

Evaluation of UV-curability of Photo-curable Materials for Acid Free Pressure Sensitive Adhesive

Ji-won Park, Sueng-Woo Lee, Young-Min Yoo, Hyun-Woo Chung,
Won-Bum Jang and Hyun-Joong Kim[†]

*Program in Environmental Materials Science, College of Agriculture & Life Science,
Seoul National University, Seoul 151-921, South Korea*

In general, pressure-sensitive-adhesive (PSA) is distinct from commonly used an adhesive material. There are many useful benefits, PSA are applied in many fields. A using of PSA are expanding on electrical and electronic product, especially PSA are used as a very important material in the field of touch screen panel (TSP). PSA is posted a indium tin oxide (ITO) films that patterned ITO layer. To preserve the layer, the existing PSA which contains acid are replaced by acid-free PSA. In order to synthesize acid free PSA, acrylic acid (AA) is replaced by the 2-ethylhexyl acrylate (2-HEA), glycidyl methacrylate (GMA) and isobonyl acrylate(IBA). To improve cohesion of acid-free PSA, two different methods, - self-crosslinking system and IPNs-system-, are introduced. Self-crosslinking system is hard method compared to the IPNs-system, but there is no residue and the system showed excellent properties.

Keywords : Pressure sensitive adhesive, Acid free, self-crosslink, IPN

1. Introduction

Compared to conventional adhesives, pressure-sensitive adhesives (PSAs) offer many advantages allowing quick, easy, and automatic procedures and thus they can be used in a wide variety of application. However, durable temperature range of PSA is limited, because its internal cohesion is relatively weak. If temperature is too high, PSA can be oozed out of substrates and bubbles can be formed inside the adhesives. This problematic feature causes a serious damage to end product [1~4].

General adhesive are composed of soft-segment and hard-segment. Roles of soft-segment are implement of flexible polymer chain and excellent wetting properties. Roles of hard-segment are implement of strong-cohesion and good adhesion. The materials as 2-EHA, n-BA, IOA, IDA are used in soft-segment and AA, GMA, HEA are used in hard-segment. Especially, AA has containing carboxyl functional group, therefore PSA containing AA has a strong-cohesion,

excellent adhesion and excellent crosslinking reactivity. However, because surface of the PSA shows acidic properties, this PSA oxidizes the surface of substrate. These reactions are particularly important in areas such as touch screen panel (TSP).

Table 1. Base composition of acid free PSA

Material	Ratio(w%)	Role
2-Ethylhexyl Acrylate	66.7	Soft segment
Isobonyl Acrylate	10.0	Hard segment
2-Hydroxyethyl Acrylate	10.0	Hydrogen bond to substrate
Glycidyl methacrylate	13.3	Reactive site

ITO thin film is assembled by the PSA. The ITO is corroded by the PSA and the lifetime of product is decreased. Therefore, acid free PSAs are required, and new materials that alternate AA are needed to improve strong-cohesion, excellent

adhesion and excellent crosslinking reactivity. To improve the internal cohesion of the adhesive, there are two major methods. First method is to use a crosslinking agent that forms chemical linkage between linear polymers as shown in Figure 1a. With a crosslinking agent added simply, cohesion strength can be greatly enhanced. But this method provides too short pot-life of application process and performance of original materials can be seriously degenerated. Furthermore, as an alternative method, there is an entanglement method. In this method, new polymer chains are created between the networks of existing polymers, resulting in semi-IPN (semi-interpenetrating polymer network) structures (Figure 1b) [5~7]. This method is commonly processed by UV/EB technology and the pot-life and performance of adhesives is relatively controllable.

