A DISSERTATION FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Characterization and Aging Behavior of Optically Clear Acrylic Adhesives for Touch Screen Panel

터치 스크린 패널용 아크릴계 광학 접착소재의

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Abstract

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Optically clear adhesive (OCA) for touch screen panel (TSP) means highly transparent pressure sensitive adhesive (PSA) which has more than 90% of visible light transmittance. This name indicates especially PSA applied for TSP assembly, for example, bonding between transparent electrode and cover window or display module. OCA needs high transparency because contents from display module reach to user's eye through it. Along with this transparency, required properties for OCA are suitable adhesion strength, anti-corrosive property, cloud point-resistance, and durability. Acrylic polymer is mainly used as OCA because of its excellent transparency. UV-curing method has employed for OCA preparation due to its high efficiency and productivity.

In capacitive TSP structure, which is used mostly in these days, OCA is contacted to transparent electrode. Therefore, OCA should not damage transparent electrode since it is closely related to TSP driving. General acrylic adhesives include acrylic acid for improving cohesion but this component can corrode transparent electrode due to carboxyl group in it. Accordingly, acid-free PSA should be prepared with excluding acidic component. In this study, N-vinyl caprolactam was chosen instead of acrylic acid.

Cloud point-resistance of PSA mean no haze appearance on cured PSA film regardless of environmental change. This property can be given to PSA as incorporating hydrophilic moiety into PSA matrix. Hydrophilic ingredient helps equal distribution of absorbed moisture in PSA matrix under humid condition thus cloudy state of PSA do not occur. Oligomeric (Methoxylated Polyethyleneglycol Acrylate, PEGA) and monomeric (2-hydroxyethyl acrylate, HEA) hydrophilic component were incorporated to the PSA in this experiment. Their effects on adhesion property and aging behavior were compared.

As a result, monomeric ingredient, HEA showed better cloud point-resistance assignment to the PSA and more stable adhesion property although it passed hygrothermal aging than those of oligomeric material incorporated one. PEGA contains ether groups in its structure and this functional group is weak to oxidation hence adhesion property of PEGA blended PSA declined when it was aged. On the other hand, HEA was well distributed owing to its low molecular weight. This phenomenon and hydroxyl group in HEA structure had relevance to better cloud point-resistance, adhesion property, and hygrothermal aging stability of prepared PSA by HEA incorporation. Both hydrophilic component was also effective to prevent corrosion of conductive substrate.

Keywords: optically clear adhesive, touch screen panel, acrylic adhesive, acid-free property, cloud point-resistance, hydrophilic component, adhesion performance, aging behavior

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Chapter 1

General Introduction and Objectives

1. Optically clear adhesive and touch screen panel

Nowadays, touch screen panel (TSP) is a very common input tool in electronic devices. Optically clear adhesive (OCA) is used to bond each layer consisting TSP, especially cover window, transparent electrode, or display module as shown in Figure 1-1. But there are other advantages for using OCA besides just attaching each component. The representative advantage is better image quality with OCA than without it. Figure 1-2 describes the image difference with and without OCA (Dexerials Corporation, 2014). The Loss of the light from the backlight unit decreased in the TSP. It is because the refractive index difference between the cover window and display module decreased by employing OCA. Accordingly, the contrast ratio is improved and the user can see clear images through cover window. This bright image can reduce the backlight unit driving power and that is related to the battery power consumption. Additionally, the vibration and impact resistance can also be improved by using OCA. The touch performance of the TSP is enhanced as well by applying OCA in comparison with that of the TSP without OCA (air gap structure) (Yi, 2013).

“Optically clear” means more than 90 % of the visible light can transmit the adhesive material. Clarity is very critical to OCA because the user sees output from display module through OCA layer. The adhesion strength and durability are also important. The anti-corrosion property to the transparent electrode and cloud point-resistance are also needed. These two properties will be described in detail in a separate section.

OCA is predominantly supplied into liquid resin type and cured film type like double-side tape, which is pressure sensitive adhesive (PSA). Tape type OCA is released as cured status, hence there is no worry about shrinkage and application on the substrates, including flexible one, is also easy and simple.

The acrylic adhesive is employed as OCA because of its excellent transparency, ease of property modification, and economical advantage. Table 1-1 lists suitable points of the acrylic adhesive as OCA compared to other types of adhesives.

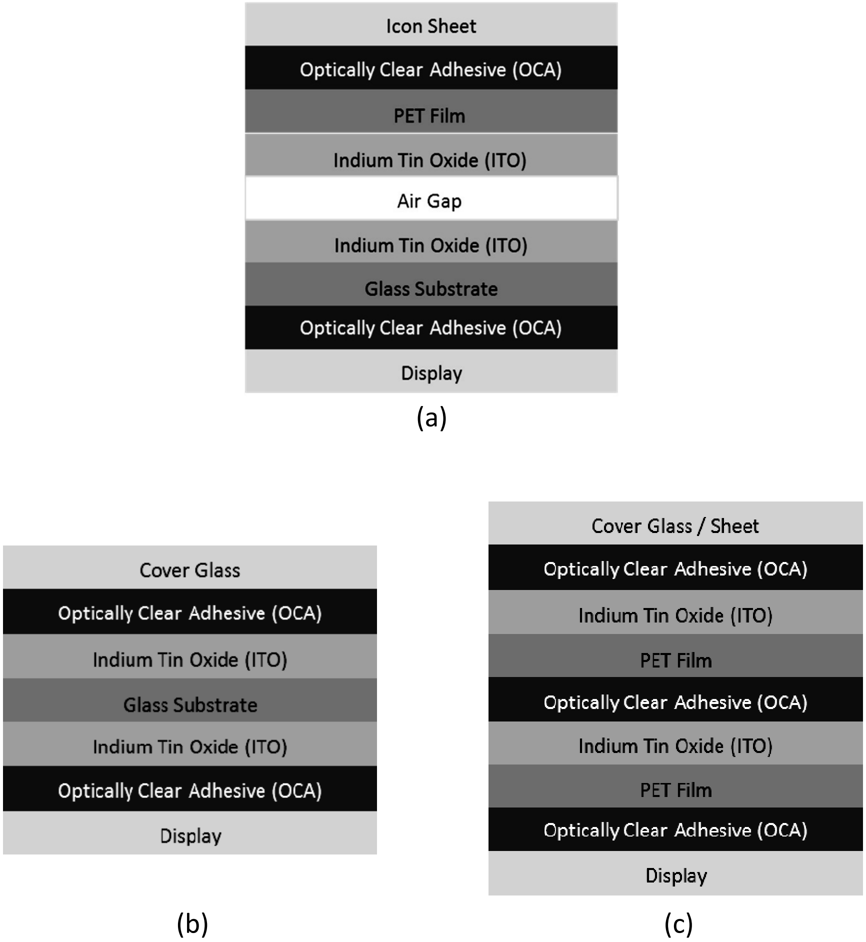


Figure 1-1. Structure of resistive (a), capacitive (glass sensor) (b), and capacitive (film sensor) (c) type of TSP (Fuji Keizai, 2011).

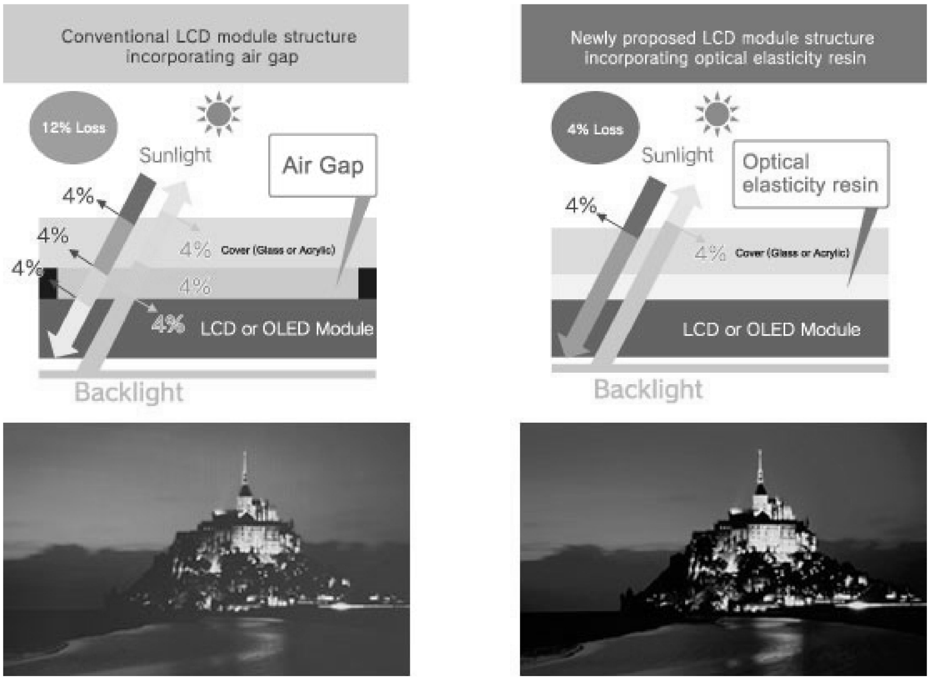


Figure 1-2. Image difference without (a) and with (b) OCA (Dexerials Corporation, 2014)

Table 1-1. Properties of each type of adhesives (Nitto Denko, 2014).

	Advantages	Disadvantages
Rubber	Cheap	Small selection of substrates Weak heat and weather Resistance
Acryl	Excellent transparency Large selection of substrates Easy modification by various monomer selection	Worse heat resistance than silicone adhesive.
Silicone	Wide use range of temperatures Outstanding resistance to heat and cold Outstanding resistance to chemicals and weather	Expensive
Polyurethane	Outstanding removability Only minor degrees of malodor and skin irritation	Outstanding moisture permeability Difficult to produce strong adhesion and tack

2. UV-curable PSA

UV-curing have been widely used because of its environmental friendliness and inducing fast reaction among reactants. It needs only several seconds for reaction. A photoinitiator should be included into PSA composition to start reaction. UV-curing is an easy and rapid way to make crosslinking polymer structure using by multifunctional monomer or oligomer. Owing to fast reaction, UV-curing can provide high efficiency and productivity. Generally, free radical and cationic polymerization occurred by UV irradiation.

Not only just curing, UV irradiation have important role for the preparation of the base resin which constitute PSA because resin can be prepared without solvent in short time at room temperature. Polymerization of a monomer mixture without solvent by UV irradiation can be a good advantage especially for OCA. OCA for TSP is applied on a substrate as relatively thick film compared to other applications. Employing UV-polymerization is a useful way to make thick PSA film because it does not need solvent therefore 100 % solid type PSA can be given. Non-solvent type PSA is easy to be coated on a substrate and form thick film after coating process, by UV-curing.

3. Acrylic OCA

Acrylic resin composed of 2-ethylhexyl acrylate, methyl acrylate, acrylic acid, vinyl pyrrolydone, and glycidyl metacrylate was used as OCA for bonding color filter and protective epoxy coating in liquid crystal display (Chang *et al.*, 2005). The relationship between co-monomer side chain length and optical property (transmittance and refractive index) has been researched. There were tries to make refractive index of OCA higher with inducing semi-IPN structure (Lee *et al.*, 2012) and incorporating inorganic materials like zirconium carboxyethyl acrylate (Kim *et al.*, 2013), titanium oxide (Lee *et al.*, 2013) or hafnium carboxyethyl acrylate (Lee *et al.*, 2014). These OCAs are based on 2-ethylhexyl acrylate, acrylic acid because the researches were only focused on improvement of refractive index to enhance image quality and contrast ratio on display.

4. Acid-free property

To OCA, it is a very important property not to any affect transparent electrode which is contacted each other in the TSP structure. Usually an acid component assigned cohesion to general acrylic PSA thus it is an essential ingredient for a good adhesion property. But this acid component can corrode transparent electrode in a long-term respect. Figure 1-3 was plotted the electrical resistance increase of the ITO as time passed under high temperature and humid condition. The acidic component, acrylic acid, contained PSA sample brought out the large electrical resistance increase of the ITO. The electrical resistance increase of the ITO is related to the transparent electrode corrosion. The corrosion of the transparent electrode can cause a problem of the TSP driving. This defect of the TSP can be connected to failure in whole electronic devices like smartphone, tablet PC, laptop, and so on, which include TSP.

Therefore the acidic component should be minimized or replaced by other cohesive materials. Common polar components can be good substitutes for assigning cohesion to acrylic PSAs. For example, N-vinyl caprolactam, N-vinyl pyrrolidone, (un)substituted acrylamide, and hydroxyl alkyl (meth)acrylate can be acceptable candidates for acid-free acrylic adhesives (Everaerts *et al.*, 2009).

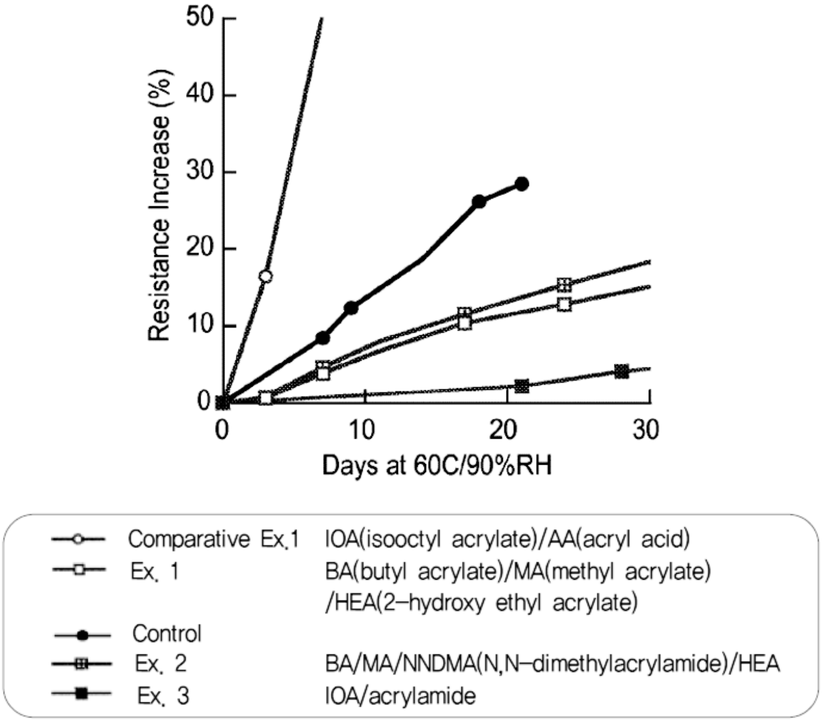
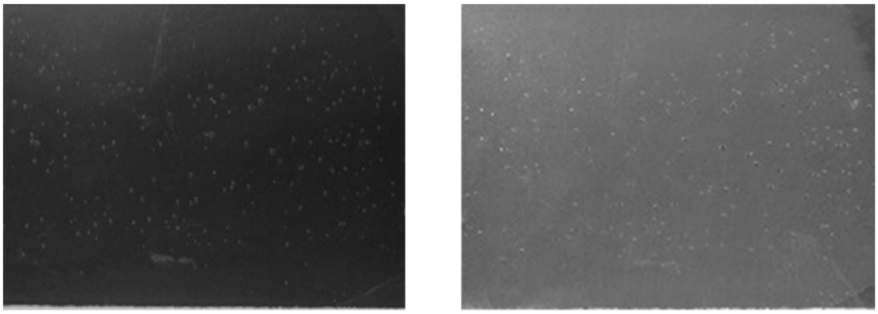


Figure 1-3. Relationship of the percent resistance increase as a function of time under high temperature and humid condition (Park *et al.*, 2012).

5. Cloud point-resistance

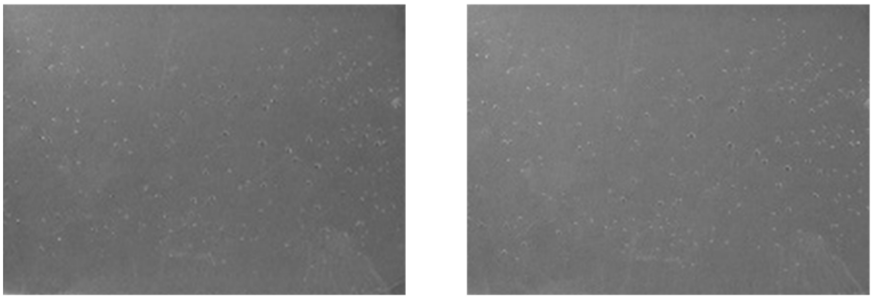
Cloud point-resistance mean haze-free property under various environment or dramatic environmental change. When a PSA has placed in high temperature and humid condition then returns to ambient temperature and humidity condition, the moisture absorbed into the PSA matrix is localized. The refractive index of the localized moisture is different with that of the continuous PSA phase therefore white or cloudy surface is observed. Figure 1-4 presents the haze of a general acrylic PSA without hydrophilic components due to an abrupt environment change. They are photos of the UV-cured PSA films on a black-color table. The PSA film was transparent before it placed under high temperature and humid condition, but it showed a cloudy state due to the moisture in it directly after it was taken from that condition.

This is a temporary phenomenon and the haze disappears with equilibration between the PSA and environment after some time. The hydrophilic component should be incorporated to solve this problem according to previous study (Everaerts *et al.*, 2013). Figure 1-5 explains the assignment of cloud point-resistance to the general PSA. The moisture can be more equally dispersed or even solubilized by incorporating the hydrophilic moiety into the PSA matrix. As a result, the phase separation do not occur between the PSA matrix and localized moisture. The refractive index difference is not developed as well. Accordingly, the PSA can keep the clear state under the sudden environmental change.



Before aging

After 2 min



After 5 min

After 10 min

Figure 1-4. Transparency change of the general acrylic PSA without hydrophilic component after taking out each sample from the high temperature and humidity conditioned oven (50 ^{o}C, 80 %RH), 3 days later.

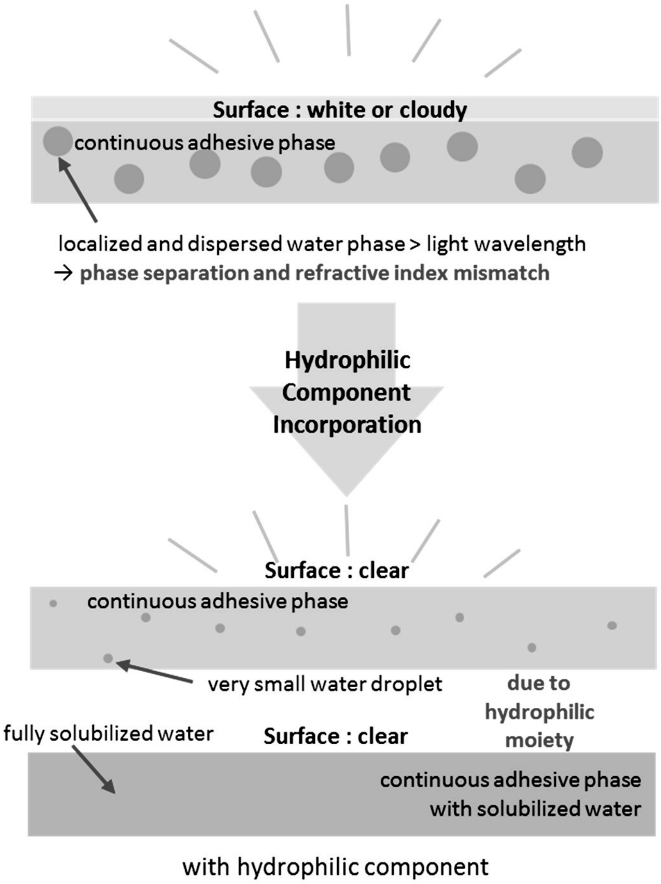


Figure 1-5. Cloud point-resistance assignment to general PSA.

6. Objectives of this study

The objectives of this study are preparing acid-free and cloud point-resistant OCA then observing aging behavior of it for TSP driving without trouble in long-term use. To assign cloud point-resistance to the PSA, oligomeric and monomeric hydrophilic materials were incorporated to the previously prepared acid-free base resin. Their effects on the adhesion performance and aging behavior were characterized to check the PSA durability. In addition, it was tried to investigate which material shows better performance and how each material led to difference on aging behavior.

6.1. Preparation of acid-free OCA

At first, the work was focused on the anti-corrosive acrylic PSA preparation with excluding an acidic component. Acrylate monomer with amide group was incorporated for cohesion assignment to the PSA instead of the acidic component. N-vinyl caprolactam (NVC) was selected for cohesion assignment purpose to the PSA. Other components were 2-ethylhexyl acrylate (2-EHA) for low glass transition temperature (T_g) of the PSA and isobornyl acrylate (IBOA) for high T_g and rigidity.

The adhesion performance and corrosion property of the PSA were examined with various amount of NVC incorporation because it is necessary to investigate how this material affect PSA property and what is appropriate amount for using it as OCA. This composition was utilized as the base resin for blending hydrophilic components which will be mentioned in next 2 sections.

6.2. Cloud point-resistance assignment by oligomeric component

Methoxylated polyethylene glycol monoacrylate (PEGA) was added to the base resin consisted of 2-EHA, IBOA, and NVC. In this time, NVC 20 wt% contained base resin was chosen based on several experiment result. PEGA have 11 repeating units composed of -C_2H_4-O- and this part is related to the hydrophilicity. The acrylate group in PEGA enables it to react with the base resin and crosslinker during the UV-curing

6.3. Cloud point-resistance assignment by monomeric component

2-Hydroxyethyl acrylate (HEA) was blended to NVC 20 wt% contained base resin like the preceding. HEA is monomer hence it was expected to show different tendency in the adhesion performance or aging behavior compared to PEGA blended PSA. HEA has hydroxyl –OH group in its structure and this part took charge of hydrophilicity. This material also includes acrylate group thus well reacted with the base resin and crosslinker without trouble.

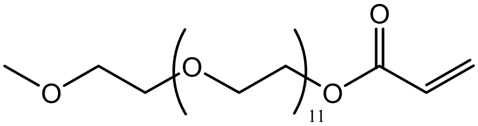


Figure 1-6. Structure of monofunctional methoxylated polyethyleneglycol acrylate (PEGA).

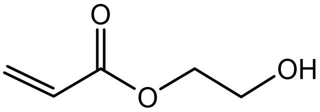


Figure 1-7. Structure of 2-hydroxyethyl acrylate (HEA).

6.4. Aging behavior characterization of OCA

Durability of OCA should be secured because the long-term use of the TSP will be expanded since various electronic devices, even in white goods, started to employ the TSP as an input tool. Therefore it is needed to monitor critical properties as OCA like adhesion strength or transparency by exposing prepared OCA under hygrothermal aging condition, which is one of the accelerating aging method. The accelerated aging is a common method to verify materials properties within relatively short time.

Each sample was taken from the conditioned oven and their adhesion strength, viscoelastic property and corrosion property were measured. The X-ray photoelectron and infrared spectra helped to know how polymer structure had changed during the aging. Chemiluminescence analysis showed the difference of the polymer degradation degree, especially about its oxidation, through signal intensity (Gijsman *et al.*, 2001).

Chapter 2

Preparation and Characterization of Acid-free Optically Clear Adhesive with N-vinyl Caprolactam

1. Introduction

It is needed to exclude acrylic acid (AA) in OCA composition to protect transparent electrode of touch screen panel, as described in chapter 1. N-vinyl caprolactam (NVC) can be good replacement instead of AA. Nitrogen atom in NVC structure has high electronegativity therefore it can be helpful for OCA to enhance cohesion. NVC has been employed in other studies for medical pressure sensitive adhesive (PSA) (Czech *et al.*, 2007; Feldstein*, et al.*, 2014), self-adhesive products such as label (Czech, 2001; Czech, 2004), drug delivery system (Cespi *et al.*, 2014), dental materials (Moshaverinia *et al.*, 2011).

So far, there are few published studies about OCA. The relationship between curing behavior and its viscoelastic property has been researched (Chang*, et al.*, 2005). Titanium oxide (Lee*, et al.*, 2013), hafnium carboxyethyl acrylate (Lee*, et al.*, 2014), and zirconium carboxyethyl acrylate (Kim*, et al.*, 2013) blended PSA also has been studied for OCA focused on high refractive index because high refractive index OCA can contribute to clear image from TSP. There are many patents about optical bonding material as a PSA type (OCA) or liquid resin type (optically clear resin, OCR) applied by various company (Everaerts*, et al.*, 2009; Determan *et al.*, 2010; Katakami, 2010; Toyama *et al.*, 2011; Everaerts*, et al.*, 2013). But there are no published research paper about acid-free OCA.

Purpose of this research is characterization of acrylic OCA incorporated NVC to main polymer backbone consisted of OCA matrix as core material for protecting transparent electrode from corrosion by OCA. Therefore PSA type OCA was prepared by adopting varied amount of NVC and then adhesion performance was observed. Durability of OCA is also important because TSP will widen its usage to long-term used electronic products like white goods or automobiles. But recent papers have not studied about that so it is necessary to be carried out. Durability of PSA prepared in this study should be checked as well. Hygrothermal aging is generally used as a test method to decide OCA suitability before actual OCA application by intentionally exposing it in harsh environment. Consequently, prepared OCA passed through property test including adhesion performance and corrosion property after placing in hygrothermal aging condition. Additionally, method for detecting corrosive property of PSA to transparent electrode was suggested as a simple one.

2. Experimental

2.1. Materials

2-Ethylhexyl acrylate (2-EHA, Samchun Pure Chemical, Republic of Korea), isobornyl acrylate (IBOA, Sigma-Aldrich, USA), and N-vinyl caprolactam (NVC, Sigma-Aldrich, USA) were used to prepare monomer premix. 1,6-Hexanediol diacrylate (HDDA, Miwon Specialty Chemical, Republic of Korea) was a crosslinking agent. Photoinitiator for premix preparation and UV-curing was α,α-dimethoxy-α-phenylacetophenone (Irgacure 651, BASF, Germany). All reagents were used without any further purification.

