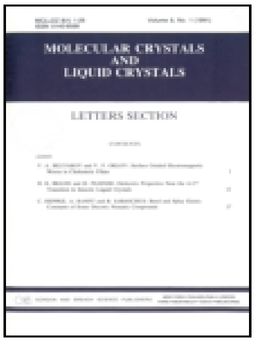


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Preparation and Characterization of UV Cured Optical Films Containing a Fluorene Compound

Jae Hwan Chun, Jung Mi Cheon, Boo Young Jeong & Nam-Ju Jo

To cite this article: Jae Hwan Chun, Jung Mi Cheon, Boo Young Jeong & Nam-Ju Jo (2015) Preparation and Characterization of UV Cured Optical Films Containing a Fluorene Compound, Molecular Crystals and Liquid Crystals, 622:1, 6-13, DOI: 10.1080/15421406.2015.1096491

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1096491

Mol. Cryst. Liq. Cryst., Vol. 622: pp. 6–13, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1096491

Preparation and Characterization of UV Cured Optical Films Containing a Fluorene Compound

JAE HWAN CHUN,[1,2] JUNG MI CHEON,[1] BOO YOUNG JEONG,[1] AND NAM-JU JO[2,*]

[1]Polymer Surface Research Team, Korea Institute of Footwear and Leather Technology, Pusan, Korea
[2]Department of Polymer Science Engineering, Pusan National University, Pusan, Korea

In this study, the high refractive coating films applicable for optical materials were produced. the conversion and the photo curing behaviors were examined through FTIR-ATR and photo-DSC, and thermal and mechanical properties of cured films were examined by using DMA and UTM, and pencil hardness, refractive index and optical transmittance of film were measured. Urethane metacrylate oligomer was synthesized by mixing bisphenoxyethanolfluorene (BPEF), polycaprolactone diol (PCL), and polytetramethylene ether glycol (PTMeG) in varying ratios. Also, as the results of mixing ethylene glycol phenyl ether acrylate (PHEA) and trimethylolpropanetriacrylate (TMPTA) in varying ratios, the more time UV irradiated, the higher conversion and the heat of enthalpy (ΔH) *and the initial curing rate increased with increasing TMPTA content up to 70%. Also, as the trifunctional monomer increased, the storage modulus and* T_g *increased, and the stress increased while the strain decreased to reach its maximum value. Also, as the BPEF ratio increased, the maximum value of stress increased while the strain decreased, the refractive index and pencil hardness increased, and light transmittance was all over 80%.*

Keywords UV cured film; Optical film; Refractive index

Introduction

The development of the coating technique for improving material's surface performance and functionality has been continued. Coating is the technique for protecting the substrates by forming the micro-thin coating thickness on the product's surface or giving new physical characteristics by reforming the substrates. Coating technique is considered the important method to implement traits or functionalities that is needed to certain industry fields. Especially, as the smartphone becomes popular, the demand for high level functionality of coating material has been increased in the industries like display, optical components, and precision electronic components [1–3].

As the concerns about environment and health has increased, the development of the reaction curing type and the solvent-free based on the VOCs(volatile organic compounds)

---

[*] Address correspondence to Prof. Nam-Ju Jo, Dept. of Polymer Science Engineering, Pusan National University, Busan 609-735, Korea. E-mail: namjujo@pusan.ac.kr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

free is accelerated, especially, instead of the VOCs, the study on photo curing using source lights that do not produce pollutants are in the process. In the industry fields, the UV curing is widely used and that kind of curing is excellent in performance per price, and energy consumption is low, and emits less VOCs, and curing equipment is simple, and the amount of heat applied to substrates is small, and after curing, it is available to make the materials excellent in chemical resistance and mechanical properties [4, 5].