2. Experimental

2.1. Synthesis of base pre-polymer

Base pre-polymers for PSA by entanglement method were prepared by solution polymerization (50% solid content). The typical procedure was as follows: 100 g of 2-EHA, 15 g of IBA, 15g of 2-H EA, 20g of GMA, 0.45 g of dimethyl 2,2' - azobis(isobutyrate) and 150 g of ethyl acetate (EAc) were mixed in a 500-ml four-neck flask equipped with overhead stirrer, a dropping funnel and a thermo-meter. The mixture was heated to 70 °C with stirring. After the exothermic reaction was completed, the temperature was maintained for 30 min. Then dimethyl 2,2' - azobis(isobutyrate) (0.15 g) in EAc (50 g) was added and the reaction mixture was stirred for 3 h. Afterwards, another dimethyl 2,2' - azobis(isobutyrate) (0.15 g) in EAc (25 g) was added and the reaction continued for 2 h to give base pre-polymer for PSA.

Table 2. Composition of UV curable acid free PSA (Self cure type)

Sample Name	Base PSA	Acrylic Acid(phr)	2-Carboxyethyl Acrylate (phr)	HP-8 (phr)
AF-AA	100	6		0.12
AF-2CEA	100		14.4	0.3

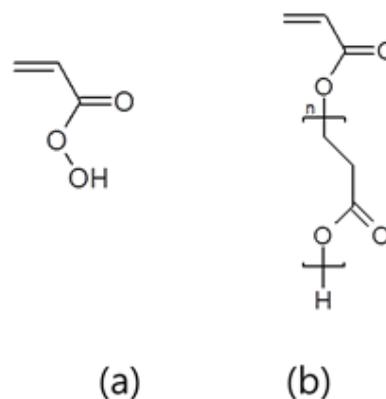


Fig. 1. (a) acrylic acid (b) 2-carboxyethyl acrylate

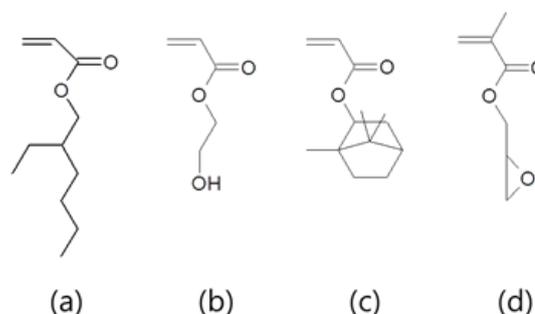


Fig. 2. (a) 2-ethylhexyl acrylate (b) 2-hydroxyethyl acrylate (c) isobronyl acrylate (d) glycidyl methacrylate

2.2 Preparation of curable PSA sample

For prepare self-crosslinking PSA, 100 g of base PSA and 6 g AA/14.4g 2-CEA were mixed in a 500-ml four-neck flask equipped with a overhead stirrer, a dropping funnel and a thermometer. The mixture was heated to 75 °C with stirring. And adding PI in synthesized PSA before coating process [Table 2].

For investigation of UV-curing behaviors, samples were prepared adding 5 phr of HP-8 to TMPTA and TMP(EO)TA respectively [Table 3]. Then prepared samples were coated as 40 μm of coating thickness and heated at 70 °C in oven with 20minute. Conveyer belt type UV irradiator equipped with mercury lamp light source was used for UV curing and UV was irradiated at 100, 200, 400, 800, 1600 mJ/cm² of light intensity.

Table 3. composition of UV curble acid free PSA (IPNs type)

Sample Name	Base PSA	TMPTA	TMP(E09) TA	HP-8(phr)
AF-I001	100	11.1	0.0	0.6
AF-I002	100	25.0	0.0	1.3
AF-I091	100	0.0	11.0	0.6
AF-I092	100	0.0	25.0	1.3

2.3 Test

2.3.1. FT-IR

IR spectra were recorded using a Jasco 6100 series FTIR spectrometer (Jasco, Japan) equipped with an attenuated total reflectance (ATR) accessory. To obtain the IR spectra of the UV-curable PSAs, each PSA was cut into 1 × 1 cm² pieces. The thickness of PSAs is not important in the ATR method, so it was not measured. It had a transmission range from 400 to 4000 cm⁻¹. The resolution of the spectra recorded was 4 cm⁻¹.

