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Original Article

Curing behavior of a UV-curable coating based on urethane acrylate oligomer: the influence of reactive monomers

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Abstract

A hybrid organic-organic urethane acrylate oligomer was synthesized by the reaction of polypropyleneglycol (PPG), 2,4-toluene diisocyanate (TDI) and 2-hydroxyethyl methacrylate (HEMA) using dibutyltin dilaurate (DBTDL) as a catalyst. The urethane acrylate oligomer's structure was characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR). Two UV-curable coatings were prepared by blending the urethane acrylate oligomer, a reactive monomer (1,6- hexanediol diacrylate (HDDA) or trimethylol propane triacrylate (TMPTA)) and a photoinitiator (2,2-dimethoxy-2-phenyl acetophenone). The UV curing process of such coatings was monitored by FT-IR and determination of the gel fraction. It was found that as the UV dose increased, the specific peaks at 1635 cm^{-1} and 810 cm^{-1}, related to the carbon-carbon double (C=C) bond, decreased. Gel fraction of the cured coating film was found to increase with increasing radiation time. Thermal properties of the cured coating were also investigated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

Keywords: UV-curable coating, urethane acrylate oligomer, gel fraction, reactive monomer, thermal properties

1. Introduction

UV-curing or photo-polymerization technique represents a major advance in the development of the coating, adhesive and ink industries (Kayaman-Apohan *et al.*, 2003). UV-curing provides many advantages such as instant drying, broad formulating range, reduced energy consumption, coating of heat sensitive substrate, high curing rate and low space and capital requirement for curing equipment (Wang *et al.*, 2008; Moon *et al.*, 2005). UV-curable coating represents a class of coating with no or low volatile organic compounds (Patel *et al.*, 2009 and Srivastava *et al.*, 2008) and has been widely used in many industries.

The main components of UV-curable coating are an oligomer, a monomer and a photoinitiator (Dzunuzovic *et al.*, 2004). The prepolymers or oligomer are often complex structures based on, for example, epoxy acrylates, urethane acrylates, polyether urethane acrylates, polyester acrylates, polyether acrylates and acrylated oils. The structures and formulations of diluent monomers and prepolymers may be varied to suit a particular application and property requirement (Allen, 1996). UV-curable urethane acrylate oligomers are commercially available with molecular weights ranging from 600 to 6000 g/mol and with functionalities ranging from 2 to 6. To improve the performance of UV-curable coatings, novel oligomers, the main component of UV-curable coatings and adhesives, have been developed by many researchers. Tasic *et al.* (2004) synthesized the hyperbranched urethane acrylates (HB-UA), based on aliphatic hyperbranched polyesters and polyethyleneglycol acrylate for use in UV-curable coatings. UV-curing kinetic and thermal properties of the HB-UA were studied by FT-IR spectroscopy and DSC, respectively. They reported that the obtained coatings have good mechanical properties and solvent resistance. Xu *et al.*

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(2006) synthesized organic–inorganic hybrid urethane acrylate hydrolytic condensate (HUA-HC) through a sol–gel method with an acid catalyst of low concentration from a hybrid urethane acrylate prepolymer (HUA), containing hydrolysable ethoxysilane groups (Si-OEt). They revealed that the cured HUA-HC film showed better performance than the cured HUA film in the investigated aspects due to more inorganic Si–O–Si linkages in HUA-HC. Park *et al.* (2009) prepared dual-curable adhesives based on various epoxy acrylate oligomers. They found that after curing the pendulum hardness and the adhesion strength of the cured films increased.

In this research work, a hybrid organic-organic urethane acrylate oligomer was synthesized and characterized by FT-IR and NMR. Two different coatings based on such hybrid urethane acrylate oligomer was prepared and polymerized by UV-irradiation. Curing behavior of the coatings was monitored using FT-IR spectroscopy and by determination of gel fraction. The influence of functionality of monomer on curing behavior of such coatings is also discussed. The thermal properties of the cured coating were studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

2. Experimental

2.1 Materials

2,4-Toluene diisocyanate (TDI), polypropylene glycol (PPG), used to synthesize the urethane prepolymer, and 2,2-dimethoxy-2-phenyl acetophenone, a photoinitiator, were purchased from Fluka. 2-Hydroxyethyl methacrylate (HEMA), 1,6-hexanediol diacrylate (HDDA), trimethylol propane triacrylate (TMPTA), monomers, and dibutyltin dilaurate (DBTDL), a catalyst, were obtained from Aldrich. N,N'-dimethylformamide (DMF), a solvent, was purchased from Merck. All the chemicals were used as received without further purification.

