

UV경화형 2-EHA/AA 점착제의 점착특성에 대한 경화제의 영향

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(2014년 7월 6일 접수, 2014년 8월 1일 수정, 2014년 9월 15일 채택)

Effect of Crosslinking Agent on Adhesion Properties of UV Curable 2-EHA/AA Pressure Sensitive Adhesive

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(Received July 6, 2014; Revised August 1, 2014; Accepted September 15, 2014)

초록: UV경화형 2-ethylhexyl acrylate(2-EHA)/acrylic acid(AA) 점착제의 점착특성에 대한 경화제 함량의 영향에 대해 조사하였다. 0.01 wt%의 극소량의 MMT가 도입된 아크릴 단량체 혼합물에 각각 0, 0.05, 0.1, 0.3 wt%의 1,6-hexanediol diacrylate(HDDA)를 경화제로 첨가하고 UV조사를 실시하여 점착제를 제조하였다. MMT 도입이 공중합체의 경화 거동과 점착제의 표면 특성에 미치는 영향은 매우 낮았으나, 점착특성의 경우 MMT의 도입으로 분자 사슬의 유연성이 제한되면서 응집파괴(cohesive failure)가 억제되는 것을 확인하였다. 그러나 0.3 wt%의 경화제가 도입된 점착제는 사슬 경직성이 크게 증가하면서 MMT의 첨가가 오히려 점착특성을 저하시키는 것으로 추측되었다. 결과를 토대로 2-EHA/AA 점착제의 경우 0.05 wt%의 낮은 함량의 경화제와 극소량의 MMT의 도입이 박리 시 응집파괴 없이 균형적인 점착특성을 부여하는 것으로 판단된다.

Abstract: UV-cured acrylic copolymer pressure sensitive adhesive (PSA) having different amounts of crosslinking agents were prepared and adhesion properties were investigated. 0.01 wt% of MMT clay was dispersed in 2-ethylhexyl acrylate (2-EHA)/acrylic acid (AA) monomer mixture containing 0, 0.05, 0.1 and 0.3 wt% 1,6-hexanediol diacrylate (HDDA) for crosslinking. It was investigated that the curing behavior and surface chemistry of PSAs were merely affected by the presence of MMT clays. On the other hand, adhesive properties were influenced by the MMT addition; a cohesive failure was restrained due to improved molecular elasticity even in uncrosslinked acrylic PSAs. However, it was also appeared that combination of 0.3 wt% crosslinking agent and MMT loading might result in the damage of adhesion properties of PSAs possibly due to the lack of chain flexibility. In our studies, it is suggested that the 2-EHA/AA PSAs incorporating 0.01 wt% of MMT and crosslinked with 0.05 wt% of HDDA exhibited the balanced adhesion properties without severe cohesive failure during strip.

Keywords: UV radiation curing, pressure sensitive adhesive, acrylic copolymer, montmorillonite, adhesion properties.

Introduction

Pressure sensitive adhesive (PSA) is a adhesive which form a bond when light pressure is applied to adhesive and can be peeled off without leaving traces.¹ The application of PSA products has been developed rapidly includes package, automotive, electric, medical, architectural industry and home appliance.^{1-5,8} Acrylic PSAs, in general, are copolymerized with low T_g monomers such as 2-ethylhexyl acrylate (2-EHA)

and *n*-butyl acrylate (*n*-BA) for tackiness and high T_g monomer such as acrylic acid (AA) for cohesive strength of PSAs.² Acrylic acid is usually copolymerized with 50~90% major polymer because of carboxylic group in its structure is useful for crosslinking and modifying cohesive strength.^{2,6} As PSAs need to be able to wet the surface of a substrate and possess a low T_g component to enable a tacky film to be obtained, they are usually prone to fail cohesively. This can be prevented in photo-initiated systems by incorporating a small amount of crosslinking agents.^{3,4}

The UV-curing process for acrylic PSAs offers several advantages compared to the typical solvent-based processes,

