of acrylic PSAs were investigated from Advanced rheometric expansion system (ARES)

Keywords: acid-free acrylic PSAs, adhesion performance, curing behaviors, methylaziridine derivative, aluminum acetylacetonate, peel strength, probe tack, gel fraction, viscoelastic property

1. Introduction

Pressure sensitive adhesive (PSA) tapes composed of acrylic copolymers have been extensively utilized in various industries, such as packaging, printing, electrical insulation and automobile. In general, the PSA properties (tack, peel adhesion, holding power) of acrylic adhesive have been controlled by blending tackifiers or dissimilar polymers, by adjusting molecular weight and its distribution, and also by copolymerization with a polar monomer and curing system. In recent years, the PSA properties of acrylic adhesives copolymer have been interpreted by considering various factors, such as dynamic mechanical properties, surface tension, and miscibility[1-6].

The most common technique of preparing PSA is the variation of glass transition temperature (T_g) using differ-

ent types and amounts of comonomers. Typically, a combination of two acrylic monomers is used for synthesis of PSAs. Monomers, whose polymers have low T_g value provide tack and flexibility of the adhesive. Addition of comonomers, whose polymers have higher T_g value with respect to 2-ethylhexyl acrylate (e.g. ethylacrylate or methylacrylate) enhance cohesion of the adhesive, hence also the adhesive shear strength. The T_g values of the synthesized polymer are proportional to the amount of added comonomer. The higher is the T_g of the base polymer, the lower are peel and tack values while increase of shear strength is observed[7]. Lower tack and peel value may be attributed to higher stiffness of polymer chains, which influences wetting process of the substrate by the adhesive. On the other hand, higher shear strength may be correlated with the higher cohesion as the consequence of higher T_g values[8].

The properties of PSAs by copolymerization of acrylic

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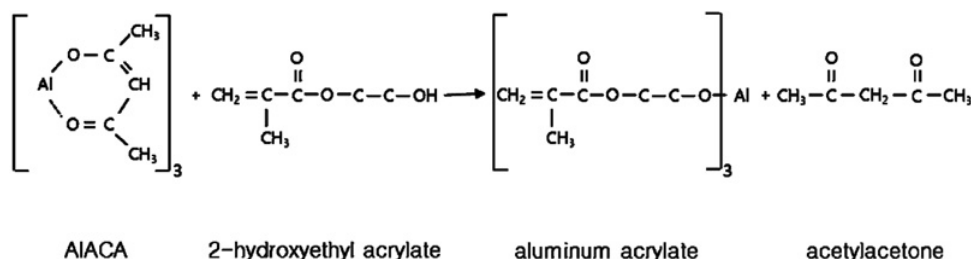


Figure 1. Reaction between aluminum acetylacetonate and 2-hydroxyethyl acrylate.

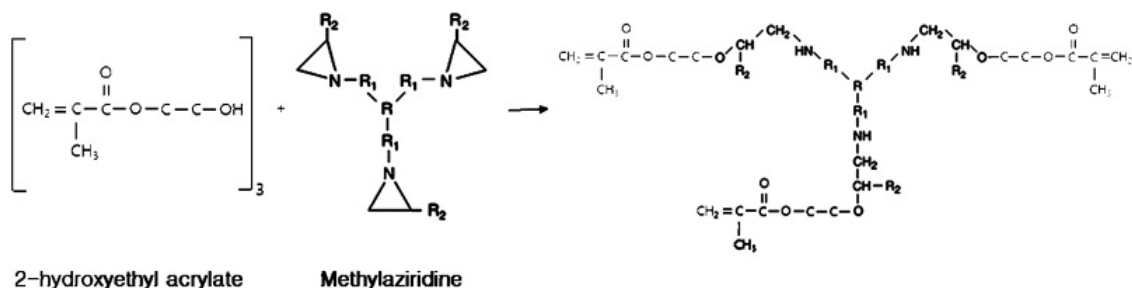


Figure 2. Reaction between methylaziridine and 2-hydroxyethyl acrylate.

monomers and formulated in organic solvent mixture are determined, to a great extent, by the kind and quantity of the crosslinking agent added to the self-adhesives. As with molecular weight, crosslinking influences the bulk properties of the film and builds shear, heat and chemical resistance, while negatively impacting the tack and peel. It is necessary to achieve inter-chain crosslinking for heat resistance, because the PSA polymers are operating in the region above their T_g values. Therefore, without crosslinks, the polymer would readily flow under heat, losing all cohesive strength. The crosslinking also builds water and chemical resistance, as well as final adhesive construction properties to enhance die cutting, slitting and roll stability[9].

