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# Optical properties and adhesion performance of optically clear acrylic pressure sensitive adhesives using chelate metal acetylacetonate



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#### ABSTRACT

Optically clear acrylic pressure-sensitive adhesives (PSAs) with different co-monomers were synthesized. This study employed metal chelate aluminum acetylacetonate and zirconium acetylacetonate as curing agents. The optical properties of the acrylic PSAs were examined by UV-visible spectroscopy and a prism coupler. In addition, the adhesion performance was obtained by assessing the peel strength, the tack, and the shear adhesion failure temperature. The decrease in the adhesion performance may be related to a higher crosslinking density, which also resulted in a higher gel content.

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# 1. Introduction

Pressure-sensitive adhesive (PSA) tapes composed of acrylic copolymers have been extensively utilized in various applications, including packaging, printing, electrical insulation and automobile parts. In general, the PSA properties (tack, peel adhesion, holding power) of acrylic adhesives are controlled by blending tackifiers or dissimilar polymers, by adjusting molecular weights and related distributions, and also by copolymerization with a polar monomer with various curing systems. In recent years, the PSA properties of acrylic adhesive copolymers have been interpreted by considering various factors, such as the dynamic mechanical properties, surface tension, and miscibility of the copolymers [1–5].

Pressure-sensitive adhesives are composed of long chain molecules confined by crosslinkages into three-dimensional networks. They are, in an uncrosslinked form, capable of sustaining very large reversible deformations under low amounts of stress. However, a few tenths of a percent of a crosslinking agent can create a pressure-sensitive adhesive in a viscoelastic fluid state with good mechanical and optical properties [6].

The properties of pressure-sensitive adhesives synthesized by the copolymerization of acrylic monomers and formulated in an organic solvent mixture are determined, to a great extent, by the type and quantity of the crosslinking agent added to the selfadhesive. As with the 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, as pressure-sensitive adhesive polymers operate in the region above their glass-transition temperature. 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 the final adhesive construction properties to enhance die cutting, slitting and roll stability [7].

Polymers containing ionic crosslinks such as carboxylates have been known for many years [8]. These "ionomers", 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, a metal salt can be chosen to ensure particular characteristics [6].

Transition metals having a coordination number greater than 2, i.e., typically those with numbers of 4, 6 or 8 (exemplified by Zn, Ni, Mn, Fe, Co, Cr, Al Ti or Zr), form with 2,4-pentanedione (acetylacetone) chelate complexes [9] known as acetylacetonates. The hydrogen atoms of the methylene group  $-CH_2$ - causing the induction effect of the neighboring ketone group are very mobile. There, the acetylacetonates show keto-enol antimerism. The central hydrogen atom of the chelate rings is accessible for electrophilic substitution [10]. Metal chelates that react with the acrylic polymer chains containing carboxylic groups are particularly efficient as crosslinking agents. They have the following formula [6] (Fig. 1). A characteristic for crosslinking systems containing metal chelates is the addition of alcohol as a stabilizer, after the vaporization of which (in the drying channel

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together with other solvents) the crosslinking starts spontaneously. Pressure-sensitive adhesive acrylics containing the above mentioned crosslinking agent are, therefore, called room temperature crosslinking pressure-sensitive adhesives [11].

Optical PSAs are being used increasingly in areas, such as LCDs, PDPs and OLEDs, due to increased optical device production rates worldwide [12]. Optical PSAs should have high contrast, clarity, a high refractive index and good reliability [13]. These properties can be achieved via curing using chelate metal acetylacetonate.

In this study, optically clear acrylic PSAs were prepared using metal chelate aluminum acetylacetonate and metal chelate zirconium acetylacetonate. Emphasis was placed on an investigation of the crosslinking properties by two metal chelate materials to improve the optical properties. Also, the curing behaviors, adhesion performance, and viscoelastic properties were examined.

# 2. Experimental

# 2.1. Materials

Experiments were conducted using solvent-based acrylic PSAs containing 15 wt% 2-ethylhexyl acrylate (2-EHA, 99.0% purity, Samchun Pure Chemical Co., Ltd, Republic of Korea), 5 wt% acrylic acid (AA, 99.0% purity, Samchun Pure Chemical Co., Ltd, Republic of Korea), and 45 wt% 2-phenoxy ethyl acrylate (2-PEA, 90.0% purity, Tokyo Chemical Industry, Japan). Lauryl acrylate (LA, 99.0% purity, Samchun Pure Chemical Co., Ltd, Republic of Korea) was employed as a 35 wt% co-monomer, as listed in Table 1.