2.2. Monomer premix preparation

A 300 mL round-bottomed flask was equipped with a mechanical stirrer, thermometer, N_2 purging tube. Then each monomer was charged into a flask as mentioned in Table 3-1. Photoinitiator amount was 0.04 phr. Five monomer premixes with different amount of NVC were prepared by irradiating UV to 2-EHA, IBOA, NVC, and photoinitiator mixture using a UV-spot cure system (SP-9, USHIO, Japan) with 40 mW/cm^2 intensity under N_2 rich atmosphere for about 3 min. Average viscosity after finishing UV irradiation was near 870 cPs which is measured by Brookfield viscometer using No. 4 spindle under 750 rpm at room temperature.

Table 2-1. Monomer ratio for premix preparation by UV irradiation

	#1	#2	#3	#4	#5
2-EHA (wt%)	60	60	60	60	60
IBOA (wt%)	40	35	30	20	0
NVC (wt%)	0	5	10	20	40
T_g of cured PSA film (^oC) [a]	-40.8	-32.1	-28	-16.6	-22.6

[a] : measured by ARES.

2.3. Coating and UV-curing

Each premix was blended with 0.1 phr of HDDA and 0.16 phr of additional photoinitiator using by a paste mixer (Daewha Tech Co. Ltd, Republic of Korea) for 5 min under 1000 rpm of rotation and revolution speed. The generated heat during blending was not considered. These mixtures were coated on PET film with 175 µm of dry thickness for peel strength measurement. They were also coated on release film with 500 µm of dry thickness for viscoelastic property measurement. Coated samples were UV-cured using by a conveyor belt type UV curing equipment with 1000 mJ/cm^2 dose and formed PSA film after UV-curing.

2.4. Gel fraction

To know the gel fraction of each sample, the UV-cured PSA film was soaked to toluene for 24 hours at 50 ^{o}C after weighing every samples. Then swelled PSA films were fully dried after eliminating toluene for 24 hours at 50 ^{o}C. After drying, samples weights were measured and finally the gel fraction was gained. The gel fraction of cured PSA film was calculated through following equation.

$$Gel\ fraction\ (\%) = (W_1/W_0) \times 100$$

Where, W_0 is the initial weight of the sample, and W_1 is the solvent extracted weight (Park *et al.*, 2013).

2.5. Transmittance

UV/visible spectrophotometer (Cary 100 UV-Vis, Agilent Technologies, USA) was an instrument for evaluating visible light transmittance of PSA film as OCA in this experiment. Measurement wavelength range was 400 to 700 nm. PSA film coated on PET film was loaded on the instrument and bare PET film was used for setting baseline corrections (100 % transmittance).

2.6. Tack and peel strength

The probe tack and peel strength were measured by a Texture Analyzer (TA.XT. plus, Stable Micro Systems, UK) at room temperature. A probe was 5 mm diameter cylinder type stainless steel. A probe contacted to PSA film surface with a 0.5 mm/s speed and 100 g/cm^2 force for 1 s. Then it detached with a speed of 10 mm/s. Maximum force when a probe detached from PSA film surface was regarded as a probe tack result. Substrates for the peel strength test specimen were glass and polycarbonate (PC) which are representative material for TSP cover window. 1 inch width of PSA film was attached to each substrate and pressed twice by a 2 kg of rubber roller. The test speed was 5 mm/s. Peel strength measurement was performed after 24 hours. The peel strength value was determined by the average force during the test.

2.7. Aging condition

Aging condition for durability and corrosion property examination of PSA film was 50 °C, 80 % RH. The UV-cured PSA film was stored in this conditioned oven for 2, 4, and 8 weeks, respectively. After that period, each PSA film was assessed in an aspect of the peel strength, corrosion property, surface property and viscoelastic property.

2.8. Corrosion test through copper foil color change and resistance increase by attaching PSA

The corrosive property of PSA to transparent electrode was tested indirectly by copper foil color change which is simple and economical method. The UV-cured PSA film was put on copper foil and stored aging condition as mentioned at section 2.7 for 2, 4, and 8 weeks, respectively. The copper foil color changed gradually as time goes by. The copper foil color was detected by a spectrophotometer (TECHKON SP 820 λ, TECHKON GmbH, Germany). Lightness (*L*), redness (*a*), and yellowness (*b*) values were determined and those values were used to calculate color change degree, ΔE as following equation.

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

Where, L_1, a_1, b_1 data before aging, L_2, a_2, b_2 data after each aging period (Pfeffer *et al.*, 2012).

Moreover, the resistance increase was measured employing actual transparent electrode, sputtered indium tin oxide (ITO) on PET film. The UV-cured PSA film adhered to the ITO film and its surface resistance was measured by a low resistivity meter (MCP-T610, Mitsubishi Chemical, Japan) before aging and after 2 and 4 weeks aging for comparison with the copper foil color change test. The measurement point was the nearest part from PSA attachment. The resistance increase was calculated as following equation.

$$\text{Resistance increase (\%)} = (R_2 - R_1)/R_1 \times 100$$

Where, R_1 is the initial surface resistance and R_2 is the surface resistance after aging period (2 and 4 weeks).

2.9. Viscoelastic property

The viscoelastic property was observed using by an advanced rheometric expansion system (ARES, Rheometric Scientific, USA). The test sample was NVC 20 wt% contained one as a representative example of PSA film to know aging behavior in this study. The temperature sweep test was carried out from -50 to 150 ^{o}C with a heating rate of 3 ^{o}C/min. The frequency was 1 rad/s and strain was 1 %. A 25 mm diameter of parallel plate accessory was used for measurement. The gap between two parallel plates was 500 µm. The shear storage modulus was plotted as increasing temperature.

2.10. Surface free energy

The substrate surface free energy was obtained through measuring contact angles using by a contact angle analyzer (Phoenix-10, Surface Electro Optics, Republic of Korea). Distilled water, diiodomethane, and formamide were used to calculate the surface free energy of glass and PC from contact angles based on Lewis acid-base theory (Jaczuk *et al.*, 1999; Wang *et al.*, 2006). The surface free energy of NVC 20 wt% contained PSA film was measured as a representative specimen before aging and after 2, 4, and 8 weeks aging, respectively.

2.11. X-ray photoelectron spectroscopy (XPS)

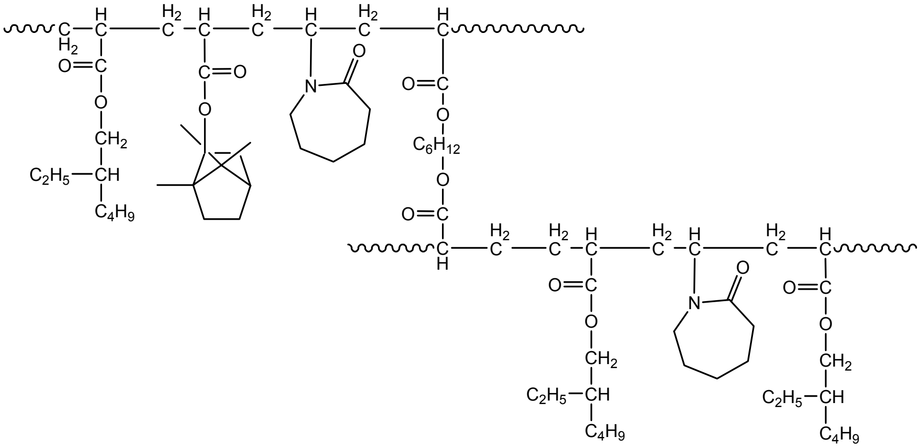
XPS instrument was Axis-HSI (Kratos Inc., UK) equipped with Mg in Mg/Al dual anode and X-ray power was 10 mA and 15 kV. Fitting method was a combination of Gaussian & Lorentzian_GL(30) using casaXPS program for element peak deconvolution. The UV-cured 500 µm of NVC 20 wt% contained PSA film was used for measurement to compare the alteration of it before and after 2 weeks aging. The C1s spectra were obtained from each separated peak related to various functional groups including carbon.

3. Results and discussion

3.1. UV-cured PSA film as OCA

All coated samples were UV-cured and formed PSA film after UV irradiation. Scheme 2-1 illustrated crosslinked structure of polymer which composed PSA. In Figure 2-1, the gel fraction of each PSA film was different whether NVC was included or not. The gel fraction was similar regardless of NVC amount after its incorporation. As incorporating NVC, the interaction among molecules was promoted due to its relatively higher polarity than that of other monomer components. High polarity was caused by nitrogen atom of NVC. The promoted reaction among molecules led to high gel fraction of the UV-cured PSA film. The polarity of NVC affected the cohesion of the UV-cured PSA film (Czech*, et al.*, 2007) and are connected to the adhesion or viscoelastic property.

The visible light transmittance of the UV-cured film was also near 100 %, so, all prepared samples had excellent clarity and satisfied optically clear status as shown in Figure 2-2. The transmittance calibration was carried out before the actual measurement, using the bare PET film which is transparent and nothing coated on it. That is, the transmittance value of the bare PET film is 100 %. For that reason, the 100 % transmittance of the specimen (PSA coated PET film) means similar clarity compared to that of the bare PET film in the actual measurement. More than 100 % of transmittance means higher transparency of coated PSA on PET film than that of bare PET film. All components were miscible, therefore, the PSA film without haze was achieved.



Scheme 2-1. Crosslinked structure of PSA material after UV-curing by HDDA.

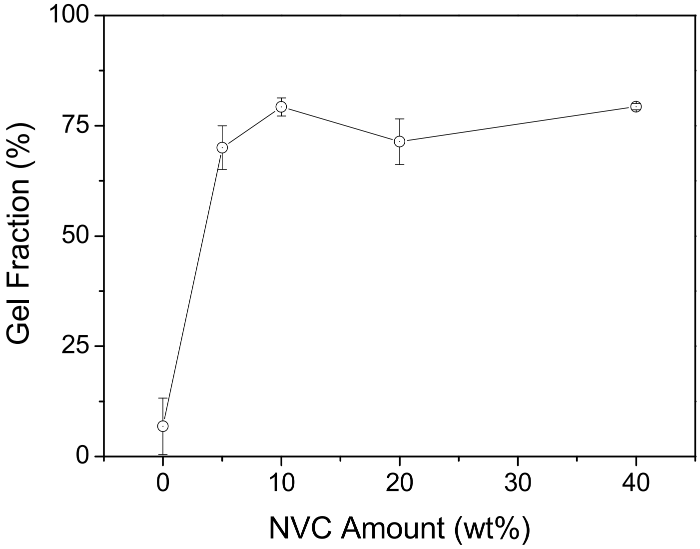


Figure 2-1. Gel fraction of the UV-cured PSA film as a function of NVC amount.

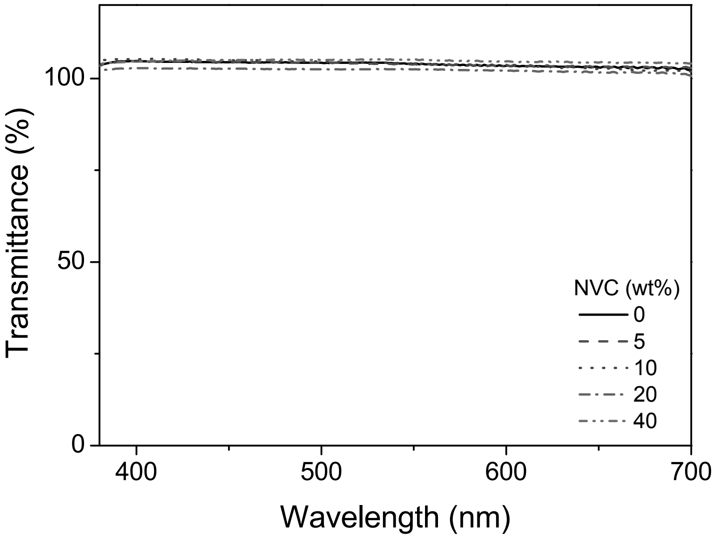
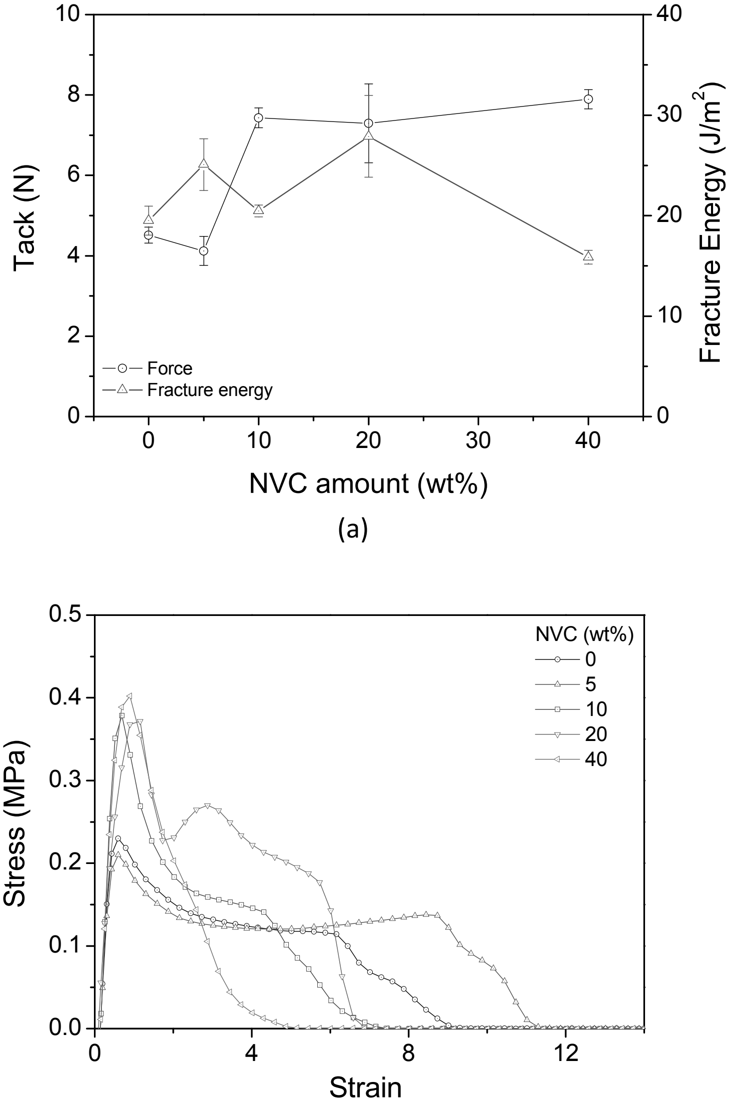


Figure 2-2. Visible light transmittance of the UV-cured PSA film on PET film (baseline : bare PET film).

3.2. Adhesion performance

3.2.1. Tack

Figure 2-3(a) shows the tack and fracture energy of the UV-cured PSA film. Figure 2-3(b) shows the debonding behavior of the samples from a stress-strain curve during the tack measurement. The tack increased with increasing NVC content because of its high polar property which came from the nitrogen atom in its structure. This polar property made the cohesion of the PSA increased. The tack of 0 and 5 wt% of NVC contained samples are similar. But, higher fracture energy was obtained for 5 wt% of NVC contained sample. This is due to higher cohesion of PSA film with NVC incorporation into the PSA composition. In Figure 2-3(b), it needed more force to debond fibril from the probe surface during the 5 wt% of NVC contained sample tack measurement than the sample without NVC. Then, the fracture energy decreased when NVC amount in the PSA was 10 wt%. It is because elevated tack and decreased fibrillation due to increased cohesion compared to samples with 0, 5 wt% of NVC. However, the fracture energy increased again after increasing NVC amount. It is considered that more increased intermolecular force owing to increased NVC led to strong fibrillation. A stress-strain curve shows the largest force is required to debond fibrillated PSA from probe surface for 20 wt% of NVC contained sample. The second peak in stress-strain curve proved it. The fracture energy decreased again at 40 wt% of NVC contained sample because of highly increased cohesion among molecules. In this case, fibrillation did not occur any more.



(a)

(b)

Figure 2-3. Probe tack value with its fracture energy (a) and stress-strain curve (b) of the UV-cured PSA film as a function of NVC amount.

3.2.2. Peel strength

The peel strength had similar tendency in Figure 2-4 on glass and PC, regardless of substrate. The peel strength increased as increasing NVC. It assigned the higher molecular interaction and the increased cohesion influenced high peel adhesion. But the peel strength also decreased for 40 wt% of NVC contained sample because too high cohesion brought out low peel adhesion. The difference of peel adhesion on different substrate arisen from surface free energy difference between two substrates. Figure 2-5 describes the surface free energy difference among 3 types of specimens : PC, glass, PSA (NVC 20 wt%). The peel strength shows high value when substrate and PSA film have similar surface free energy (Peykova *et al.*, 2012). The UV-cured PSA film expressed similar surface free energy compared to PC and quite different (lower) surface free energy compared to glass. Accordingly, peel strength was higher on PC than on glass substrate.

Meanwhile, the thermodynamic work of adhesion (W_a) can be obtained from following equation.

$$W_a = 2\sqrt{\gamma_{SLW(adh)}\gamma_{SLW(sub)}} + 2\sqrt{\gamma_{S(adh)}^{-}\gamma_{S(sub)}^{+}}\sqrt{\gamma_{S(adh)}^{+}\gamma_{S(sub)}^{-}}$$

The subscripts *adh* and *sub* refer to the adhesive and substrate, respectively. γ_{SLW} means dispersive component. γ_s^- and γ_s^+ means acid and base component, respectively (Kowalski *et al.*, 2013). Calculated W_a of the NVC 20 wt% contained PSA to glass substrate was 138.9 mN/m and to PC substrate was 126.7 mN/m. W_a value means amount of work that is expended under reversible or equilibrium conditions to inhibit the interface formation. W_a of the adhesive joints increased with the surface energy of the substrates (Kowalski*, et al.*, 2013). The W_a of PSA to glass substrate was higher than that to PC substrate. It indicates more effort was needed to form chemical bonding between glass substrate and PSA. Therefore the peel strength on glass substrate was lower than that on PC substrate.

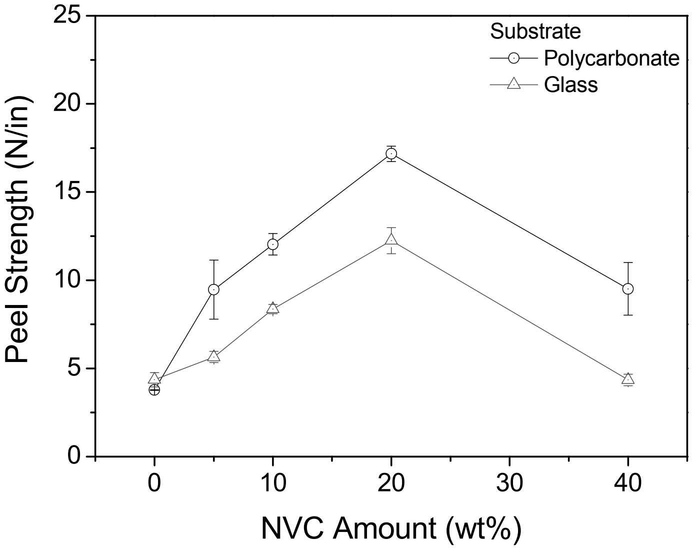


Figure 2-4. Peel strength of the UV-cured PSA film with different amount of NVC amount.

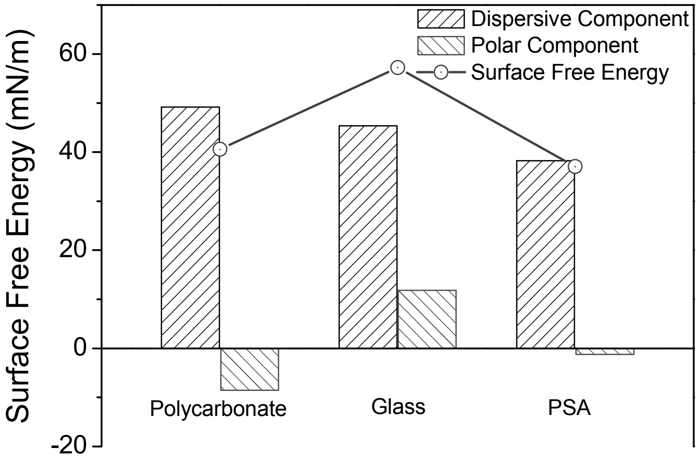


Figure 2-5. Surface free energy of various substrates used and the UV-cured PSA film.

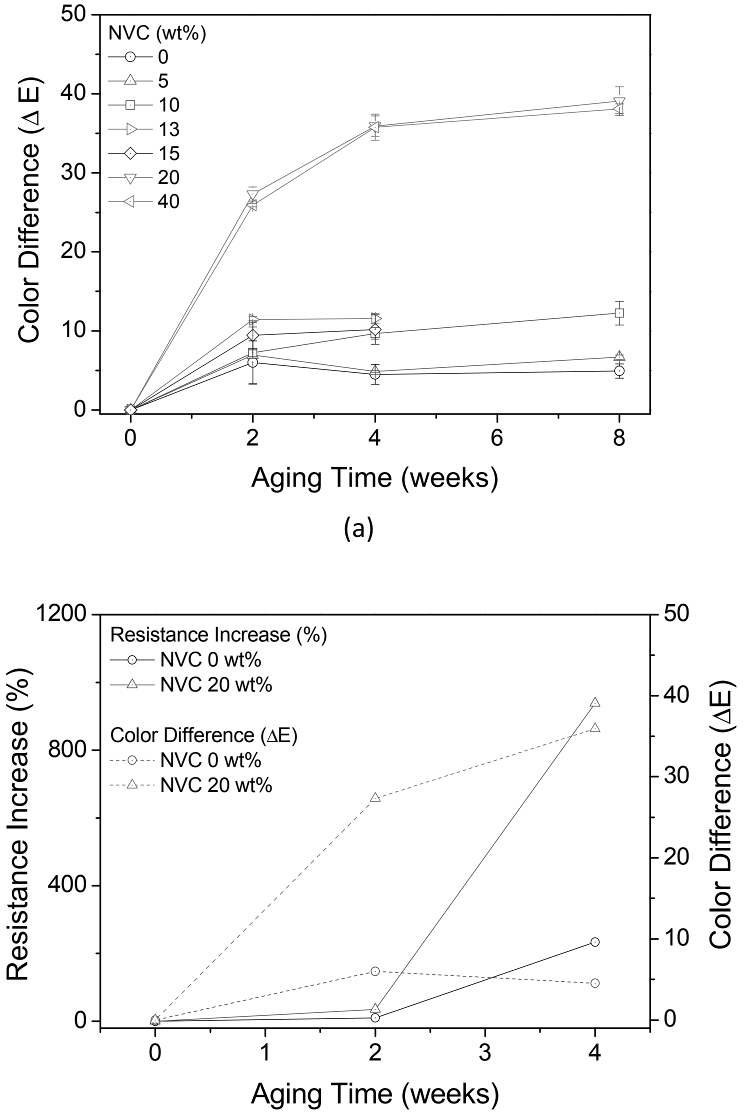
3.3. Aging behaviors

3.3.1. Corrosion property

In Figure 2-6(a), the copper foil color change by attaching PSA was monitored for 8 weeks under aging condition. More than 20 wt% of NVC amount affected the severe copper foil color change. 5 wt% of NVC did not change the copper foil color, so the effect of small amount of NVC to copper foil was not large. 10 wt% of NVC made the slight *ΔE* increase of copper foil to around 10. This result implies too much amount of polar material might bring out latent corrosion by reaction between PSA and copper in long range perspective although acidic component was excluded. More than 20 and 40 wt% of NVC amount made the copper foil color almost black, which is more than 25 of *ΔE* value. This black color is the color of copper oxide (FitzGerald *et al.*, 2006). The high electronegativity of nitrogen atom in NVC structure and carboxyl group by caprolactam ring opening helped easy oxidation of copper under hygrothermal aging condition. The caprolactam ring opening reaction will be discussed again at section 3.3.4. The Copper ion was formed by losing electron and reacted with oxygen. Finally copper oxide was formed and color change was observed during aging.

The actual resistance increase of ITO by PSA adhesion and *ΔE* were plotted together in Figure 2-6(b). The resistance increase measurement was carried out for 4 weeks because *ΔE* did not change dramatically between 4 and 8 weeks as shown in Figure 2-6(a). Measured samples were 0 and 20 wt% of NVC contained samples representatively because the difference of *ΔE* was largest between those samples, whereas the NVC 5 wt% and 10 wt% contained samples showed similar *ΔE* to NVC 0 wt% contained sample. Then

NVC 20 wt% and 40 wt% contained samples indicated similar *ΔE* value with each other. The resistance increased significantly for 4 weeks as obtained in *ΔE* result. The resistance increase of the NVC 20 wt% contained sample was higher than that of NVC 0 wt% sample, which is consistent to the *ΔE* change tendency. The corrosion property of PSA can be judged early through the copper foil color change test compared to the actual resistance increase measurement. The reason is that the *ΔE* of copper foil showed sharp increase than resistance increase within 2 weeks. The copper foil color change test can give early response about the PSA corrosion property rather than resistance increase measurement.



(a)

(b)

Figure 2-6. Copper foil color change due to the UV-cured PSA film attachment (a) and comparison between resistance increase measurement and color change (*ΔE*) value (b) under aging condition.