2.2 Characterization

^{1}H NMR spectra were recorded on a NMR spectrometer, Bruker Avance 400 MHz, using $CDCl_3$ as the solvent. Differential scanning calorimetry (DSC), Perkin Elmer Pyris Diamond 7, were performed under nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 300°C. Thermal gravimetric analysis was carried out with Mettler Toledo TGA/SDTA 851e at a heating rate of 10°C /min from 30 to 600°C under nitrogen atmosphere. FT-IR spectra were recorded on FT-IR spectrometer, Perkin Elmer system 2000 FT-IR, and the percent conversion (X) of C=C bond was calculated by the equation (Tasic *et al.*, 2004):

$$X(\%) = \frac{(A_{810} / A_{1730})_0 - (A_{810} / A_{1730})_t}{(A_{810} / A_{1730})_0} \times 100\%$$

where $(A_{810} / A_{1730})_0$ and $(A_{810} / A_{1730})_t$ are relative absorbance of C=C bonds before curing and at a given curing time t, respectively.

2.3 Synthesis of urethane acrylate oligomer

The polymerization was performed in a round-bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser under nitrogen atmosphere. The urethane acrylate oliglmer was synthesized by the reaction of TDI (0.02 mol equiv.) and PPG (0.01 mol equiv.) in N,N'-dimethylformamide using DBTDL as the catalyst. The reaction was performed at 60°C under a dry nitrogen atmosphere for 6 h. The urethane prepolymer obtained was cooled to 40°C and then HEMA (0.02 mol equiv.) was added into the mixture of the prepolymer and the reaction was monitored for about 2 h until the signal for -NCO groups (at 2270 cm^{-1}) in the IR spectrum disappeared.

2.4 Preparation of UV-curable coating

Two different formulations of UV-curable coating consisting of oligomer based on urethane acrylate, monomer and photoinitiator were prepared (Table 1). Chemical structures of the monomers and the photoinitiator used are shown in Figure 1. In each formulation the chemicals were mixed in a round-bottom flask equipped with a mechanical stirrer, a thermometer, and a condenser under nitrogen atmosphere at

Table 1. Formulation used to prepare UV-cured coating.

Component		Weight (g)	
Oligomer	Urethane acrylate oligomer	5	5
Monomer	1,6-Hexanediol diacrylate (HDDA)	5	-
	Trimethylol propane triacrylate (TMPTA)	-	5
Photoinitiator	2,2-Dimethoxy-2-phenylacetophenone	0.1	0.1
Name		AD1	AD2

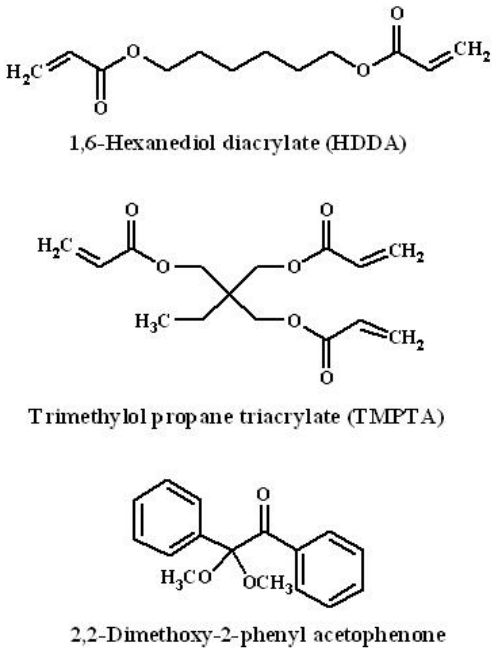

Figure 1. Molecular structure of the acrylate monomers and photo-initiator.

room temperature for 1.5 h. For further characrterization of the coatings, the UV-cured films, with the thickness of about 50 mm, were prepared by coating such mixtures on a transparent polycarbonate sheet and irradiating under 2-W UV light source. The distance of the sample to the focal point of the UV-lamp was 2 cm.