Because compounds containing the acryl readily react with the radical formed by light and heat so that the polymerization occurs. Using this property, it is applied to the various optical coating and optical materials. Plastic lens, coating film of reflecting plate, optical film of BLU(back light unit) are common applications [6–8]. In the recent optical applications, as the optical materials used in holography, LCD(liquid crystal display) reflecting plate of back light unit, and prism sheet are needed to be high refractive, the development of the polymer with high refractive index is necessary. Though the polymer having high refractive index was mainly made by introducing the halogen substituents, there were environmental problems and material's malfunctions from deterioration by halogen. So, recently, interest in the aromatic compounds and the sulfur atoms introduced compounds is increasing [8–10].

Therefore, in this study, by synthesizing high refractive oligomer introduced the compounds containing fluorene of the aromatic ring compound, we prepared the material that can be used as the optical materials that is needed to be high refractive. In this study, we synthesized the urethane acrylate oligomers using polyols of the various contents with bisphenoxyethanolfluorene (BPEF) and by adding the reactive diluents with the various content and the number of functional group, we examined the photo curing behaviors, and thermal, mechanical, optical properties.

Experiment

Bisphenoxyethanolfluorene (BPEF, Mn = 438.51 g/mol, TCI), polycaprolactone diol (PCL, Mn = 2000 g/mol), polytetramethylene ether glycol (PTMeG, Mn = 1000 g/mol) were dried at 90°C under 1-2 mmHg for 3h before use. methylene-bis(4-cyclohexylisocyanate), dibutyltin dilaurate (DBTDL), 2-hydroxyethyl methacrylate, ethylene glycol phenyl ether acrylate (PHEA), trimethylolpropane triacrylate (TMPTA), diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO), 1-hydroxycyclohexyl phenyl ketone, were purchased from Sigma Aldrich. PET film of 40 μm thickness was supplied by SK Chemical (South Korea). Bisphenoxyethanolfluorene based urethane acrylate prepolymers were prepared in a two step synthesis. First, 1 mol of BPEF, PCL, PTMeG were mixed with 2 mol of methylene-bis(4-cyclohexylisocyanate) under vacuum at 80°C for 4 h for a complete reaction. The second step consisted of adding 2 mol 2-hydroxyethyl methacrylate below 60°C. With this stoichiometry, all the isocyanate groups reacted with 2-hydroxyethyl methacrylate as confirmed by the IR measurements (Table 1). A mixture of oligomer containing fluorene compound, a photoinitiator (TPO, 1-hydroxycyclohexyl phenyl ketone), and PHEA and TMPTA as reactive diluents were heated slightly above the ambient temperature to ensure homogeneous mixing. Coating compositions are shown in Table 2. Approximately 40 μm thick films were prepared by pouring the viscous liquid formulations onto a Teflon coated steel mold and UV curable coatings were coated onto a PET film using a bar coater and cured. UV curing of the coated films were carried out through the exposure of the samples in the following: a high-pressure mercury UV lamp (100 W/cm, main wavelength: 365 nm).

Table 1. Synthesis for fluorene based urethane methacrylate oligomers

	Composition					
	Molar ratio					
Sample code	PCL	PTMeG	BPEF	H_{12}MDI	2-HEMA	DBTDL
UABF 1	0.637	0.273	0.09	2	2	1∼2drop
UABF 2	0.539	0.231	0.23	2	2	1∼2drop
UABF 3	0.469	0.201	0.33	2	2	1∼2drop
UABF 4	0.413	0.177	0.41	2	2	1∼2drop
UABF 5	0.35	0.15	0.5	2	2	1∼2drop