3.3.2. Viscoelastic property

The glass transition temperature was shifted to higher temperature range as displayed in the storage modulus of Figure 2-7. It correlated with restricted molecular mobility. The storage modulus in rubbery plateau area also increased with aging time passed, which means more crosslinked structure was formed (Mitra *et al.*, 2014). The glass transition temperature shift and storage modulus increase have relevance to increased molecular interaction and crosslinked structure. Hydrogen bonding can be the reason of increased molecular interaction in this experiment. It is supposed that structure change of molecules, which construct PSA, occurred under the high temperature and humidity condition. Thus, surface free energy analysis and XPS monitoring was performed to investigate the origin of viscoelastic property change.

3.3.3. Surface free energy

The surface free energy increased as aging time passed. The increased surface free energy is related to increase of polar component. Figure 2-8 shows the surface free energy which is sum of the polar component and dispersive component. In this graph the increase trend of the polar component can be seen clearly. It means polar functional group increased on the PSA film surface thus the PSA turned into polar structure. This fact can be related to the glass transition temperature shift of PSA mentioned at 3.3.2, inducing attraction among molecules as observed in viscoelastic property.

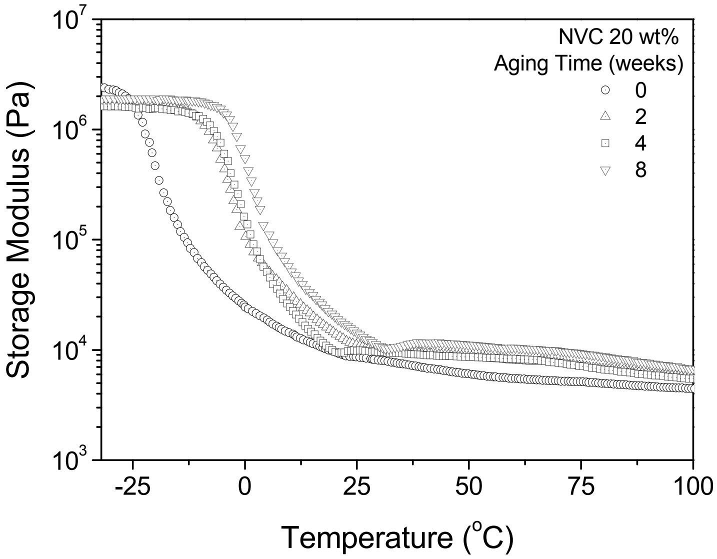


Figure 2-7. Variation of shear storage modulus of the aged samples contained 20 wt% of NVC with aging time.

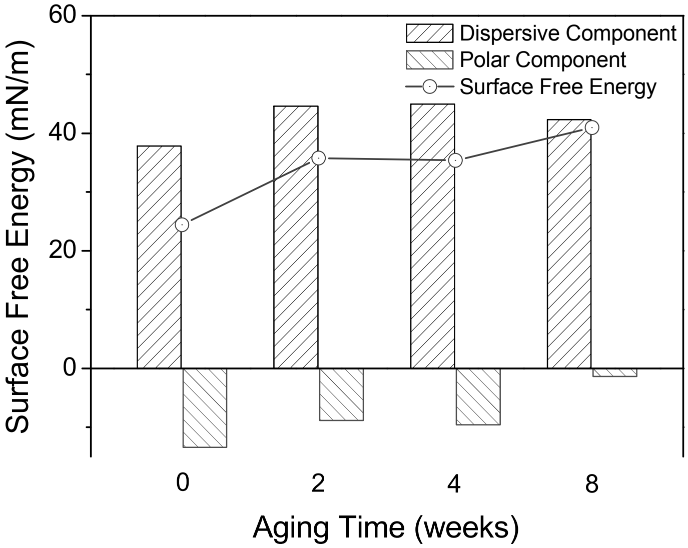


Figure 2-8. Surface free energy change of the NVC 20 wt% contained PSA film during aging.

3.3.4. XPS spectra

Figure 2-9 are XPS C1s spectra of difference of XPS spectra before and after hygrothermal aging. The viscoelastic property largely altered after 2 weeks aging, the XPS spectra were characterized before and after 2 weeks aging on that account. After aging, the (C=O)N related peak (Cheng *et al.*, 2004; Walters *et al.*, 2006) disappeared and then the O-C=O carboxyl group related broad peak (Briggs *et al.*, 1992; Wang *et al.*, 2002) was presented. It reflects the (C=O)N group in caprolactam ring changed into the –NH group by reaction under humid condition. The carboxyl group was also formed as a result of ring opening reaction with (C=O)N dissipation. This phenomena contributed to the surface free energy and viscoelastic property change caused by the polar group increase. Figure 2-10 shows expected caprolactam ring opening reaction by moisture corresponded to XPS result.

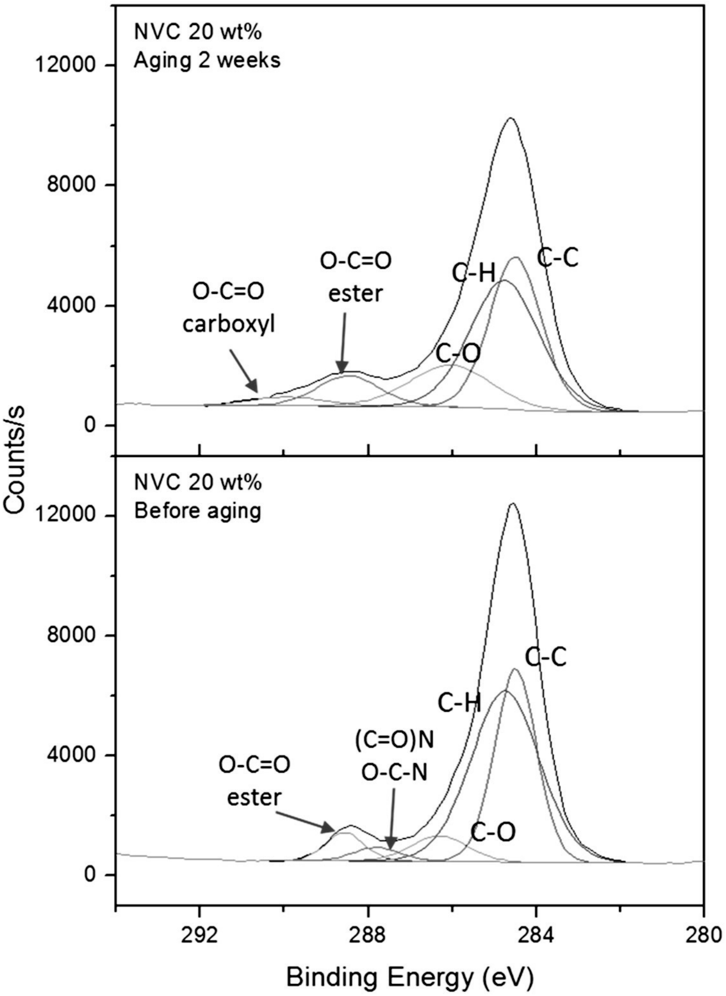


Figure 2-9. C1s spectra of the NVC 20 wt% contained sample before (down) and after aging (up).

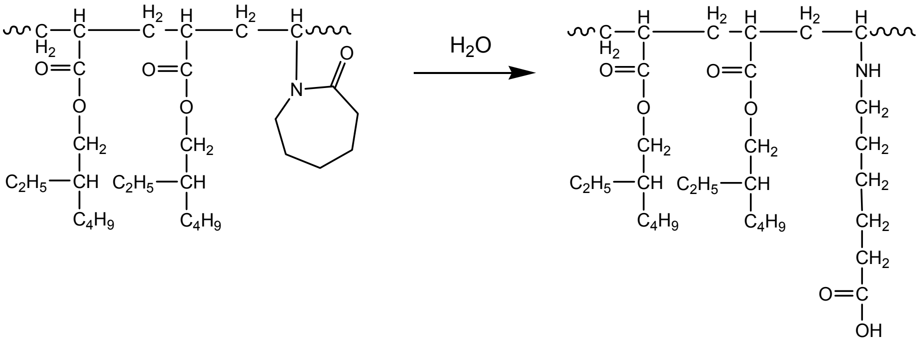
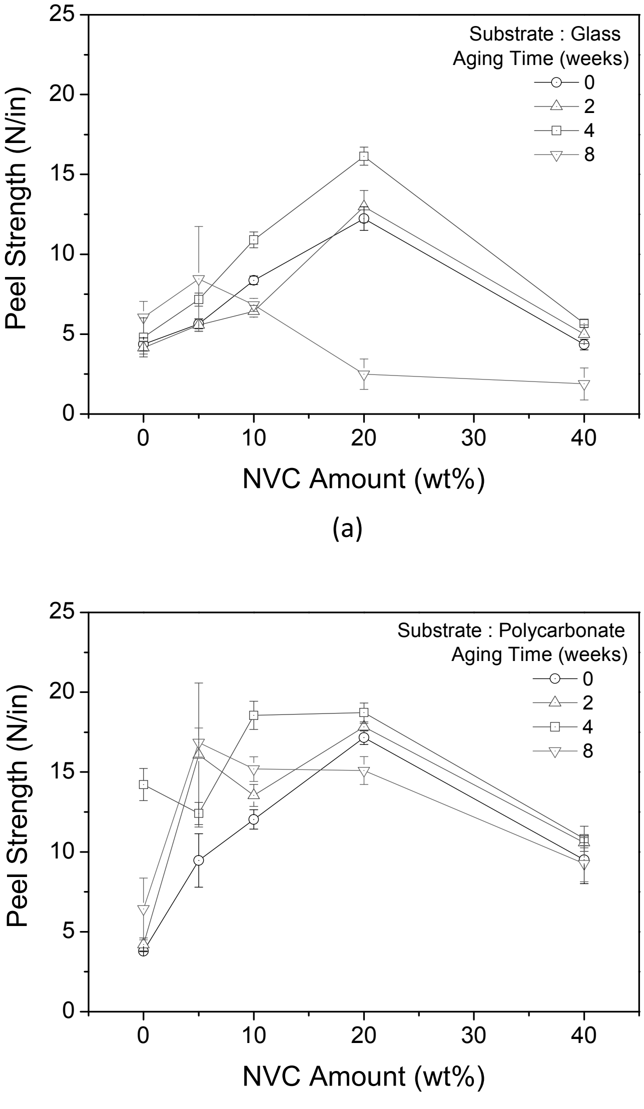


Figure 2-10. Schematic diagram of the expected caprolactam ring open reaction under humid condition.

3.3.5. Peel strength

The peel strength of samples under hygrothermal aging condition is plotted in Figure 2-11. The peel strength change showed similar trend in both substrate although the value was little different. The peel strength increased for the 4 weeks aged sample but decreased for the 8 weeks aged sample, especially for the 20 and 40 wt% of NVC contained samples. This occurrence is especially remarkable on glass substrate. The reason of increased peel strength during aging is considered since raised molecular interaction by formation of the –NH and –COOH functional group with the caprolactam ring opening as suggested by the XPS result. These groups are highly polar and can induce the hydrogen bonding among other molecules hence PSA film cohesion could be increased. Too much increased cohesion caused the decreased peel strength. Especially on the glass substrate, the definite peel strength decrease can be explained in the point of large polarity of glass as shown in Figure 2-5. The -NH and -COOH polar group consisted of PSA polymer side chain might be easily oriented toward glass substrate compared to PC substrate during period between sample preparation and peel strength measurement. The highly increased intermolecular force hindered bonding formation between the PSA and substrate at the interface. This consequence caused the lower adhesion strength.



(a)

(b)

Figure 2-11. Peel strength change on the glass substrate (a) and PC substrate (b) for 8 weeks under aging condition.

4. Conclusion

NVC was employed to prepare non-corrosive PSA for TSP, which is positioned to bond transparent electrode and each component layer. The prepared PSA film showed excellent transparency and did not seriously affect conductive substrate (copper foil) until 15 wt% of NVC was included to PSA matrix. The corrosion test method of UV-cured PSA using copper foil was effective because it showed early response with direct use of transparent electrode. To examine the UV-cured PSA stability under high temperature and humidity condition, the viscoelastic property was observed. The storage modulus at rubbery plateau increased and T_g moved to high temperature during aging due to increased molecular interaction caused by hydrogen bonding from polar functional group. It is considered that opened caprolactam ring formed carboxyl group under humid condition and this group induced hydrogen bonding. Accordingly, the UV-cured PSA film surface turned into more polar structure as well. This result was proved by the surface free energy and XPS measurement. The peel strength of samples increased until 4 weeks aging owing to the increased polar property of the PSA, but decreased after 8 weeks aging because of too high interaction and cohesion among molecules, especially more than 20 wt% of NVC contained sample had that tendency.

Chapter 3

Cloud Point-resistant Optically Clear Adhesive by Incorporating Monofunctional Methoxylated Polyethyleneglycol Acrylate

1. Introduction

In previous chapter, acid-free optically clear adhesive (OCA) was prepared with excluding acrylic acid and incorporating N-vinyl caprolactam to protect transparent electrode from corrosion. But there is the other important property to OCA. It is cloud point-resistance. Cloud point-resistance means haze did not show up in PSA film even under sudden environmental change. OCA ought to be kept clear regardless of user's environment because in TSP, light from backlight unit pass through bonding layer which OCA used and finally arrive at user's eye. To impart cloud point-resistance to OCA, hydrophilic moiety should be adopted to molecular structure of adhesive. Figure 1-5 explains this phenomenon. Useful hydrophilic component is poly(ethylene oxide) segment, hydroxyl functionality, or a combination thereof, for example, polyethyleneglycol acrylate, 4-hydroxybutyl acrylate, and 2-hydroxyethyl acrylate (Everaerts*, et al.*, 2013).

U.S. Patent (Everaerts*, et al.*, 2013) about cloud-point resistant property of OCA has been applied but there is not many published studies about this material, especially property change in accelerated aging test. Hydrophilic component is essential material for OCA preparation so it is important to observe how this material contribute to PSA property or behavior including those during aging. There are several kinds of accelerated aging test. Thermal shock test, high temperature and humidity (hygrothermal) resistance test, photodegradation test by UV irradiation, and so on (Katakami, 2010). Hygrothermal aging test is representatively used as an evaluation tool of adhesion property change and assessment of OCA stability in harsh environment. It can be used as an estimation tool for OCA suitability for TSP.

Accordingly, in this study, polyethylene glycol acrylate was incorporated to the acrylic copolymer base resin which is prepared by 2-ethylhexyl acrylate, isobornyl acrylate, and N-vinyl caprolactam. The cloud-point resistance was evaluated preferentially, and other properties such as basic adhesion performance (tack and peel strength) was measured according to polyethylene glycol acrylate blending. For checking PSA durability, the cured PSA film was put in high temperature and humid environment, then the change of the peel strength and viscoelastic property was measured. It is also important for OCA not to give any effect on transparent electrode, a key component of TSP. Consequently, the corrosion property of the prepared PSA was monitored under high temperature and humid condition.

2. Experimental

2.1. Materials

2-Ethylhexyl acrylate (2-EHA, Samchun Chemicals, Republic of Korea), isobornyl acrylate (IBOA, Sigma Aldrich, USA) N-vinyl caprolactam (NVC, Sigma Aldrich, USA) were used to prepare monomer premix as base resin. 1,6-Hexanediol diacrylate (HDDA, Miwon Specialty Chemical, Republic of Korea) was blended to monomer premix as a crosslinker. Photoinitiator was α,α-dimethoxy-α-phenylacetophenone (Irgacure 651, BASF, Germany). Methoxylated polyethyleneglycol acrylate (PEGA) was supplied from Sartomer (Product Code : CD553, France). All materials were used without further purification.

2.2. Monomer premix preparation

2-EHA (60 wt%), IBOA (20 wt%), NVC (20 wt%) were placed into a 300 ml round-bottom flask and UV was irradiated to the flask with intensity of 40 mW/cm^2 for 10 minutes. The UV main wavelength was 365 nm and the equipment was SP-9 (Ushio, Japan). The monomer mixture was stirred during the UV irradiation and kept room temperature. After UV irradiation finishing, the viscosity of premix was around 870 cPs, which is measured by Brookfield viscometer using spindle no. 4 under 750 RPM at room temperature.

2.3. Coating and UV-curing

Table 4-1 shows the formulation of the mixture for OCA preparation with hydrophilic component. 2, 5, 10, and 20 phr of PEGA was blended to prepared premix using by paste mixer (Daewha Tech, Republic of Korea) with additional 0.15 phr of photoinitiator. The rotation and revolution speed were 1000 rpm, respectively. All components were mixed uniformly and coated on the PET film with 175 μm of thickness for the peel strength measurement and 500 μm of thickness for the viscoelastic property measurement. Coated each sample was UV-cured with 1000 mJ/cm^2 dose. All samples were well cured and formed transparent pressure sensitive adhesive (PSA) film.

2.4. Gel fraction

The gel fraction was calculated from equation as following.

$$\textit{Gel fraction (\%)} = W_1/W_0 \times 100$$

Where, W_1 is the solvent extracted weight of the PSA film and W_0 is the initial weight of the PSA film. Solvent was toluene. The cured PSA film was soaked into toluene at 50 ^{o}C and the solvent extracted components were eliminated after 24 hours. Then the remained PSA film was dried for 24 hours at 50 ^{o}C. The weight of fully dried film was measured and the gel fraction was obtained.

Table 3-1. Formulation for cloud-point resistant OCA with oligomeric hydrophilic component

	#1	#2	#3	#4	#5
	Base resin (2-EHA : 60 wt%, IBOA : 20 wt%, NVC : 20 wt%)				
HDDA (phr)	0.1	0.1	0.1	0.1	0.1
Photoinitiator (phr)	0.15	0.15	0.15	0.15	0.15
PEGA (phr)	0	2	5	10	20

2.5. Aging condition

The aging condition for the PSA durability test was 50 ^{o}C and 80 %RH. The cured PSA films were positioned in temperature and humidity conditioned oven for 2, 4, and 8 weeks. After each aging period, the PSA films were taken from the oven and tested about the cloud-point resistance, peel strength, viscoelastic property, and corrosion property to transparent electrode using copper foil.

2.6. Transmittance

Transparency is important property of OCA. In this experiment, the transmittance of cured PSA film was monitored by using UV/vis spectrophotometer (Cary 100, Agilent Technologies, USA). The measurement wavelength range was 200 − 900 nm. The reference was bare PET film which is not coated with any material, and the transmittance of the PET film coated with PSA was measured. The cloud point-resistance of the PSA also checked by same method, the transmittance at 550 nm of UV-cured PSA film was directly measured after taking sample from 50 ^{o}C and 80 %RH conditioned oven. The test equipment was Visible Spectrophotometer (SECOMAM® PRIM, France)

2.7. Tack and peel strength

The tack of the cured PSA film was measured using Texture Analyzer (TA.XT.Plus, Stable Micro Systems, UK). The used probe was 5 mm diameter cylinder type stainless steel. The contact force was 100 g_f and the contact time was 1 sec. The test speed was 1 mm/sec. The maximum force was regarded as the tack value and the integrating area under the graph divided by the probe area was counted by the fracture energy.

The 180 ° peel strength measurement was carried out using the same instrument with tack measuring. The substrates were glass and polycarbonate (PC) because these two substrates are generally used as a cover window substrate in TSP. After attaching samples on those substrates, they were pressed twice using by 2 kg rubber roller. The test speed was 5 mm/sec and the average value during the measurement was considered as the peel strength value.

2.8. Corrosion test through copper foil color change

The corrosion test of the PSA to transparent electrode was carried out with attaching PSA on copper foil as an indirect method by measuring the color change of copper foil during aging. The samples adhered to the copper foil were exposed to aging conditioned oven as mentioned in section 2.5. The color difference of the copper foil by the PSA was detected using spectrophotometer (Techkon GmbH, Germany) after 2, 4, and 8 weeks. The lightness (*L*), redness (*a*), yellowness (*b*) values were measured before and after aging. Overall color difference, ΔE was calculated by following equation.

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

Where, L_1, a_1, and b_1 are data before aging, L_2, a_2, and b_2 are data after each aging period (Pfeffer*, et al.*, 2012).

2.9. Chemiluminescence (CL) analysis

The CL analysis equipment (CLA-FS1A, Tohoku Electronic Industrial Co., Ltd., Japan) was used to compare the degree of aging of each sample. The CL intensity measurement was carried out under two methods. One is non-isothermal method at a rate of 7 ^{o}C/min temperature elevation from room temperature to 150 ^{o}C. The other is isothermal method at 150 ^{o}C for 90 min after non-isothermal method. The light from 300 to 650 nm wavelength was measured. Circular shape UV-cured PSA films, which had 30 mm diameter and 500 μm thickness, were prepared. Their CL signals were monitored with different hygrothermal aging conditions.

2.10. Fourier-transform infrared (FT-IR) spectroscopy

The IR spectra were obtained for detecting the change of the PSA matrix during the hygrothermal aging. The instrument was FT-IR 6100 (JASCO, Japan) equipped with attenuated total reflectance (ATR) accessory. A 500 μm thickness film after each hygrothermal aging test was used in this measurement. The transmission range of the ATR crystal was 4000 – 650 cm^{-1} and IR spectra taken with a resolution of 4 cm^{-1} (Park*, et al.*, 2013). The positions of the peaks related to molecular structure change were ester group at 1159 cm^{-1}, ether group at 1110 cm^{-1}, carbonyl (ketone, aldehyde, and carboxyl) group at 1728 cm^{-1}, and methyl group at 2956 and 2928 cm^{-1} (Socrates, 2004). Each peak increased or decreased with molecular structure alteration as the aging progressed.

2.11. Thermogravimetric analysis (TGA)

TGA (TGA 4000, PerkinElmer, USA) was employed to demonstrate the increased intermolecular force of the samples after aging. The temperature was elevated at a rate of 10 ^{o}C/min during the test from room temperature to 600 ^{o}C under nitrogen atmosphere. The 10 phr of PEGA contained samples, which had been not aged and 2, 4, 8 weeks aged ones, were used as a representative example for the analysis.

2.12. Viscoelastic property

The viscoelastic property of aged PSA films were observed using advanced rheometric expansion system (ARES, Rheometric Scientific, UK). The test mode was temperature sweep mode from -50 to 150 ^{o}C at a rate of 3 ^{o}C/min. 0 (not aged), 4 and 8 weeks aged samples, which contained 10 phr of PEGA, were measured one by one after each aging period to investigate the difference before and after aging.

3. Results and discussion

3.1. UV-cured PSA film as OCA and its cloud point-resistance

The cured PSA films were highly transparent, near 100 % of transmittance as shown in Figure 3-1. Additionally blended PEGA had good miscibility with monomer premix composed of 2-EHA, IBOA, and NVC. The gel fraction was more than 60 % in all samples regardless of PEGA amount as plotted in Figure 3-2. In this study, the objective of incorporating PEGA is improving cloud-point resistance of prepared PSA for OCA application. Therefore, the upgraded visible light transmittance was observed at 550 nm. Figure 3-2 presented also visible light transmittance of samples with hydrophilic component, PEGA, directly after taking from high temperature and humid condition. The reference was transparent multi-layer composed of release film, UV-cured PSA film, and substrate PET film, which shows 100 % of transmittance, and clear status. The transmittance decreased without PEGA after directly taking it from hygrothermal condition but improved with adding PEGA to the PSA. The transmittance improved as increasing added the PEGA amount. It was effective to solve cloud state appearance of the existing PSA.

The reason of the increased transmittance by blending hydrophilic component is described already in Figure 1-5. This principle can be applied to the improved transmittance result. When there is no hydrophilic component, localized water phase in continuous adhesive phase made phase separation between moisture and polymer in the PSA. This phase separation led to refractive index mismatch hence the surface of the PSA film is seen white or cloudy. However, the moisture can be dispersed uniformly or fully solubilized in the PSA matrix by incorporating hydrophilic component. As a result, moisture do not cause phase separation and clear surface can be observed (Everaerts*, et al.*, 2013).

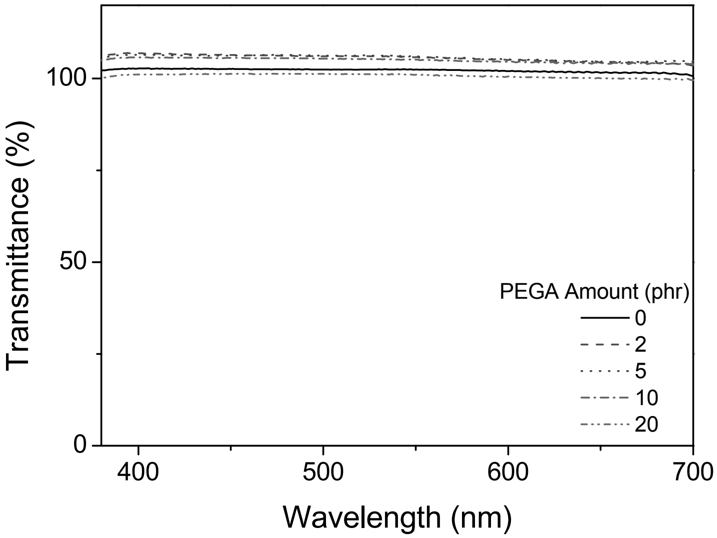


Figure 3-1. Visible light transmittance of UV-cured PSA on PET film (baseline : bare PET film).