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which is solvent free, environmentally compatible, consuming less energy.^{3,4,6} To enhance the mechanical properties and thermal stability, multi-functional monomers has been used such as butandiol diacrylate (BDDA), hexandiol diacrylate (HDDA) and diethylene glycol diacrylate (DEGDA).⁷ Usually a high degree of crosslinking lowers the peel and tack, but not always.⁸ As crosslinking of PSAs exerts a more complex influence on the peel, an improvement of peel adhesion may be expected as a crosslinking.⁸ It has been reported that addition of small amount of nanoclay such as montmorillonite (MMT) into PSAs improve several properties.^{3,8} This depends on the dispersity of nanoclay in the polymer matrix. The improved properties of polymer nanocomposite would be also desirable in the field of PSAs, but only a few studies about the effect of nanoclay addition on acrylic PSAs are available.^{3,9} J. Kajtna *et al.* recently presented the development of nanocomposite UV crosslinkable acrylic PSAs (2-EHA/AA/t-BA) and measured adhesion properties.³ They found that the major influence of clay addition on adhesion properties of PSAs is shear strength and this was determined by increase of storage modulus (G') and decrease of $\tan\delta$ value from the DMA analysis.³ J. Kajtna *et al.* also published the study of the effect of acrylic polymer/MMT nanocomposite PSAs type and amount of MMT clays on adhesion properties.^{3,9} They were prepared nanocomposite PSAs by suspension polymerization.^{3,9}

In this paper, a series of UV irradiated acrylic PSAs containing MMT has been synthesized and crosslinked with different mass use level of 1,6-hexanediol diacrylate (HDDA) crosslinking agent. 2-ethylhexyl acrylate (2-EHA, $T_g=-70$ °C), commonly available monomer that yields soft and tacky polymer, will be used as a main monomer. In order to raise the T_g of major monomer, acrylic acid (AA, $T_g=106$ °C) will be copolymerized with 2-EHA, which may increase peel adhesion at room temperature at moderate peel rate.^{8,10} The influence of MMT clays on adhesion properties especially failure mode will be also investigated. It is expected that the nanoscale size and the large specific area of MMT may result in an improvement in the cohesion of polymer molecules. The adhesion properties of the photo-crosslinked PSAs were evaluated by investigating the variations in contact angle, probe tack, peel strength and viscoelastic properties at various crosslinking agent concentrations.

Experimental

Materials. Monomers, 2-ethylhexyl acrylate (2-EHA), acrylic

acid (AA) and crosslinking agent 1,6-hexanediol diacrylate (HDDA) were purchased from Sigma-Aldrich (St.Louise, MO). They were used without further purification. Photoinitiator bis(2,4,6-trimethyl benzoyl)-phenyl phosphine oxide (BAPO, Irgacure[®]819) was supported from BASF (Floham Park, NJ) and also used in the commercially available form without further purification. Bisacyl phosphine oxides were introduced as a new class of α -cleavage photoinitiators over the year, which has an absorption bands in the near UV/visible region.^{11,12} Cloisite 15A (CEC=125 meq/100 g, Southern Clay Products, Gonzales, TX), organically treated with quaternary ammonium salt montmorillonite (MMT) was added as a nanoclay without further surface treatment.

Preparation of Pressure Sensitive Adhesive. The reaction mixture consisted of 2-EHA, AA and HDDA were filled to 200 mL glass reactor. Photoinitiator and MMT were added to the mixture and followed by agitation using mechanical stirrer. After 20 min mixing, the mixture was applied at PET film with a bar coater. The thickness of PSA films obtained was 50 μm . All adhesive coatings were exposed to UV light for 10 min by medium mercury lamp of 31 mW/cm² and with an emission at 365 nm (UVA SPOT 400/T, Dr. Hönle, Germany) equipped with nitrogen purging. Table 1 shows different formulation of monomer mixture in order to determine the influence of crosslinking agent concentration on adhesion properties.