An acrylic copolymer whose chains are only crosslinked via hydrogen bonds or interpenetrating systems (IPN) can hardly be cohesively loaded. But a few tenths of a percent of crosslinking agent make it a PSA having good mechanical properties[10]. Traditional methods of crosslinking polymers, which include sulfur vulcanization, peroxide curing and radiation curing, give networks whose crosslink densities cannot be examined by simple means[11]. Crosslinking based on amine, ether, ester or amine bonds located at suitable sites along the polymer can be used as both stoichiometry and reaction can be controlled[12]. For instance, the formation of carbamates from isocyanates and hydroxyl groups and the formation of ureas from iso-

cyanates and amines are both well known[10]. Polymers containing ionic crosslinks such as carboxylates have been known for many years[13]. These “ionomer”, as they are called, tend to exhibit both rapid stress relaxation and marked creep under load. Nonetheless, ionic linkages are attractive for crosslinking in that the reactions can be controlled to achieve the desired properties. If the ionic crosslink is metal mediated, the metal salt might be chosen for some particular spectroscopic characteristic[10].

The transition metals having a coordination number greater than 2, typically 4, 6 or 8 (exemplified by Zn, Ni, Mn, Fe, Co, Cr, Al, Ti or Zr), form with 2,4-pentanedione (acetylacetone) chelate complexes[14] known as acetylacetonates. The hydrogen atoms of the methylene group $-CH_2-$ accordingly the induction effect of the neighboring ketone group are very mobile. Therefore, the acetylacetonates show the keto-enol antimerism. The central hydrogen atom of the chelate rings is accessible to electrophilic substitution[15,16]. Crosslinking of the polymer chains with a view to the selected composition of functional monomers will only be affected by the functional carboxyl groups and hydroxyl groups protruding out of the chains[10].

Acrylic PSAs often include 3~10 wt% acrylic acid and 90~97 wt% of alkyl soft acrylate composed of butyl acrylate, hexyl acrylate, 2-ethylhexylacrylate, isooctyl acrylate or decyl acrylate. Copolymers containing acrylic acid

are commonly used for manufacture of acrylic PSAs with excellent adhesive performance[17]. But acrylic acid in PSAs may occurs unexpected reactions such as corroding adherends or making by-products when it applied within electronic devices.

In this study, acid-free PSAs were prepared based on 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate and butyl acrylate. There used two types of curing agents. One was chelate metal acetylacetonate and the other was aziridine derivative. Then adhesion performance and viscoelastic properties were checked with different coating thickness. Finally, conversion and reaction rates were investigated using gel fraction determination to study curing behaviors.

2. Experimental

2.1. Materials

Acrylic monomers, 2-ethylhexyl acrylate (2-EHA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea), butyl acrylate (BA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea) and 2-hydroxyethyl acrylate (2-HEA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea) were commercially available and used without purification. 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemical, Japan) was used as the thermal initiator. Ethyl acetate (EAc, Samchun Pure Chemical Co., Ltd, South Korea) was used as solvent. Aluminum acetylacetonate (AlACA, Dongsan Chemical, South Korea) and methylaziridine derivative (MAZ, DSM Neoresins, USA) were prepared as curing agents

2.2. Methods

2.2.1. Synthesis of Acrylic PSAs

Acrylic monomers (2-EHA, BA and 2-HEA) were synthesized as 40/40/20 wt%, respectively, by solution polymerization. Ethyl acetate (EtAc, Samchun Pure Chemical Co., Ltd, South Korea) and 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemical, Japan) were used as the solvent and thermal initiator, respectively, without purification. The mixture was placed into a 500 ml four-neck flask equipped with a stirrer, condenser and thermometer, and heated to 75°C with stirring. At the end of the exothermic reaction, the temperature was maintained for 30 min and a blend of EtAc and AIBN was added. The reaction was allowed to proceed for 0.5 h and 2.5 h. Finally, polymerization was terminated by cooling the mixture to room temperature.