Infrared spectra analysis was performed on a Nicolet FT-IR iS5 spectrometer in the 4 cm^{-1} resolution mode. 32 scans were averaged for each sample using an ATR (ZnSe crystal) apparatus. Photo-DSC analysis was performed using a DSC Q-1000 (TA Instrument, USA). The photo-DSC experiments were equipped with a photocalorimetric accessory (Novacure 2100 at NICEM, Seoul National University), which utilized light from a 100 W medium-pressure mercury lamp under a nitrogen atmosphere. The UV light intensity at the sample was 55 mW/cm^2 over the wavelength range, 300–545 nm. Mechanical properties of the films were determined by standard tensile stress–strain tests in order to measure the stress and strain at break. Stress–strain measurements were carried out at room temperature by using an universal testing machine (DTU-900MHA, extension rate of 500 mm/min). A DMA Q 800 (TA, USA) in the tension mode was used to acquire dynamic mechanical thermal analysis spectra. Samples were cut using an ASTM D1043 die with the ends cut to the proper length. The frequency of testing was 3 Hz. The temperature range tested was –100 to 100°C with a heating rate of 5°C/min. The pencil hardness of the UV-cured PUA films was determined by ASTM D 3363. Pencil hardness test was applied on coated PET films. UV-visible spectroscopy (V-670, Jasco) was used to examine the transmittance

Table 2. Composition of the UV-curing resins containing fluorene based urethane methacrylate oligomers (units in wt%, except in PI (phr))

		Monomer		Photo Initiator (phr)	
Sample code	Oligomer	PHEA	TMPTA	TPO	C-184
U1PT 30	60 (UABF 1)	28	12	5	0.5
U2PT 30	60 (UABF 2)	28	12	5	0.5
U3PT 30	60 (UABF 3)	28	12	5	0.5
U4PT 30	60 (UABF 4)	28	12	5	0.5
U5PT 0	60 (UABF 5)	40	0	5	0.5
U5PT 30	60 (UABF 5)	28	12	5	0.5
U5PT 50	60 (UABF 5)	20	20	5	0.5
U5PT 70	60 (UABF 5)	12	28	5	0.5
U5PT 100	60 (UABF 5)	0	40	5	0.5

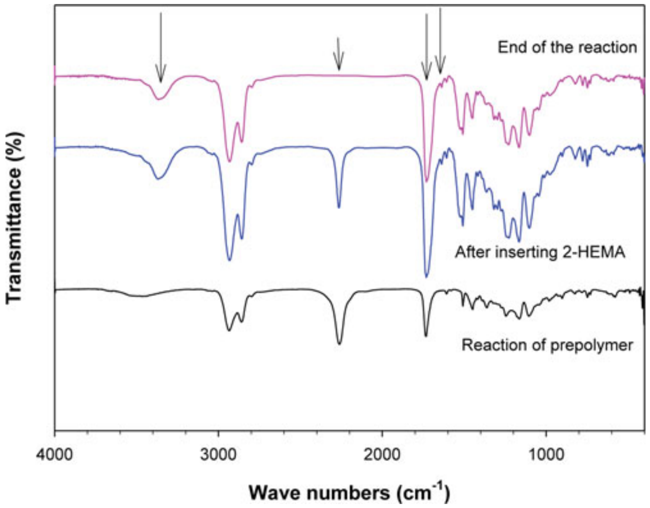
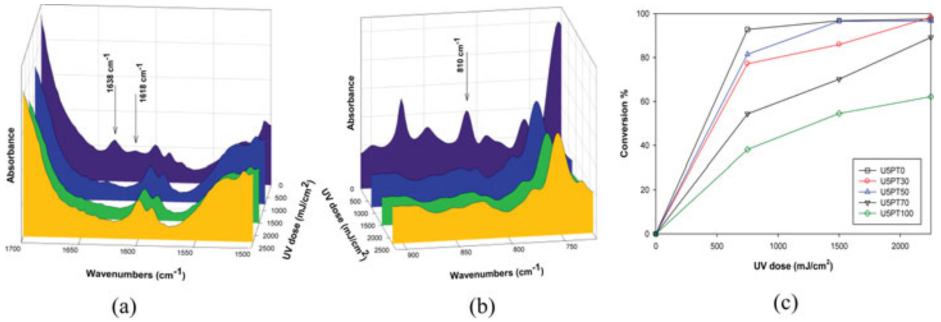


Figure 1. FTIR spectra of the synthesis reaction of the fluorene compound based the urethane methacrylate oligomer (UABF 4).

of the UV-cured films. The transmittance was determined to be in the visible range of 400–800 nm. The refractive index of the UV cured films were detected by using a prism coupler (SPA4000, Sairon, 632.8 nm laser). The prism and film were joined and the incidence angle of the laser beam was varied and so, the refractive index in both the thickness and plane directions can be determined.

