Thesis for the Degree of Master of Science

Study on the Synthesis and Photopolymerization of UV Curable Oligomers

by

Mi Na Park

Department of Chemistry

The Graduate School

Pukyong National University

February 2008

Study on the Synthesis and Photopolymerization of UV Curable Oligomers

(UV 경화 가능한 올리고머의 합성과 광중합에 관한 연구)

Advisor : Prof. Young Soo Kang

by

Mi Na Park

A thesis submitted in partial fulfillment of the requirements
for the degree of

Master of Science

in Department of Chemistry, The Graduate School,
Pukyong National University

February 2008

Study on the Synthesis and Photopolymerization of UV Curable Oligomers

A dissertation

by

Mi Na Park

Approved by:

____
(Chairman)

____
(Member)

____
(Member)

February 26, 2008

Study on the Synthesis and Photopolymerization of UV Curable Oligomers

Mi Na Park

Department of Chemistry, The Graduate School
Pukyong National University

Abstract

Three types of poly(alkyl urethane) acrylate oligomers such as poly(methyl urethane) acrylate oligomer (MUAO), poly(ethyl urethane) acrylate oligomer (EUAO), and poly(2-ethylhexyl urethane) acrylate oligomer (2-EHUAO) were synthesized from single hydroxyl-terminated polyacrylate oligomers in this research. And each oligomer was blended with epoxy urethane acrylate oligomers (EUA) and hyperbranched urethane acrylate oligomers (HUA, HUA-s, and HUA-p), and then, photopolymerized by UV irradiation. The oligomers were characterized by FT-IR, FT-NMR, rheometer, GPC, and DSC. Each oligomer was blended and photopolymerized by UV irradiation, and their thermal resistance, ball tack, and gel content were confirmed by peeling tester and ball tack tester. Photopolymerized polymers can be used for UV curable coatings, inks and adhesives.

Contents

ABSTRACT ·· i

I. INTRODUCTION ·· 1

II. EXPERIMENTATIONS AND DISCUSSIONS ·· 6

Part I. Synthesis and Characterization of Poly(alkyl urethane) Acrylate Oligomers for UV Curable Coating Agent ·· 6

1. Experiment ·· 6
- 1.1. Materials ·· 6
- 1.2. Preparation of hydroxyl-terminated poly(alkyl) acrylate oligomers ·· 6
- 1.3. Synthesis of poly(alkyl urethane) acrylate oligomers ··········· 7
- 1.4. Characterization ·· 8

2. Results and Discussion ·· 9
- 2.1. Structure analysis on the AUAOs ································ 10
  - *2.1.1. FT-IR analysis* ·· 10
  - *2.1.2. FT-NMR analysis* ··· 12
  - *2.1.3. GPC analysis* ·· 13
- 2.2. Thermal behavior analysis on AUAOs ····························· 15
  - *2.2.1. DSC analysis* ·· 15
- 2.3. Rheological behavior analysis on the AUAOs ····················· 17
  - *2.3.1. Rheometer analysis* ·· 17

3. Conclusion ·· 20

Part II. Photo-Polymerization of Poly(Alkyl Urethane) Acrylate Oligomers Using Hyperbranched Polymer by UV Irradiation for Curable Coating •• 21
1. Experiment •• 21
1.1. Materials •• 21
1.2. UV curable formulations •••••••••••••••••••••••••••••••••••••• 23
1.3. Preparation of process for UV curing ••••••••••••••••••••••••••• 25
1.3.1. Selection of light source and arrangement •••••••••••••••• 25
1.3.2. Selection of line speed and distance between light source and materials •• 26
1.4. Characterization •• 27
2. Results and discussion •• 28
2.1. Physical properties of standard components •••••••••••••••••• 28
2.1.1. Physical properties of low T_g component for permanent adhesive •• 28
2.1.2. Physical properties of high T_g component for removal adhesive •• 29
2.1.3. Selection of standard components for UV curable adhesives •• 31
2.2. Physical properties of components added multifunctional oligomers (MFOs) •• 31
2.2.1. Physical properties of components added MFOs for permanent adhesive •• 31
2.2.2. Physical properties of components added MFOs for removal adhesive •• 34
2.3. Final formulations •• 36
3. Conclusion •• 38
III. SUMMARY •• 39