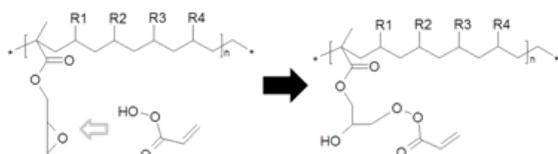


Fig. 3. Epoxy-carboxylic acid reaction in pendant of PSA main chain

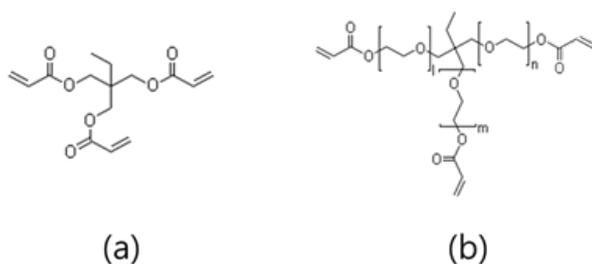


Fig. 4. Entanglement agent in IPNs system (a) TMPTA (b) TMP(E0)9TA

2.3.2. Photo-DSC

Photo-DSC experiments were conducted using a TA Instruments Q-1000 DSC equipped with a photo-calorimetric accessory, which used light from a 100 W middle-pressure mercury lamp. Light intensity was determined by placing an

empty DSC pan on the sample cell. UV light intensity at the sample was 40 mW/cm² over a wavelength range of 300–545 nm. The weight of the sample was about 3 mg and the sample was placed in an open aluminum DSC pan. Measurements were carried out at 25 °C.

2.3.3. Peel test

The specimen was cut into 25 mm width, attached to stainless steel substrate and pressed 2 times (2.7 km/in) on stainless steel using rubber roller (2 kg). The measurements were carried out at an angle of 180° with a crosshead speed of 300 mm/min at 20 °C based on ASTM D3330. The force was recorded in g during seven different runs, and the average value was reported in g/25mm.

2.3.4. Probe Tack

The tack measurements of the PSAs were carried out using a TA-XTi Texture Analyzer (Texture Technologies Co., UK) at 20 °C with a probe tack consisting of a polished stainless steel (type 304) sphere-shape probe. It was performed at a debonding speed of 0.5 mm/s, a constant pressure of 100 g/cm² and a swell time of 1 second.

3. Result

3.1. Self-crosslinkable PSA

To synthesize self - cross-linked PSA, AA and 2-CEA were used. To verify the sunthesis of each material pended to main chain of PSA, FT-IR is measured. Hydroxyl bond structure was confirmed by disappearing of epoxy bond [Figure 5]. Disappearing structures of epoxy are founded at 1250, 910, 790 cm⁻¹ of FT-IR measurement. When AA was used, changings of absorption line was founded at 1250, 950 cm⁻¹ [Figure 5]. Also, peak of carboxylic acid are appeared at 1750, 3000 cm⁻¹ and the peak is decreased by increasing reaction time. However, when 2-CEA is introduced to PSA; changings of peak line are very small in the entire graph. There is a lack of miscibility between ester of 2-CEA which is repeated in the pending chain and AF-PSA. So, there are no reactions with these materials. Haze that caused by mixing two materials can be also

interpreted the same result.