2.5 Gel fraction

The gel fraction was determined by immersing the cured sample (about 0.1 g) in hexane at 50°C. After 24 h., the sample was filtered out and dried in a vacuum oven at 50°C until constant weight. The gel fraction was calculated by equation (Park *et al.*, 2009):

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

where W_0 is the original weight and W_t is the weight after drying.

3. Results and Discussion

3.1 Synthesis and characterization of urethane acrylate oligomer

The urethane acrylate oligomer was synthesized by reacting polypropyleneglycol (PPG) with 2,4-toluene diisocyanate (TDI) to produce the urethane prepolymer. Then the urethane prepolymer was end-capped by 2-hydroxyethyl methacrylate (HEMA) (Figure 2.). The polyurethane acrylate oligomer product was characterized by ^{1}H NMR ($CDCl_3$) as shown in Figure3: d (ppm) 6.14 (-C(CH_3)=CH_2 cis), 5.59-5.60 (-C(CH_3)=CH_2 trans), 1.94-1.95 (-C(CH_3)=CH_2), 4.99 (-NH-), 4.27-4.39 (–O-CH_2-CH_2- of HEMA), 3.39-3.87 (broad peak–O-CH-CH_2- of PPG), 2.14-2.17 (-CH_3 of TDI), 1.10 (-CH_3 of PPG). The results are in good accordance with the results reported by Burel *et al.* (1999) and Thames *et al.* (1996). The urethane acrylate oligomer obtained was also characterized by FT-IR. Figure 4 shows the FT-IR spectrum of the urethane

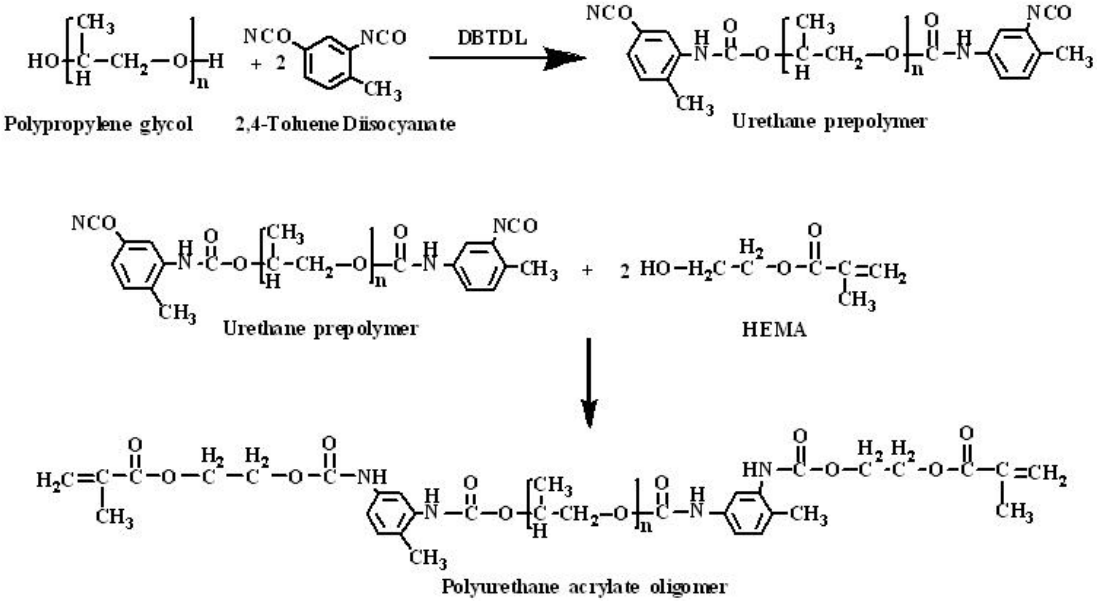

Figure 2. Synthesis of urethane acrylate oligomer.