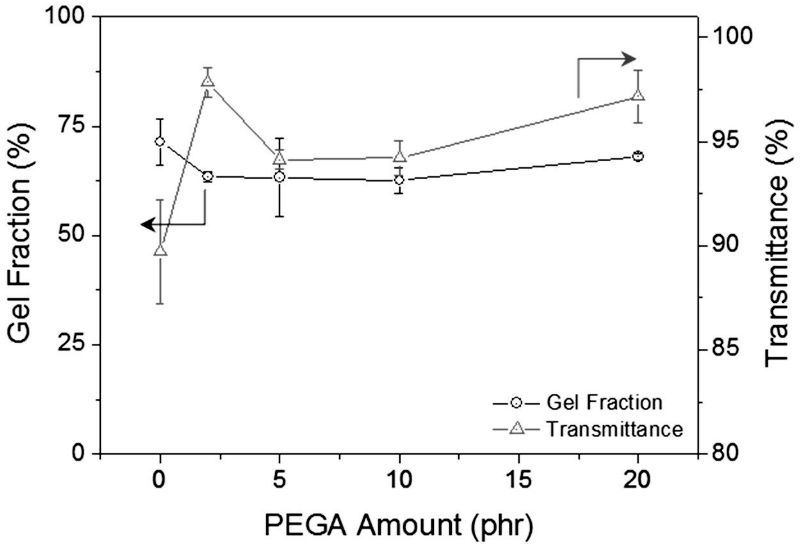


Figure 3-2. Gel fraction of UV-cured PSA film as function of PEGA amount and improved visible light transmittance due to hydrophilic component PEGA directly after taking sample from 50 °C, 80 %RH chamber.

3.2. Adhesion performance

3.2.1. Tack

Figure 3-3 shows the tack and fracture energy. The tack increased with incorporating PEGA and kept constant value then decreased when 20 phr of the PEGA was blended. PEGA has long hydrophilic segment consisted of -O-C_2H_4- repeating unit. This hydrophilic segment is polar enough to bring out active molecular interaction. The increased molecular interaction in the PSA matrix required more force to detach probe from the cured PSA film surface. Too much amount of polar group lowered tack value because of high cohesion among the PSA molecules. The fracture energy initially increased due to enhanced molecular interaction then decreased by highly increased cohesion with blending PEGA.

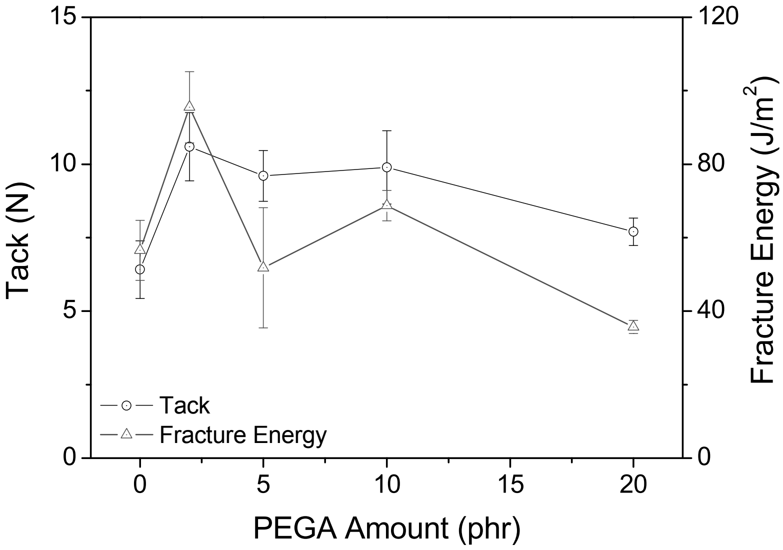


Figure 3-3. Probe tack and fracture energy of UV-cured PSA film as a function of PEGA amount.

3.2.2. Peel strength

The OCA application window was proposed for suitable OCA in terms of peel strength because adhesion strength is also important factor as shown in Figure 3-4. The peel strength increased temporarily as incorporating 2 phr of PEGA and decreased continuously with increasing PEGA amount. This phenomenon is because the increased molecular interaction owing to polar ingredient, PEGA addition. Increased amount of PEGA, which is more than 5 phr, assigned excessively increased cohesion to the cured PSA film. The molecular mobility was restricted by the reinforced molecular interaction on account of enhanced polar property and resulted in peel strength decrease (Joo *et al.*, 2006). In other words, too much increased cohesion of the PSA could cause adhesion decrease of PSA (Czech *et al.*, 2006).

The polar property was given to the PSA by blending PEGA so there is not much difference between the peel strengths on two substrates. The high peel strength of the PSA can be revealed on substrate which has similar surface free energy to PSA (Peykova*, et al.*, 2012). PC is non-polar substrate and glass is polar substrate. The ascribed polar property to the PSA led to small difference between peel strengths on two substrates because the surface free energy of the PSA became polar, which is close to glass.

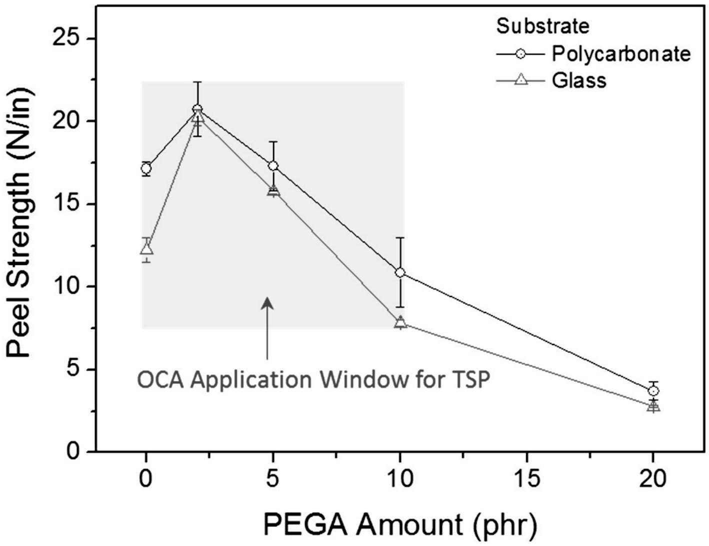


Figure 3-4. OCA application window of UV-cured PSA film with different amount of PEGA amount.

3.3. Aging behaviors

3.3.1. Corrosion property

Figure 3-5 shows the color difference of the copper foil, which PSA adhered on it, as a corrosion property test by PSA attachment. The corrosion property was improved due to PEGA incorporation. The color of the copper foil underwent large change without PEGA under hygrothermal aging condition. The reason of the copper foil color change is the formation of copper oxide owing to oxidation of copper through losing electron on copper atom. The copper foil color turned to black. The base resin was consisted of 2-EHA, IBOA, and NVC. NVC hold nitrogen atom in its structure and it has high electronegativity therefore nitrogen atom might accelerate for copper atom to lose electron under moisture existence. The lost electron from copper atom is transferred to oxygen and formed copper oxide.

The copper foil color did not change and was kept stable for 8 weeks since 2 and 5 phr of PEGA was added. It is considered that PEGA prevented copper foil from corrosion by including moisture in its structure as incorporated to the PSA matrix because PEGA is hydrophilic component. Moisture could not move to interface between the PSA and the copper foil hence the corrosion of the copper foil did not occur. But too much amount of PEGA cannot protect copper foil from corrosion like in case of 10 and 20 phr of PEGA blending to the PSA matrix. As time goes by, the copper foil color changed significantly by 10 and 20 phr of PEGA contained PSA. The *ΔE* curve was plotted as straight shape in that case. Sufficient amount of hydrophilic component attracted enough moisture. Then it made for copper to be oxidized due to polarity of hydrophilic component and increase amount of moisture at interface between copper foil and PSA. Finally, the copper reacted with the attached PSA film on it. Consequently, the dark copper foil color reflected the oxidized copper.

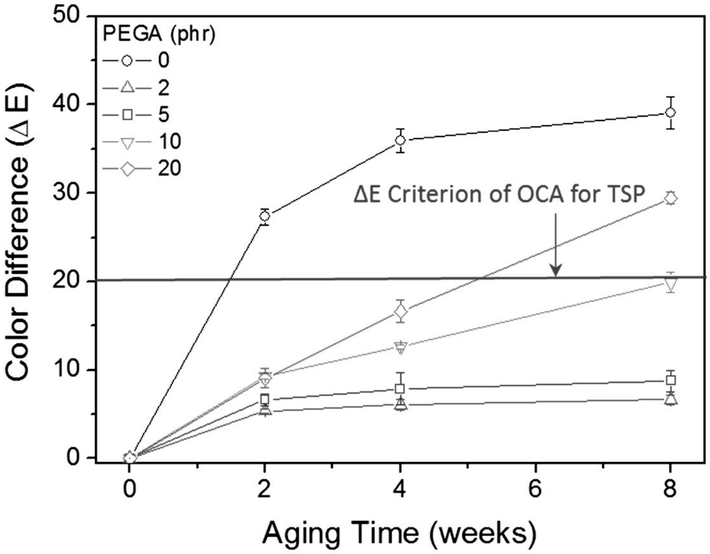


Figure 3-5. Copper foil color difference due to cured PSA film attachment for 8 weeks under aging condition.

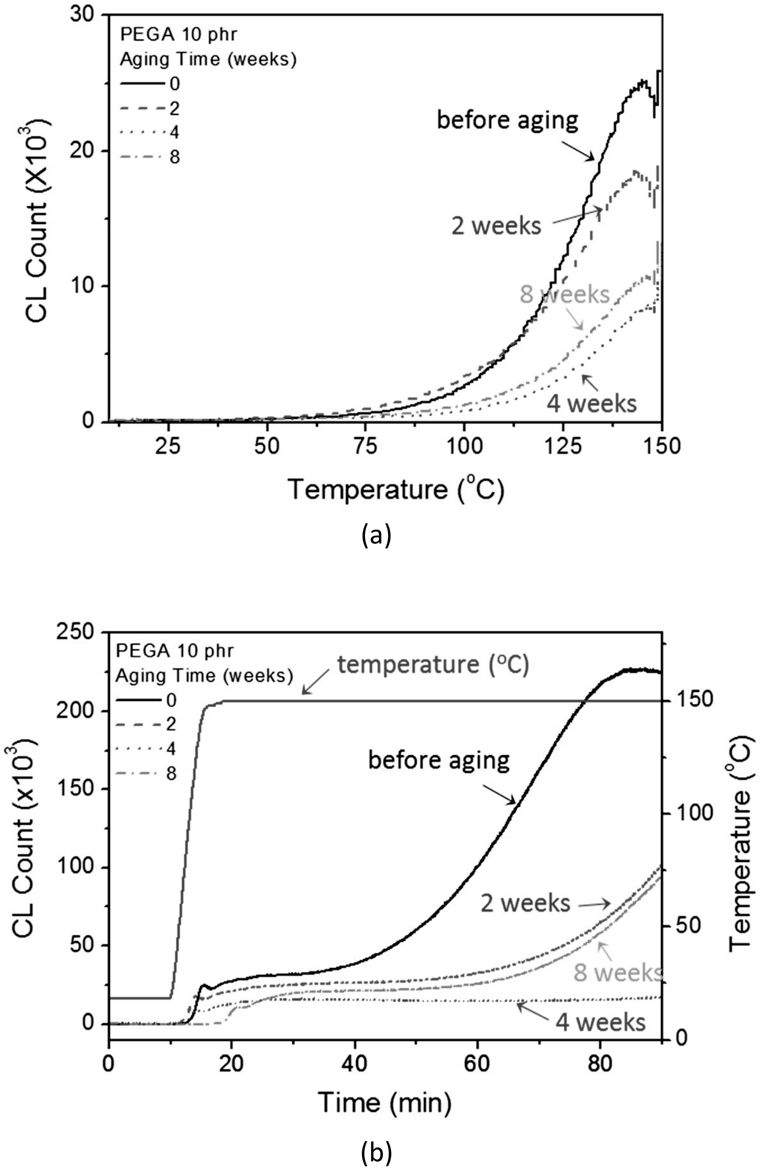
3.3.2. Polymer structure change observed by CL analysis and IR spectra

Figure 3-6 describe the CL analysis result. The non-isothermal CL result of the PEGA 10 phr contained PSA film was exemplified in Figure 3-6(a). Then Figure 3-6(b) was plotted about the CL result as measurement time passed, with isothermal condition for 70 minutes after temperature elevation up to 150 ^{o}C. CL signal is observed when carbonyl group was formed and oxygen was lost in polymer backbone under oxygen rich atmosphere flow. Scheme 3-1 shows when CL signal is observed with oxidation under oxygen atmosphere during the test (Rychlý *et al.*, 2011; Rychlý *et al.*, 2011). It is also known that CL intensity is related to concentration of peroxides (Gijsman*, et al.*, 2001). Scheme 3-2 is outlined oxidative attack point in polymer backbone and how polymer structure can be changed during non-isothermal CL analysis in this experiment (Rychlý*, et al.*, 2011; Rychlý *et al.*, 2013). These schemes can be applied to the aging process of the prepared OCA in this study. In Figure 3-6(a), the CL value tended to increase as increasing temperature because it became gradually easy for polymer to be oxidized due to the raised temperature. It means carbonyl group was formed during non-isothermal test as a result of degradation.

The CL peak decreased as sample aging had progressed in both test, non-isothermal and isothermal test. Relatively high CL intensity of certain material at specific temperature means that material can be easily oxidized by oxidative attack. Accordingly, more aged samples showed lower CL peak and it suggests relatively substantial molecular structure, which is stable against oxidation, was formed during aging. This phenomenon related to carbonyl group formation in PSA matrix during aging and this functional group can induce hydrogen bonding between molecules. For that reason, polymer structure which consisted of PSA could be substantial. There is another possible reason for low CL peak of aged sample. Before aging, there were many ether groups in PEGA. This ether group can be attacked by oxygen easily compared to ester group. Ether group changed into ester group or hydroxyl group as aging progressed by oxidation. These groups are relatively hard to be attacked by oxygen. Therefore CL peak could not be high. The 8 weeks aged sample showed higher CL peak than that of 4 weeks aged sample. It is considered that the polymer structure turned to weak one, which can be easily attacked by oxygen after 8 weeks aging. The reason of the weak polymer structure is supposed the chain scission after 8 weeks aging (Chiantore *et al.*, 2000). Oxygen can approach to attack point easily in scissored polymer structure and it brought out higher CL peak.

Figure 3-7 shows the IR spectra of PEGA 10 phr contained sample at each aging period for the support, which are the expected reactions between molecules during the aging. The peak at 1160 cm^{-1} related to ester group increased while the peak at 1110 cm^{-1} related to ether group (Kaczmarek *et al.*, 2006) decreased as confirmed in Figure 3-7(a). Ether group of PEGA in the PSA matrix can be partially changed into ester group due to the oxidation during the aging. Meanwhile, the peak at 1725 cm^{-1} is related to general carbonyl group, especially ester, aldehyde, ketone, and carboxyl group (Socrates, 2004; Lau *et al.*, 2006; Mun *et al.*, 2008). In the main backbone of PSA, side chain can be scissored thus carboxyl group and aldehyde group can be formed. Therefore the peak at 1725 cm^{-1} increased because of ketone, aldehyde, carboxyl group formation as indicated in Figure 3-7(b). The chain scission also can occur by further reaction via carbonyl group formation in the main backbone. On that account, the peak at 2950 and 2925 cm^{-1} related to alkyl group (CH_3 or CH_2 in alkane) increased as manifested in Figure 3-7(c)

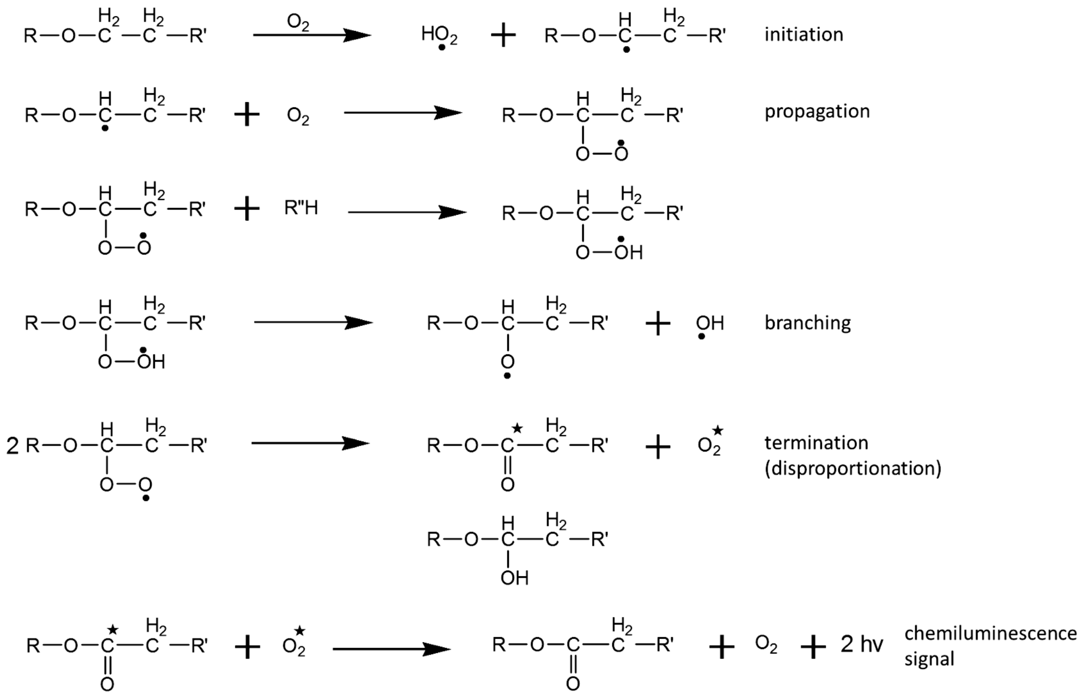
(Lin *et al.*, 2006). Scheme 3-3 is suggested based on previously mentioned reaction. These changes had relation to PSA property change which will be discussed next section. The IR peak variation was not large but these changes were significantly reflected in PSA property.



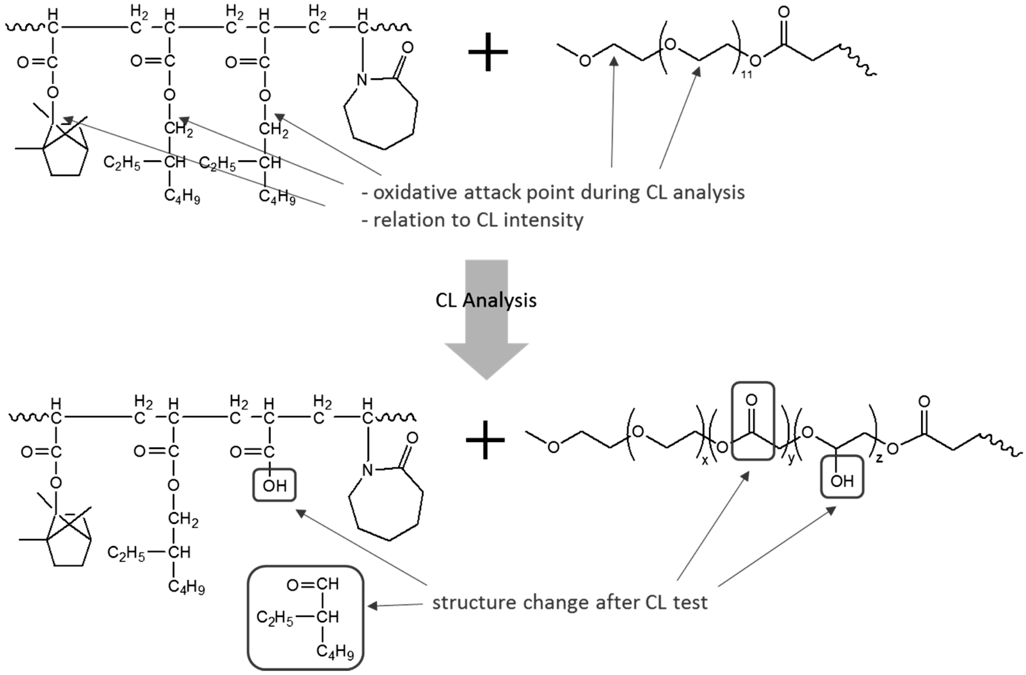
(a)

(b)

Figure 3-6. Chemiluminescence analysis result under temperature elevation from room temperature to 150 °C (a) and isothermal chemiluminescence test result at 150 °C (b) of PEGA 10 phr contained PSA film before and after aging under oxygen atmosphere.



Scheme 3-1. The mechanism of free radical oxidation and formation of carbonyl group related to the principal of chemiluminescence (CL) signal (Rychlý*, et al.*, 2011).

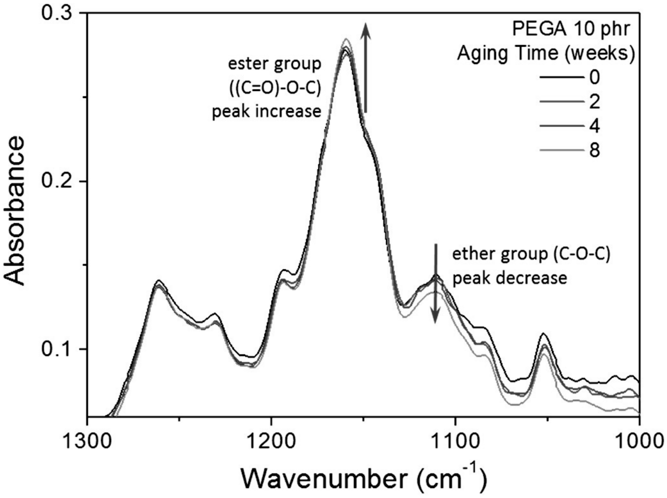


- oxidative attack point during CL analysis
- relation to CL intensity

CL Analysis

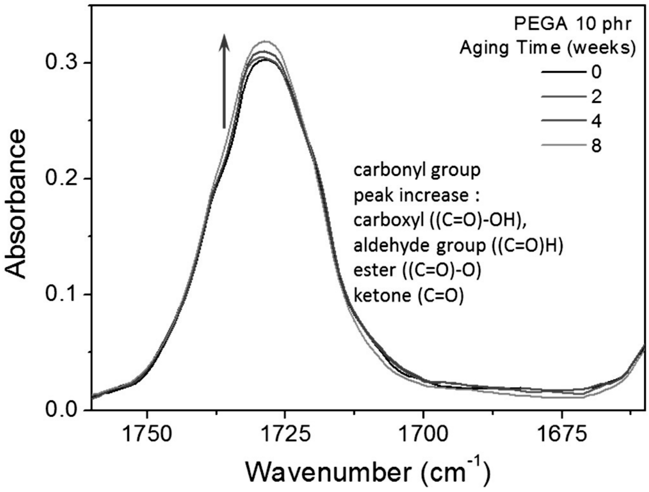
structure change after CL test

Scheme 3-2. Example of possible polymer oxidation reaction related to CL intensity in the PSA matrix during CL analysis.



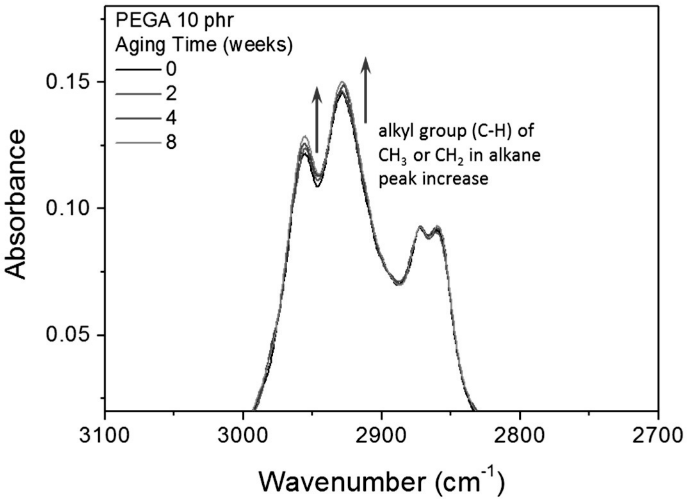
0.3
0.2
0.1
Absorbance
1300
1200
1100
1000
Wavenumber (cm^{-1})
PEGA 10 phr
Aging Time (weeks)
0
2
4
8
ester group
((C=O)-O-C)
peak increase
ether group (C-O-C)
peak decrease

(a)



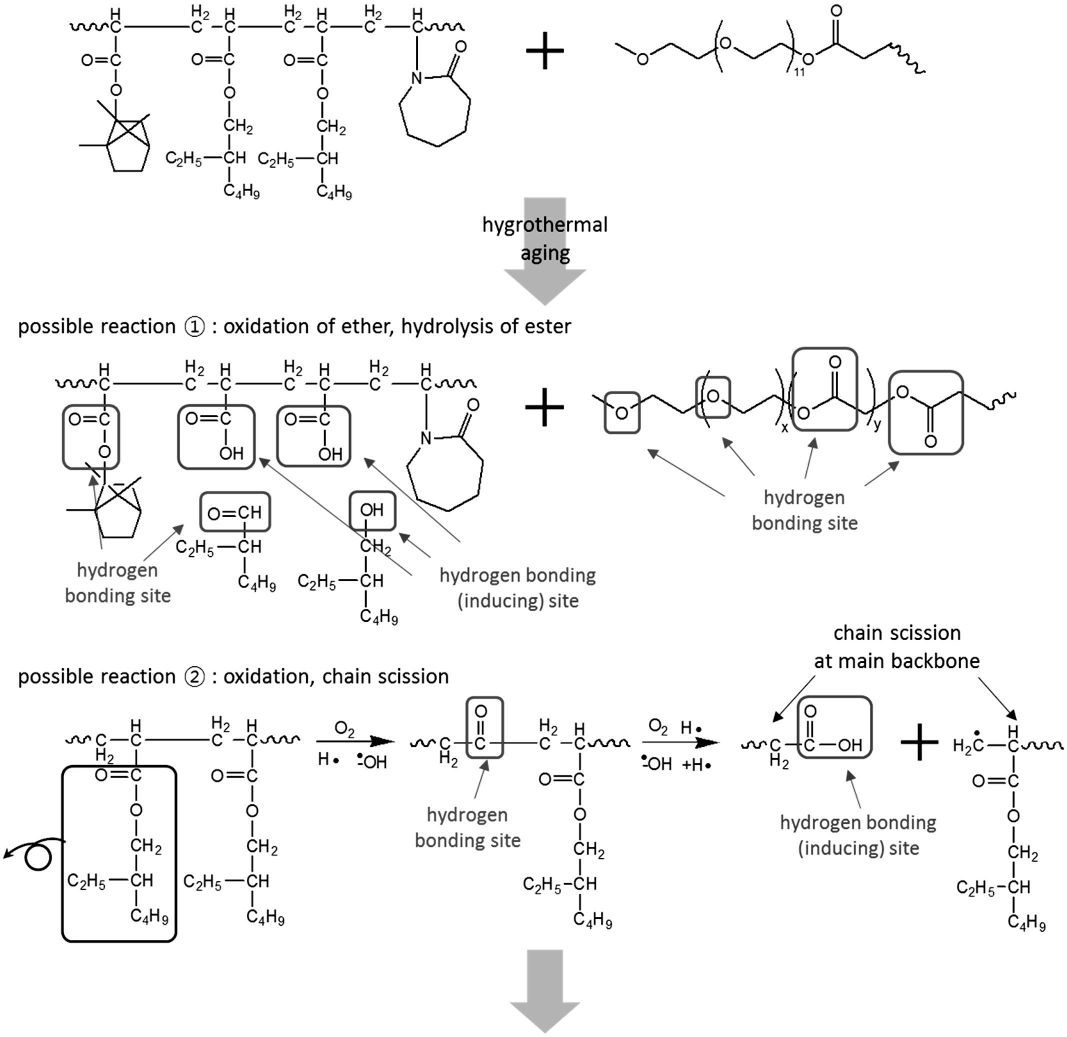
0.3
0.2
0.1
0.0
Absorbance
1750
1725
1700
1675
Wavenumber (cm^{-1})
PEGA 10 phr
Aging Time (weeks)
0
2
4
8
carbonyl group
peak increase :
carboxyl ((C=O)-OH),
aldehyde group ((C=O)H)
ester ((C=O)-O)
ketone (C=O)

(b)



(c)

Figure 3-7. Polymer structure change during aging observed by IR spectra : peak increase and decrease related to ester group and ether group (a), peak increase related to carbonyl group (b), and peak increase related to alkyl group (c).



