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Mi Na Park [a] , Sun Wha Oh [b] , Byung Hyun Ahn [c] , Myung Jun Moon [d] & Young Soo Kang [e]

[a] Department of Chemistry, Pukyong National University, Busan, Korea

[b] Basic Science Research Institute, Pukyong National University, Busan, Korea

[c] School of Material Science and Engineering, Pukyong National University, Busan, Korea

[d] Department of Industrial Chemistry, Pukyong National University, Busan, Korea

[e] Department of Chemistry, Sogang University, Seoul, Korea

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Mi Na Park[1], Sun Wha Oh[2], Byung Hyun Ahn[3], Myung Jun Moon[4], and Young Soo Kang[5]
[1]Department of Chemistry, Pukyong National University, Busan, Korea
[2]Basic Science Research Institute, Pukyong National University, Busan, Korea
[3]School of Material Science and Engineering, Pukyong National University, Busan, Korea
[4]Department of Industrial Chemistry, Pukyong National University, Busan, Korea
[5]Department of Chemistry, Sogang University, Seoul, Korea

The poly(alkyl urethane) acrylate oligomers (AUAOs) were obtained by the reaction of alkyl acrylate oligomers and 2-isocyanatoethyl acrylate. Synthesis of AUAOs were done with 2-mercaptoethanol (2-MEOH), alkyl (methyl, butyl, 2-ethylhexyl) acrylate, 2,2′-azobisisobutyronitrile (AIBN, initiator) and dibutyltin dilaurate as a catalyst. Then 2-MEOH was used for functional chain transfer agent. The oligomers were characterized by FT-IR, FT-NMR, rheometer, and DSC. Each oligomer was blended and photopolymerized by UV light, and their ball tack, adhesiveness, and thermal resistance were confirmed by ball tack tester and so on. Photo-polymerized AUAOs can be used for UV curable coatings, inks and adhesives.

Keywords: adhesive; poly(alkyl urethane) acrylate oligomer; UV curing

INTRODUCTION

During the last 20 years, UV coatings have grown from their first application in furniture coatings to embrace many industries including

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Address correspondence to Young Soo Kang, Department of Chemistry, Pukyong National University 599-1, Daeyeon-3-dong, Nam-gu, Busan 608-737, Korea. E-mail: yskang@pknu.ac.kr

electronics, printing and automotive [1]. It can be cured at low temperatures and promote high productivity due to their fast production rates. In most of these applications the UV-curable resin is applied onto the flat substrate (wood, metal, plastic, and paper) and cured online by a brief passing under a powerful UV lamp [2].

Usually the UV-curable coating is formulated with three basic components including prepolymer, diluent, and photoinitiator [3]. The most commonly used UV-curable formulations contains unsaturated acrylates. Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties used as prepolymer [4]. PU can be easily prepared by a simple polyaddition reaction of polyol, isocyanate, and a chain extender [5]. Its well known that, polyurethane acrylates among polymer containing PUs are widely used as a prepolymer for UV coatings which provide excellent physical and mechanical properties such as adhesion on substrates, flexibility and impact strength [6].

In this study, a step-wise successive method for the synthesis of hydroxyl or isocyanate terminated prepolymers was used for the preparation of mono functional acrylic urethane acrylate oligomers. The NCO group can be reacted generally with compounds containing active hydrogen atoms. Therefore, the use of little excess of isocyanate cause the formation of light structure products containing urethane groups. The adhesion property of isocyanate-based adhesives involves the combination of several chemical properties. The characteristics of isocyanates are well known for their reactivity with other functional group and solubility in many organic materials [7].

Three types of poly(urethane acrylate) oligomers (AUAOs) were synthesized from single hydroxyl-terminated poly(alkyl acrylate) oligomers (HTPAAOs) and they were UV-cured in this study. From this experiment, we can obtain oligomers having low glass transition temperature (T_g) compared with that reported in the previous study [8] and studied their physical properties after UV curing. T_g is a very important characteristic property of polymers [9]. Its an important factor in determining the upper use temperature of a polymer used as a plastic or fiber in load bearing applications [10]. However, T_g shows considerable increase with the chemical conversion during the UV curing [11]. By synthetic method including the addition of 2-isocyanatoethyl methacrylate, T_g value of synthesized materials can be lowered as –10°C as compared with that reported in the previous study [8]. Therefore, we can expect lower T_g and lower viscosity for better production efficiency.