2.2.2. Formation of PSA Films

All acrylic PSAs were coated onto the corona treated polyethylene terephthalate (PET, SK Chemical, Republic of Korea) film using coating bars, kept at room temperature for 1 h and then dried in an oven at 80°C for 20 min. These dried films were kept at $22 \pm 2^\circ\text{C}$ and $60 \pm 5\%$ RH for 24 h before performing the other tests

2.2.3. Preparation of Cured Acrylic PSAs

Acrylic PSAs were cured using two types of curing agents. The curing agents were multifunctional methylaziridines and aluminum acetylacetonate. The crosslinking of PSAs is based mainly on the hydroxyl groups within the polymeric chain (Figures 1~2). The oxygen of the nucleophilic hydroxyl group causes ring opening of the tense aziridine rings, whereas the hydrogen atoms accompanying the hydroxyl groups protonate the nitrogen atoms [18]. And characteristic for crosslinking systems containing metal chelates is the addition of alcohol as a stabilizer, after the vaporization of which (in the drying channel together with other solvents) the crosslinking starts spontaneously[19].

2.2.4. Gel Fraction

The gel fraction of the cured acrylic PSAs after mixing was measured. Firstly, the sample weight was measured before 24 h immersion in toluene at room temperature (W_0). The immersed sample was filtered through a 200 mesh wire net and oven dried at 70°C for 24 h. The weight was then measured (W_{24}). The gel content was estimated using the following equation.

$$\text{Gel contents (\%)} = \frac{W_{24}}{W_0} \times 100$$

2.2.5. Advanced Rheometric Expansion System (ARES) Analysis

The viscoelastic properties of the acrylic PSAs were determined using an advanced rheometric expansion system (ARES, Rheometric Scientific, UK, in NICEM at Seoul National University) equipped with an 8 mm parallel plate mode. The typical temperature scan range was -60 to 200°C, and the heating rate was 5 °C/min. The frequency was 1 Hz and the gap between the plates was 1 mm. Also the $\tan \delta$ curves from the temperature sweep tests suggested glass transition temperature (T_g) data.

2.2.6. Peel Strength

The peel strength was also measured using a Texture Analyzer. The specimens were prepared as 25 mm width samples. The specimens were pressed onto the stainless steel substrate by 2 passes of a 2 kg rubber roller and stored at room temperature over 12 h. The peel strength was determined at a 180° angle with a crosshead speed of 300 mm/min at 20°C based on ASTM D3330. The peel strength is the average force on the debonding process. The force was recorded in g units for 5 different runs and the average force was reported in g/25 mm.

2.2.7. Probe Tack

The probe tack was measured using a Texture Analyzer (Micro Stable Systems, TA-XT2i) with a 5 mm diameter stainless steel cylinder probe at 20°C. The standard probe tack test was divided into three stages : approaching the surface of the PSAs, contact and detachment from the surface of the PSAs. The speed of the probe was 0.5 mm/s, the contact time on the PSAs surface was 1 s under a 100 g/cm² constant force and the separation rate was 10 mm/s. In the debonding process, the probe tack was obtained at the maximum debonding force.

3. Results and Discussion

3.1. Adhesion Performance

The adhesion performance, such as the peel strength and probe tack of acrylic PSAs were influenced by types and contents of curing agents. The change in the glass transition temperature of acrylic PSAs and crosslinking density affected by curing agents are important factors for controlling the adhesion performance[20]. In Figure 3, the peel strength of all samples decreased with increasing curing agent contents. But the peel strength of samples with AIACA decreased more sharply than one with MAZ when less than 30 phr (in binder) curing agent contents was used regardless of coating thickness. In particular, at MAZ contents < 30 phr (in binder), cohesive failure occurred when the acrylic PSA sample was detached from the SUS surface. However, all samples with AIACA showed interfacial failure, which means that there was no residue after peeling. These results could be indicated by more strong network formation of the acrylic PSA with increasing AIACA contents. The cohesion force of the acrylic PSA was increased by forming a crosslinked structure, resulting in a concomitant increase in peel strength.