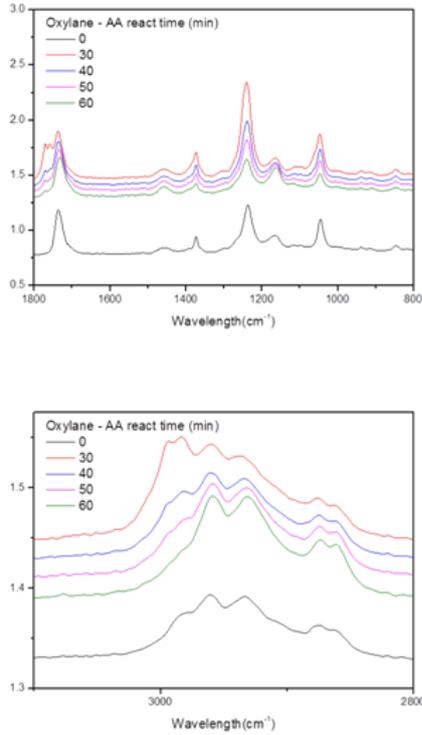
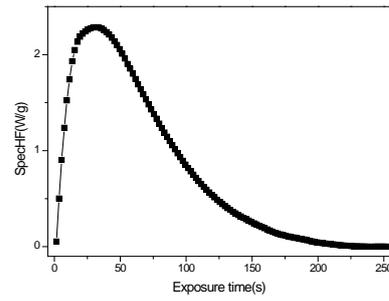


Fig. 5. FT-IR result of react between carboxylic acid and epoxide group in self-crosslinking PSA

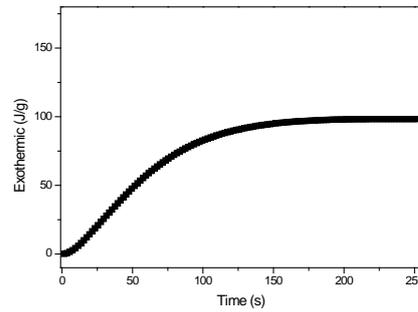
Figure 6-a is result of analyzing photo reactivity of self-cross-linked adhesive by photo-DSC. Photo-DSC can be measured exothermic heat flow in the process of combining C=C double bond by free-radical reaction. The weight of AA in entire wetting-PSA is only 2.34%.

Figure 6-b is recalculated result of photo reaction rate of AA participation in the PSA. When this result compared with conventional UV-curable adhesive, the reaction rate (whole reaction time: 4 min) is very slow. Therefore, degree of freedom of C=C structure of acrylate pended with PSA chain that has larger molecule weight than general UV-curable materials is low. Based on these results, chain reaction of C=C structure pended with PSA is confirmed, although the reaction is slow.

Figure 7 is PSA performance of self-crosslinkable PSA. At peel test, AAP(PSA that contain AA) show interfacial failure mode in all cases. While 2-CEAP(PSA that contain

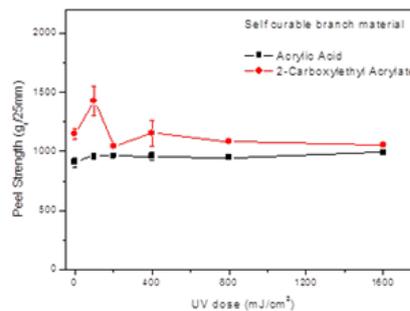


(a)

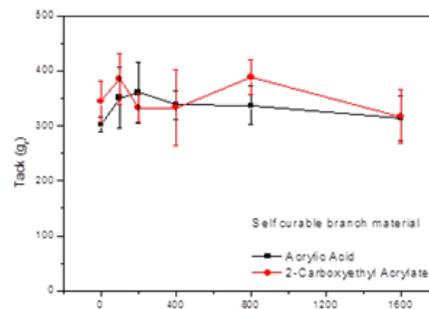


(b)

Fig. 6. Photo reactivity of self-crosslinking PSA by photo-DSC (a) specific heat flow (b) exothermic area



(a)



(b)

Fig. 7. Performance of self-crosslinking PSA (a) peel test (b) tack test

2-CEA) show cohesion failure. The reaction between polymers of low molecular weight is occurred by UV exposure. The reaction makes intermolecular networks and effect on improving the properties. As a result, the properties of the AAP are increase by UV increasing.