Measurement. Attenuated total reflectance (ATR) measurement was used for determining the conversion of monomer during crosslinking reaction by JASCO ATR PRO450-S (Jasco International Co. Ltd., Tokyo, Japan). The samples for ATR spectroscopy were prepared using following procedures. Monomer mixture was coated on PET film and then crosslinked under UV lamp for 10 min. The conversion of each sample can be evaluated by monitoring ATR spectra at the characteristic bands 810 cm⁻¹ for acrylic double bonds.⁸ All the sampling process was executed in the dark room in order to inhibit the additional reaction. To investigate the effect of

Table 1. Reaction Mixture Formulations

| Material (wt%) | PSA 01 | PSA 02 | PSA 03 | PSA 04 |
|----------------|--------|--------|--------|--------|
| 2-EHA | 89.9 | 89.9 | 89.8 | 89.6 |
| AA | 10.05 | 9.95 | 10 | 10 |
| BAPO | 0.05 | 0.05 | 0.05 | 0.05 |
| MMT | 0 | 0.05 | 0.05 | 0.05 |
| HDDA | 0 | 0.05 | 0.1 | 0.3 |

MMT loading on gel formation, gel phase content of nanocomposite was determined by Soxhlet extraction using tetrahydrofuran (THF) (Sigma-Aldrich Co., St. Louis, MO) under reflux during 24 h. The gel content of the UV-cured nanocomposite PSAs was then determined using following equation.

$$\text{Gel content (\%)} = \frac{W_a}{W_b} \times 100 \quad (1)$$

Where W_b and W_a are the sample weight before and after extraction, respectively.

The measurement of contact angle was performed at 25 °C 12 min with a Goniostar contact angle goniometer (Surface Tech. Co., Trenton, NJ). Drops of de-ionized water (5~5.2 mm diameter) were prepared with a micro-syringe and were dropped onto the surface of nanocomposite PSAs. Viscoelastic properties of PSAs materials were determined by HAAKE MARS III rheometer (Thermo Fisher Scientific Inc., Sunnyvale, CA) apparatus. PSAs were tested under temperature range from -90 to 40 °C at a heating rate of 2 °C/min and subjected to a constant frequency 1 Hz. A 25 mm diameter parallel plate and a gap size of 50 μm were used.

PSA Testing. Probe tack test was carried out using TE-6001 probe tack tester (Tester Sangyo, Co. Ltd, Saitama-ten, Japan) according to ASTM D2979-01. The test machine measures the force required to separate aluminum probe tip from the PSAs under low pressure and short contact time. Probe tack was evaluated with a 200 g/cm contact pressure, 1 s dwell time and at the rate of 0.1 cm/s. 180° peel test was conducted on a universal testing machine (UTM) (Instron, Norwood, MA) according to ASTM D903-49, where the peeling rate was controlled to 200 mm/min at room temperature. The test strips with 25 mm width were bonded to aluminum test panels by rolling a 3 kg rubber roller over the test strips 3 times. An average value of 5 times measurements was calculated for adhesion properties determination. Dynamic shear strength was measured using UTM according to the ASTM D-2370 after the sample was aged in a vacuum oven for 24 h. Five specimens were prepared per each PSA and tested respectively, and the shear strength for samples was averaged out to report. The crosshead speed was fixed at 20 mm/min.¹³

Results and Discussion

Conversion of 2-EHA/AA PSAs. ATR spectra from 4000 to 650 cm^{-1} of monomer mixture with and without MMT clay

after 10 min of UV irradiation is shown in Figure 1. The kinetics of UV crosslinking of acrylic PSAs can be investigated by evaluation of diminishing of absorption band at 810 cm^{-1} , which corresponds to =CH out-of-plane bending modes.⁸ Strong signal at 1720 cm^{-1} is attributed to the ester C=O bond in PET film.⁸ From the results, the final conversion of acrylic monomer is between 85~90% and the presence of MMT clay in monomer did not influence on conversion of prepolymer.

Figure 2 shows the influence of the presence of crosslinking agent added to monomer mixture on the kinetics of photopolymerization reaction. From the result, the highest level of conversion is observed less than 2 min at HDDA concentration of 0.3 wt%, which is significantly higher than that measured for sample without crosslinking agent. The final conversion of all monomer mixture showed a plateau maximum around 7 min of UV radiation time and then was not clearly affected by HDDA concentration.