Results and Discussion

To verify the synthesis of the urethane acrylate oligomer, FT-IR was measured (Figure 1). We found that the NCO peak of the isocyanate group disappear at 2270 cm^{-1} and the C=C peak of the acrylate group appear at both 1637 cm^{-1} and 1618 cm^{-1}. Also, the characteristic peak of C=O and N-H of urethane bond appeared at 1734 cm^{-1} and 3373 cm^{-1}, respectively. From that, we verified that urethane acrylate oligomer was well synthesized.



(a) (b) (c)

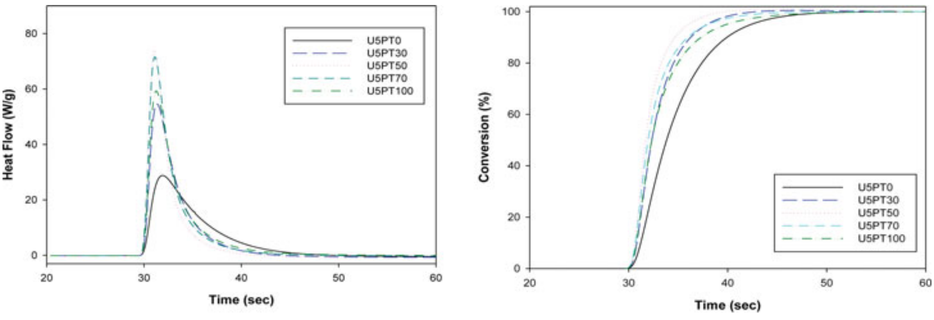
Figure 2. FTIR-ATR spectra of the UV-cured film (U5PT50) with different UV dose at (a) 1638 cm^{-1}, 1618 cm^{-1} and (b) 810 cm^{-1}, and (C) conversion of UV-cured film with the various reactive diluent contents and UV dose.

Figure 2 (a), (b) shows the change of the characteristic peak of the composition (U5PT50) which is using TMPTA as 50% of the reactive diluent, according to the dose of UV. Before irradiation, the peak of the C=C stretching band and the 810 cm^{-1} (C-H out of plane bending in C=C double bond) twisting band which are in the UV curable resin were measured at around 1,638 cm^{-1} and 1,618 cm^{-1}, it significantly decreased as the C=C bond of acrylate group broke with the radical photochemical reaction after irradiation. Also, we can see that the peak value of 1,638 cm^{-1} and 1,618 cm^{-1} decreased as an increasing UV dose, but it remained without extinction. It is because there were remained monomers couldn't be cured as the curing rate of the tirfunctional monomer TMPTA of reactive diluent was fast so that the external curing on the surface that was in contact with the air occurred in a very short time. Also, we investigated the photo curing behavior by measuring the conversion of the cured film according to the UV irradiation. The method of measuring the amount of the double bond existed in an acryl monomer by calculating the area of peak of 1,638 cm^{-1}, 1,618 cm^{-1}, 810 cm^{-1}

$$\text{Conversion of UV} - \text{cured group}\,(\%) = \frac{A_0 - A_t}{A_0} \times 100$$

was used, the conversion of the curing film according to the UV irradiation was calculated following equation below. A_0 is the area of each of absorption bands before the UV irradiation, and A_t is the area of each of absorption bands after the UV irradiation [11].