The other hand, 2-CEAP has unreacted monomer, the monomer are reacted by UV irradiation independent of base PSA. Miscibility between new molecules chains produced by the reaction and base PSA were poor. And mono-functionality monomer is not suitable for IPN. So, the reaction is not expected for methods of crosslinking between intermolecular. As a result, despite the hardening process, the fracture mode is not changed.

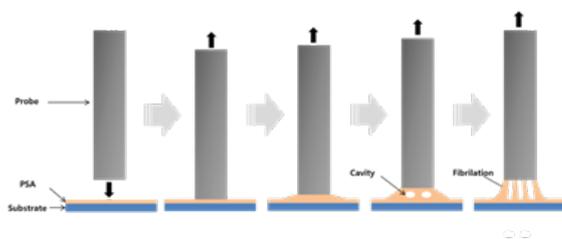


Fig. 8. Fracture scheme of track test

Results of track test show the similar results. Figure 8 shows a scheme where the process is the expression of fibrillation phenomena of PSA. When there are the lack of cohesion of adhesive, fibrillation phenomenon are caused in the tack in the experiment. Such as this phenomenon, substrate pollution and residual problem are caused. Tack of AAP is modest rise and decreased by progress of UV curing. Initially, increased levels of crosslinking between adhesive molecules will improve the cohesion. Since UV curing is more progressed, freedom of molecules mobility is decreased and wetting of the probe is also decreased. These results are the similar to the general trend of UV curable adhesive.[5-7]

2-CEAP shows no inclination results which include fibrillation phenomenon in the entire section. Based on these results, AA showed superior results for application to self-cure adhesive material adhesive.

3.2. IPNs system PSA

Properties of IPNs system adhesive are

controlled by degree of UV curing of entanglement agent. Two selection of the entanglement agents are TMPTA and the TMP (EO) TA. Each basic structure is the same, but three chains of TMP(EO)TA have ethoxylated structures. Because of these differences, each of the reaction may be different. In UV curing process, flexibility and degrees of freedom of UV-curing materials are very important. Because, these molecules are react with other materials in a fixed location. Ethoxylated structure of configure TMP(EO)TA also affects the flexibility and degree of freedom.

Table 4. Functionality numbers of UV-curable materials and PI per unit

Sample	Mw	Fn/ molecules	Fn/g (mole)	FN ratio (PI set=1)
Photo Initiator	164.21	2	0.0122	1
TMPTA	296.32	3	0.0101	0.83
TMP(EO)9TA	692.81	3	0.0043	0.36

Table 5. Functionality ratio between UV-curable materials and PI

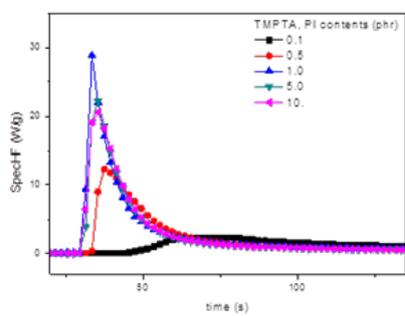
PI (phr)	Fn ratio in TMPTA		Fn ratio in TMP(EO)9TA	
	PI	TMPTA	PI	TMP(EO)9TA
0.1	0.12	100.00	0.28	100.00
0.5	0.60	100.00	1.41	100.00
1	1.20	100.00	2.81	100.00
5	6.02	100.00	14.06	100.00
10	12.03	100.00	28.13	100.00

Figure 9 is results of heatflow of TMPTA and TMP(EO)TA by P-DSC. To evaluate external factor of UV curing of TMPTA and TMP(EO)TA, UV-curability was measured by varying concentration of initiator.