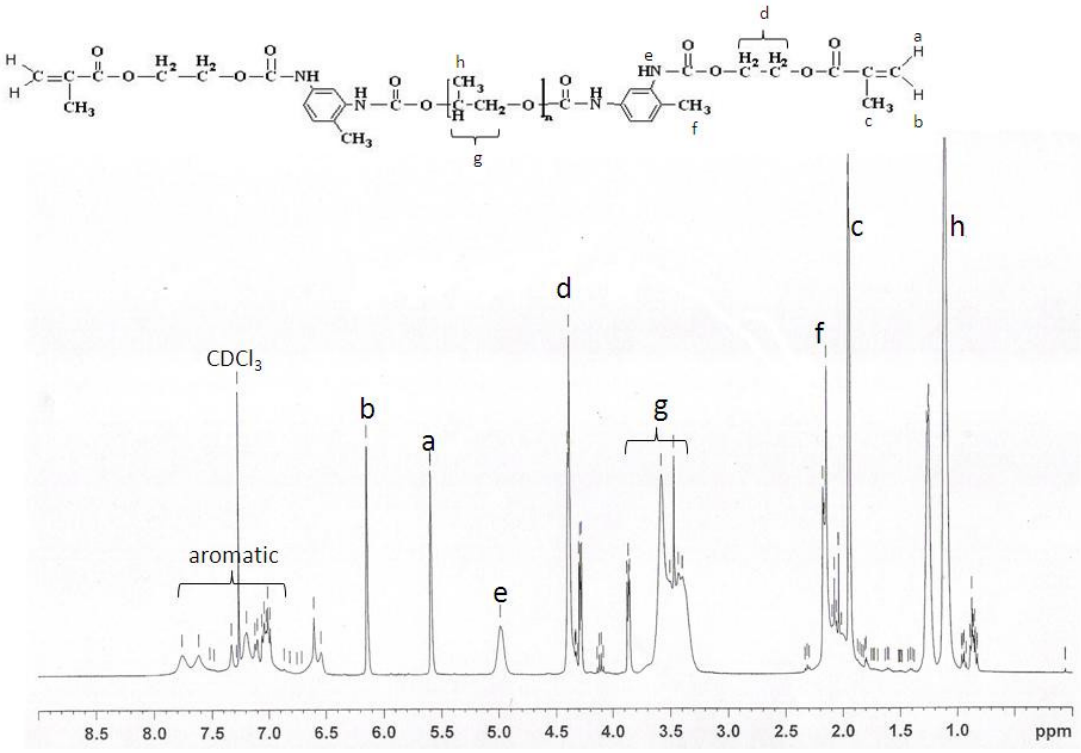

Figure 3. ^{1}H NMR spectrum of urethane acrylate oligomer.

acrylate oligomer. The absorption bands at 3390, 1730 and 810 cm^{-1} relate to –NH stretching, C=O stretching and C=C twisting of acrylate, respectively. From the IR spectra, the disappearance of the characteristic absorption band at 2270 cm^{-1} related to isocyanate group (-NCO) indicates the completion of the reaction (Bayramoglu *et al.*, 2006).

3.2 Curing behavior monitored by FT-IR

Figure 5 shows FT-IR spectra of AD1 and AD2 UV-curable coatings as a function of time for 2 W UV-irradiation. It was found that both formulations showed the absorption band of acrylate group (C=C) at 1635 cm^{-1} and 810 cm^{-1}, which decreased with increasing UV-curing time. This is because C=C bonds in the reactive monomers took part was the cross-linking reaction by photopolymerization (Park *et al.*, 2009).

Conversion of acrylate bonds in both AD1 and AD2 versus irradiation times is shown in Figure 6. It can be seen from the figure that as the UV-curing time increased, the conversion of acrylate bonds increased very fast during the first five seconds and then became constant. However, AD1 has a slightly lower conversion than AD2. This was because the conversion of acrylate bonds is based on the functionality of the monomer, the higher functionality of monomer, the faster increase in the conversion of acrylate bonds. The reaction rate and extent of UV-curing in AD2, that contains three reactive sites per monomer molecule, were higher than those in AD1, which contains two reactive sites per monomer molecule.