FT-IR and FT-NMR were used to characterize their molecular structure. The thermal properties and rheologic behavior of the

synthesized oligomers were also investigated by a differential scanning calorimetry (DSC) and a rheometer. The adhesion properties of adhesives including several chemical properties were identified with ball tack tester and so on in this study.

EXPERIMENTAL

Materials

For this study, methyl acrylate (99%, MA), butyl acrylate (99%, BA), 2-ethylhexyl acrylate (99%, 2-EHA), 2-mercaptoethanol, 2-isocyanatoethyl methacrylate, dibutyltin dilaurate (DBTDL), di(ethylene glycol) ethyl ether acrylate (90+% , DEGEEA), and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Aldrich Chemical Co. and used without any further purification. All solvents were obtained from Junsei Chemical Co. and used without further purification.

Preparation of Poly(alkyl urethane) Acrylate Oligomers

AUAOs (**2**) were obtained by the reaction of HTPAAOs (**1**) and 2-isocyanatoethyl methacrylate in an equal mole dissolved in toluene and stirring at room temperature for 1.5 hrs in the presence of dibutyltin dilaurate as a catalyst until the peak at 2270 cm^{-1} of NCO group in FT-IR spectrum disappeared. After cooling to room temperature, large excess of n-hexane was added into reaction mixture. The precipitate was redissolved in chloroform to yield hydroxyl-terminated HTPAAO (1). As a solvent, toluene and residues were distillated under the reduced pressure for 3 hrs 50°C. The obtained oligomers were transparent and very sticky.

UV Curing

Three AUAOs samples were mixed with Irgacure 184 (3 wt%) and drawn on glass plates with a 20 μm applicator, respectively, then exposed to an UV lamp (120 w/cm) at 30 m/min of line speed in air.

Measurements

The functional groups of AUAOs were confirmed by means of FT-IR spectroscopy (Perkin Elmer SPECTRUM 2000 of single beam). The structure of synthesized oligomers was identified with 400 MHz FT-NMR spectroscopy (JEOL, JNM-ECP400) using acetone-d_6 as the solvent. The thermal property was investigated by a differential

scanning calorimetry (DSC) (Perkin Elmer, Pyris 1). The controlled shear stress versus shear rate and viscosity using reactive diluents were obtained with a rheometer (Carri-Med Ltd, CSL 500). After curing, AUAOs' adhesiveness was identified with ball tack tester. Their thermal resistance was designated when sample is detached from SUS304 plate as 0.1 m. 25 × 25 mm of sample was attached to one side of SUS304 plate. And a balance was weighted to its other side. The sample was put in the oven and its temperature was increased as 5°C/min of ratio. Then, first temperature was measured as temperature resistance when sample detached from SUS304 plate over 0.1 m.

RESULTS AND DISCUSSION

HTPAAOs using acrylate monomer were synthesized according to the previous report [8]. The different molar ratios of AIBN, alkyl acrylate, and 2-mercaptoethanol for the synthesis of AUAOs were as follows. The molar ratio of AIBN, alkyl acrylate, and 2-mercaptoethanol was 2:800:50 for the synthesis of poly(methyl urethane) acrylate oligomer (MUAO) and poly(butyl urethane) acrylate oligomer (BUAO), and that for synthesis of poly(2-ethylhexyl urethane) acrylate oligomer (2-EHUAO) was 2:800:100. The reaction temperature and time were chosen as a practical point of view because the acrylates have a high reactivity [12,13].

We successfully prepared AUAOs by the reaction of HTPAAOs and 2-isocyanatoethyl methacrylate in toluene in the presence of dibutyltin dilaurate as a catalyst. The reaction scheme for the synthesis of AUAOs is given in Figure 1. In the synthetic procedure of AUAOs, 2-isocyanatoethyl methacrylate was used for the formation of urethane groups containing carbon double bond in AUAOs. Because it has NCO group in the molecule with end of vinyl groups [14]. So, vinyl group can be changed from double bond to single bond after photo-polymerization by UV curing. This indicates that AUAOs containing urethane group possibly do UV cure at the same time.

The structure of MUAO (**2a**), BUAO (**2b**), and 2-EHUAO (**2c**) were confirmed with ^{1}H-NMR. The assignments of peaks in the spectra of AUAOs were described in detail as follows.

2a: (acetone-d_6, ppm) 1.93 (CH_3), 1.99–2.03, 2.25–2.31 and 2.59–2.79 (broad peaks, all kinds of CH_2 and CH), 3.18–3.24 ($NHCH_2$), 3.67 (CH_3, methyl acrylate), 4.41–4.45 (CO_2CH_2), 5.58(C=CH_2, trans to methyl), 6.15 (C=CH_2, cis to methyl), 8.00 (NH).