Aluminum acetylacetonate (AIACA, Tokyo Chemical Industry, Japan) and zirconium acetylacetonate (ZrACA, Tokyo Chemical



acrylic PSA with acid functionality



aluminum acetylacetonate



Fig. 1. Reaction between acrylic PSAs with carboxylic acid and aluminum acetylacetonate [6].

# Table 1

Monomer compositions, molecular weight  $(M_w)$  and polydispersity index (PDI) of the acrylic binder.

	2-EHA	AA	2-PEA	LA	$M_w$	PDI
Binder	15	5	45	35	550,000	7.1

Note: All monomers were based on weight percent.

Industry, Japan) were used as crosslinking agents. Ethyl acetate was used as the organic solvent at its boiling point temperature of about 77 °C. A solution of 0.1 wt% 2,2′-azobisisobutyronitrile (AIBN, Junsei Chemical, Japan) was used as the thermal initiator to start the radical polymerization process.

# 2.2. Methods

## 2.2.1. Synthesis of acrylic PSAs

Acrylic PSAs were synthesized by solution polymerization. The solid content in the solution was 50%. The mixture was placed into a 500 ml four-neck flask equipped with a stirrer, condenser and thermometer and was heated to 78 °C with constant stirring. At the end of the exothermic reaction, the temperature was maintained for 30 min, and a blend of ethyl acetate and AIBN was added. The reaction was allowed to proceed for 0.5 h or 2.5 h. Finally, polymerization was terminated by cooling the mixture to room temperature.

# 2.2.2. Preparation of cured acrylic PSAs

Cured PSAs were prepared by blending polymerized binders and two metal chelate materials. The amounts of the two metal chelate materials were 1, 2, 5 and 10 phr of binder. The mixture was stirred with a mechanical stirrer at room temperature for about 5 min. Cured PSAs were coated onto polyester films (PET, 50- $\mu$ m-thick, SKC, Republic of Korea) using a No. 18 bar coater (wet thickness 41.1  $\mu$ m) and were then dried at 70 °C for 5 min. The thickness of each sample was approximately 25  $\mu$ m.

# 2.2.3. Optical properties

2.2.3.1. UV-visible spectroscopy. UV-visible spectroscopy (UV-1650PC Shimadzu, Japan) was used to examine the transmittance of the UV-cured acrylic PSAs. Both the bare PET as a control and the acrylic PSA sample coated onto the PET film were set on the instrument. The transmittance was determined in the visible range of 380–700 nm.

2.2.3.2. Prism coupler. The refractive index of the acrylic PSAs coated on a PET film was detected at wavelengths of 404, 532, 632.8 and 829 in the visible range using a prism coupler 2010/M (Metricon, USA). Acrylic PSAs were UV-cured after coating prepolymers onto the PET film to produce PSA films that would not reach the point of cohesive failure. A bare PET film was used as the reference. The prism and film were joined, and the incidence angle of the laser beam was varied so that the refractive index in both the thickness and planar directions could be determined.

#### 2.2.4. Gel content

The gel content provides a degree of crosslinking. The weights of the samples were measured. Then, for 24 h the samples were immersed in toluene at room temperature, after which the insoluble polymers were removed by filtration through a 200 mesh wire net. Then, the samples were dried at 70 °C until they reached a constant weight. The gel contents were calculated using the following equation:

Gelcontent (%) =  $W_t/W_0 \times 100$ 

Here,  $W_0$  is the weight before immersion, and  $W_{24}$  is the weight after immersion.

## 2.2.5. Adhesion performance

*2.2.5.1. Peel strength.* The peel strength was measured using a Texture Analyzer (Micro Stable Systems, TA-XT2i). The specimens were prepared as 25-mm-wide samples. The specimens were pressed onto a stainless steel substrate by two passes of a 2 kg rubber roller and were stored at room temperature for 12 h. The

peel strength was determined at an angle of  $180^{\circ}$  with a crosshead speed of 300 mm/min at  $20 \text{ }^{\circ}\text{C}$  based on ASTM D3330. The peel strength is the average force on the deboning process. The force was recorded in g units for five different runs, and the average force was reported as g/25 mm.

2.2.5.2. 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 and contact and detachment from the surface of the PSAs. The speed of the probe was 0.5 mm/s, and the contact time on the PSAs surface was 1 s under a constant force of 100 g/cm<sup>2</sup>. The separation rate was 10 mm/s. In the debonding process, the probe tack was obtained as the maximum debonding force.