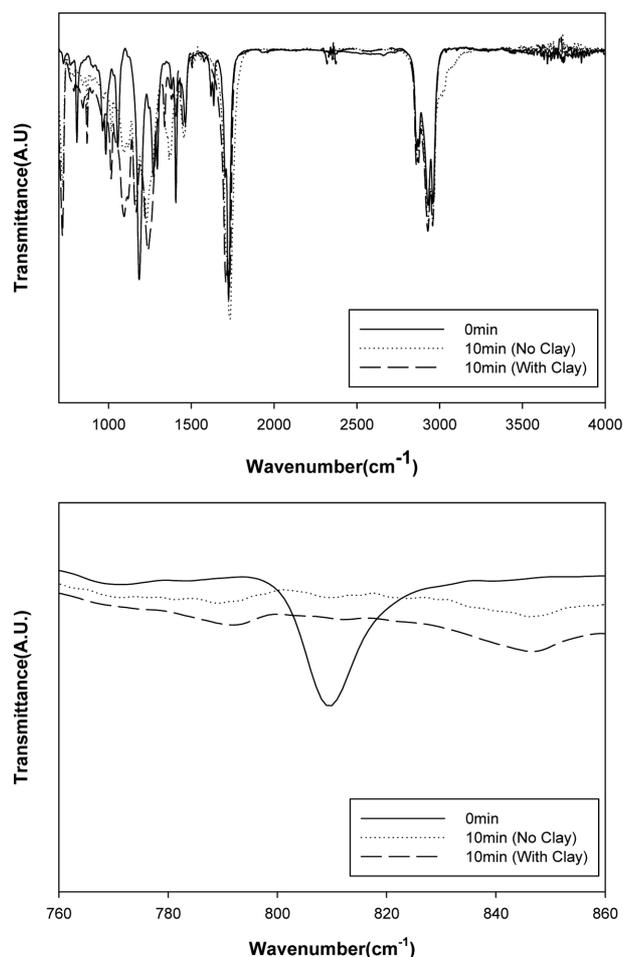


Figure 1. Transmittance of 2-EHA/AA PSA and nanocomposite PSA.

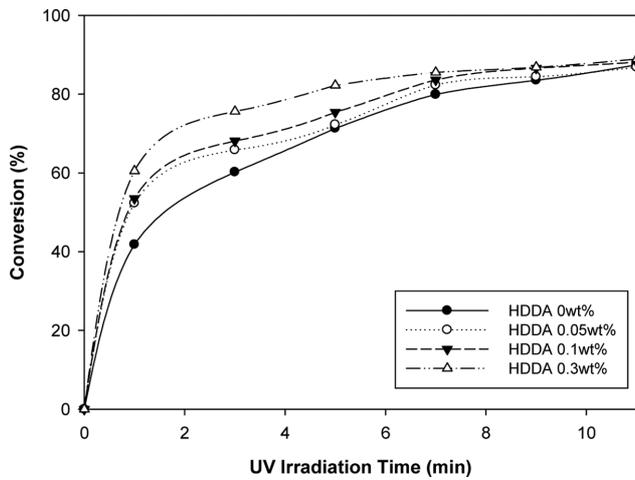


Figure 2. Conversion (%) of 2-EHA/AA PSAs with UV irradiation time.

Table 2. Gel Contents of 2-EHA/AA PSA and Nanocomposite PSA

| HDDA Content (wt%) | Gel content (wt%) | |
|--------------------|-------------------|-----------|
| | No Clay | With Clay |
| 0 | 1.7 | 5.0 |
| 0.05 | 61.5 | 72.2 |
| 0.1 | 73.5 | 78.6 |
| 0.3 | 86.8 | 81.9 |

The gel amount of PSAs measured by Soxhlet extraction is presented in Table 2. It is determined that gel content of polymer nanocomposite increase with HDDA concentration and reached a maximal value at 0.3 wt%. As also can be seen in Table 2, a relatively lower gel amount of PSAs in presence of MMT at 0.3 wt% of HDDA is observed. It may be considered that intercalated, not exfoliated MMT platelets may hinder the crosslinking process.¹⁰

Adhesion Properties of 2-EHA/AA/MMT Nanocomposite PSAs. In probe tack tests, the tip of a probe is brought into contact with a supported adhesive under low contact pressure for a short time and then pulled way at a fixed rate, followed to the measurement of the peak force of separation.⁸ As shown in Figure 3, tack value of the sample without crosslinking agent was higher than the sample crosslinked with 0.05 wt% and above, but severe cohesive failure would be happened for uncrosslinked PSAs with no MMT added. It can be evident that the restriction in the mobility of polymer chains caused by well-dispersed MMT layer inhibits cohesive failure of PSAs during detachment from a probe.³ According to the contact