- ester, carbonyl, carboxyl group formation after hygrothermal aging → hydrogen bonding increase
- change related to TGA result, viscoelastic property, peel strength of PSA during aging

Scheme 3-3. The suggested mechanism of the polymer structure change in PSA matrix during the hygrothermal aging (50 ^{o}C, 80 %RH) based on IR spectra.

3.3.3. Thermogravimetric analysis

Figure 3-8 shows TGA curve of PEGA 10 phr contained PSA films aged for 2, 4, and 8 weeks. Magnified part between room temperature and around 300 ^{o}C appeared separately. It was obviously seen that the weight decrease of aged samples were slower than that of unaged sample. In addition, the point which sample weight started to decrease sharply around 300 ^{o}C was delayed little for aged samples. This result suggests reinforced intermolecular interaction of aged polymer, which made difficult for polymer to degrade. Enhanced intermolecular force might originate from interaction between carbonyl group, carboxyl group, and hydroxyl group which are product of degradation (Rychlý*, et al.*, 2011) as checked by IR spectra. The CL result implied formation of the carbonyl group occurred in the polymer backbone during aging process as attacked by oxygen. As aging time passed, the carbonyl group was formed more, and hydrogen bonding could be formed easily. This phenomenon led to lowered weight loss during thermogravimetric test as shown in Figure 3-8. Although the chain scission was carried out, hydrogen bonding was valid. So weight loss of the 8 weeks aged PSA film was delayed like 2 and 4 weeks aged sample.

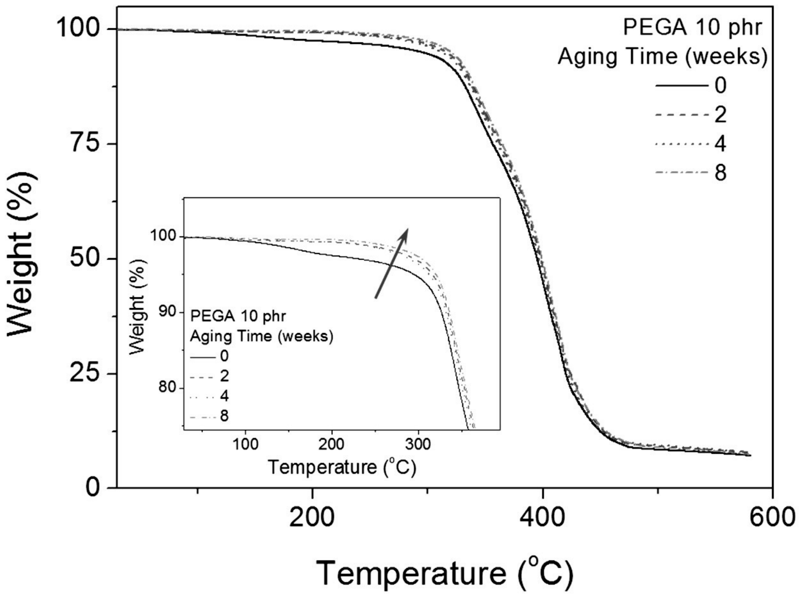


Figure 3-8. TGA curves of 10 phr PEGA contained PSA film.

3.3.4. Viscoelastic property

The shear storage moduli of the PEGA 10 phr contained sample during the aging were plotted in Figure 3-9 as a representative example. After 4 weeks aging, the storage modulus increased around whole temperature range. The glass transition temperature (T_g) shifted to the high temperature significantly after the 4 weeks aging. However, the storage modulus decreased at low temperature range after 8 weeks aging. The T_g of PSA film aged for 8 weeks also decreased compared to 4 weeks aged sample. Moreover, the temporary decrease of the storage modulus around room temperature for the 8 weeks aged sample indicated looser polymer structure than that of other aged samples. These loose structure resulted from the chain scission caused by hygrothermal aging and related to the general decrease of storage modulus. Until 4 weeks aging, the effect of the aging to the polymer structure was crosslinking by hydrogen bonding with the carbonyl group or hydroxyl group which is formed as polymer structure of PSA was degraded.

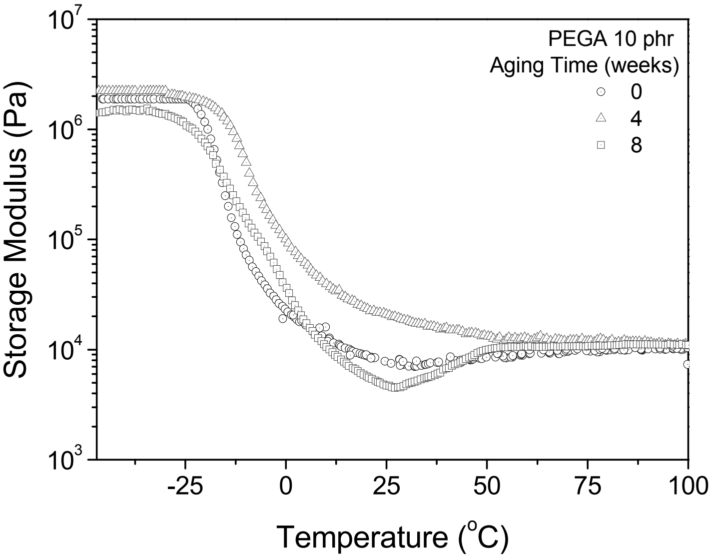
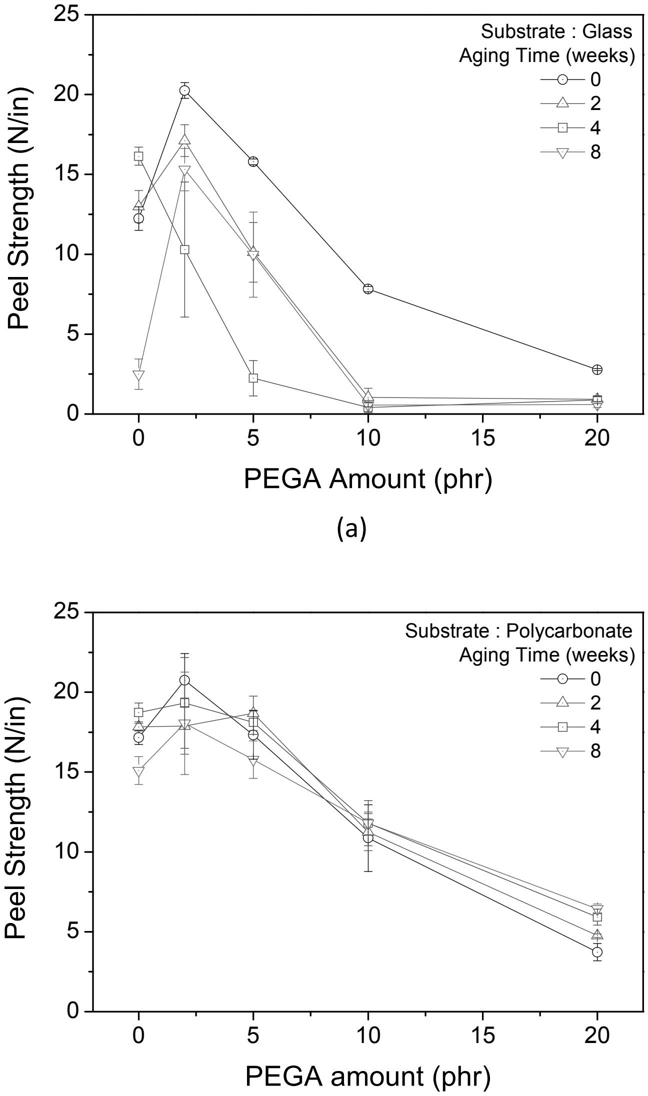


Figure 3-9. Shear storage modulus with 10 phr of PEGA contained cured film under aging condition (50 °C, 80 %RH).

3.3.5. Peel strength

The peel strength decreased for the 2 and 4 weeks aged PSA films and increased again for the 8 weeks aged PSA film as shown in Figure 3-10(a). This tendency corresponds to the CL analysis result. The CL intensity of the 2 and 4 weeks aged samples decreased and that of the 8 weeks aged sample increased. The polymer molecule which consisted of PSA might form crosslinked structure between PEGA and base resin by hydrogen bonding via carboxyl group, aldehyde group, and ester group which are formed during the aging. After the 8 weeks aging, the polymer backbone was broken and this occurrence accord to the mobility of the polymer molecules. Therefore these broken molecules and increased polar functional group helped the wetting of the PSA be improved then adhesion strength elevated again.

But the peel strength did not show large change on PC substrate in comparison with that on glass substrate during the aging as shown in Figure 3-10(b). It is considered that phenomenon came from polarity difference between two substrates because peel strength is related to surface free energy between substrate and PSA film (Peykova*, et al.*, 2012). As aging time increased, the PSA film turned to more polar structure as discussed above. Glass is polar substrate and the peel strength of the PSA film on glass substrate was affected from polar property change of the PSA film. On the other hand, PC is non-polar substrate and the peel strength of the PSA film on PC substrate was not much affected from polar property change of the PSA film.



(a)

(b)

Figure 3-10. Peel strength change on glass (a) and PC substrate (b) for 8 weeks under aging condition (50 ^{o}C, 80 %RH).

4. Conclusion

The summary of this study was illustrated in Figure 3-11. Hydrophilic component, PEGA was blended to the base resin composed of 2-EHA, IBOA, and NVC to assign cloud-point resistant property to PSA for OCA application. PEGA blended PSA film showed cloud-point resistance. The peel strength and tack initially increased and decreased by PEGA blending because PEGA imparted high cohesion to the PSA film due to its polar property. PEGA was effective also to prevent conductive substrate from corrosion by PSA attachment but too much amount of it could not protect substrate from corrosion. During the aging, the polar property of the PSA film increased by hydrogen bonding owing to carbonyl, hydroxyl and carboxyl group formation, which is confirmed by using CL analysis and IR spectra, as a result of degradation. This polar property made the intermolecular interaction active and the overall polymer structure grew tight. The decreased CL peak showed the changed polymer structure which is difficult to be attacked by oxygen as aging progressed. The shear storage modulus reflects this phenomenon thus the storage modulus of 4 weeks aged sample increased then that of 8 weeks aged sample decreased again because of the chain scission. The peel strength decreased as the aging had progressed due to high cohesion and molecular interaction then increased once more after 8 weeks aging by increased wetting property due to degraded polymer structure and polar functional group formation by chain scission in PSA matrix.

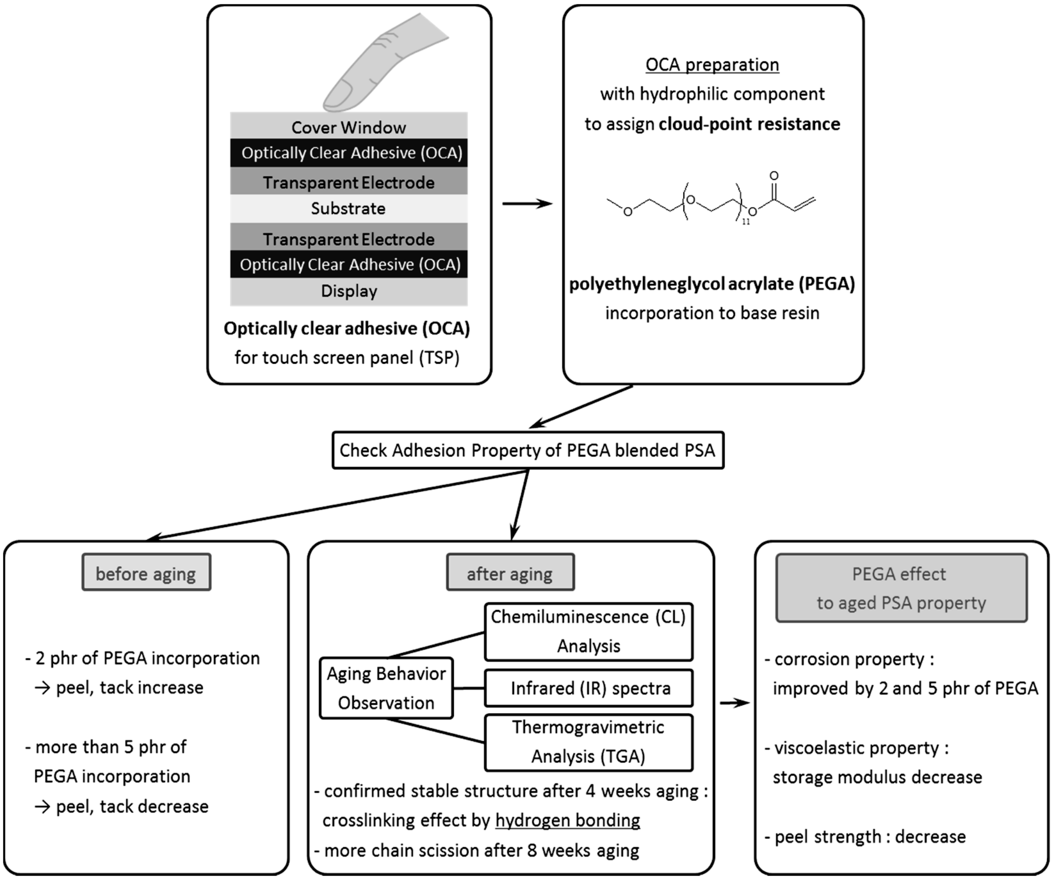


Figure 3-11. Schematic diagram of OCA preparation with hydrophilic component and its aging behavior.

Chapter 4

Cloud Point-resistant Optically Clear Adhesive by Incorporating 2-Hydroxyethyl Acrylate

1. Introduction

In view of the cloud point-resistance impartment, hydrophilic component is vital for the OCA preparation. The patent has been applied (Everaerts*, et al.*, 2013) but paper has not been published yet about this topic. Hydrophilic PSA has been designed using poly(ethylene glycol) and poly(N-vinyl caprolactam) and its property has been tested (Feldstein*, et al.*, 2014) but that work was not focused on OCA application. Apart from this case, hydrophilic PSA is mainly employed as a medical application like a transdermal patch for drug delivery system (Czech*, et al.*, 2007; Cilurzo *et al.*, 2012; Dana *et al.*, 2013; Banerjee *et al.*, 2014), biosensing (Wang *et al.*, 2013), biodegradable one (Czech *et al.*, 2013), paper recycling-friendly PSAs contained in a mixture of recycled-fiber sources (Yan *et al.*, 2004).

Polyethylene glycol acrylate (PEGA), oligomeric hydrophilic component was added to acid-free OCA which is composed of 2-ethylhexyl acrylate, isobornyl acrylate, and N-vinyl caprolactam in preceding chapter. PEGA was effective to impart cloud point-resistance to OCA. However, PEGA made PSA structure vulnerable against to the oxidation due to ether group in it. From this point, adhesion strength decreased as increasing aging time. Therefore, the aspect of the PSA stability was not good with PEGA blending.

On that account, monomeric hydrophilic component, 2-hydroxyethyl acrylate added acrylic PSA was studied as OCA in this research. The comparison will be possible between oligomeric and monomeric hydrophilic components blended PSAs. Basic properties and durability of monomeric hydrophilic component blended PSA were examined as OCA. Hygrothermal aging method, which is one of the common accelerating aging test, was employed. Acrylic OCA was prepared by UV irradiation to acrylic monomer blend. Several properties, which are needed as OCA, visible light transmittance, tack, and peel strength, were surveyed with increasing hydrophilic component. The aging behavior was monitored to inspect what change occurred and how this change was connected to the adhesion property change.

2. Experimental

2.1. Materials

2-Ethylhexyl acrylate (2-EHA, Samchun Chemicals, Republic of Korea), isobornyl acrylate (IBOA, Sigma Aldrich, USA), N-vinyl caprolactam (NVC, Sigma Aldrich, USA) were used for preparing the monomer premix, which forms base resin. 2-Hydroxyethyl acrylate (HEA, Samchun Chemicals, Republic of Korea) was blended to the partially polymerized monomer premix associated to cloud point resistance property. The photoinitiator was α, α-dimethoxy-α-phenylacetophenone (Irgacure 651, BASF, Germany). 1,6-Hexanediol diacrylate (HDDA, Miwon Specialty Chemical, Republic of Korea) functioned as a crosslinking agent. All materials were used as received without further treatment.

2.2. Monomer premix preparation

The monomer premix was prepared by irradiating UV to 2-EHA, IBOA, and NVC monomer mixture as listed in Table 5-1. The monomer mixture was charged to a 300 mL of round-bottom flask with a photoinitiator. The UV intensity was 40 mW/cm^2. N_2 gas was purged to the flask with a rate of 20 mL/min and temperature was also controlled to room temperature during irradiation. After partial polymerization by UV, the viscosity of the monomer premix was 870 cPs, which was measured by Brookfield viscometer using spindle No.4 under 750 RPM at room temperature.

Table 4-1. Formulation for cloud point-resistant OCA with monomeric hydrophilic component

	#1	#2	#3	#4	#5
	Base resin (2-EHA : 60 wt%, IBOA : 20 wt%, NVC : 20 wt%)				
HDDA (phr)	0.1	0.1	0.1	0.1	0.1
Photoinitiator (phr)	0.15	0.15	0.15	0.15	0.15
HEA (phr)	0	2	5	10	20

2.3. Coating and UV-curing

Various amount of HEA (2, 5, 10, 20 phr) was blended to the monomer premix using by paste mixer (DAEWHA Tech., Republic of Korea). The prepared mixture was coated on PET film with 175 µm for the peel strength and visible light transmittance measurements and 500 µm on release film for other experiments. The coated mixture was cured by conveyor belt type UV curing equipment with 1000 mJ/cm^2 UV dose to form a PSA film.

2.4. Gel fraction

To check the curing degree according to blended amount of HEA, the gel fraction of the cured PSA film was calculated from following equation.

$$\text{Gel fraction (\%)} = (W_1/W_0) \times 100$$

Where, W_0 is the initial weight of the sample, and W_1 is the solvent extracted weight of the sample (Park*, et al.*, 2013).

The cured PSA film was soaked into toluene in 50 °C for 24 hours. After that, soaked PSA film was dried at 50 °C again for 24 hours to remove solvent from PSA film. The dried PSA film weight was obtained then finally gel fraction was calculated.

2.5. Aging condition

The aging condition was 50 °C and 80 %RH for investigating the property change and cloud point resistance of the prepared PSA as OCA. All samples were placed in the temperature and humidity set oven. Each sample was taken from the oven after 2, 4, and 8 weeks, respectively for the checking adhesion and corrosion property change including the aging behavior of the prepared PSA.

2.6. Transmittance

The visible light transmittance of the prepared OCA was monitored using UV/vis spectrophotometer (Cary 100, Agilent Technologies, USA). The transmittance spectrum was recorded in the range of 200 − 900 nm. PSA films were coated on the PET film substrates and their average thickness were 175 μm. The bare PET film was the reference when the transmittance was measured.

Meanwhile, another visible spectrophotometer (SECOMAM® PRIM, France) was employed for checking whether cloud point resistance was revealed or not in the prepared PSA film. The measurement wavelength was 550 nm. The effect of hydrophilic component to solve cloudy state of the PSA film was confirmed when the PSA film immediately return to ambient temperature from the high temperature and humidly conditioned environment for OCA application.

2.7. Tack, peel strength and tensile strength

Texture analyzer (TA.XT.Plus, Stable Micro Systems, UK) was employed to evaluate the adhesion property and the tensile strength of the PSA film during the aging. The tack of the cured PSA film was measured only before the aging for checking effect of HEA blending to the adhesion property. The probe was 5 mm diameter of stainless steel cylinder. It approached with a speed of 1 mm/sec and contacted to the PSA surface for 1 sec with 100 g_f then separated with a speed of 1 mm/sec. The maximum value, when the probe was detached, was regarded as the tack value. The integrated value under the stress-strain curve area during the tack measurement was determined as the fracture energy.

The 180 ^{o} peel strength measurement was conducted using the 1 inch width cured PSA film strip, which is coated on the PET film. The samples were attached on the polycarbonate (PC) and glass substrate then pressed using a 2 kg rubber roller twice. The test speed was 5 mm/sec and the average force during the peeling was regarded as the peel strength. PC and glass was adopted because they can be used most generally as a cover window, which is frequently contacted to OCA in TSP.

The tensile strength was also done in the same speed with peel strength measurement. The only difference is the sample shape was used for tensile strength test 500 μm of thickness free film without any substrate. The both ends of the film released from release liner was fixed and extended. The stress-strain curve was obtained. Through stress-strain curve from the tensile strength measurement, the characteristic transition of the PSA film was observed with aging time.

2.8. Corrosion test through copper foil color change

The corrosion property of the cured PSA film was assessed by applying indirect method, which is economical and simple. Originally, OCA is applied on transparent electrode as illustrated in Figure 1-1 but in this experiment copper foil was used as an alternative substrate instead of actual transparent electrode. The copper foil was prepared and the cured PSA film adhered onto it. Then this specimen was placed in 50 °C and 80 %RH conditioned oven as mentioned in 2.5. The specimens were taken out from the oven in sequence during each aging period, like 2, 4, and 8 weeks. If any color change did not occur on the copper foil, the PSA do not affect transparent electrode while if there was color change on the copper foil, it means the attached PSA corroded transparent electrode. The changed color of the copper foil caused by attached PSA film was detected by spectrophotometer (Techkon GmbH, Germany). The *L* (darkness-lightness), *a* (redness-greenness), *b* (blueness-yellowness) values of the copper foil color were determined and the color difference *ΔE* value was calculated by following equation.

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

Where, L_1, a_1, b_1 data before aging, L_2, a_2, b_2 data after each aging period (Pfeffer*, et al.*, 2012).

2.9. Viscoelastic property

Advanced rheometric expansion system (ARES, Rheometric Scientific, UK) was used to know viscoelastic property change of HEA contained PSA film during the aging. The 500 um thickness of the cured PSA film was loaded on 25 mm diameter of parallel plate accessory in ARES equipment. The storage modulus was measured under temperature sweep mode at a rate of 3 ^{o}C/min to know overall behavior change of the PSA during the aging through the temperature elevation. The measured samples were before aging, 2, 4, and 8 weeks aged ones.

2.10. Chemiluminescence (CL) analysis

The CL analysis was performed to understand the change of the polymer structure in the PSA matrix after the aging. The samples, aged during the each aging period, were put in the instrument (CLA-FS1A, Tohoku Electronic Industrial Co., Ltd., Japan) one by one. Non-isothermal method was initially executed and temperature was elevated from room temperature to 150 ^{o}C at a rate of 7 ^{o}C/min. Then temperature was kept isothermally at 150 ^{o}C for 90 min. The CL signal was recorded during the test. The specimen thickness was 500 μm.

2.11. Fourier-Transform Infrared (FT-IR) spectroscopy

The IR spectra of the samples were investigated using FT-IR 6100 (JASCO, Japan). The wavenumber measurement range was from 4000 − 650 cm^{-1} and a resolution was 4 cm^{-1}. The samples had a change during the aging and it can be verified what functional group appeared or disappeared in the PSA matrix by observing the increase or decrease of absorbance peak in the spectra. In this experiment, the peak at 1725 cm^{-1} related to carbonyl group, 1159 cm^{-1} related to ester and alcohol group, 2956 and 2928 cm^{-1} related to alkyl group were observed especially (Socrates, 2004).