2.2.5.3. Shear adhesion failure temperature (SAFT). The cohesion force was measured by checking both the shear adhesion failure temperature (SAFT) and the holding power. To assess the SAFT, the samples,  $25 \times 25$  mm size, were attached to a stainless steel substrate by rolling with a 2 kg rubber roller twice, and were then loaded with a 500 g weight. The samples were held in an oven at a heating rate of 0.4 °C/min, and the temperature when shear failure occurred was checked.

## 2.2.6. Characterization of the acrylic PSAs

2.2.6.1. 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) equipped with an 8 mm parallel plate mode. A typical temperature scan range was -40 °C to 80 °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 temperature sweep tests determined glass transition temperature ( $T_g$ ).

# 3. Results and discussion

# 3.1. Optical properties

The optical properties of the PSAs were measured by UV–visible spectroscopy and a prism coupler. Acrylic PSAs should show high transmittance ( > 95%) in order to be used in optical films [14]. This property can be obtained using metal chelate curing agents. Likewise, the reflective index of acrylic PSAs depends on the co-monomer and curing degree by the curing agents. Different amounts of metal chelates aluminum acetyl acetonate (AIACA) and zirconium acetylacetonate (ZrACA) (0.25 and 0.50 wt%, respectively) were added to the acrylic bonder, as shown in Fig. 2. The synthesized PSA were coated onto a PET film, and bare PET film was measured as the reference. While minor differences were considered, the transmittance values of all PSAs were > 95%, showing excellent transparency in the visible wavelength.

The refractive index parameter in the optical properties attracts the greatest amount of research attention, as it depends on the brightness as well as the contrast ratio in optical displays, such as those on mobile phones and tablet PCs. The refractive index of a polymer containing a high refractive index functional group is higher than that of the monomer that is typically used. Thus, the PEA in all PSAs, which has a high refractive index of 1.518, shows a higher polymer refractive index due to the presence of a phenyl group [13]. The influence of the concentration of the external crosslinker metal chelates aluminum acetylacetonate (AIACA) and zirconium acetylacetonate (ZrACA) on the refractive index is described in Fig. 3. As expected, the amount of the increase of the metal chelate crosslinking agent corresponds to the increase of the



Fig. 2. Transmittance of acrylic PSAs with AIACA and ZrACA contents in the visible area of 380–700 nm.



Fig. 3. Refractive index of acrylic PSAs with the AIACA and ZrACA contents.

refractive index of the acrylic PSAs in the visible wave length. With ZrACA in comparison AlACA, better optical properties resulted. This result shows that crosslinking by ZrACA as compared to AlACA leads to more synthesized acrylic PSAs due to the additional functional reactive sites.

## 3.2. Gel contents

The crosslinking efficiency by the crosslinking agents was roughly estimated by gel fraction measurements (Fig. 4). The amount of gel phase that was measured is defined as the amount of both crosslinked molecules as highly entangled and coiled polymer molecules. In the latter case, crosslinking occurs only though entanglement. Moreover, it is not truly a polymeric network, which usually consists of interconnected polymeric molecules. There, the gel phase can vary due to the change in the polymer molecular weight [15,16]. The gel fraction increased with an increasing the amount of crosslinking agent, and then reached a constant value of 85% regardless of the type of crosslinking agent used. Such a high gel fraction upon saturated crosslinking indicates that the agents overcrosslinked the PSAs [17]. Furthermore, an additive amount of 0.25 wt% of AlACA brought the gel fraction to a constant value, whereas 0.125 wt% of ZrACA was required to reach that value. From this result, nearly twice as much AIACA was required compared to ZrACA for overcrosslinking. This clearly shows that more efficient crosslinking is obtained with ZrACA than with AlACA. The major difference in efficiency is likely due to the structure of the agents. The reaction point on ZrACA is the zirconium atom, which is larger than the aluminum atom. Also, the reactive sites of the zirconium atom are greater in number compared to the number of such sites on the aluminum atom. There, the crosslinking environment of ZrACA is sterically preferred.