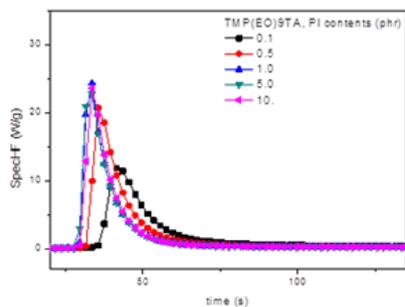
Generally, it is not easy to set an end point of UV-curing process. Testing time of P-DSC is set 100s, because the curing condition stands to fit for the self-crosslinkable PSA. Self-crosslinkable PSA are cured by 1600mJ/cm² of UV, and UV intensity

in the curing progress is 16mW. When the 0.1phr of initiator, curing speed is very slow, and a peak of the curing reaction rate is difficult to distinguish. However, the amount of initiator is increased over 0.5phr, the cure rate is rapidly increased. But, if the amount is more than 1.0 phr of initiator, curing rate does not increase any more.

Figure 10 is exothermic area which is calculated based on the results of P-DSC. As in the result, heat flow is increased by increasing amount of initiator. But above 1.0phr, exothermic is not increased. Table 4 is the value-number of functional groups based on unit mass of photo initiator, TMPTA and TMP(EO)TA.



(a)

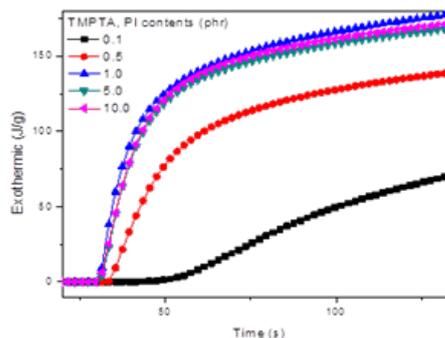


(b)

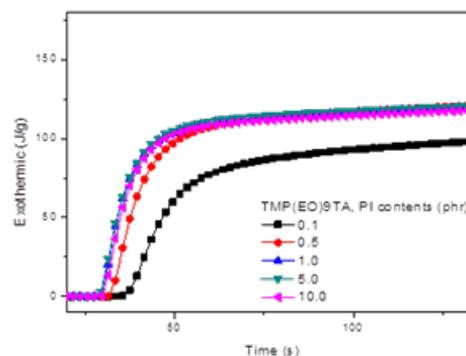
Fig. 9. Specific heatflow of UV-curable materials (a) TMPTA (b) TMP(EO)9TA

Table 5 is the ratio of functionality between UV-curable monomer and photo initiator which are calculated based on values of Table 4. Based on the results, the functionality ratio of initiator and the exothermic area/peak of heat flow was re-plotted [Figure 11].

TMPTA and TMP (EO) 9TA tend to show the similar results. The result was combined at one graph and re-plotted by functionality ratio of

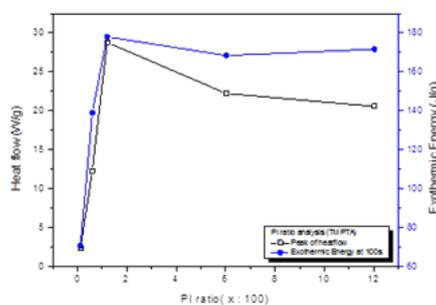


(a)

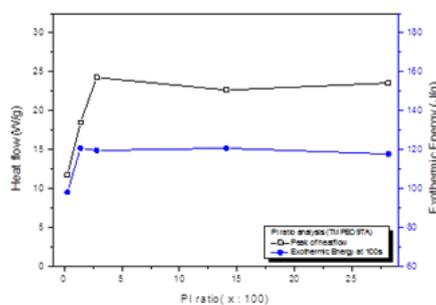


(b)

Fig. 10. Exothermic area (=integrate of heatflow) of UV-curable materials (a) TMPTA (b) TMP(EO)9TA



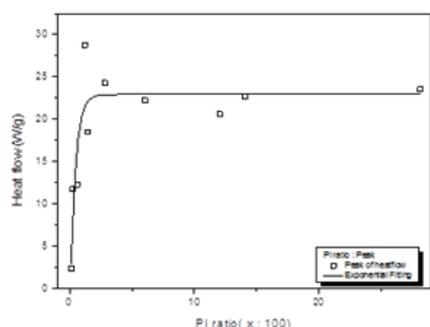
(a)