2.12. Fourier-Transform (FT) Raman spectroscopy

FT-Raman instrument (FRA 160/S, Bruker, Germany) was used for monitoring the change of the PSA film to the depth direction. The light source laser wavelength used for the measurement was 633 nm. The assessed wavenumber range was 4000 − 100 cm^{-1} with a resolution of 0.5 cm^{-1}. The scanning were carried out 5 times at a surface, 20, 40, 60, and 80 μm, respectively, for one sample. The measured samples were cured PSA film which contained HEA 10 phr, before and after aging. The areas under the peaks from 3000 to 2800 cm^{-1} and from 1520 to 1425 cm^{-1} were compared with each other. Those peaks showed evident differences in whole Raman spectrum scale. The peak between 3000 and 2800 cm^{-1} is related to alkyl groups. The peak 1520 to 1425 cm^{-1} is related to peroxy acid group (Socrates, 2004).

2.13. Thermogravimetric analysis (TGA)

After the aging, TGA (TGA-4000, PerkinElmer, USA) test was also implemented to know the alteration in the PSA matrix. Temperature was elevated from room temperature to 600 ^{o}C at a rate of 10 ^{o}C/min. The samples were HEA 10 phr contained PSA films before and after aging. The TGA curves of samples were compared with each other.

3. Results and discussion

3.1. UV-cured PSA film as OCA and its cloud point-resistance

The curing of the PSA for the tacky film formation was progressed and all samples showed adequate curing. The gel content of the PSA film was more than 60 %, which is good curing degree (Figure 4-1).

The transmittance of the PSA film after curing is very important. Accordingly, it was investigated first. Figure 4-2 shows the transmittance spectra of the samples in the visible light region. The reference was bare PET film without any coatings. The transmittance was nearly 100 % regardless of PSA coating. There was no haze on the cured PSA films. All components were compatible well in the PSA matrix.

The next examination of the prepared PSA film was cloud point resistance. In this experiment, HEA was incorporated to prevent haze of the PSA film under any circumstance. The cured PSA film was placed in the high temperature and humidity conditioned oven for 72 hours. After that, the samples were taken from oven and their transmittance was measured at 550 nm within 10 minutes. The haze appeared temporarily and disappeared after some time because the PSA consisted polymer was balanced with environment, which is like moisture migration. The haze of the PSA film was evaluated through transmittance value. The transmittance was improved by incorporating HEA and the amount was not largely associated to the result as shown in Figure 4-3(b). This result also implies that haze problem was not solved only by regulating NVC amount which is essential for cohesion of the PSA in this research as shown in Figure 4-3(a). Hydroxyl group in the PSA matrix made moisture dispersed well, and haze did not appear on the PSA film. As a result, HEA was effective to avoid haze problem caused by sudden environmental change.

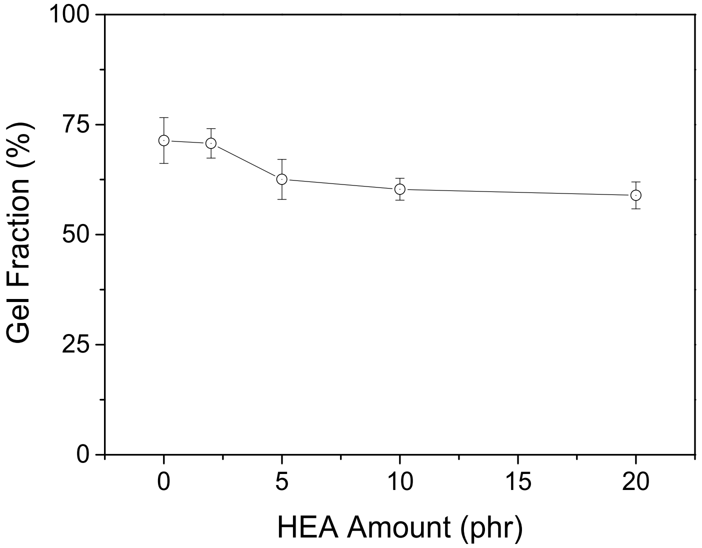


Figure 4-1. Gel fraction of UV-cured PSA film as a function of HEA amount.

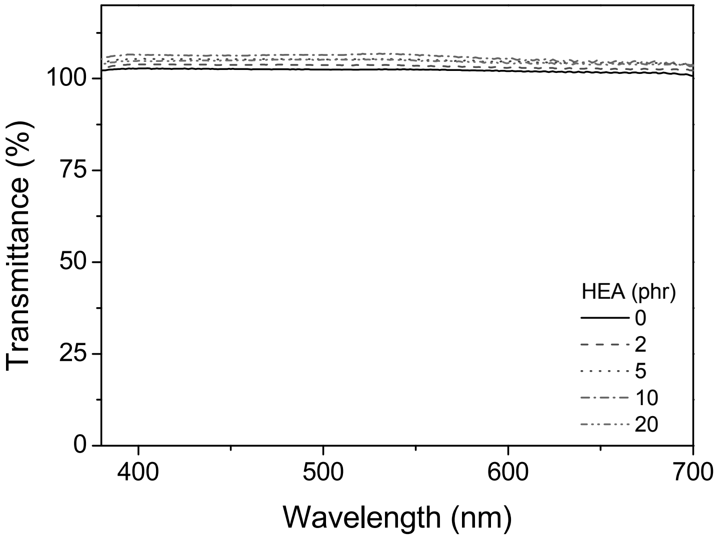
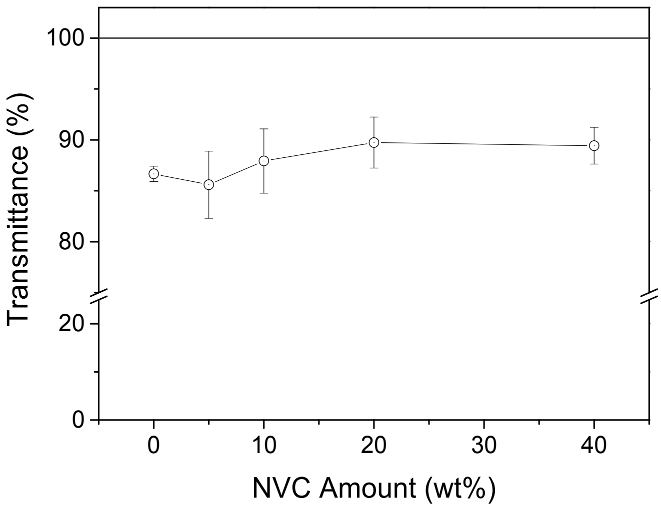
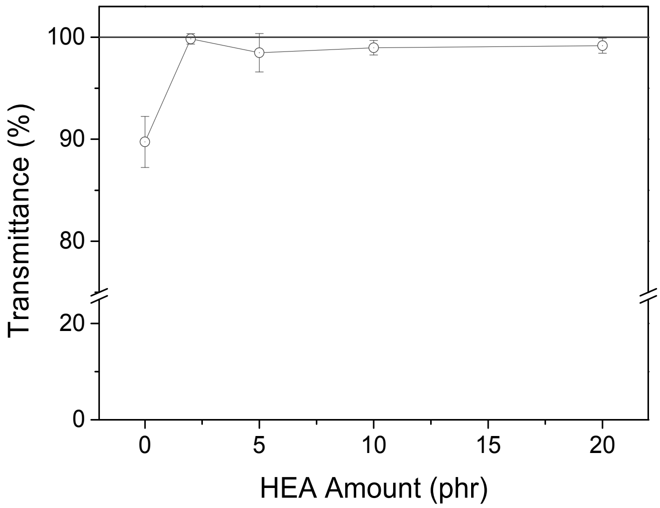


Figure 4-2. Visible light transmittance of UV-cured PSA on PET film
(baseline : bare PET film)



(a)



(b)

Figure 4-3. Visible light transmittance of typical acid-free PSA (a) and improved visible light transmittance by incorporation HEA (b) directly after taking sample from 50 °C 80 %RH chamber.

3.2. Adhesion performance

3.2.1. Tack

The tack tended to increase by HEA blending due to its polar property as indicated in Figure 4-4 although it temporarily decreased when 10 phr of HEA was blended. But the difference was not remarkable with considering standard deviation of 10 phr and 20 phr of HEA blended specimen. The fracture energy also showed the same tendency with tack but kept steady value after 10 phr of HEA addition. The hydroxyl group in HEA induced hydrogen bonding between ester or amide group in the polymer side chain. Therefore the cohesion of the PSA film can be increased and the tack also increased. The most effective polar component amount by deriving molecular interaction was 2 and 5 phr of HEA.

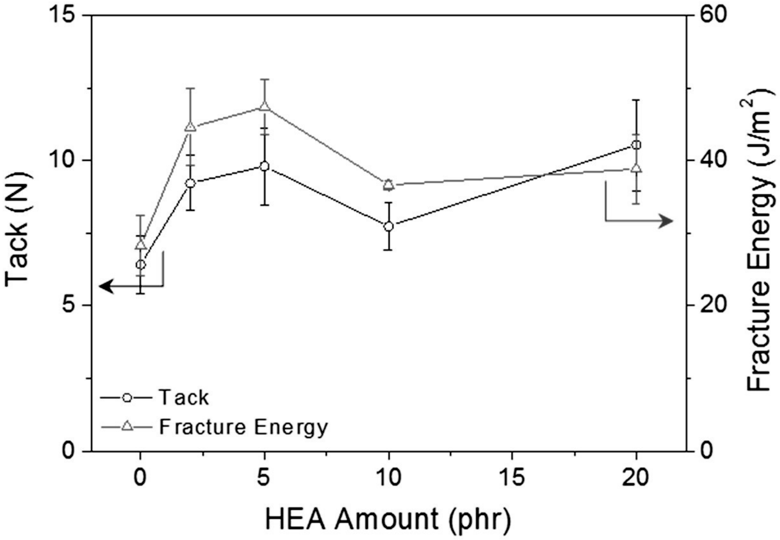


Figure 4-4. Probe tack and fracture energy of the UV-cured PSA film as a function of HEA amount.

3.2.2. Peel strength

In Figure 4-5, peel strength showed the same tendency with tack result. It increased initially but decreased after 10 phr of HEA incorporation. The values were close between HEA 10 phr and 20 phr contained sample. The cohesion increase of the PSA film also had core role in the peel strength increase like the case of the tack. The peel strength is related to the wettability of the PSA as well. The wettability was also influenced by the increase of PSA polarity, which is promoted improvement of wettability, by hydroxyl group of HEA.

As increasing HEA amount in the PSA matrix, the difference of the peel strength on PC and glass substrate decreased gradually because of the modification of the PSA character to more polar one due to hydroxyl group. The difference of the peel strength on discrete substrate is related to surface free energy of PSA film and substrate. PC is non-polar substrate and PSA film is also generally non-polar. On the other hand, glass is polar substrate. The PSA film turned to polar owing to hydroxyl group and this result brought out peel strength increase on glass substrate. Peel strength is high when surface free energy is similar between PSA film and substrate (Peykova*, et al.*, 2012). So the peel strength difference on two substrates decreased by modifying PSA property with increasing HEA amount.

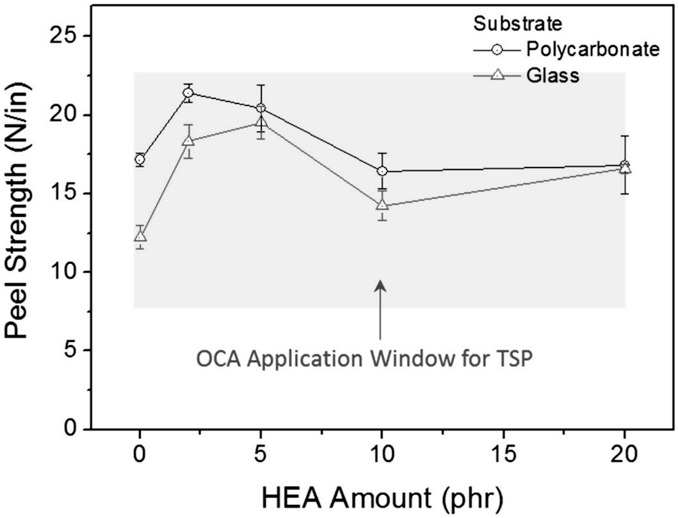


Figure 4-5. Peel strength of the UV-cured PSA film with different amount of HEA on glass and PC substrates.

3.3. Aging behaviors

3.3.1. Corrosion property

Figure 4-6 showed corrosion property of PSA film as observed by indirect method using copper foil during the aging. The interesting result is that hydrophilic component can inhibit color change of copper which meant copper corrosion did not occur. There was significant color difference before and after HEA blending. Before HEA blending, color difference value (*ΔE*) was already large within 2 weeks aging. Less than 10 phr of HEA maintained stable state while 20 phr of HEA, too much hydrophilic component, can corrode copper as time goes by. It is considered that adequate amount of hydrophilic compound is able to disperse moisture into the PSA matrix not to contact to copper but abundant hydrophilic compound attract moisture and helped it reach copper. From that reason, copper corrosion arose. *ΔE* was low until 4 weeks aging regardless of HEA amount, whereas the gap of the *ΔE* value was observed after 8 weeks aging.

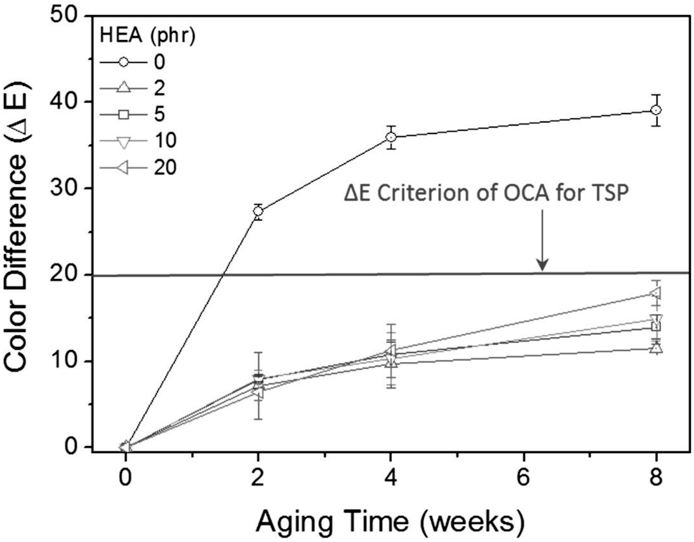


Figure 4-6. Corrosion property test using copper foil by the UV-cured PSA film attachment for 8 weeks under hygrothermal aging condition.

3.3.2. Polymer characteristics change through viscoelastic, thermal property, and stress-strain curve

Viscoelastic curve can give useful information about adhesive behavior depending on temperature range (Benedek *et al.*, 2008). Accordingly storage moduli among samples were compared under temperature sweep mode before and after aging in this research. The shear storage moduli of samples during the aging were plotted with increasing temperature in Figure 4-7. The glass transition temperature (T_g) was also shifted to the high temperature range during the aging. This change is obvious between not aged sample and 2 weeks aged one. The change of the storage modulus is reflected the change of the polymer structure in the PSA matrix. The increase of the glass transition temperature and modulus in the rubbery plateau or glass-like temperature range indicates that molecular interaction became more active.

This tendency can be perceived in TGA curve. In Figure 4-8, TGA curve showed initial difference of weight loss curve. The weight loss was delayed as the aging period of the sample was long. It means it was hard for PSA film to be decomposed during the TGA test. This result also suggested that intermolecular force, which is speculated as hydrogen bonding, is increased by structure change of the polymers constituting PSA.

The stress-strain curve difference is exhibited during the aging through Figure 4-9. Tensile strength means cohesive strength of the material, and maximum elongation at break is proportional to free volume within the polymer (Novikov *et al.*, 2003). The cohesion of the PSA increased when this result inferred from the tensile strength for 2 weeks aging. After 4 weeks aging, both strain and stress increased hence this phenomenon suggested that not only cohesive strength but also free volume increased for 2 more weeks aging. The molecular structure got tight by increased intermolecular force as aging had progressed, thus strain and stress increased simultaneously until 4 weeks aging. The sample became weak so it broke earlier during the test compared to other samples after 8 weeks aging.

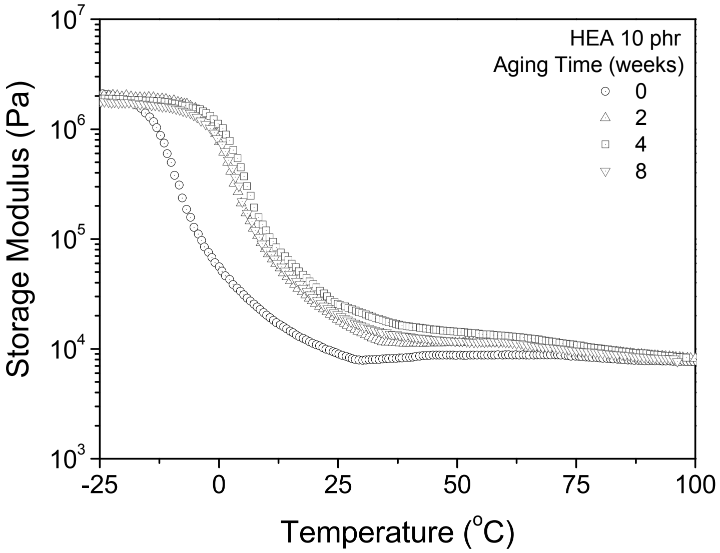


Figure 4-7. Shear storage moduli of HEA 10 phr contained PSA film during the hygrothermal aging.

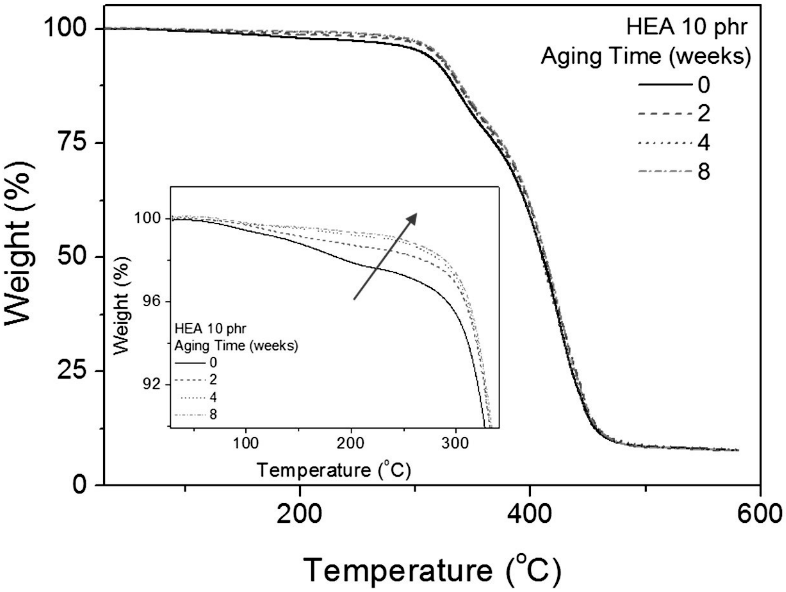


Figure 4-8. Initial difference of thermogravimetric curves among the aged PSA samples during the hygrothermal aging.

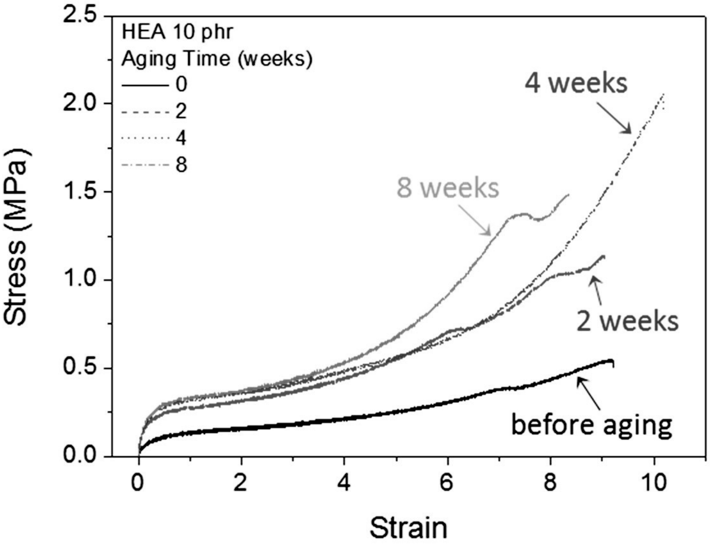


Figure 4-9. Stress-strain curves of the HEA 10 phr contained specimens as hygrothermal aging time passed.

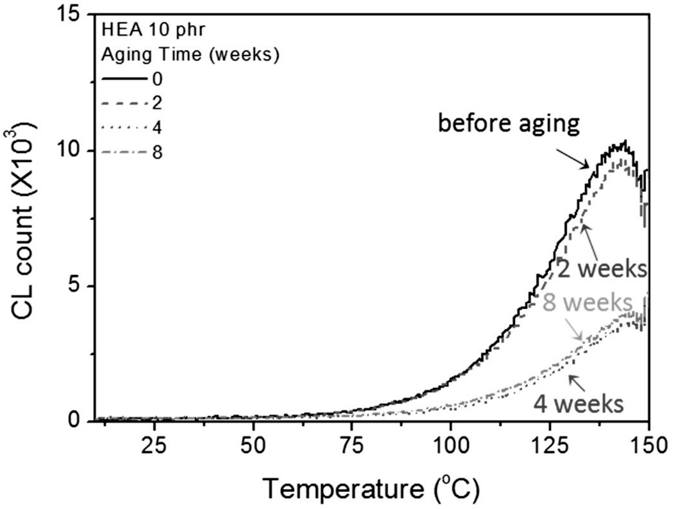
3.3.3. Polymer structure change observed by CL, IR, and Raman analysis

To know what change occurred in the polymer structure during the aging, CL signal, IR and Raman spectra were measured. At first, the CL signal was presented in Figure 4-10. CL signal can be detected when carbonyl group is formed after polymer chain is attacked by oxygen as described in Scheme 3-1 (Rychlý*, et al.*, 2011). Therefore, the difference of the CL intensity come from how easily the polymer structure can be attacked by oxygen. The attack point is mainly lateral carbon from oxygen. Scheme 3-1 is about oxidization of ether group and this group can be more easily oxidized than ester group (Rychlý*, et al.*, 2011). However, there is no ether group and only ester group in the prepared PSA. Ester group can be changed to carboxyl and aldehyde group as a result of oxygen attack. Scheme 4-1 illustrated the structure change of the polymers after CL test. This occurrence can be applied to suppose aging sequence of samples in this experiment. The polymer structure can experience such change by oxidation under hygrothermal condition.

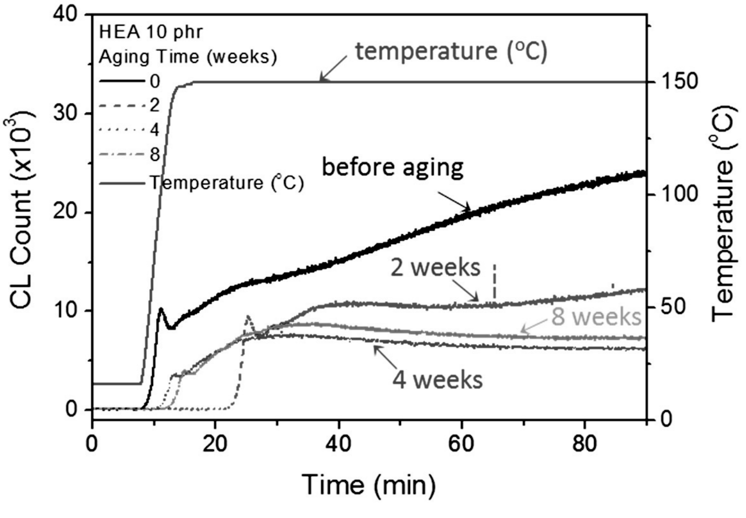
Figure 4-10(a), which is non-isothermal CL analysis result, imparts the polymer structure got stable because the CL signal decreased as aging time goes by. Once ester group changed to aldehyde group or carboxyl group due to degradation during the aging, following reaction by oxygen cannot occur any more in CL analysis. Figure 4-10(b) also represented same result. The clearer difference among samples was provided with higher CL intensity than that of non-isothermal test. The CL signal increased definitely due to active reaction by oxygen attack with elevating temperature and the polymer structure became difficult to be attacked during the analysis. The common result in Figure 4-10(a) and 4-10(b) is the polymer structure was easy to be oxidized after 8 weeks aging. This is because the chain scission occurred after relatively long aging time. The shortened polymer chain readily allowed oxygen approaching to the site that is not oxidized.