IV. REFERENCES ·· 40

V. KOREAN SUMMARY ·· 42

List of Figures

Fig. 1-1 Preparations of poly(alkyl urethane) acylate oligomers (AUAOs) •• 7

Fig. 1-2 FT-IR spectra for; (a) MUAO, (b) EUAO, and (c) 2-EHUAO ••••• 11

Fig. 1-3 Molecular weight of AUAOs measured by GPC; (a) MUAO, (b) EUAO, and (c) 2-EHUAO •• 14

Fig. 1-4 The glass transition temperature (T_g) for: (a) MUAO (b) EUAO, and (c) 2-EHUAO •• 17

Fig. 1-5 Shear stress versus shear rate and viscosity for AUAOs in 20 wt% of phenoxyethyl acrylate as a diluent at 25 ℃ •••••••••••••••••••• 18

Fig. 2-1 Synthetic scheme and structure of epoxy urethane acrylate oligomer (EUA) •• 22

Fig. 2-2 Structures of hyperbrenched urethane acrylate oligomers (HUA); HUA, HUA-s, and HUA-p •• 22

Fig. 2-3 UV curor •• 26

Fig. 2-4 Adhesiveness and ball tack of low T_g component for permanent adhesive •• 28

Fig. 2-5 Heat resistance of low T_g component for permanent adhesive •• 29

Fig. 2-6 Adhesiveness and ball tack of high T_g component for removal adhesive •• 30

Fig. 2-7 Heat resistance of high T_g component for removal adhesive •• 30

Fig. 2-8 Adhesiveness and heat resistance curves of LT-6 according to the content of multifunctional oligomers ••••••••••••••••••••••••••••• 32

Fig. 2-9 Adhesiveness and heat resistance curves of permanent adhesive

according to the content of C-9 as a tackifier •••••••••••••••••••••• 34
Fig. 2-10 Adhesiveness and heat resistance curves of removal adhesive according to the content of C-9 as a tackifier •••••••••••••••••••••• 36
Fig. 2-11 Gel content and ball tack of permanent and removal type of adhesives ••• 37

List of Equations

Eq. 2-1 Fox equation for selection of standard component ••••••••••••••••• 23
Eq. 2-2 Equation of UV dose for calculation of cure rate •••••••••••••••••• 26

List of Tables

Table 1-1 Molecular weight of AUAOs ••••••••••••••••••••••••••••••••••••••• 15
Table 2-1 T_g and viscosity according to the components for permanent and removal adhesive; (a) low T_g component and (b) high T_g component •• 24
Table 2-2 Arrangement of UV lamps consisted of metal halide and mercury lamps •• 25
Table 2-3 Adhesiveness and heat resistance of LT-6 according to the content of multifunctional oligomers for permanent adhesive •••••••••• 32
Table 2-4 Components including LT-6, multifunctional oligomers, and tackifier for permanent adhesive ••••••••••••••••••••••••••••••••• 33
Table 2-5 Components including HT-1, multifunctional oligomers, and tackifier for removal adhesive •••••••••••••••••••••••••••••••••••• 35

I. Introduction

Growing concern for environmental protection has driven industry toward the use of solvent-free polymerization system, where UV-radiation curing has become a viable alternative to conventional thermal curing of solvent-containing polymer formulations [1]. During the last 20 years, UV coatings have grown from their first application in furniture coatings to embrace many industries including electronics, printing and automotive [2]. Much work has been devoted to the cure behavior and properties of crosslinked acrylates especially [3-11].