# 3.3. Adhesion performance

The concentration of the curing agents' dependence of the peel strength was evaluated by a 180° peel test. The test was carried out at room temperature. The dependence cannot be attributed to the crystalline aggregate of the long alkyl side group [6,18–21]. As shown in Fig. 5, the adhesions of the PSAs crosslinked by AlACA and ZrACA decreased with an increase in the concentration of the curing agents up to 10 wt%. The adhesion clearly depends on the type of crosslink agent used, as both PSAs consist of the same acrylic copolymer. As mentioned above, crosslinking using ZrACA as opposed to AlACA is efficient due to the additional reactive sites. At higher values of added ZrACA (0.125 wt%) and AlACA (0.25 wt%), acrylic PSAs mostly lose their adhesive characteristics. The reduction of the peel strength can be attributed to the increased polymer crosslinking. Crosslinking improves the cohesive strength of the adhesive, which influences the degree of deformation and hence causes lower force during the debonding process. It is known that the formation of a crosslinked polymer structure affects the peel strength of the adhesive [6,22,23]. Investigated tack values against the amounts of curing agents, presented in



Fig. 4. Gel contents of acrylic PSAs with AlACA and ZrACA contents.



Fig. 5. The peel strength of acrylic PSAs with the AlACA and ZrACA contents.

Fig. 6, indicate a decrease of the tack. Tack is an adhesion performance, which means the ability of the adhesive to adhere to a substrate in a short time and at a low pressure, tack is highly dependent on the degree of polymer molecular mobility. The decrease may be attributed to the fact, that crosslinking decrease the polymer molecular mobility, which limits the optimal wetting of the stainless steel probe and decreases the adhesion area between the substrate and the adhesive coating. For this reason, the tack decreased in the acrylic PSAs with a higher concentration of the curing agent, especially considering the higher crosslinking density in ZrACA than AlACA [24]. It can be suggested by the comparison of the peel strength and tack values that both properties decrease with an increase in the amount of added curing agent due to the higher crosslinking density. However, it can be shown that the tack is less affected by crosslinking as compared to the peel strength. The relative reduction of the tack from its initial value to the value with the highest addition of the curing agent is more than that of the peel strength. This may be related to that fact that the tack is primarily affected by the polymer structure at the surface of the microspheres [24]. The following plot was adopted, in the case of the shear adhesion failure temperature (SAFT) measurement in Fig. 7. The cohesion force also increased as regards the SAFT. This suggests that the cohesion force of acrylic PSAs against the temperature increases with an increase in the amount of the curing agents, which is in agreement with the published results of other studies



Fig. 6. The tack of acrylic PSAs with the AlACA and ZrACA contents.



Fig. 7. Shear adhesion failure temperature (SAFT) of acrylic PSAs with the AlACA and ZrACA contents.



Fig. 8. Tan delta of acrylic PSAs with ZrACA contents.

## 3.4. Characterization of synthesized acrylic PSAs

The viscoelastic properties, which play a key role in the adhesion performance of acrylic PSAs with added ZrACA, were tested by ARES measurements [25]. Fig. 8 indicates the temperature-dependence of the tan delta of the PSAs. The tan delta curve of the PSAs increased with an increase in the amount of ZrACA due to crosslinking. The  $T_g$  of the acrylic PSAs (temperature at the tan delta peak) increased and values of the tan delta decreased with an increase in the amount of ZrACA. This means that the behavior of tan delta is strongly related to crosslinking and polymer mobility against the temperature.

## 4. Conclusion

Optically clear acrylic PSAs with different co-monomers were synthesized and cured by using the chelate curing agents, AlACA and ZrACA. According to the results, the following conclusions can be drawn. Minor differences were determined between AlACA and ZrACA in terms of the optical properties of the transmittance and the refractive index. However, ZrACA, having more functional reactive sites than AlACA, showed lower values due to higher crosslinking with respect to the peel strength and the tack. The proof may be seen in the increase of the gel content. The decrease in the peel strength may be attributed to the improved cohesiveness of the microsphere particles, which influences the degree of deformation and causes lower force during the debonding process. The tack also decreased but the decrease is not as rough as in the case of the peel strength, as the crosslinking process on the particle surface decreased the degree of polymer mobility, which prevented the optimal wetting of the stain less steel probe [24].

We expect that the results will upgrade basic and application knowledge pertaining to optically clear pressure-sensitive adhesives for current optical devices such as mobile phones with touch screens, and tablet PCs and that they will aid in the design of acrylic PSAs with metal chelate curing agents.