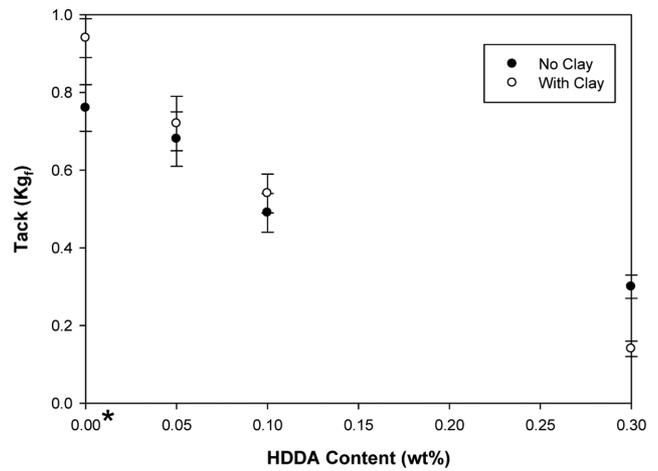


Figure 3. Probe tack of 2-EHA/AA PSA with HDDA(*cohesive failure).

Table 3. Contact Angle of 2-EHA/AA PSA

| HDDA Content (wt%) | Contact angle (deg.) | |
|--------------------|----------------------|-----------|
| | No Clay | With Clay |
| 0 | 73.6 | 73.2 |
| 0.05 | 71.2 | 70.8 |
| 0.1 | 74.5 | 73.3 |
| 0.3 | 75.9 | 75.8 |

angle data of PSAs in Table 3, it can be seen that the introduction of MMT did not affect the surface chemistry of PSAs. Previous work speculated that Cloisite 15A did not migrate on the PSAs surface due to its very hydrophobic nature.^{3,9}

Figure 4 shows peel strength data of PSAs with different

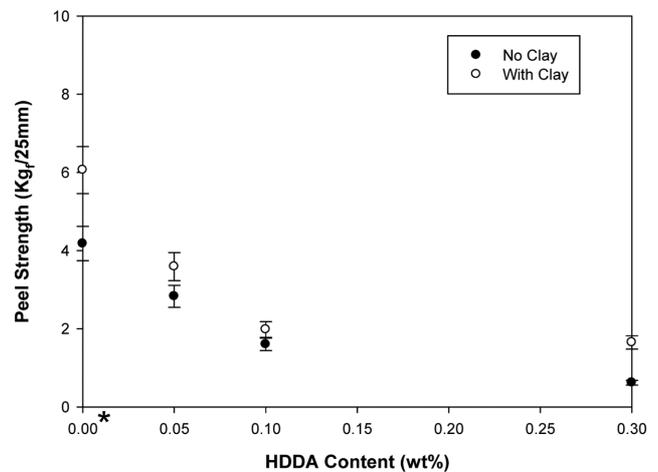


Figure 4. Peel strength of 2-EHA/AA PSA with HDDA (*cohesive failure).

amount of HDDA. Increasing molecular weight and degree of crosslinking are usually expected to cause a decrease in peel adhesion because these factors may increase the modulus of elasticity and decrease the polymer chain mobility.^{3,8,10} The 180° peel adhesion of the sample without crosslinking agent is highest as shown in Figure 4, but severe cohesive failure leaving visually noticeable residue was happened during stripped similar to the result of probe tack test. It is also noteworthy that compared with the sample without MMT, the introduction of 0.01 wt% MMT effectively restrained the cohesive failure of PSAs. Although adhesion properties of 2-EHA/AA nanocomposite PSAs decrease with increasing crosslinking agent, the proper balance between tack and peel strength was obtained by PSAs cured by 0.05 wt% of crosslinking agent.