They 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 a flat substrate (wood, metal, plastic, paper) and cured on–line by a brief passing under a powerful UV lamp [12]. UV cured materials have high resistance to weather, ozone, aging, frictional wear, and heat. Besides they can absorb the shock and resist rust with the film thickness. This solvent-free technology is now commonly used in various industrial applications to achieve an ultrafast hardening of protective coatings, printing inks, adhesives, varnishes and composites [13].

Usually, the UV-curable coating is formulated with the three basic components including prepolymer, diluent, and photoinitiator [14]. The most commonly used UV-curable formulations contain unsaturated acrylates. The main types of acrylic oligomers are epoxy acrylates, polyester acrylates, polyether acrylates, urethane acrylates and silicone acrylates [15]. Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties as a prepolymer [16]. And PU can easily be prepared by a simple polyaddition reaction of polyol, isocyanate, and a chain extender [17]. As well known, polyurethane acrylates among polymer including 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 [18].

UV Irradiation-Curable PU Systems

PU-based acrylate-terminated polymers have been introduced for use in UV-cured elastomer coatings. They are usually used in conjugation with di- or trifunctional acrylate resins such as 1,6-hexane diol diacrylate (HDDA) whose function is to control hardness and flexibility in the final elastomeric lacquer.

The primary advantage of such PU elastomers is their freedom from solvent use and hence 100% solids content of their coatings. A typical formulation for UV curing would contain the following:

monomers;
urethane acrylates;
photoinitiators and /or amine synergists;
additives for use as flow aids and defoamers.

Typical monomers are of the polymerizable plasticizer type based on functionally active acrylates. A difunctional acrylate would be used for chain-extension purposes, while a trifunctional one would be primarily used to control crosslink density and hence cure state. Both would have low viscosity, approximately 100 cps, and hence during processing act as plasticizers.

Photoinitiators

Two classes are known based on free radicals and hydrogen abstraction techniques, respectively. Free residual types are receptive to UV irradiation by absorbing radiation energy such that free radicals result and these produce a chain polymerization reaction and eventually a solid polymer matrix. An example of the photoinitiation reaction sequence, which follows a Norrish I-type cleavage. Another photoinitiator would be benzoin butyl ether.

Hydrogen Abstraction

Such types are typified by benzophonone and function by UV light exciting the singlet to the triplet state, whence a hydrogen atom is extracted from an adjacent donor molecule, e.g. amine synergist leading to free radical deformation and hence to polymerization.

Urethane Acrylates

These are made by reaction of an acrylate monomer with the diisocyanate, usually in the presence of a catalyst such as dibutyltin dilaurate. An example of a typical urethane acrylate reaction results in a flexible elastomer, based on hydroxyl ethyl acrylate.

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 react generally with compounds containing active hydrogen atoms. Therefore, the use of a small excess of isocyanate caused the formation of light structure products containing urethane groups. The characteristics of isocyanates are well known for reactivity with other functional groups, and solubility in many organic materials [19]. The adhesion property of isocyanate-based adhesives will be examined in detail. These characteristics are summarized as follows:

1. Isocyanates react readily with a variety of other functional groups.
2. Di- and polyisocyanates can undergo self-polymerization to form three-dimensional resins in situ.
3. Isocyanates are quite soluble in many organic substances, and due to their small molecular size it readily permeates insoluble porous structures.
4. The reaction of di- and polyisocyanates with hydroxyl-bearing polyesters and polyethers, co-reactants in many isocyanate adhesive applications, produces the strong, polar, hydrogen-bonded, and flexible polyurethanes which, when wet, intimately contact and show strong attraction for a variety of surfaces.
5. Isocyanates provide elastomer-metal bonds with flexible to rigid gradation in physical properties between elastomer and metal which afford superior fatigue life.
6. Isocyanates react with hydrated oxide layers on metal surfaces, thus producing an in-situ clean surface, and therein most probably allowing the urea groups of the adhesive to form chemical bonds with the residual valencies of the metal lattice.