Figure 2 (c) shows the conversion factor of urethane acrylate resin according to the UV dose (range from 0 to 2250 dose). In the process of UV curing, the characteristic peak rapidly decreased, and variation of the conversion of 1,638 cm^{-1} and 1,618 cm^{-1} and the conversion of 810 cm^{-1}, according to the UV irradiation dose, are nearly similar. Also, as the ratio of TMPTA, the reactive diluent, increased to 0%, 30%, 50%, 70, 100%, the conversion were 99.5%, 99.1%, 98.6%, 96.8%, 57.4%, respectively. When only using the TMPTA, the conversion was the lowest, and as the content of TMPTA increased, the conversion decreased. The reason is assumed that as the content of trifunctional monomer increase, the C=C double bond remained unreactive by the photoinitiator locked in the crosslinked polymer network. Also, we can derive that the conversion did not reach 100%, in the all cases, the complete cure did not occured. This is because oxygen in the air stopped the radical reaction acting as the inhibitor.



(a) (b)

Figure 3. Photo-curing behaviors of UV-curing resins according to contents of reactive diluents: (a) heat flow and (b) conversion.

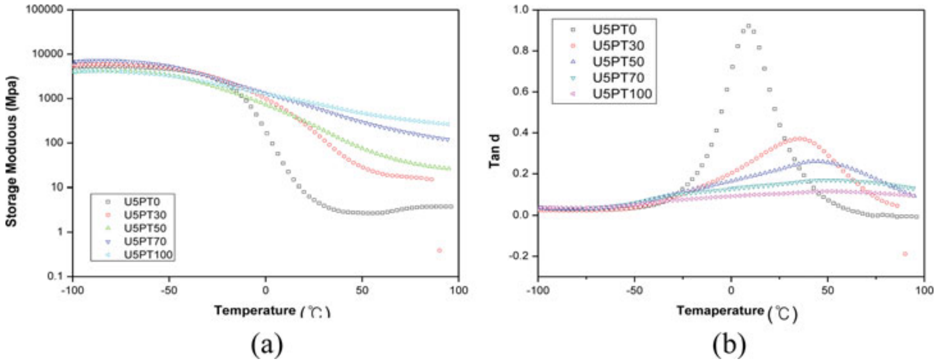


Figure 4. Viscoelastic property for UV-cured films with varying reactive diluent contents (a) storage modulus and (b) Tan d.

As shown in Figure 3, as the content of trifunctional monomer increased, the enthalpy radiated during photo curing gradually increased, and the highest value appeared when the content of TMPTA was 70%. The total enthalpy of U5PT0 and U5PT70 was 171.3 J/g and 208.2 J/g respectively. The more content of TMPTA, the shorter time of being value of the maximum curing peak, when the content of TMPTA was 0% and the content of PHEA was 100%, the maximum curing peak time was 31.87 sec, while the shortest time of maximum curing peak was 31.07 sec when TMPTA's content was 70% and PHEA's content was 30%. The rate of photo curing and the total enthalpy are not directly proportional to the amount of content of trifunctional monomer, but it decreases over the certain amount of content. As the trifunctional monomer increases, the content of the double bond per unit mass increases so that both the enthalpy and the initial curing velocity increase. But, if there are so many trifunctional monomer, the crosslinking density become so high, and that disturb for the photoinitiator to break the double bonds. This implies that the total enthalpy and the crosslinking rate decrease because the crosslinking reaction progress is hindered [12].