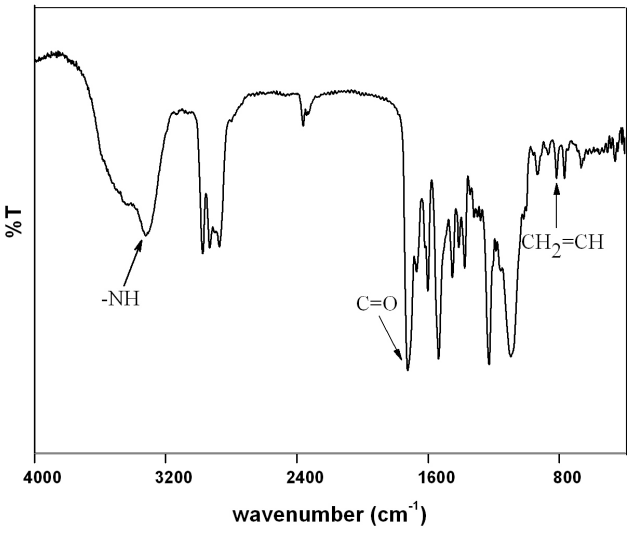

Figure 4. FT-IR spectra of urethane acrylate oligomer.

3.3 Gel fraction

Figure 7 shows the gel fraction of the cured film of AD1 and AD2 as a function of time. In the first five seconds,

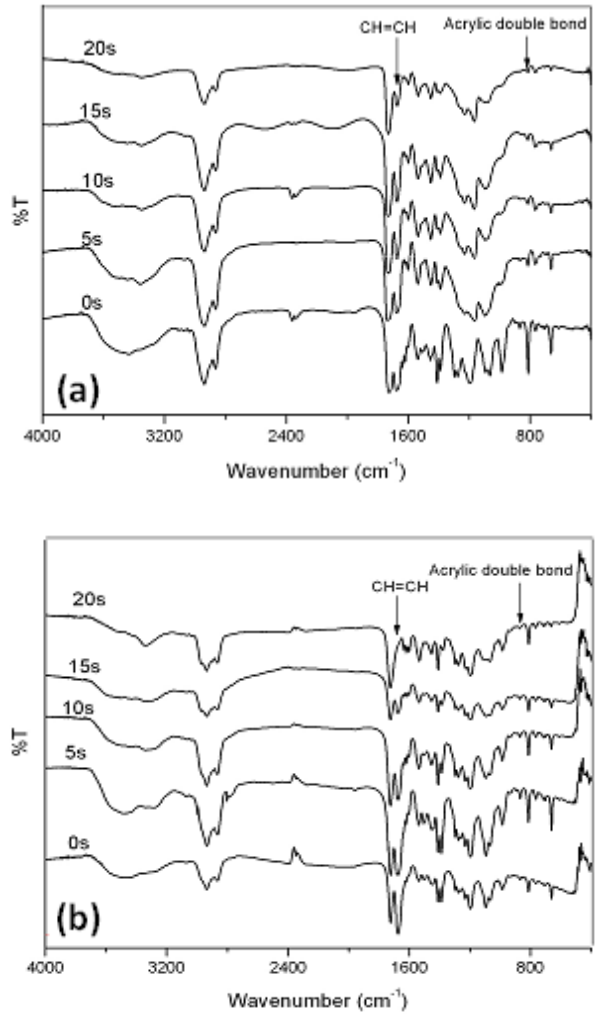

Figure 5. FT-IR spectra of (a) AD1 and (b) AD2 UV-curable coating as a function of time at 1635 cm^{-1} and 810 cm^{-1}.