The glass transition temperature (T_g) is also a very important characteristic property of polymers [20]. It is of major importance in determining the upper use temperature for a polymer used as a plastic or fiber in load bearing applications [21]. However, T_g shows considerable increase with the chemical conversion during the UV curing [22]. By synthetic method including the addition of 2-isocyanatoethyl methacrylate, T_g value of synthesized materials could be lowered as -10 ^{o}C as compared with that reported in the previous study [23]. Therefore, we can anticipate by implementation of this research that lower T_g and lower viscosity affected by it are better for the production efficiency.

Three types of poly(alkyl urethane) acrylate oligomers such as poly(methyl

urethane) acrylate oligomer (MUAO), poly(ethyl urethane) acrylate oligomer (EUAO), and poly(2-ethylhexyl urethane) acrylate oligomer (2-EHUAO) were synthesized from single hydroxyl-terminated polyacrylate oligomers in this research. And each oligomer was blended with hyperbranched urethane acrylate oligomers (HUA, HUA-s, and HUA-p) and then photopolymerized by UV irradiation.

The poly(alkyl urethane) acrylate oligomers were obtained by the reaction of hydroxyl-terminated alkyl acrylate oligomers and 2-isocyanatoethyl acrylate. Synthesis of poly(alkyl) acrylate oligomers were done with 2-mercaptoethanol (2-MEOH), alkyl (methyl, ethyl, 2-ethylhexyl) acrylate, 2,2-azobisisobutyronitrile (AIBN, initiator) and dibutyltin dilaurate as a catalyst. Then 2-MEOH was used for functional chain transfer agent. FT-IR, FT-NMR, and GPC were used to characterize their molecular structure. The thermal property and rheologic behavior of the synthesized oligomers were also investigated by a differential scanning calorimetry (DSC) and a rheometer. Each oligomer was blended and photopolymerized by UV irradiation. And then, the adhesion properties of isocyanate-based adhesives including thermal resistance, ball tack, and gel content were confirmed with peeling tester and ball tack tester. Photopolymerized poly(alkyl urethane) oligomers can be used for UV curable coatings, inks, and adhesives.

II. Experimentations and Discussions

Part I. Synthesis and Characterization of Poly(alkyl urethane) Acrylate Oligomers for UV Curable Coating Agent

1. Experiment

1.1. Materials

For this study, methyl acrylate (99%, MA), ethyl acrylate (99%, EA), 2-ethylhexyl acrylate (99%, 2-EHA), 2-mercaptoethanol, 2-isocyanatoethyl methacrylate, dibutyltin dilaurate (DBTDL), and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Aldrich Chemical Co. and used without any further purification. All solvents (HPLC grade) were obtained from Junsei Chemical Co. and used without further purification.

1.2. Preparation of hydroxyl-terminated poly(alkyl) acrylate oligomers

To prepare single hydroxyl-terminated poly(alkyl) acrylate oligomers, a solution of AIBN, alkyl acrylate, 2-mercaptoethanol in toluene was stirred at 65 ℃ for 1.5 hrs under N_2. 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 poly(alkyl) acrylate oligomers (HTP(alkyl)AO) (**1**). As a solvent, toluene and residues were distillated under the reduced pressure for 3 hrs 50 ℃. The obtained oligomers were transparent and very sticky.

1.3. Synthesis of poly(alkyl urethane) acrylate oligomers

Poly(alkyl urethane) acrylate oligomers (**2**) were obtained by the reaction of single hydroxyl-terminated polyacrylate oligomers (**1**) and 2-isocyanatoethyl methacrylate in an equal mole dissolved in toluene and stirring for 1.5 hrs at room temperature in the presence of dibutyltin dilaurate as a catalyst until the peak at 2270 cm^{-1} of NCO group in FT-IR spectrum disappeared. The reactant was dried under a vacuum system.