DMA was measured to investigate the effect of the cured film according to the ratio of reactive diluents on the viscoelasticity. As shown in Figure 4 (a), as TMPTA, the trifunctional monomer, increased, the value of storage modulus increased in the rubbery plateau. In other words, if trifunctional monomer increases, the cross linked density also

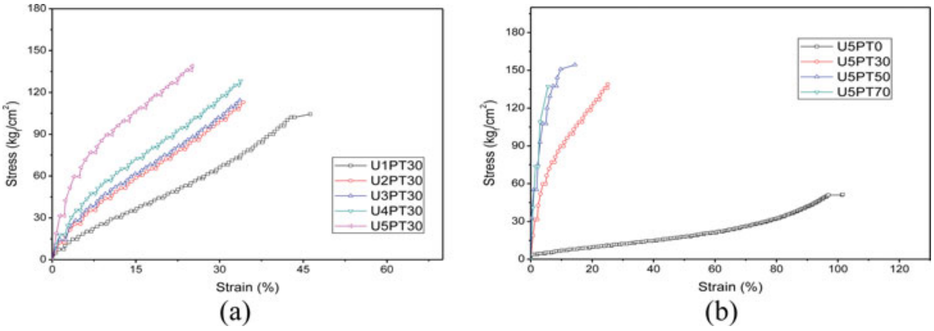


Figure 5. Stress and strain at break of UV-cured films.

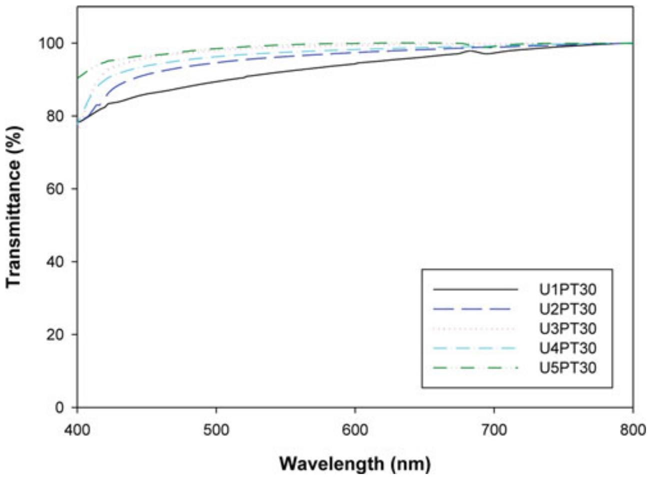


Figure 6. The transmittance of UV-cured films, 400-800 nm with contents of fluorene compound as a polyol in the urethane methacrylate.

increases. As the ratio of PEHA/TMPTA, the trifunctional monomer, increased like 100/0, 70/30, 50/50, 30/70, 0/100, respectively, and the Tg which was calculated maximum value of tan δ in Figure 4 (b) increased like 79°C, 35.38°C, 44.19°C, 49.88°C, 51.05°C, respectively. Also, as the trifunctional monomer increased, the value of tan δ decreased, and it appeared over the wide range. So, it is assumed that because cross linked structure disturbed the movement of the molecular chain, the maximum peak of tan δ moved to the high temperature and, the value of tan δ decreased [13].

As shown in Figure 5 (a), as BPEF content increased, the maximum stress increased while the strain decreased. it is assumed that the BPEF molecule is so strong that the stress increased and the strain decreased as BPEF content increased. Also, the mechanical property was examined according to the content of reactive diluents, as the ratio of the PHEA to the TMPTA decreased like 100:0, 30:70, 50:50, the stress increased while the strain decrease. Over 70% of the content of TMPTA, both stress and strain decreased, especially, at the 100% TMPTA content, the film was too hard that the stress couldn't be measure (Figure 5 (b)). We found out that if the content of TMPTA, the trifunctional reactive diluent, was over the particular ratio, the degree of crosslinking was too high that it formed the hard film and decreased the film's property. Also, by analyzing this result based on the FTIR-ATR spectrum and the result of the Photo-DSC, it is assumed that the existence of many monomers that were not cured made the conversion be lowered.

The pencil hardness of UV cured film which was coated on PET was measured. When synthesizing the polyurethane acrylate oligomer with increasing the BPEF ratio, the pencil hardness was much the same, and the range was from HB (U1PT30∼U3PT30) to 1H (U4PT30, U5PT30). Though it was the minute difference, it showed the tendency that as the BPEF content increased, the pencil hardness also increased.