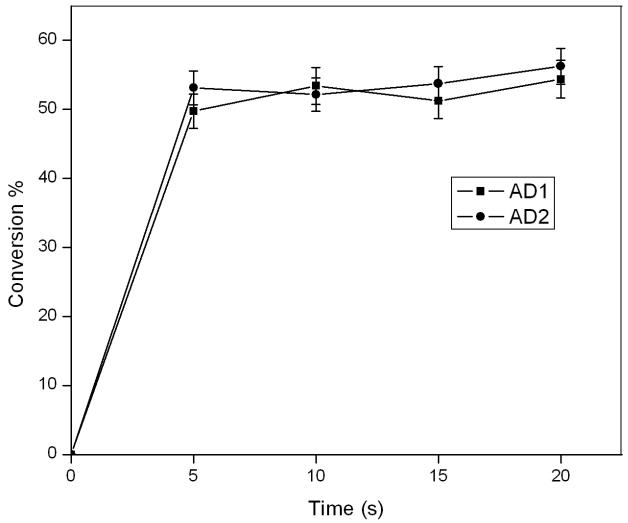

Figure 6. UV-curing profiles of UV-curable coating based on urethane acrylate oligomer measured by FT-IR spectroscopy.

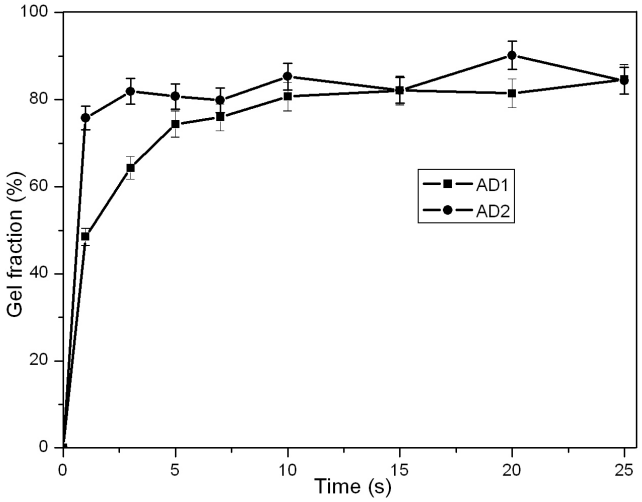

Figure 7. Gel fraction of UV-curable coating based on urethane acrylate oligomer as a function of time.

the gel fraction of both AD1 and AD2 increase rapidly with UV-irradiation and then became constant. It was also found that the gel fraction of AD2 was higher than that of AD1 regardless of time. This was because the gel fraction depends on the functionality of the monomer. The acrylate monomers contain C=C bonds, as the reactive site. In AD2 formulation, TMPTA with triacrylate group was used as a monomer while in AD1 formulation, the monomer HDDA used has two reactive sites. Therefore, AD2 with TMPTA monomer containing more C=C bonds resulted in higher crosslinked films when incorporated into UV curable resin.

3.4 Thermal properties

The glass transition temperatures (T_g) of the cured sample were analyzed by DSC. It was found from the DSC thermograms that the T_g values of AD1 and AD2 were 180 and 195°C, respectively (Figure 8). An increase in monomer functionality accelerated the curing reactions, therefore

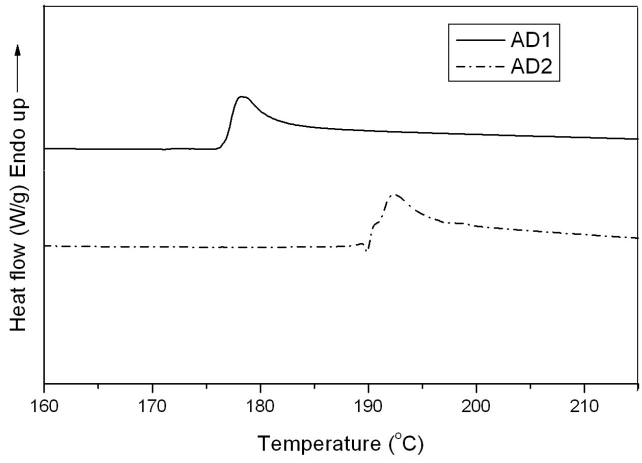

Figure 8. DSC thermogram of UV-curable coating based on urethane acrylate oligomer.