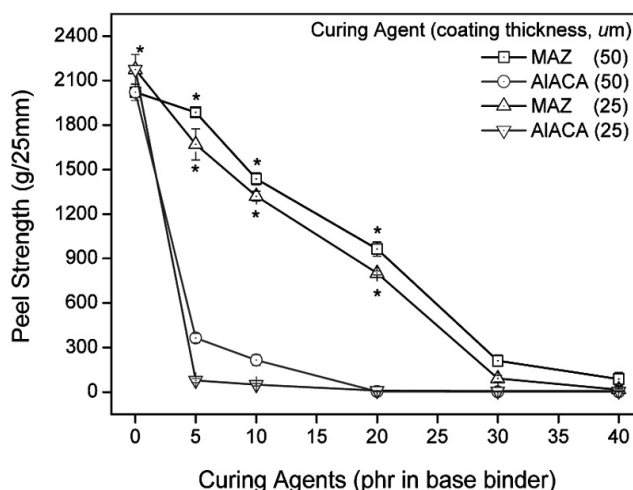


Figure 3. Peel strength as a function of curing agents with different coating thickness (*: cohesive failure).

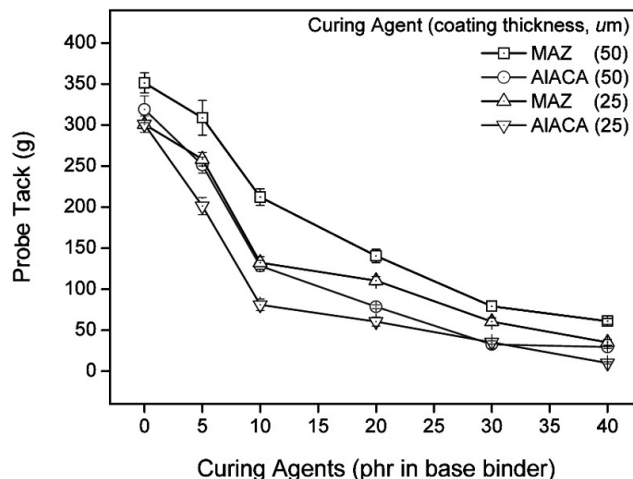


Figure 4. Probe tack as a function of curing agents with different coating thickness.

Also, the probe tack decreased steadily with increasing curing agent contents and happened no fibrillation between the stainless steel probe and acrylic PSAs without no cured samples (Figure 4). This is because with increasing curing agent contents, the acrylic PSAs showed greater cohesion force to endure probe tack force.

This suggests that a greater AIACA contents has less affinity to attach to the SUS surface and the T_g increases with increasing AIACA contents. Acrylic PSAs with a higher T_g mean more rigid structures resulting in a less peel strength. Also, the storage modulus of acrylic PSAs decreased with increasing AIACA contents.

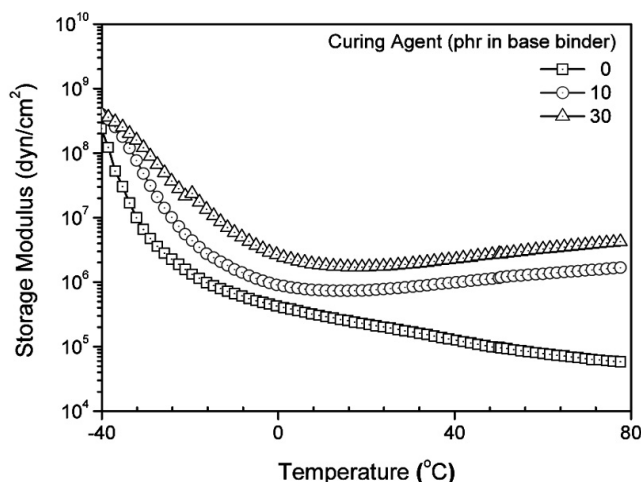


Figure 5. Change in the storage modulus after curing with AlACA.

3.2. Viscoelastic Properties

The viscoelastic properties that play a key role in the adhesion performance of acrylic PSAs blended with different AlACA contents were tested by ARES measurements[21]. The storage modulus (G') is associated with the hardness of the adhesive, and the loss modulus (G'') is related to energy absorption. $\tan \delta$ is the value determined by the following equation:

$$\tan \delta = \frac{G''}{G'}$$

where G' and G'' is the storage and loss modulus, respectively. The value shows the balance of the viscoelastic behavior. Figure 5 shows that the storage modulus of acrylic PSAs are different at temperatures. The storage modulus increased with increasing AlACA contents. It can be investigated that acrylic PSAs' cohesion is getting higher with increasing AlACA contents. Not only the plateau area of the storage modulus at the high temperature region suggests that acrylic PSA formed an entanglement structure but also it appeared a rubbery plateau at high temperatures compared to the acrylic PSA without AlACA. Because the storage modulus at high temperatures is directly related to the thermal resistance of acrylic PSA, acrylic PSAs become more elastic at high temperatures. Figure 6 indicates the $\tan \delta$ curve of acrylic PSA. The T_g of the acrylic PSAs (temperature at $\tan \delta$ peak) increased and the values of the $\tan \delta$ decreased with increasing AlACA. This means that at the high temperature region, the storage modulus of the acrylic PSAs is strong-

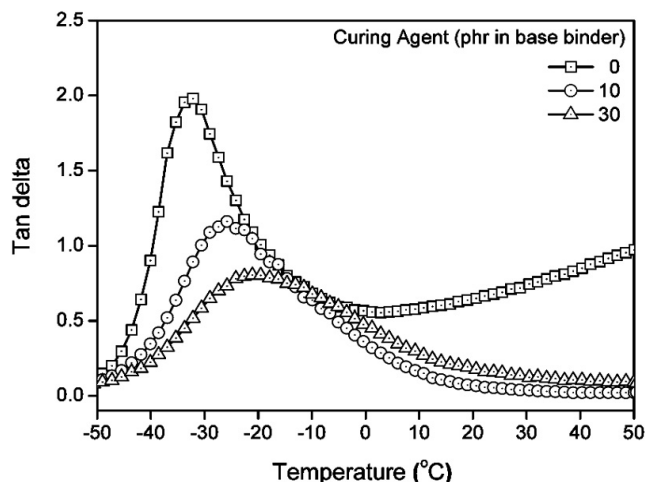


Figure 6. Change in $\tan \delta$ after curing with AlACA.

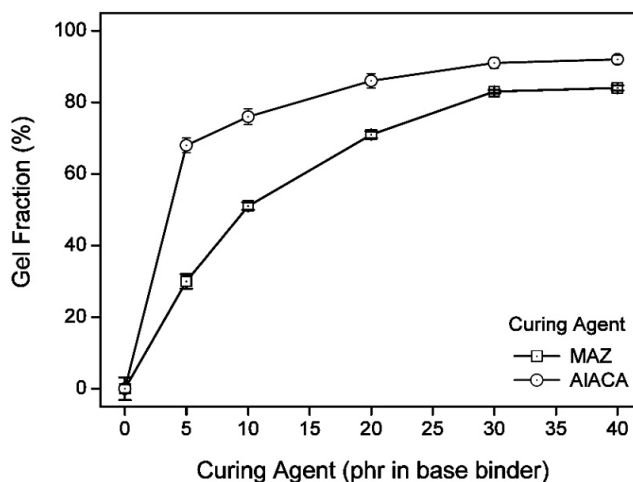


Figure 7. Gel fraction as a function of curing agents.

ly related to AlACA contents.

3.3. Gel Fraction

The gel fraction was calculated to determine the degree of curing of acrylic PSAs by measuring the insoluble material remaining[22]. The gel fraction increased gradually after curing the acrylic PSAs by MAZ and AlACA, as shown in Figure 7. However, the rate of the increase was decreased by increasing contents of curing agents. AlACA had a higher conversion rate than MAZ because of the formation of a tightly cross-linked network. Also, the gel fraction did not reach at 100% both AlACA and MAZ. It suggests that unreacted monomers exist after curing reactions.

4. Conclusion

In general, acrylic PSAs include acrylic acid as hard segments which makes acrylic PSAs more cohesive and influences physical properties considerably. However, acrylic acid may corrode adherends which are related to specific fields of electronic devices and indicate unexpected byproducts. So, acid-free acrylic PSAs based on 2-EHA, BA and 2-HEA were prepared. Curing behaviors, viscoelastic properties and adhesion performance were obtained by blending two types of curing agents, MAZ and AlACA, respectively. The reactivity of AlACA was > MAZ in spite of equal functionality number. It suggests that acrylic PSAs with AlACA formed higher cross-linked structures. Furthermore, the gel content of the acrylic PSAs increased with increasing contents of curing agents. This is because the conversion of the remaining monomer into a polymer obtained a rigid structure.

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