To verify the effect of MMT on cohesion of PSA, dynamic shear strength was measured and the result is shown in Figure 5. It is reported that the cohesion of PSA is closely related to the internal structural resistance of the polymer. Therefore, the measurement of shear strength of PSA is accepted as criteria for the cohesion of PSA.¹³ As shown in Figure 5, PSA did not show cohesive failure in MMT loading, which is similar to the result of tack and peel strength. From the result shown in Table 3, it may be thought that the presence of MMT influence the relative C=C bond concentration in case of no crosslinking agent added. It can be said that the presence of MMT into PSA increases the cohesion of polymer by strong interaction between polymer chain and MMT surface, which may has the similar influence as a crosslinking.

Viscoelastic properties of acrylic PSAs were tested by using rheometer analysis and the information about the elastic and

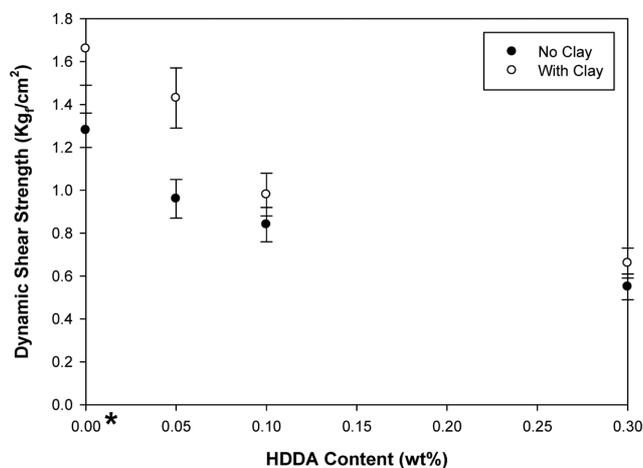


Figure 5. Dynamic shear strength of 2-EHA/AA PSA with HDDA (*cohesive failure).

damping contribution of the materials with storage modulus and $\tan\delta$ over a temperature range were shown in Figure 6 and 7, respectively. Both T_g and storage modulus in rubbery region of PSAs increased with increasing crosslinking agent content. This enhancement in viscoelastic properties might be attributed to the rigid structural stability of the acrylic polymer matrix by UV crosslinking.^{6,7,14} It was also interesting to note that higher value of G' and lower value of $\tan\delta$ at 25 °C was obtained in the case of PSAs with MMT clays as can be seen in Table 4. The difference of G' and $\tan\delta$ value between PSAs and nanocomposite PSAs was clearly observed at 0.3 wt% of crosslinking agent added. This also may correspond to lower measured adhesion properties for nanocomposite PSAs with added 0.3 wt% crosslinking agent.

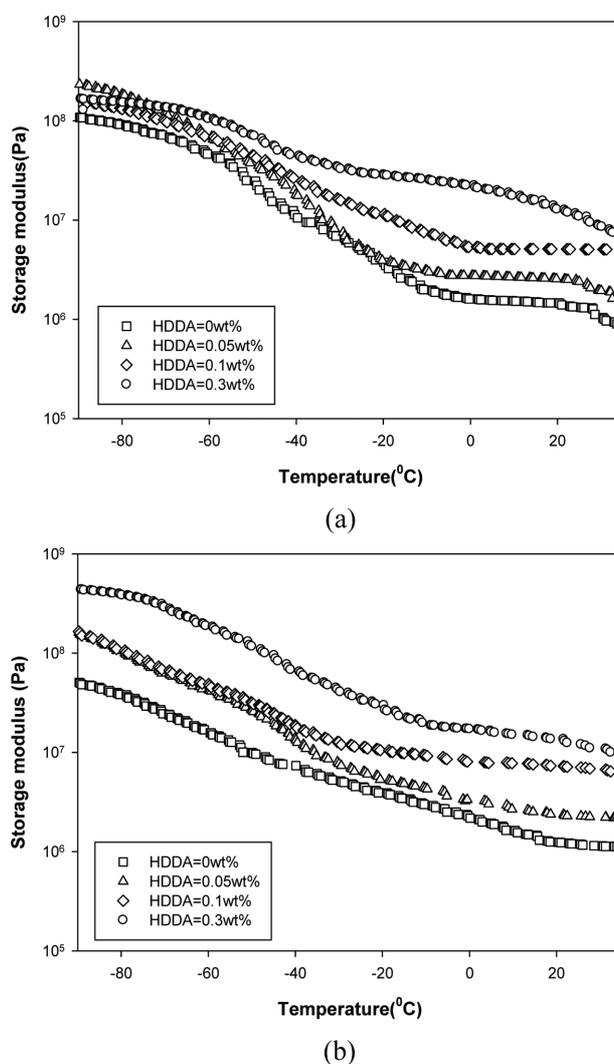


Figure 6. Temperature dependence of G' for PSA and nanocomposite PSA (a) without MMT; (b) 0.01 wt% MMT added.