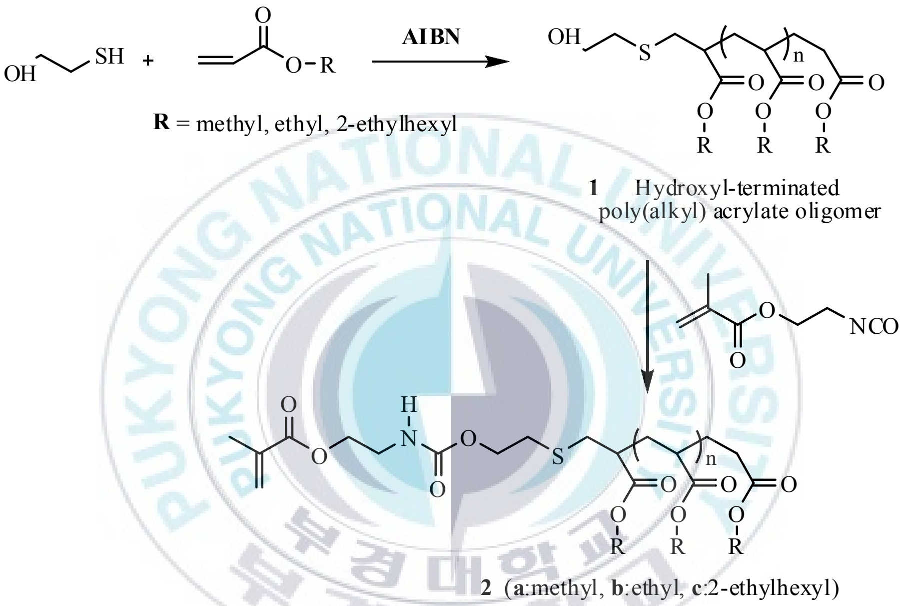


Fig. 1-1. Preparations of poly(alkyl urethane) acylate oligomers (AUAOs).

1.4. Characterization

The functional groups of poly(alkyl urethane) acrylate oligomers were confirmed by means of FT-IR spectroscopy (Perkin Elmer SPECTRUM 2000 of single beam) using solutions of oligomers with chloroform. Scanning number was 20 at a resolution of 4 cm^{-1} within the range 400 - 4000 cm^{-1}. The structure of synthesized oligomers was identified with 400 MHz FT-NMR spectroscopy (JEOL, JNM-ECP400) using acetone-d_6 as the solvent. The chemical shifts were obtained for the acetone-d_6 signal at 2.00 ppm as an internal reference for ^1H-NMR. The number average molecular weight (M_n) and polydispersity index (PDI) of AUAOs were obtained with gel permeation chromatography (GPC) (Agilent Technologies, Agilent 1100) after calibration with standard polystyrene. The thermal property was investigated by a differential scanning calorimetry (DSC) (Perkin Elmer, Pyris 1). All samples of 9.600 mg were subjected to the same thermal history, which consisted of a cooling scan from ambient temperature down to -50 ℃, follows by a heating scan from that temperature up to 50 ℃. The heating rate was 10 ℃/min and N_2 gas was flowed as the rate of 50 mL/min in the all case. Glass transition temperature (T_g) was taken as the midpoint temperature. The controlled shear stress versus shear rate and viscosity using reactive diluents were obtained with a rheometer (Carri-Med Ltd, CSL 500). The phenoxyethyl acrylate (20 wt%) having mono functional group was used as reactive diluents for getting lower viscosity which is proper to UV curing.

2. Results and discussion

Functional chain-transfer agents are useful for preparing single hydroxyl-terminated polyacrylate oligomers [24,25] because they have both –SH and –OH in the molecule and have potential for a wide range of applications because of the presence of hydroxyl functional groups at the chain end for the sites for chemical modification. This can affect the physical properties of the resulting polymers [26]. It means that –SH group as chain transfer and –OH as functional group for formation of urethane group after reaction with isocyanate group exist in the molecule. 2-Mercaptoethanol was used as chain transfer agent by the reason of above-mentioned advantages.