AD2, containing the three-acrylate-reactive-site monomer, produced the cured film with higher crosslink density compared with the cured film produced from AD1 formulation. It can be concluded that T_g of the cured film depends on the functionality of the reactive monomer (Choi and Kim, 2004).

The summary of TGA results of the cured samples (2 W, 15 s) is given in Table 2 and the thermogravimetric (TG) and differential thermogravimetric (DTG) analysis curves for cured films are shown in Figure 9. The weight loss at the temperature less than 300°C was due to the trapped volatile materials were released (Chattopadhyay and Webster, 2009). Then the thermal decomposition of the crosslinked polyurethane started via the degradation of polymer side chains, occurring at about 300°C. The next step was due to the decomposition of aromatic structure between 350 and 450°C. The temperatures above 450°C indicated the complete decrosslinking and thermal degradation of the cured films (Kayaman-Apohan *et al*., 2005). In Table 2, AD2 showed higher thermal stability than that of AD1 due to AD2 contained triacrylate monomer while AD1 contained diacrylate monomer. Curing reaction of AD2, therefore, resulted in highly crosslinked density polymer which exhibited better heat-diffusion inhibition characteristics.

4. Conclusions

The urethane acrylate oligomer was synthesized successfully in two steps. Firstly, TDI was reacted with PPG using DBTDL as catalyst in order to prepare urethane prepolymer. Then, the urethane prepolymer was reacted with HEMA to form the urethane acrylate oligomer. The reaction between the urethane acrylate oligomer and HEMA was monitored by both FT-IR and NMR. From the FTIR spectra, the disappearance of the characteristic absorption band at 2270 cm^{-1} (-NCO) indicated the completion of the reaction. The UV-curable coatings were prepared by mixing oligomer, monomer and photoinitiator at room temperature. The FT-IR spectra showed a decrease in the intensity of specific peak at 1635 cm^{-1} and 810 cm^{-1} related to C=C bond with increasing UV-curing time indicating the proceeding of photo-polymerization reaction. The conversion of both AD1 and AD2 was increased with increasing irradiation time. However, AD2 showed slightly higher percent conversion than AD1. The reaction rate and extent of UV-curing depended on the functionality of the monomer. The monomer with higher functionality possessed more reactive sites and, therefore, showed higher rate and extent of crosslink reaction. In addition, T_g and thermal stability of cured films increased with increasing the monomer reactive site.

Acknowledgments

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Table 2. TGA results for UV-cured films.

Composition	Weight loss % at 100 °C	5% weight loss Temperature (°C)	50% weight loss Temperature (°C)	Maximum weight loss % Temperature (°C)	Residue (%)
AD1	0.94	206	407	426	6.45
AD2	1.23	187	434	442	10.43

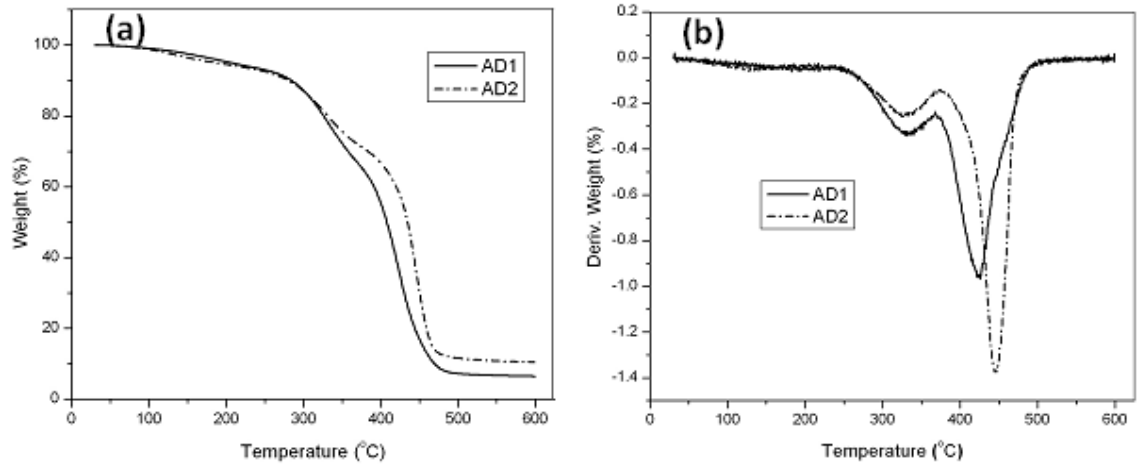

Figure 9. TGA (a) and DTG (b) thermogram of UV-cured films based on urethane acrylate oligomer.