In IR spectra, there were the increase of the peak related to both ester group and primary alcohol (Figure 4-11(a)), carbonyl group (Figure 4-11(b)), alkyl group (Figure 4-11(c)) (Socrates, 2004). In the case of the peak at 1160 cm^{-1}, if there were the ether group, the ester group increased as a consequence of the oxidization reaction but there was no ether group thus it might be more reasonable that increase of this peak is related to primary alcohol (Socrates, 2004) formation as a result of ester hydrolysis under hygrothermal aging condition (Lin*, et al.*, 2006). The reason of alcohol decrease after 8 weeks aging is considered owing to reaction between alcohol and aldehyde, which form hemiacetal. Ketone, aldehyde, and carboxyl groups are related to carbonyl group and the increase of these groups by oxidation during the aging affected IR absorbance peak at 1728 cm^{-1}. The band from 1600 to 1675 cm^{-1} is related to amide group in caprolactam ring. The shoulder at 1625 cm^{-1} is associated with hydrogen bonded amide group in caprolactam ring with hydroxyl group and 1644 cm^{-1} peak have relevance to amide group hydrogen bonded with water (Maeda *et al.*, 2002; Spěváček *et al.*, 2012). Before aging, there was hydroxyl group from HEA therefore amide in caprolactam ring could form hydrogen bond with it. As aging time passed, amide group from caprolactam ring gradually formed hydrogen bonding with moisture under hygrothermal aging condition. Thus 1644 cm^{-1} peak increased while 1625 cm^{-1} shoulder almost disappeared. Finally after 8 weeks aging, 1644 cm^{-1} peak decreased again and this result is assumed that caprolactam ring was opened by moisture. Alkyl groups, especially CH_3 or CH_2 in alkane structure, related to peak at 2956 and 2928 cm^{-1}, increased as well because of the chain scission probably, inside the polymer chain. The decrease of these peaks after 8 weeks aging is considered because of hemiketal formation. Hydroxyl group from HEA and carbonyl group of ketone from intermediate during the oxidation in the polymer main backbone can react each other then hemiketal is able to be formed as a product. Before the chain scission step, ketone reacted with alcohol therefore methyl group could not be formed.

Figure 4-12 expressed depth profiling result measured by Raman analysis. Figure 4-12(a) is the Raman spectra of HEA 10 phr contained sample before aging from film surface to 80 μm depth as a representative one. Other samples had analogous spectrum shape. The peak between 3000 and 2800 cm^{-1} is evident and this peak increased as increasing depth. For the clear comparison, integrated values under peak area from 3000 to 2800 cm^{-1} (Figure 4-12(b)) and from 1520 to 1425 cm^{-1} (Figure 4-12(c)) were plotted as a function of depth as aging time passed. The value tended to increase and slightly decrease again with scanning into the inner part of the PSA film. The peak is related to methyl, methylester, and methylketones (Socrates, 2004). Therefore increase of this peak means more methyl groups exist in the inside of the PSA film compared to those at surface. The methyl group increase is connected to chain scission because methyl group can be formed as an end group. From this point, it can be known the chain scission is more active in the inside of the film. In addition, this peak is related to aldehyde group, which is the product of degradation of ester group, linked to IR result (Socrates, 2004). Figure 4-12(c) also shows the increase of the peaks. This peak is related to peroxy acid group in the polymer chain and that group is formed as an intermediate group when degradation of polymer is progressed as shown in Scheme 4-2. The peroxy acid group increased along with the methyl group. These peaks existed initially although aging had not progressed because they are related to alkane CH_2 symmetric stretching and deformation. Then methyl and peroxy acid group were formed due to the aging, peaks increased resultingly. On the other hand, the integrated values increased until 2 weeks aging but decreased again and held similar value to that of one before aging during the rest aging period. It is thought this phenomenon arose from reaction between aldehyde or ketone with alcohol like the result shown from IR spectra. The hemiacetal and hemiketal structure, which is the product of the reaction, can lead to decrease of aldehyde and peroxy group. Lastly, based on these observations, the suggested polymer structure change was outlined in Scheme 4-3.

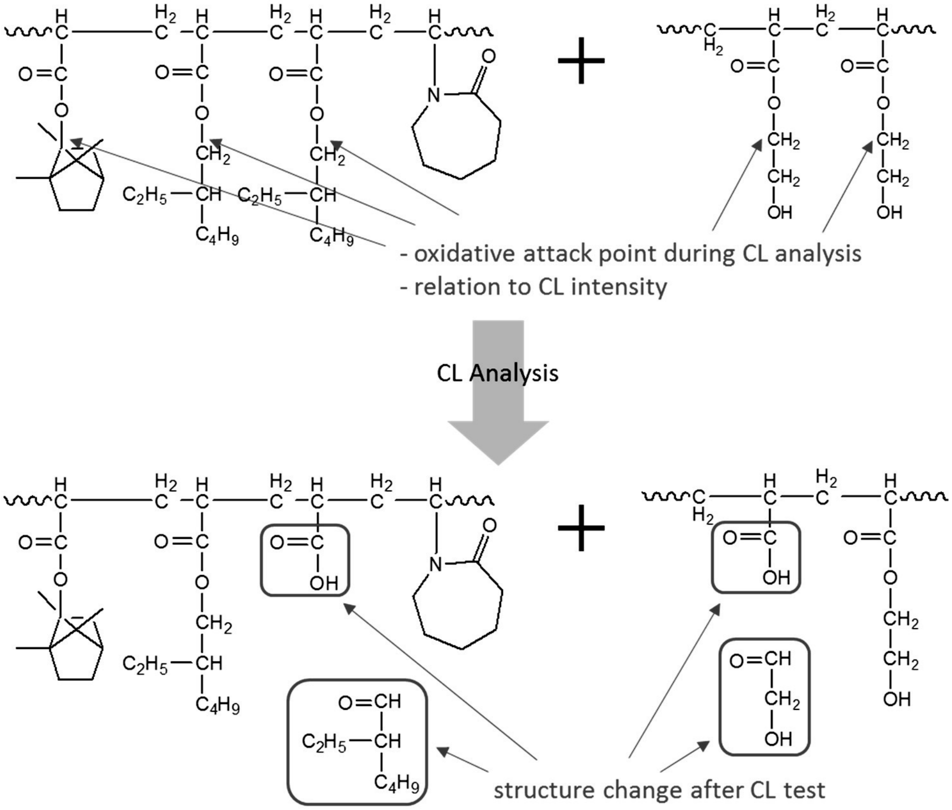


(a)

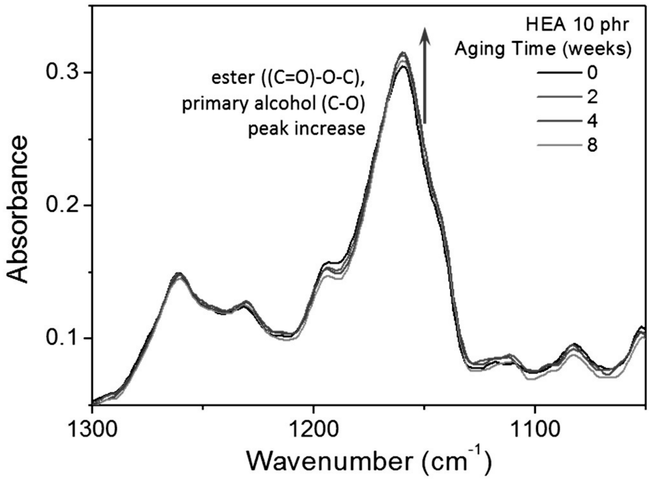


(b)

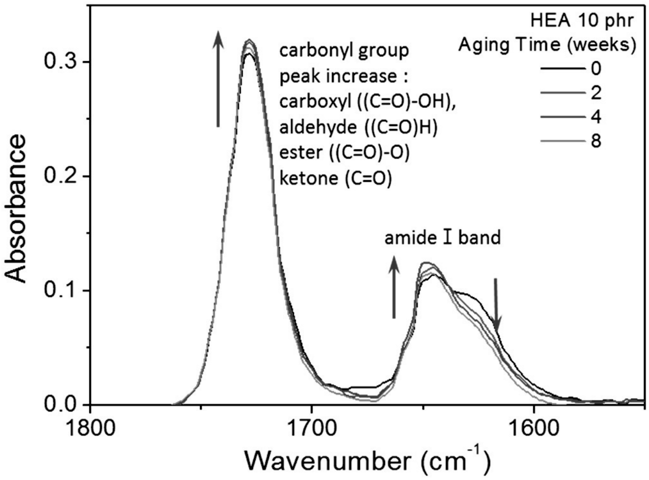
Figure 4-10. Chemiluminescence (CL) signal of HEA 10 phr contained PSA film during the non-isothermal (a) and isothermal (b) analysis before and after hygrothermal aging.



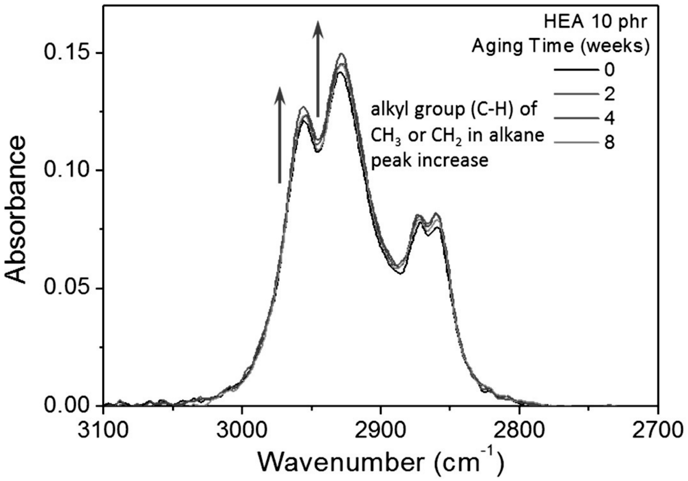
Scheme 4-1. Expected structure change of polymer consisted of PSA matrix during the CL test by oxidation.


HEA 10 phr
Aging Time (weeks)
0
2
4
8
ester ((C=O)-O-C),
primary alcohol (C-O)
peak increase
Absorbance
0.1
0.2
0.3
1300
1200
1100
Wavenumber (cm^{-1})

(a)

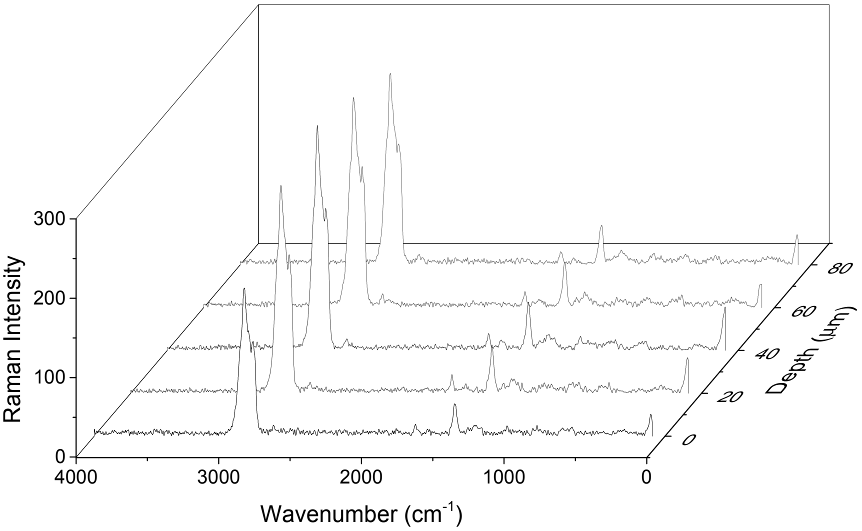

HEA 10 phr
Aging Time (weeks)
0
2
4
8
carbonyl group
peak increase :
carboxyl ((C=O)-OH),
aldehyde ((C=O)H)
ester ((C=O)-O)
ketone (C=O)
amide I band
Absorbance
0.0
0.1
0.2
0.3
1800
1700
1600
Wavenumber (cm^{-1})

(b)

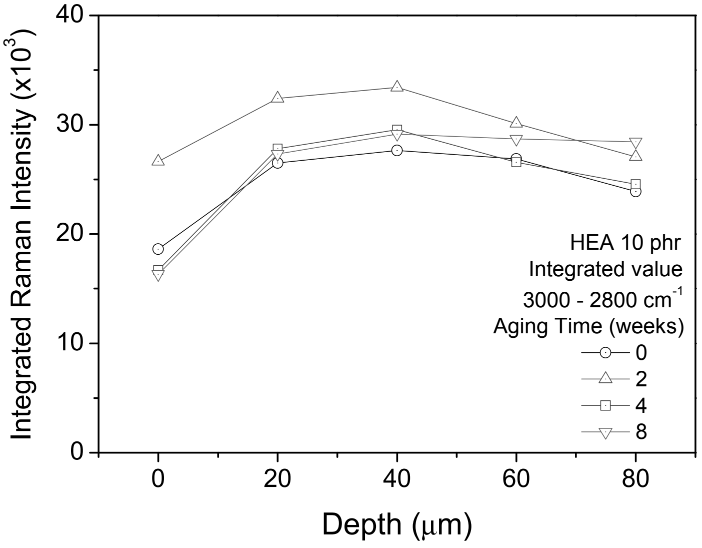


(c)

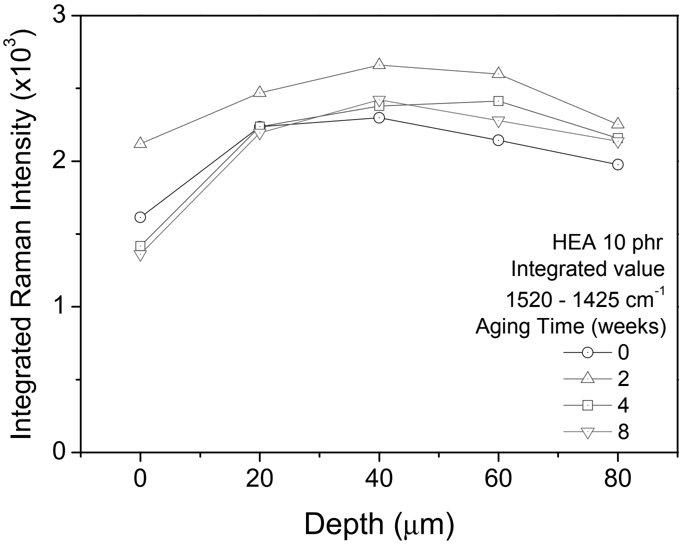
Figure 4-11. IR spectra of HEA 10 phr contained sample during the hygrothermal aging (50 ^{o}C, 80 %RH) : the peak related to ester and primary alcohol group (a), carbonyl group (b), and alkyl group (c).


Raman Intensity
0
100
200
300
4000
3000
2000
1000
0
Wavenumber (cm^{-1})
Depth (μm)
0
20
40
60
80

(a)

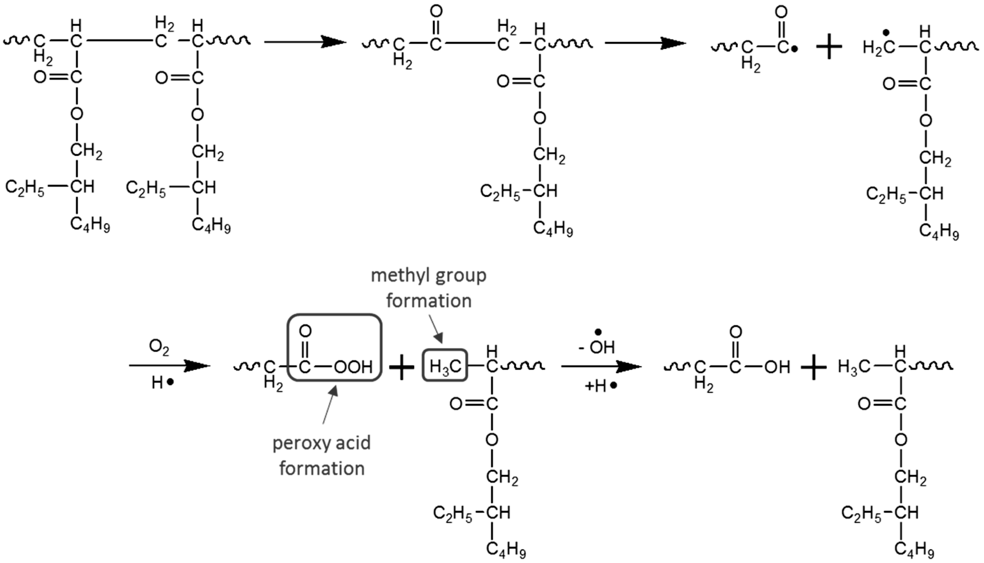


(b)

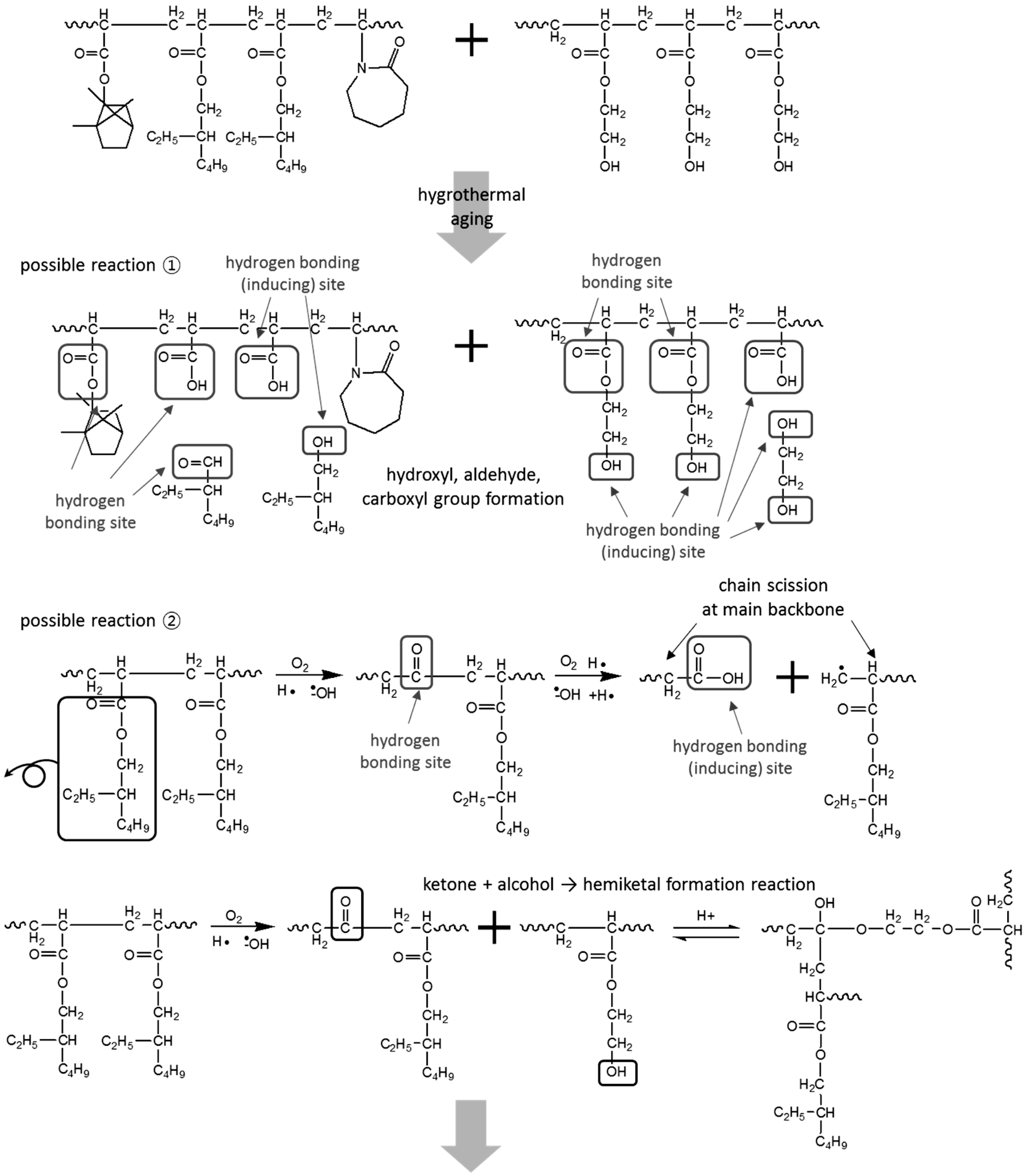


(c)

Figure 4-12. Raman spectra of HEA 10 phr contained PSA film from surface to the inside before aging (a), integrated value of the area under the peak between 3000 and 2800 cm^{-1} (b), and between 1520 and 1425 cm^{-1} (c) during the hygrothermal aging.



Scheme 4-2. Peroxy acid and methyl group formation during the hygrothermal aging in this experiment.

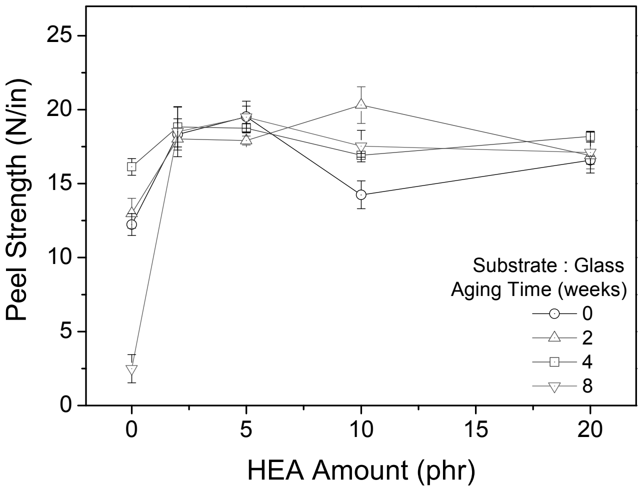


- carboxyl, alcohol, aldehyde group formation after hygrothermal aging → hydrogen bonding increase
- change related to TGA result, viscoelastic property, peel strength of PSA during the aging

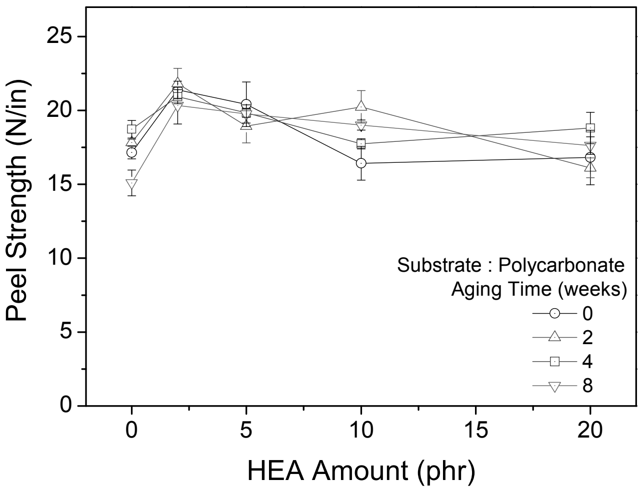
Scheme 4-3. Suggested reaction of the HEA blended PSA during the hygrothermal aging

3.3.4. Peel strength

Figure 4-13(a) and 4-13(b) shows the peel strength during the aging on the different substrates. Overall, there was no obvious difference or drop of the peel strength during the aging, especially on PC substrate, which is non-polar substrate. The peel strength was generally kept stable during the aging, although that of HEA 10 phr contained sample increased after 2 weeks aging. The polymer structure change during the aging did not bring about large change of the peel strength especially between 4 and 8 weeks aging since HEA amount increased in the PSA matrix. As aging time passed, the cohesion of the PSA film increased because of the polar carboxyl or aldehyde group formation, which is the result of degradation. The formation of these groups were confirmed by the IR and Raman analysis. They can induce hydrogen bonding among molecules with ester and hydroxyl groups which originally existed. This change was actively carried out at relatively inside of the PSA film than surface of it as investigated in Raman spectroscopy depth profiling. Peel strength measurement is related to the phenomena of interface between PSA film and substrate so peel strength did not change greatly during the aging. Another possible reason for stable peel strength during the aging is that hydroxyl group also induced hemiketal formation with ketone before chain scssion thus peel strength did not much decrease.



(a)



(b)

Figure 4-13. Peel strength change on glass (a) and PC substrate (b) for 8 weeks under hygrothermal aging condition.

4. Conclusion

In this research, HEA was incorporated to the acrylic base resin for preparing cloud point resistant OCA. The results of this work were summarized in Figure 4-14. HEA assigned cloud point resistance to the PSA film under various circumstances by its hydrophilic property of hydroxyl group. In addition, it did not any affect the visible light transmittance of the PSA film after UV curing at ambient temperature. The cohesion of the PSA was also enhanced owing to HEA hence the tack and peel strength increased. The corrosion resistance of the PSA film was highly improved with HEA addition but the corrosion of the conductive substrate by the PSA film attachment was weakly observed again as increasing HEA amount. The noteworthy feature is, there was no dramatic decrease of the adhesion strength during the aging in the HEA incorporated samples. The adhesion strength was retained and this tendency was marked in the peel strength on the PC substrate. The aging behavior observed by IR and Raman spectra signified carboxyl, hydroxyl, aldehyde, peroxy acid and methyl group formation as a result of chain scission, which is the degradation of the polymer chain. This polar functional group like carboxyl and hydroxyl group led to hydrogen bonding among molecules and intermolecular force increased. The hydroxyl group from HEA somewhat prevented the chain scission of the polymer. For this reason, polymer structure was substantial as aging time passed and this change was reflected to viscoelastic properties, which are the increase of the T_g and storage modulus on rubbery plateau.