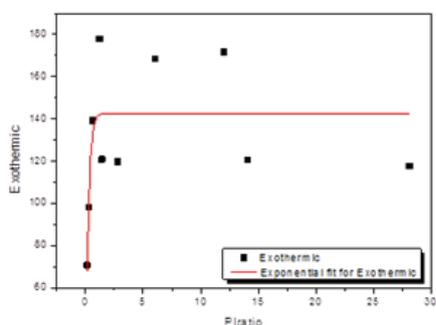
(b)

Fig. 11. Replotted graph with the functionality ratio of initiator and the exothermic are/peak of heat flow (a) TMPTA (b) TMP(EO)9TA

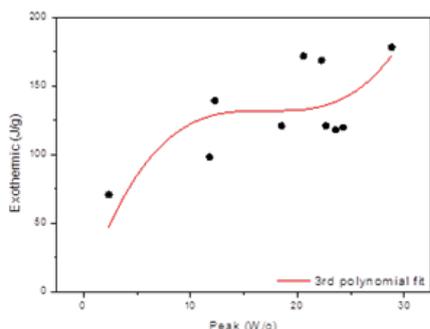
initiator [Figure 12]. There are exponential relation ($R_2 = 0.76$) between functionality ratio of initiator and peak of heat flow.



(a)



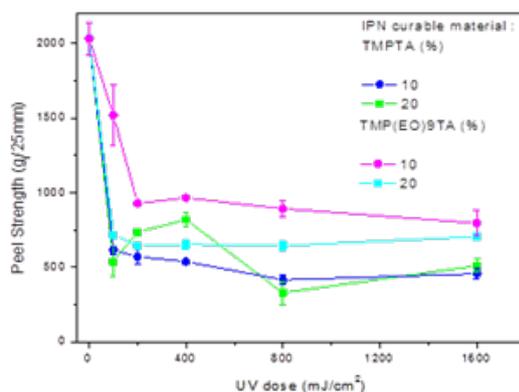
(b)



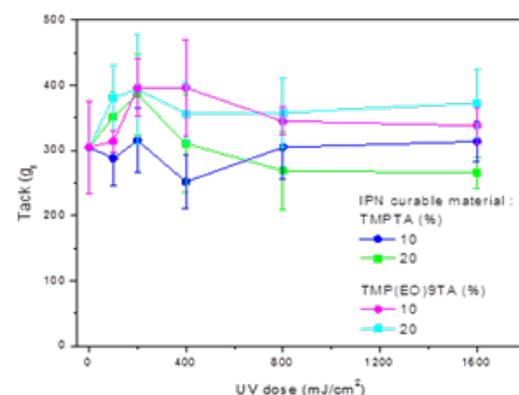
(c)

Fig 12. Fitting of PI ratio and photo-curable properties (a) spec. heatflow (b) exothermic area (c) spec. heatflow with exothermic area

Likewise, exponential relation ($R_2 = 0.39$) exist. in the between functionality ratio of initiator and exothermic area. Peak of heat flow and functionality ratio of initiator have great relevance, but functionality ratio of initiator and the exothermic area have not a great relationship.



(a)



(b)

Fig. 13. Performance of IPNs system introduced PSA (a) peel test (b) tack test

Peak of heat flow is associated with the instantaneous reaction rate, while exothermic area is associated with the overall conversion rate.

The conversion rate is dependent on not only functionality ratio of initiator but internal factors influenced by freedom of functional groups such as viscosity and molecule structure. Based on these results, examination of the relationship between heat flow and exothermic area shows a very high correlation (3rd polynomial fit, $R_2 = 0.96$) [Figure 12-(c)].

In this result, with increasing peak of heat flow, conversion ratio is highly increased. The result indicates that the amount of initiator greatly effects on the overall conversion. The ratio of initiator primarily influence to heat flow, and when the reaction rate is optimized, better conversion is

expected.