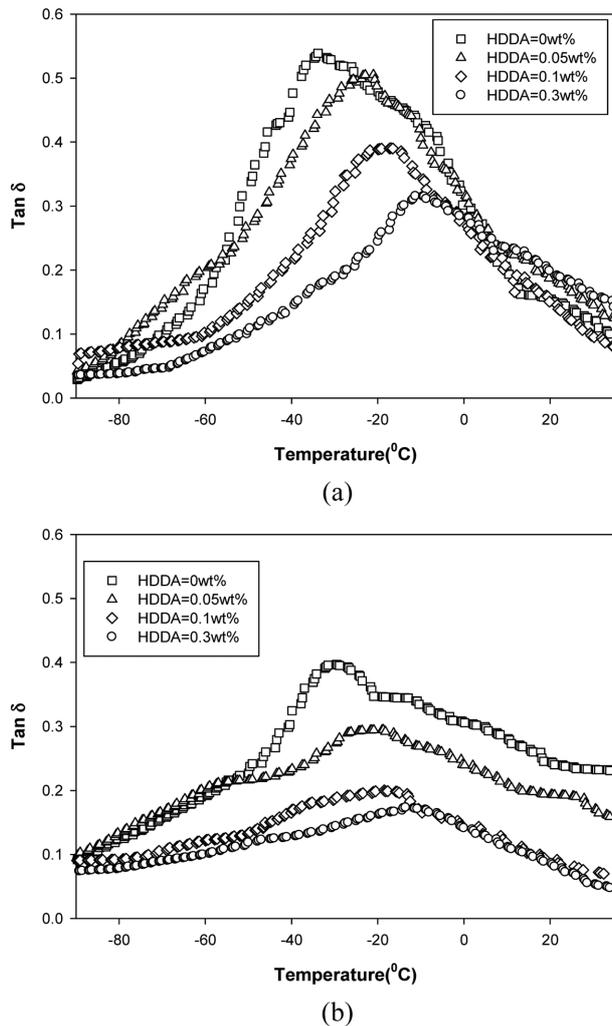


Figure 7. Temperature dependence of $\tan\delta$ for PSA and nanocomposite PSA (a) without MMT; (b) 0.01 wt% MMT added.

Table 4. Storage Modulus and $\tan\delta$ for PSA and Nanocomposite PSA at 25 °C

| HDDA content (wt%) | $G'(\text{Pa}) \times 10^6$ | | $\tan\delta$ | |
|--------------------|-----------------------------|------|--------------|------|
| | No MMT | MMT | No MMT | MMT |
| 0 | 1.32 | 1.19 | 0.14 | 0.24 |
| 0.05 | 2.40 | 2.28 | 0.17 | 0.19 |
| 0.1 | 5.07 | 7.06 | 0.12 | 0.08 |
| 0.3 | 10.9 | 12.0 | 0.18 | 0.07 |

Conclusions

UV irradiated 2-EHA/AA/MMT nanocomposite PSAs has been prepared and cured with different amount of 1,6-hexanediol diacrylate (HDDA) as a crosslinking agent. It was

observed that the addition of 0.01 wt% MMT clay in the monomer mixture did not have any influence on polymerization kinetics and surface chemistry of PSAs. It can be also found that both tack and peel strength of PSAs somewhat improved and cohesive failure of sample was also prevented by the incorporation of MMT clay. On the other hand, the presence of MMT results in decline of adhesion properties in case of highly crosslinked structure at 0.3 wt% of HDDA. It can be suggested that 0.01 wt% of MMT and small amount added crosslinking agent under 0.3 wt% revealed high restriction in the mobility of polymer chain, which may result in the improvement of adhesion properties. It may be considered that HDDA showed an optimum concentration at 0.05 wt% for proper balance between tack and peel strength without cohesive failure during adhesive during debonding process.

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