## References

- Yang HWH. Water-based polymers as pressure-sensitive adhesives-viscoelastic guidelines. Journal of Applied Polymer Science 1995;55:645–52.
- [2] Chang EP. Viscoelastic windows of pressure-sensitive adhesives. Journal of Adhesion 1991;34:189–200.
- [3] Kano Y, Akiyama S. Poly(butyl acrylate)/(polyvinylidene fluride-co-hexa-fluoroacetone) blends as pressure-sensitive adhesives. Journal of Applied Polymer Science 1997;63:307–13.
- [4] Kim H-Y, Mizumachi H. Miscibility and peel strength of acrylic pressuresensitive adhesive: acrylic copolymer-tackifier resin systems. Journal of Applied Polymer Science 1995;56:201–9.
- [5] Tse MF. Studies of triblock copolymer-tackifying resin interactions by viscoelasticity and adhesive performance. Journal of Adhesion Science and Technology 1989;3:551–70.
- [6] Czech Z, Wojciechowicz M. The crosslinking reaction of acrylic PSA using chelate metal acetylacetonates. European Polymer Journal 2006;42:2153–60.
- [7] Ooka M, Ozawa H, Recent developments in crossiliking technology for coating resins. Progress in Organic Coatings 1994;23:325–38.
- [8] Holliday L. Ionic polymers. NY: John Willey and Sons; 1975.
- [9] Flatau K, Musso H. The structure of mercury compounds of 2,4-pentanediones. Angewandte Chemie International Edition 1970;9:379–80.
- [10] Colmann JP. Reactions of metal acetylacetonates. Angewandte Chemie 1965;77(4):154–61.
- [11] Milker R, Czech Z. Vernetzung von Copolymeren auf Acrylatbasis, 9. Munchener Klebstoff-und Veredelungsseminar, Munchen, Germany; 1984. 85–91.
- [12] Chang EP, Daniel H. Electrooptical light-management material: low-reflectiveindex adhesives. Journal of Adhesion 2005;81:925–39.
- [13] Miyamoto M, Ohta A, Kawta Y, Nakabayashi M. Control of refractive index of pressure-sensitive adhesives for the optimization of multilayered media. Japanese Journal of Applied Physics 2007;46:3978–80.
- [14] Chau JLH, Lin Y-M, Li A-K, Su W-F, Chang K-S, Hsu L-C, et al. Transparent high refractive index nanocomposites thin films. Materials Letters 2007;61:2908–10.
- [15] Kajtna J, Likozar B, Golob J, Krajnc M. The influence of the polymerization on properties of an ethylacrylate/2-ehtyl hexylacrylate pressure-sensitive adhesive suspension. International Journal of Adhesion and Adhesives 2008;28 (7):382–90.
- [16] Kajtna J, Golob J, Krajnc M. The effect of polymer molecular weight and crosslinking reactions on the adhesion properties of microsphere water-based acrylic pressure-sensitive adhesives. International Journal of Adhesion and Adhesives 2008;29(2):186–94.
- [17] Murakami H, Futashima K, Nanchi M, Kawahara S. Unique thermal behavior of acrylic PSAs bearing long alkyl side group and crosslinked by aluminum chelate. European Polymer Journal 2011;47:378–84.
- [18] Czech Z. Crosslinking of PSA based on water-borne acrylate. Polymer International 2003;52:347-57.
- [19] Milker R, Czech Z. Solvent-coating acrylate contact adhesives. Adhesion 1989;6:20–5.
- [20] Milker R, Czech Z. A novel method for the production of crosslinked acrylic contact adhesives. Adhesion 1991;35(4):13–5.
- [21] Jordan Jr EF, Artymyshyn B, Speca A, Wrigley AN. Side-chain crystallinity. II. Heats of fusion and melting transitions on selected copolymers incorporating *n*-octadecyl acrylate or vinyl stearate. Journal of Polymer Science Part A: Polymer Chemistry 1971;9:3349–65.
- [22] Asahara J, Hori N, Takemura A, Ono H. Crosslinked acrylic pressure-sensitive adhesives. I. Effect of the crosslinking reaction on the peel strength. Journal of Applied Polymer Science 2003;87:1493–9.
- [23] Czech Z. New copolymerizable photoinitiators for radiation curing of acrylic PSA. International Journal of Adhesion and Adhesives 2007;27:195–9.
- [24] Kajtna J, Krajnc M. UV crosslinkable microsphere pressure sensitive adhesiveinfluence on adhesive properties. International Journal of Adhesion and Adhesives 2011;31:29–35.
- [25] Lim D-H, Do H-S, Kim H-J. PSA performances and viscoelastic properties of SIS-based PSA blends with H-DCPD tackifiers. Journal of Applied Polymer Science 2006;102:2839–46.