nology Development Agency and from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education is gratefully acknowledged. Acknowledgement also goes to Compart Precision (Thailand) Co., Ltd. and the Faculty of Science, Burapha University.

References

Allen, NS. 1996. Photoinitiators for UV and visible curing of coatings: mechanisms and properties. Journal of Photochemistry and Photobiology A: Chemistry 100, 101-107.

Bayramoglu, G., Vezir Kahraman, M., Apohan, NK. and Güngör, A. 2006. Synthesis and characterization of UV curable dual hybrid oligomers based on epoxy acrylate containing pendant alkoxysilane groups. Progress in Organic Coatings 57, 50-55.

Burel, F., Lecamp, L., Youssef, B., Bunel, C. and Saiter, JM. 1999. Synthesis and photoinitiated polymerization of a new urethane acrylatemonomer: influence of polymerization temperature. Thermochimica Acta 326, 133-141.

Chattopadhyay, DK. and Webster, DC. 2009. Thermal stability and flame retardancy of polyurethanes. Progress in Polymer Science 34, 1068-1133.

Choi, JH. and Kim, HJ. 2004. Curing behaviors and coating performance of UV curable epoxy acrylate coatings for wooden flooring. M.S. Thesis. Seoul National University, Seoul, Korea.

Dzunuzovic, E., Tasic, S., Bozic, B. and Babic, D. 2004. UV-curable hyperbranched urethane acrylate oligomers containing soybean fatty acids. Progress in Organic Coatings 52, 136-143.

Kayaman-Apohan, N., Amanoel, A., Arsu, N. and Güngör, A. 2003. Synthesis and characterization of UV-curable vinyl ether functionalized urethane oligomers. Progress in Organic Coating 49, 23-32.

Kayaman-Apohan, N., Demirci, R., Cakir, M. and Gungor, A. 2005. UV-curable interpenetrating polymer networks based on acrylate/vinylether functionalized urethane oligomers. Radiation Physics and Chemistry 73, 254-262.

Moon, JH., Shul, YG., Hong, SY., Choi, YS. and Kim, HT. 2005. A study on UV-curable adhesives for optical pick-up: I. Photo-initiator effects. International Journal of Adhesion and Adhesives 25, 301-312.

Park, YJ., Lim, DH., Kim, HJ., Park, DS. and Sung, IK. 2009. UV- and thermal-curing behaviors of dual curable adhesives based on epoxy acrylate oligomers. International Journal of Adhesion and Adhesives 29, 710-717.

Patel, MM., Patel, KI., Patel, HB. and Parmar, JS. 2009. UV-curable Polyurethane Coatings Derived from Cellulose. Iranian Polymer Journal 18, 903-915.

Srivastava, A., Agarwal, D., Mistry, S. and Singh, J. 2008. UV curable polyurethane acrylate coatings for metal surfaces. Pigment & Resin Technology 37, 217-223.

Thames, SF., Yu, H., Schuman, TP. and Wang, MD. 1996. Acrylated lesquerella oil in ultraviolet cured coatings. Progress in Organic Coating 28, 299-305.

Tasic, S., Bozic, B. and Dunjic, B. 2004. Synthesis of new hyperbranched urethane-acrylates and their evaluation in UV-curable coatings. Progress in Organic Coatings 51, 320-327.

Wang, F., Hu, JQ. and Tu, WP. 2008. Study on microstructure of UV-curable polyurethane acrylate films. Progress in Organic Coatings 62, 245-250.

Xu, J., Pang, W. and Shi, W. 2006. Synthesis of UV-curable organic–inorganic hybrid urethane acrylates and properties of cured films. Thin Solid Films 514, 69-75.