Single hydroxyl-terminated polyacrylate oligomers using acrylate monomer were synthesized according to the previous report [23]. The different molar ratios of AIBN, alkyl acrylate, and 2-mercaptoethanol for the synthesis of poly(alkyl urethane) acrylate oligomers (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(ethyl urethane) acrylate oligomer (EUAO), and that for 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 [27,28]. Moreover, acrylates are easily polymerized from monomer state at 60 ℃ [29,30].

We successfully prepared mono-functional acrylic urethane acrylate oligomers by the reaction of single hydroxyl-terminated polyacrylate oligomers 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 Fig. 1-1. In the synthetic procedure of AUAO, 2-isocyanatoethyl methacrylate was used for the formation of urethane groups containing carbon double bond in

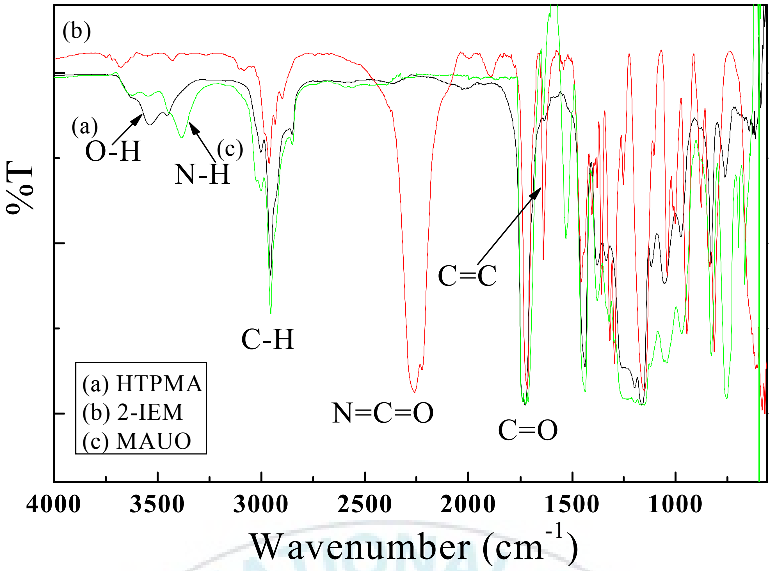
AUAOs, because it has NCO group in the molecule with end of vinyl groups [31]. So, vinyl group can be changed from double bond to single bond after photo-polymerization by UV curing. This indicates that AUAOs containing urethane group possibly do UV cure at the same time.

2.1. Structure analysis on the AUAOs

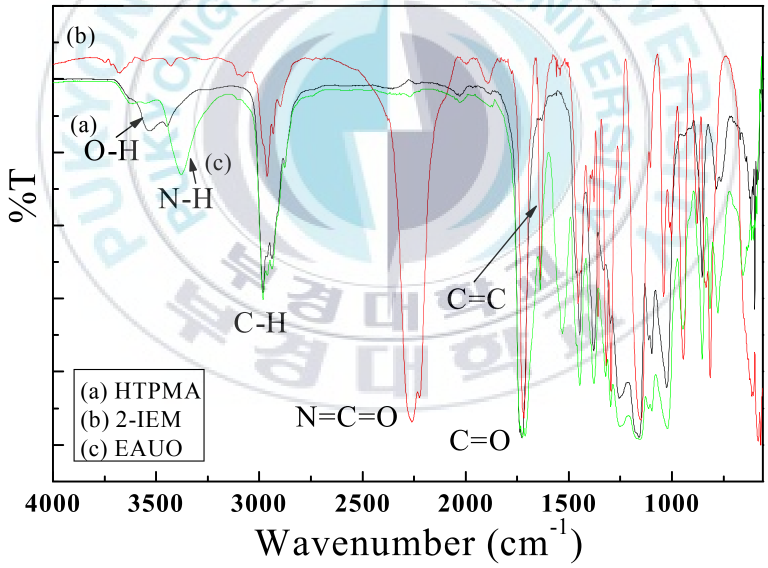
The structure of poly(methyl urethane) acrylate oligomer (**2a**, MUAO), poly(ethyl urethane) acrylate oligomer (**2b**, EUAO), and poly(2-ethylhexyl urethane) acrylate oligomer (**2c**, 2-EHUAO) were confirmed with FT-IR, ^{1}H-NMR, and GPC. The assignments of peaks in the data for identification of their structures of MUAO, EUAO and 2-EHUAO were described in detail as follows.