The refractive index of the UV cured film manufactured according to the BPEF content was measured using the prism coupler. In this study, the wavelength was set to 632.8 nm, and the refractive index of the film whose thickness is about 23∼24 μm was measured. When synthesizing polyurethane acrylate oligomer, as the proportion of BPEF increased in the total polyol content, the refractive index increased to 1.502, 1.508, 1.515, 1.521, 1.528, respectively. The polyol containing fluorene group contains benzene ring compound which is the high refractive material. So, the refractive index increased as the content increased in this experiment.

Also, Figure 6 shows the result of measuring optical transmittance of UV cured film in the wavelength range from 400 nm to 800 nm. In the process of oligomer synthesizing, as the BPEF content of polyol increased, the optical transmittance increased a little.

Conclusion

In this study, urethane acrylate oligomer was synthesized according to the BPEF content and UV curable resin composition were manufactured according to the various PHEA and TMPTA mixing ratio. As the UV dose increased, the conversion also increased, and when using TMPTA only, the conversion was the lowest, and the more content of TMPTA, the lower the conversion. As TMPTA content increased, the heat of enthalpy increased gradually, when TMPTA content was 70%, it showed the highest heat of enthalpy and the fastest rate of UV curing. As TMPTA content increased, the storage modulus increased in the rubbery plateau, and the maximum of tan δ also increased. In terms of tensile property, as the BPEF ratio increased, the maximum value of stress increased and the strain decreased, and the stress increased until the TMPTA ratio became 50%. The pencil hardness of coated film on PET was in the range from HB to 1H, and as the BPEF ratio increased, the refraction index also increased. As the BPEF content of polyol increased, the optical transmittance increased.

References

[1] Cho, J. D., & Hong, J. W. (2005). *Eur. Polym. J.*, *41*, 367.

[2] Uhlmann, P., Frenzel, R., Voit, B., Mock, U., Szyszka, B., Schmidt, B., Ondratschek, D., Gochermann, J., & Roths, K. (2007). *Prog Org Coat*, *58*, 122.

[3] Brock, T., Groteklaes, M., & Mischke, P. (2000). *European Coatings Handbook*, Editor, Vincentz, Hannover.

[4] Glöckner, P., Jung, T., Struck, S., & Studer, K. (2008). *Radiation Curing - Coatings and Printing Inks*, Editor, Vincentz Network, Hannover.

[5] Kumari, S., Mishra, A. K., Chattopadmay, D. K., & Raju, K. V. S. V. (2007). *J. Polym. Sci. Part A: Polym. Chem.*, *45*, 2673.

[6] Srivastava, A., Agarwal, D., Mistry, S., & Singh, J. (2008). *Pigment & Resin Technol.*, *37*, 217.

[7] Woutens, M., Wolfs, D., Van der linde, M., Hovens, J., & Tinnemans, A. (2004). *Prog. Org. Coat.*, *51*, 312.

[8] Yu, Y. Y., & Chen, W. C. (2003). *Mater. Chem. & Phys.*, *82*, 388.

[9] Matsuda, T., Funae, Y., Yoshida, M., Yamamoto, T., & Takaya, T. (2000). *J. Appl. Polym. Sci.*, *76*, 50.

[10] Seesukphronrarak, S., Kawasaki, S., Kobori, K., & Takata, T. (2007). *J. Polym. Sci., Part A: Polym. Chem.*, *45*, 3073.

[11] Jancovicova, V., Mikula, M., Havlinova, B., & Jakubikova, Z. (2013). *Prog. Org. Coat.*, *76*, 432.

[12] Han, A. R., Kim, J. G., Hong, J. W., & Kim, H. K. (2012). *J. adhes. interface*, *13*, 1.

[13] Kunwong, D., Sumanochitraporn, N., & Kaewpirom, S. (2011). *Songklanakarin J. Sci. Technol.*, *33*, 2.