Figure 13 is properties of measurements of IPN system applied to acid-free adhesive. Peel result has the same tendency as the typical UV curable adhesive, because cured UV-curable material harms the movement of molecular chains of the PSA. Result of PSA containing 20% of TMPTA shows increasing once curve. At that time fracture mode is changed from cohesion to interfacial mode. TMP(EO)9TA is also enough to crosslink low-molecular weight PSA. As a result over the appropriate level, multifunctional monomers are need to realize entanglement system in PSA. Result of tack test also showed the evidences of both the cohesion failure.

4. Conclusion

To improve internal cohesion of acid-free adhesive, these experiments were preceded by introducing two kinds of system. Self-crosslinking of acrylic adhesive material can be synthesized and defined by FT-IR. In addition, UV curing speed is slowly compared with conventional UV cure adhesive, but they are self-crosslinked each other. Furthermore, application to OCA process are likely defined, because controlling of adhesive properties are easier than other's. IPN systems are typically used for UV cure adhesive system. UV-curable materials have different reactivity by the ratio between the number of functional groups and PI. And there are optimized ratios of number of functional groups and PI. Conversion of the material depends also on the ratio. However, IPNs applied acid-free adhesive properties are poor and not enough for cohesion. More precise relationship of reactivity of UV curing material and factors which effect on the properties can be determined by additional experiments.

References

[1] Hayashi, S.; Kim, H. J.; Kajiyama, M.; Ono, H.; Mizumachi, H.; Zufu, Z., *J. Appl. Pol. Sci.*, **71**, 651 (1999)

[2] Kim, H. J.; Hayashi, S.; Mizumachi, H., *J. Appl. Pol. Sci.*, **69**, 581 (1998)

[3] Kim, H. J.; Mizumachi, H. *J. Appl. Pol. Sci.*, **56**, 201 (1995)

[4] Satas, D. *Handbook of Pressure Sensitive Adhesive Technology*; Satas & Associates: New York, (1999)

[5] Do, H. S.; Kim, S. E.; Kim, H. J., *Preparation and Characterization of UV-Crosslinkable Pressure-Sensitive Adhesives in Adhesion-Current Research and Applications*; Wiley-VCH: Weinheim (2005)

[6] Hyo-Sook Joo, Young-Jun Park, Hyun-Sung Do, Hyun-Joong Kim, Si-Yong Song, Kil-Yeong Choi, "The curing performance of UV-curable semi-interpenetrating polymer network structured acrylic pressure-sensitive adhesives", *J. Adhesion Sci. Technol.*, **21**(7), 575~588 (2007)

[7] Hyun-Sung Do, Young-Jun Park, Hyun-Joong Kim, "Preparation and adhesion performance of UV-crosslinkable acrylic pressure sensitive adhesives", *J. Adhesion Sci. Technol.*, **20**(13), 1529~1545 (2006)

[8] Timothy F. Scott, Wayne D. Cook, and John S. Forsythe, "Photo-DSC cure kinetics of vinyl ester resins. I. Influence of temperature", *Polymer*, **43**(22), 5839-5845 (2002)

[9] Timothy F. Scotta, Wayne D. Cook, a, and John S. Forsythea, "Photo-DSC cure kinetics of vinyl ester resins II: influence of diluent concentration", *Polymer*, **44**(3), 671-680 (2003)

[10] Jung-Dae Cho and Jin-Who Hong, "Photo-curing kinetics for the UV-initiated cationic polymerization of a cycloaliphatic diepoxide system photosensitized by thioxanthone", *European Polymer Journal*, **44**(2), 367-374 (2005)

[11] Enos, H. I.; Harris, G. C.; Hedrick, G. W, *Encyclopedia of Chemical Technology*, 2nd ed.; Wiley: New York (1968)

[12] Das, S.; Maiti, S.; Maiti, M. J., *Journal of Macromolecular Science, Part A*, **17**, 1177 (1982)