2b: (acetone-d_6, ppm) 0.96–1.00 ($CH_3CH_2CH_2CH_2$), 1.33–1.38 ($CH_3CH_2CH_2CH_2$), 1.55–1.58 ($CH_3CH_2CH_2CH_2$), 1.93 (CH_3), 1.95–2.03, 2.59–2.65 and 2.72–2.80 (broad peaks, all kinds of CH_2 and CH),

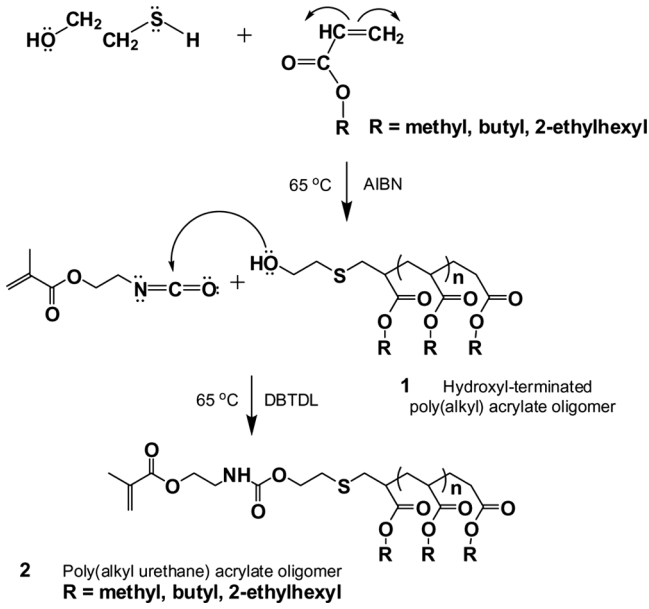

FIGURE 1 Synthetic scheme of AUAOs using HTPAAOs and 2-isocyanatoethyl methacrylate at 65°C in toluene.

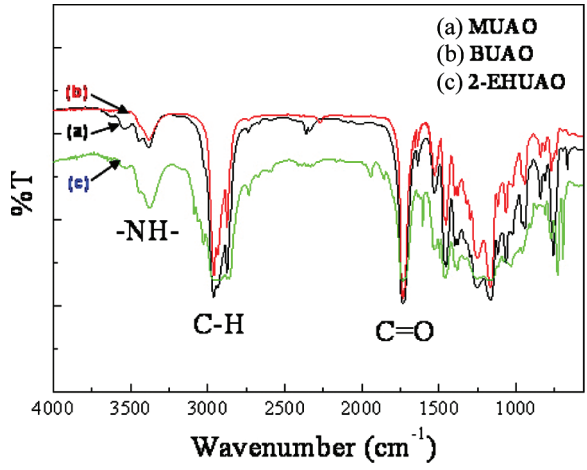

FIGURE 2 FT-IR spectra of AUAOs.

TABLE 1 Thermal and Rheologic Behavior of AUAOs

Oligomer	MUAO	BUAO	2-EHUAO
T_g (°C)	−34.06	−13.13	−9.17
Viscosity (cps)	52.92	0.986	2.431

3.24–3.30 ($NHCH_2$), 4.08–4.13 ($CH_3CH_2CH_2CH_2$), 4.40–4.46 (CO_2CH_2), 5.71 (C=CH_2, trans to methyl), 6.38 (C=CH_2, cis to methyl), 8.20 (NH).

2c: (acetone-d_6, ppm) 0.96–1.06 (CH_3), 1.93 (CH_3–C=CH_2), 1.25–1.29, 1.57–1.65, 1.99–2.06, 2.25–2.29 and 2.72–2.79 (broad peaks, all kinds of CH_2 and CH), 3.20–3.29 ($NHCH_2$), 4.41–4.45 (CO_2CH_2), 5.80 (C=CH_2, trans to methyl), 6.25 (C=CH_2, cis to methyl), 8.18 (NH).

From Figure 2, we can check the peaks of main absorption bands in the FT-IR spectra of AUAOs. Absorption peak of -NH- groups was assigned at 3390 cm^{-1} instead of disappearance of -OH groups at 3530 cm^{-1}. Therefore, for the UV curing, peak of C=C bonds at the end groups of 2-isocyanatoethyl methacrylate was confirmed at 1640 cm^{-1}. From the obtained FT-IR data, we identified that the synthesized material had functional groups for UV curing and urethane groups for lower T_g.