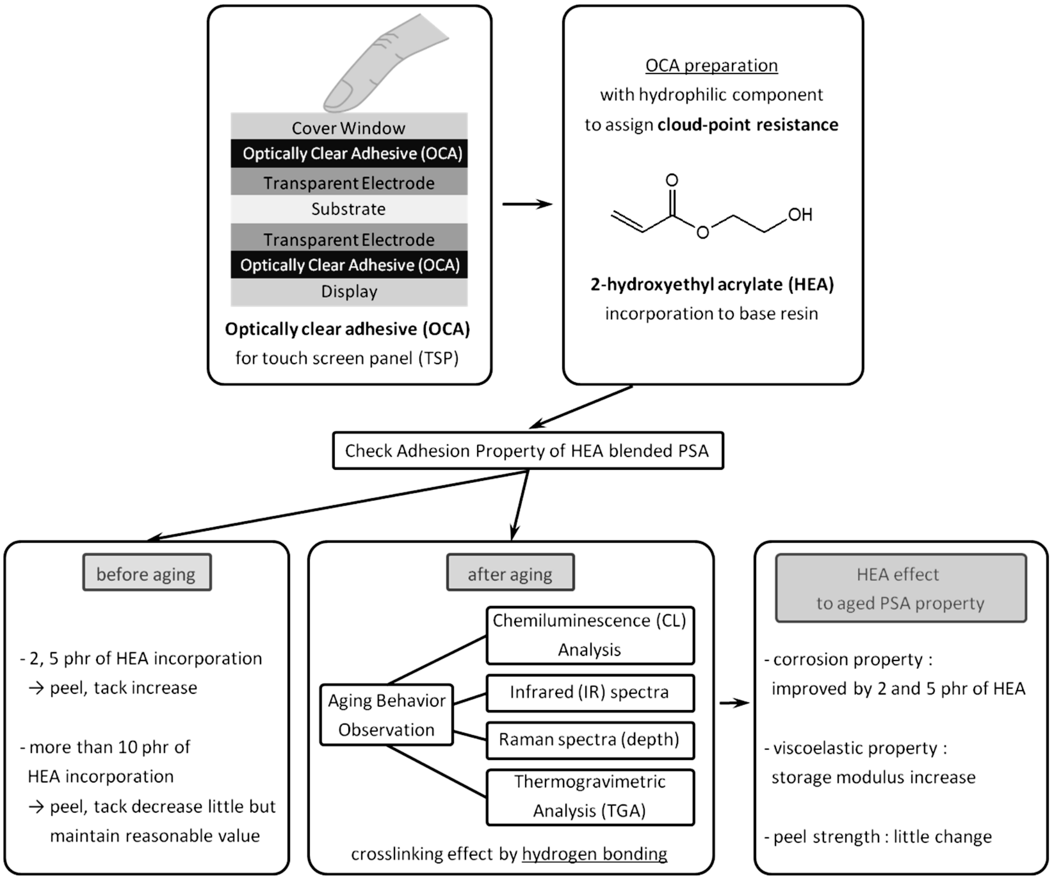


Figure 4-14. The objective of HEA blending into PSA matrix and its effect on hygrothermal aging behavior and adhesion property.

Chapter 5

Concluding Remarks

Optically clear adhesive (OCA) is indispensable material to assemble touch screen panel (TSP). The position of OCA in the TSP structure is predominantly contacted to transparent electrode. Therefore, no influence to transparent electrode by OCA is important because possible influence is related to TSP operation. Usually OCA is acrylic polymer due to its excellent transparency but it needs to exclude an acidic component, which is included owing to cohesion improvement of PSA. Acid-free PSA preparation for OCA application was the first objective of this study then the oligomeric and monomeric hydrophile components were blended respectively for imparting cloud point-resistance to the PSA. The alteration of the adhesion performance and aging behavior in accordance with each hydrophilic material were observed.

1. Preparation of acid-free optically clear adhesive

N-vinyl caprolactam (NVC) was chosen for preparing the acid-free OCA. 2-Ethylhexyl acrylate (2-EHA), isobornyl acrylate (IBOA), and NVC were photopolymerized then formed monomer premix by UV irradiation. This monomer premix was coated and UV-cured then transparent pressure sensitive adhesive (PSA) film was finally made. NVC contained PSA film showed appropriate adhesion property. Indirect and economical method using copper foil to investigate the corrosion property of the PSA was employed. The color change of the copper foil by attaching the PSA film under hygrothermal aging condition can be a criterion for corrosive property of the PSA. In this experiment, NVC prevent the corrosion of the copper foil but more than 20 wt% of NVC led to moderate color change probably due to its polar property. The adhesion strength also decreased appreciably at more than 20 wt% of NVC contained sample after 8 weeks hygrothermal aging. It is because the increased cohesion by the hydrogen bonding with the caprolactam ring opening.

2. Cloud point resistant optically clear adhesive by incorporating monofunctional methoxylated polyethyleneglycol acrylate

Monofunctional methoxylated polyethyleneglycol acrylate (PEGA) was blended to the base resin consisting of 2-EHA, IBOA, and NVC for providing cloud point-resistance to the PSA as OCA. It was effective to impart cloud point-resistance to the PSA and protect transparent electrode from corrosion. But more than 5 phr of PEGA made the adhesion performance of the PSA declined. In addition, PEGA contains ether groups which are vulnerable to oxygen attack (oxidation) during the aging. This weakness is related with the chain scission after the aging, then it caused the adhesion strength and overall storage modulus decreased. The caprolactam ring opening, hydrolysis of the ester group in the acrylates, and oxidation of the main backbone induced the hydrogen bonding hence the adhesion strength and glass transition temperature (T_g) increased until 4 weeks aging. But overall storage modulus and T_g decreased after 8 weeks aging owing to the chain scission, which is the result of the further progressed aging.

3. Cloud Point-resistant Optically Clear Adhesive by incorporating 2-hydroxyethyl acrylate

2-Hydoxyethyl acrylate (HEA) was blended to the base resin which is the same one as mentioned above. Cloud point-resistance was effectively realized by HEA compared to PEGA because HEA was well-dispersed in the

PSA matrix due to its low molecular weight. The adhesion property was also affordable. After adding more than 10 phr of HEA, the adhesion strength decreased slightly due to the increased cohesion by its polarity but it was enough to be used as OCA. HEA blended cloud point-resistant PSA showed more stable adhesion performance during the aging because it does not have ether group thus it is relatively stable structure against for oxidation. The hydroxyl group supported stable structure by forming the hydrogen bonding. But the hydrolysis of the ester group in the acrylate could not help occurring during the aging because this composition includes many acrylates. It is assumed that the chain scission also arose. The hydrogen bonding was induced as well by this phenomena therefore T_g of the PSA increased during the aging. The reactions during the aging more activated at the inside of the PSA film compared to the surface. Accordingly, the adhesion strength did not much change because the adhesion is the phenomena at the interface between the PSA and substrate. As a result, the monomeric hydrophilic component was better in aspects of the cloud point-resistance assignment and adhesion property maintenance.

References

Banerjee, S., Chattopadhyay, P., Ghosh, A., Datta, P., Veer, V. 2014. Aspect of adhesives in transdermal drug delivery systems. International Journal of Adhesion and Adhesives. 50: 70-84.

Benedek, I., Feldstein, M. M. 2008. Fundamentals of Pressure Sensitivity. CRC Press, Boca Raton.

Briggs, D., Beamson, G. 1992. Primary and secondary oxygen-induced C1s binding energy shifts in X-ray photoelectron spectroscopy of polymers. Analytical Chemistry. 64(15): 1729-1736.

Cespi, M., Casettari, L., Palmieri, G. F., Perinelli, D. R., Bonacucina, G. 2014. Rheological characterization of polyvinyl caprolactam–polyvinyl acetate–polyethylene glycol graft copolymer (Soluplus®) water dispersions. Colloid and Polymer Science. 292(1): 235-241.

Chang, E. P., Holguin, D. 2005. Curable Optically Clear Pressure-Sensitive Adhesives. The Journal of Adhesion. 81(5): 495-508.

Cheng, Z., Teoh, S.-H. 2004. Surface modification of ultra thin poly (ε-caprolactone) films using acrylic acid and collagen. Biomaterials. 25(11): 1991-2001.

Chiantore, O., Trossarelli, L., Lazzari, M. 2000. Photooxidative degradation of acrylic and methacrylic polymers. Polymer. 41(5): 1657-1668.

Cilurzo, F., Gennari, C. G., Minghetti, P. 2012. Adhesive properties: a critical issue in transdermal patch development. Expert opinion on drug delivery. 9(1): 33-45.

Czech, Z. 2001. Solvent-based pressure-sensitive adhesives for PVC surfaces: A special report. Advances in Polymer Technology. 20(1): 72-85.

Czech, Z. 2004. Development in the area of UV-crosslinkable solvent-based pressure-sensitive adhesives with excellent shrinkage resistance. European Polymer Journal. 40(9): 2221-2227.

Czech, Z., Kurzawa, R. 2007. Acrylic pressure-sensitive adhesive for transdermal drug delivery systems. Journal of Applied Polymer Science. 106(4): 2398-2404.

Czech, Z., Wilpiszewska, K., Tyliszczak, B., Jiang, X., Bai, Y., Shao, L. 2013. Biodegradable self-adhesive tapes with starch carrier. International Journal of Adhesion and Adhesives. 44: 195-199.

Czech, Z., Wojciechowicz, M. 2006. The crosslinking reaction of acrylic PSA using chelate metal acetylacetonates. European Polymer Journal. 42(9): 2153-2160.

Dana, S. F., Nguyen, D.-V., Kochhar, J. S., Liu, X.-Y., Kang, L. 2013. UV-curable pressure sensitive adhesive films: effects of biocompatible plasticizers on mechanical and adhesion properties. Soft Matter. 9(27): 6270-6281.

Determan, M. D., Everaerts, A. I., Moore, C. L., Olson, D. B. 2010. High refractive index pressure-sensitive adhesives. United Sates Patent. US 2010/0048804 A1.

Dexerials Corporation 2014. "Optical elasticity resin for small-to-medium sized FPDs Technical data." 2014, from http://www.dexerials.jp/en/products/b3/svr1120.html.

Everaerts, A. I., Xia, J. 2009. Indium-tin-oxide compatible optically clear adhesive. United States Patent. US 2009/0087629 A1.

Everaerts, A. I., Xia, J. 2013. Cloud point-resistant adhesives and laminates. United States Patent. US 8361632 B2.

Feldstein, M. M., Bovaldinova, K. A., Bermesheva, E. V., Moscalets, A. P., Dormidontova, E. E., Grinberg, V. Y., Khokhlov, A. R. 2014. Thermo-Switchable Pressure-Sensitive Adhesives Based on Poly (N-vinyl caprolactam) Non-Covalently Cross-Linked by Poly (ethylene glycol). Macromolecules. 40: 5759-5767.

FitzGerald, K. P., Nairn, J., Skennerton, G., Atrens, A. 2006. Atmospheric corrosion of copper and the colour, structure and composition of natural patinas on copper. Corrosion Science. 48(9): 2480-2509.

Fuji Keizai. 2011. Special Adhesives and Passivation Materials · Market Outlook and Application 2012. Tokyo.

Gijsman, P., Verdun, F. 2001. The influence of polymer type, stabilizers and sample geometry on the relationship between chemiluminescence and oxygen uptake. Polymer Degradation and Stability. 74(3): 533-542.

Jaczuk, B., Biaopiotrowicz, T., Zdziennicka, A. 1999. Some Remarks on the Components of the Liquid Surface Free Energy. Journal of Colloid and Interface Science. 211(1): 96-103.

Joo, H.-S., Do, H.-S., Park, Y.-J., Kim, H.-J. 2006. Adhesion performance of UV-cured semi-IPN structure acrylic pressure sensitive adhesives. Journal of Adhesion Science and Technology. 20(14): 1573-1594.

Kaczmarek, H., Szalla, A. 2006. Photochemical transformation in poly(acrylic acid)/poly(ethylene oxide) complexes. Journal of Photochemistry and Photobiology A: Chemistry. 180(1-2): 46-53.

Katakami, E. 2010. Photocurable resin composition for laminating optically functional material. Japan Patent. WO 2010/027041 A1.

Kim, S., Lee, S.-W., Lim, D.-H., Park, J.-W., Park, C.-H., Kim, H.-J. 2013. Optical properties and adhesion performance of acrylic PSAs; influence of functionalized monomer and curing agent. Journal of Adhesion Science and Technology. 27(21): 2265-2277.

Kowalski, A., Czech, Z., Byczyński, Ł. 2013. How does the surface free energy influence the tack of acrylic pressure-sensitive adhesives (PSAs)? Journal of Coatings Technology and Research. 10(6): 879-885.

Lau, K. K., Gleason, K. K. 2006. Initiated chemical vapor deposition (iCVD) of poly (alkyl acrylates): an experimental study. Macromolecules. 39(10): 3688-3694.

Lee, S.-W., Park, J.-W., Kwon, Y.-E., Kim, S., Kim, H.-J., Kim, E.-A., Woo, H.-S., Swiderska, J. 2012. Optical properties and UV-curing behaviors of optically clear semi-interpenetrated structured acrylic pressure sensitive adhesives. International Journal of Adhesion and Adhesives. 38: 5-10.

Lee, S.-W., Park, J.-W., Park, C.-H., Kim, H.-J. 2014. Enhanced optical properties and thermal stability of optically clear adhesives. International Journal of Adhesion and Adhesives. 50: 93-95.

Lee, S.-W., Park, J.-W., Park, C.-H., Kwon, Y.-E., Kim, H.-J., Kim, E.-A., Woo, H.-S., Schwartz, S., Rafailovich, M., Sokolov, J. 2013. Optical properties and UV-curing behaviors of optically clear PSA-TiO_2 nano-composites. International Journal of Adhesion and Adhesives. 44: 200-208.

Lin, Y., Chen, X., Zhang, H., Wang, Z. 2006. Effects of hygrothermal aging on epoxy-based anisotropic conductive film. Materials Letters. 60(24): 2958-2963.

Maeda, Y., Nakamura, T., Ikeda, I. 2002. Hydration and phase behavior of poly (N-vinylcaprolactam) and poly (N-vinylpyrrolidone) in water. Macromolecules. 35(1): 217-222.

Mitra, S., Ahire, A., Mallik, B. 2014. Investigation of accelerated aging behaviour of high performance industrial coatings by dynamic mechanical analysis. Progress in Organic Coatings. 77(11): 1816-1825.

Moshaverinia, A., Chee, W. W., Brantley, W. A., Schricker, S. R. 2011. Surface properties and bond strength measurements of N-vinylcaprolactam (NVC)-containing glass-ionomer cements. The Journal of prosthetic dentistry. 105(3): 185-193.

Mun, G. A., Nurkeeva, Z. S., Dergunov, S. A., Nam, I. K., Maimakov, T. P., Shaikhutdinov, E. M., Lee, S. C., Park, K. 2008. Studies on graft copolymerization of 2-hydroxyethyl acrylate onto chitosan. Reactive and Functional Polymers. 68(1): 389-395.

Nitto Denko 2014. "Adhesive Design Technology." from http://www.nitto.com/rd/base/adhesive/specificat/.

Novikov, M. B., Roos, A., Creton, C., Feldstein, M. M. 2003. Dynamic mechanical and tensile properties of poly(N-vinyl pyrrolidone)–poly(ethylene glycol) blends. Polymer. 44(12): 3561-3578.

Park, C.-H., Lee, S.-W., Park, J.-W., Kim, H.-J. 2013. Preparation and characterization of dual curable adhesives containing epoxy and acrylate functionalities. Reactive and Functional Polymers. 73(4): 641-646.

Park, E.-S., Park, J.-W., Kim, H.-J. 2012. Adhesive and Pressure Sensitive Adhesive Materials for Displays. Polymer Science and Technology. 23(1): 47-60.

Peykova, Y., Lebedeva, O. V., Diethert, A., Müller-Buschbaum, P., Willenbacher, N. 2012. Adhesive properties of acrylate copolymers: Effect of the nature of the substrate and copolymer functionality. International Journal of Adhesion and Adhesives. 34: 107-116.

Pfeffer, A., Mai, C., Militz, H. 2012. Weathering characteristics of wood treated with water glass, siloxane or DMDHEU. European Journal of Wood and Wood Products. 70(1-3): 165-176.

Ruiz-Rubio, L., Vilas, J. L., Rodríguez, M., León, L. M. 2014. Thermal behaviour of H-bonded interpolymer complexes based on polymers with acrylamide or lactame groups and poly(acrylic acid): Influence of N-alkyl and α-methyl substitutions. Polymer Degradation and Stability. 109: 147-153.

Rychlý, J., Lattuati-Derieux, A., Lavédrine, B., Matisová-Rychlá, L., Malíková, M., Csomorová, K., Janigová, I. 2011. Assessing the progress of degradation in polyurethanes by chemiluminescence and thermal analysis. II. Flexible polyether- and polyester-type polyurethane foams. Polymer Degradation and Stability. 96(4): 462-469.

Rychlý, J., Matisová-Rychlá, L., Csomorová, K., Janigová, I., Schilling, M., Learner, T. 2011. Non-isothermal thermogravimetry, differential scanning calorimetry and chemiluminescence in degradation of polyethylene, polypropylene, polystyrene and poly(methyl methacrylate). Polymer Degradation and Stability. 96(9): 1573-1581.

Rychlý, J., Rychlá, L., Stloukal, P., Koutný, M., Pekařová, S., Verney, V., Fiedlerová, A. 2013. UV initiated oxidation and chemiluminescence from aromatic–aliphatic co-polyesters and polylactic acid. Polymer Degradation and Stability. 98(12): 2556-2563.

Socrates, G. 2004. Infrared and Raman characteristic group frequencies: tables and charts. John Wiley & Sons,

Spěváček, J., Dybal, J., Starovoytova, L., Zhigunov, A., Sedláková, Z. 2012. Temperature-induced phase separation and hydration in poly(N-vinylcaprolactam) aqueous solutions: a study by NMR and IR spectroscopy, SAXS, and quantum-chemical calculations. Soft Matter. 8(22): 6110-6119.

Toyama, Y., Inoue, S., Nagata, M., Hosokawa, T. 2011. Pressure-Sensitive Adhesive Composition for Optical Films, Pressure-Sensitive Adhesive Optical Film and Image Display. United States Patent. US 7862888 B2.

Walters, K. B., Hirt, D. E. 2006. Grafting of end-functionalized poly(tert-butyl acrylate) to poly(ethylene-co-acrylic acid) film. Polymer. 47(19): 6567-6574.

Wang, J., Wang, L. 2006. The lower surface free energy achievements from ladder polysilsesquioxanes with fluorinated side chains. Journal of Fluorine Chemistry. 127(2): 287-290.

Wang, P., Pan, C.-Y. 2002. Preparation of styrene/acrylic acid copolymer microspheres: polymerization mechanism and carboxyl group distribution. Colloid and Polymer Science. 280(2): 152-159.

Wang, X., Nilsson, D., Norberg, P. 2013. Printable microfluidic systems using pressure sensitive adhesive material for biosensing devices. Biochimica et Biophysica Acta. 1830(9): 4398-4401.

Yan, Z., Luo, Y., Deng, Y., Schork, J. 2004. Water-soluble/dispersible cationic pressure-sensitive adhesives. II. Adhesives from emulsion polymerization. Journal of Applied Polymer Science. 91(1): 347-353.

Yi, D. 2013. Touch Panel Report - OCA/OCR for Touch Panel - 2013. IHS.

초 록

터치 스크린 패널의 사용은 스마트폰의 등장 이래 빠른 속도로 증가하여 노트북 컴퓨터, 태블릿 PC, 모니터 등 현재 많은 전자기기에서 채용되고 있으며 이를 조립하기 위해서는 광학용 접착소재가 필수적이다. 터치 스크린 패널에서 광학용 접착소재가 사용되는 부분은 주로 투명 전극과 최상층의 커버 윈도우 및 디스플레이 모듈 사이이다. 이러한 광학용 접착소재는 대다수가 무용제 타입으로서 UV 경화를 통해 제조되며, 터치 패널의 구조상 디스플레이 모듈로부터 재현되는 화면이 광학용 접착소재를 통과하여 사용자의 눈에 들어오기 때문에 우수한 투명성이 필요로 되어 아크릴계 고분자가 주로 사용된다.

광학용 접착소재에 요구되는 물성은 상기 언급한 이유로 인한 가시광선 투과율 90% 이상의 고투명성과 더불어 적절한 접착물성 및 내구성, 투명 전극에 대한 내식성, 운점 저항성 등이다.

현재 터치 패널의 구조는 대부분 정전용량 방식이 사용되고 있으며, 이 경우 광학용 접착소재는 투명전극과 맞닿게 되므로 접착소재가 투명전극에 영향을 끼쳐서는 안 된다. 투명전극의 손상은 터치 패널의 구동과 밀접한 관련이 있기 때문이다. 일반적으로 아크릴계 접착소재에 응집력을 부여하기 위해 포함되는 아크릴산의 경우, 카르복실 그룹으로 인한 산 성분 때문에 투명전극이 영향을 받아 투명전극의 저항이 변화될 위험이 있어 산 성분은 배제되어야 한다.

또한 운점 저항성은 접착소재가 어떠한 환경에서도 탁도가 증가하는 일 없이 투명함을 유지하는 성질을 의미하며, 탁도 증가 현상은 특히 고온 고습 조건에 접착소재가 노출되었다가 갑자기

상온 조건으로 돌아왔을 때 관찰될 수 있다. 운점 저항성을 접착소재에 부여하기 위해서는 친수성 성분을 도입하는 것이 효과적이라고 알려져 있는데, 이는 고온 고습 조건에서 접착제 내부로 흡수되었던 수분을 고르게 분산시킬 수 있기 때문이다.

따라서 본 연구에서는 아크릴계 광학용 접착소재를 제조함에 있어 산 성분을 배제시키면서 응집력을 부여하기 위해 N-비닐 카프로락탐 (NVC) 모노머를 도입하였으며, 그 함량에 따라 접착물성 및 투명 전극의 부식에 미치는 영향을 살펴보면서 적절한 함량을 찾고자 하였다. 특히 접착소재가 투명 전극의 저항 증가에 미치는 영향을 알아보기 위한 방식은 간편하면서도 경제적인 간접적 측정 방법으로서, 전도성 기재인 구리 호일에 경화된 점착필름을 부착시켜 고온 고습 조건에 노출시킴에 따라 나타나는 구리 호일의 색깔 변화를 관찰하여 부식에 영향을 미치는지의 여부를 알아보고자 하였다. NVC 의 함량이 증가함에 따라 택과 접착력이 증가하였으며, 고온 고습 조건에 노출시킨 노화 시간이 길어질수록 20 wt% 이상의 함량에서는 구리 호일의 색이 변화됨과 동시에 8 주 후에는 접착력도 크게 저하되었는데 이는 유리 기재에서 더욱 확연한 경향을 보였다.

이후, 접착력이 가장 높았던 20 wt% 의 NVC 를 함유한 조성의 베이스 레진에 대하여 운점 저항성을 부여하기 위한 친수성 그룹을 도입하였으며, 분자량이 상대적으로 큰 올리고머 계열과 분자량이 작은 모노머 계열의 두 가지 소재를 선택하였다. 올리고머 계열은 메톡실레이티드 폴리에틸렌글리콜 모노아크릴레이트 (PEGA), 모노머 계열은 2-하이드록시에틸 아크릴레이트 (HEA) 를 선정하여 도입함으로써 같은 친수성 소재일지라도 접착물성 및 노화 거동에 어떤 변화를 야기하는지 고찰하고자 하였다. 두 성분 모두 운점

저항성을 부여하는 데에 효과가 있었으나, 모노머 성분인 HEA 의 효과가 더 좋게 나타났다.

올리고머 성분인 PEGA 의 경우, 2 phr의 함량까지는 택 및 접착력이 증가하였으나 그 함량이 증가할수록 택과 접착력이 감소하는 현상을 보였다. 투명 전극에 끼치는 영향 또한 PEGA 도입을 통해 크게 감소시킬 수 있었지만 20 phr 에서는 구리 호일의 변색을 보여 너무 많은 양의 친수성 성분은 투명전극에 영향을 끼칠 수 있음을 확인하였다. PEGA 가 도입된 점착필름의 노화 후 접착력은 감소하다가 일시적으로 증가하는 현상을 보여주었으며 이는 고분자 사슬의 절단으로 인한 젖음성 향상 때문으로 사료된다. 또한 PEGA 에는 상대적으로 에테르 그룹이 많아 이로 인해 산화에 취약한 모습을 보여 이것이 물성의 저하로 이어진 것으로 추측된다.

반면 모노머 성분인 HEA 의 경우, 5 phr 의 함량까지는 택 및 접착력이 증가하였으며 10 phr 이상부터는 감소 경향을 보였으나 그 값이 충분히 광학용 접착소재로서 쓰일 수 있을만한 수준이며, 노화 후에도 접착력이 크게 저하되지 않으면서 노화 전과 비슷한 수준을 나타내었다. 또한 HEA 를 도입함으로써 PEGA 와 마찬가지로 전도성 기재에 대한 영향을 확연히 낮출 수 있었다. 화학발광분석법의 결과에 따르면 PEGA 가 도입된 점착필름에 비해 HEA 가 도입된 점착필름은 훨씬 낮은 시그널을 보여 산화에 안정한 성질을 보여주었으며, 라만 스펙트럼을 통한 두께방향 프로파일링 결과로부터 표면보다 필름 내부에서 노화로 인한 반응이 활발하게 일어나 계면현상인 접착력에는 큰 영향을 미치지 않은 것으로 추정되었다. 이와 더불어, 점착제의 노화에 따른 에스테르 그룹의 가수분해나 산화로 인한 카르보닐 그룹의 증가, 사슬 절단 등의 반응은 제조된 점착제들에서 공통적으로 관찰되었다.

따라서 광학용 접착소재로 쓰이기 위한 점착제에의 운점 저항성 부여 및 투명 전극에 미치는 영향, 노화 거동 등을 종합적으로 고려하였을 때, 분자량이 큰 친수성 그룹보다는 분자량이 작은 모노머 형태의 친수성 소재가 안정하면서도 우수한 접착 물성을 구현 가능한 것으로 판단되었다.

주요어: 광학용 점착제, 터치 스크린 패널, 아크릴계 점착제, 비산성, 운점 저항성, 친수성 성분, 접착 물성, 노화 특성

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