In Table 1, T_g of AUAOs using DSC scanned from −50°C to 50°C shows the lower value of T_g than that of the previous material [8]. Reported T_g value of HTPMAO was about −25°C, but that of MUAO containing urethane groups was measured as −34°C. From this data, we can know that the lower concentration of polar groups leads to the lower T_g. This is because the polar groups, have a high cohesive force, and participate in intermolecular hydrogen bonding and restrict the

TABLE 2 Composition, T_g, and Viscosity of Each Sample Having Low T_g

Sample Name	LT-1	LT-2	LT-3	LT-4	LT-5	LT-6	LT-7	LT-8
[1]BUAO	75	75	50	50	25	25	0	0
[2]MUAO	25	25	50	75	75	75	75	100
[3]2-EHUAO	0	0	0	0	0	0	25	0
[4]DEGEEA	50	75	75	50	100	150	150	150
Igarcure 184	3	3	3	3	3	3	3	3
T_g (°C)	−31.2	−35.1	−37.8	−38.0	−42.2	−44.7	−44.4	−46.4
Viscosity (cps) × 1000	7.7	6.4	9.2	34	16	4.6	5.8	2.8

[1]Poly(butyl urethane) acrylate oligomer (BUAO).
[2]Poly(methyl urethane) acrylate oligomer (MUAO).
[3]Poly(2-ethylhexyl urethane) acrylate oligomer (2-EHUAO).
[4]Di(ethylene glycol) ethyl ether acrylate (DEGEEA).

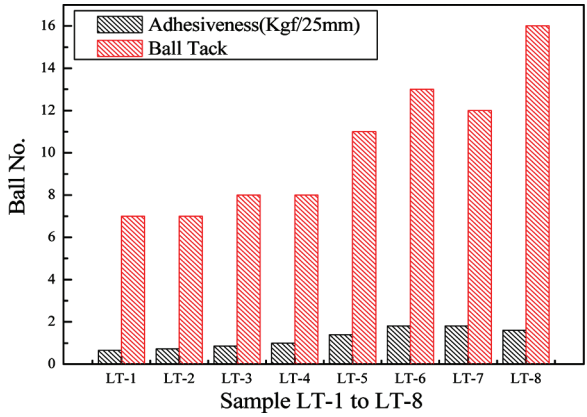

FIGURE 3 Adhesiveness and ball tack graph of each composition.

rotation of polymer segment. This results in a higher hardness and smaller elongation at break [15]. Also, viscosity of AUAOs according to the different measuring temperatures appears in Table 1. As a soft segment, urethane group of AUAOs interferes to flow main chain and branches at appointed temperatures. Generally, the length of the main chain and branch affected the viscosity. The short and soft segment results in the higher hardness of polyurethane.

This is due to an increase in polar groups and cohesive energy density [16,17].

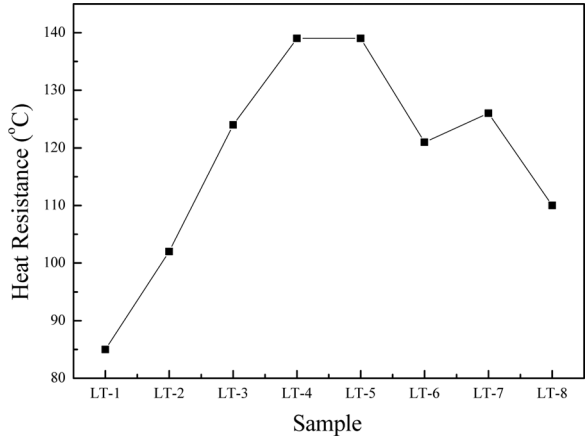

FIGURE 4 Heat resistance graph of each composition.

From Table 2 and Figure 3, we can confirm that ball tack is increased with decrease of T_g. But, LT-6 and LT-7 have maximum adhesiveness due to the balance of cohesive strength between T_g and ball tack.

Figure 4 shows the thermal resistance of each sample. In spite of high T_g, LT-1 and LT-2 have low thermal resistance because their liquidity is decreased. So, they can't have enough contact area and adhesion for a glass plate.

CONCLUSION

Poly(alkyl urethane) acrylate oligomers (AUAOs) were synthesized from hydroxyl-terminated poly(alkyl acrylate) oligomers (HTPAAOs) and 2-isocyanatoethyl methacrylate for the UV curing. AUAOs had the lower T_g and viscosity than those reported in the previous study [8]. Lower T_g and viscosity of the reactants are better for the production efficiency. After UV curing, oligomers having low T_g are easily processed by lower cost and higher efficiency.

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