2.1.1. FT-IR Analysis

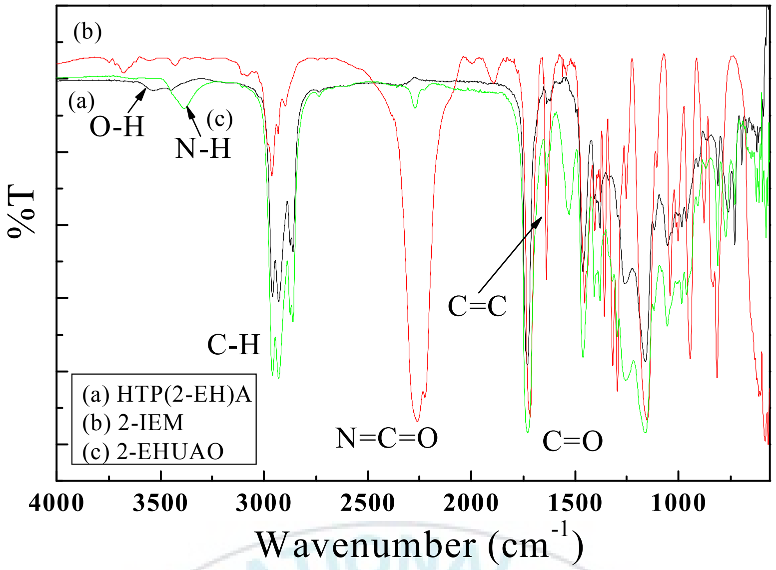
From Fig. 1-2, we can check the compared assignments of main absorption bands in the FT-IR spectra of AUAOs with hydroxyl-terminated poly(alkyl) acrylate oligomer (HTPAAOs). Because AUAO includes urethane groups after the reaction of 2-isocyanatoethyl methacrylate and HTPAAOs, the changed functional groups can be confirmed by the comparison of assignments of absorption peak. 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.



(a) FT-IR spectra for MUAO.



(b) FT-IR spectra for EUAO.



(c) FT-IR spectra for 2-EHUAO.

Fig. 1-2. FT-IR spectra for; (a) MUAO, (b) EUAO, and (c) 2-EHUAO.

2.1.2. FT-NMR Analysis

NMR spectra are useful in polymer characterization and allow us to have a deep insight into the structure of the polymer chains [32]. By comparing peaks of HTPAAOs and AUAOs, we can decide that AUAOs were successfully synthesized completely. The ^{1}H-NMR spectra assignments of AUAOs are shown as follows.

2a: Poly(methyl urethane) acrylate oligomer : ^{1}H-NMR (acetone-d$_6$, ppm) 1.93 (s, 3H, CH_3), 1.99-2.03, 2.25-2.31 and 2.59-2.79 (m, , all kinds of CH_2 and CH), 3.18-3.24 (m, 2H, $NHC\underline{H_2}$), 3.67 (s, 3H, $C\underline{H_3}$, methyl acrylate), 4.41-4.45 (m, 2H, $CO_2C\underline{H_2}$), 5.58(dd, 1H, J = 1.5 Hz and J = 15.0 Hz, $C{=}CH_2$, trans to methyl), 6.15 (dd, 1H, J = 1.2 Hz and J = 8.0 Hz, $C{=}CH_2$, cis to methyl), 8.00 (NH).

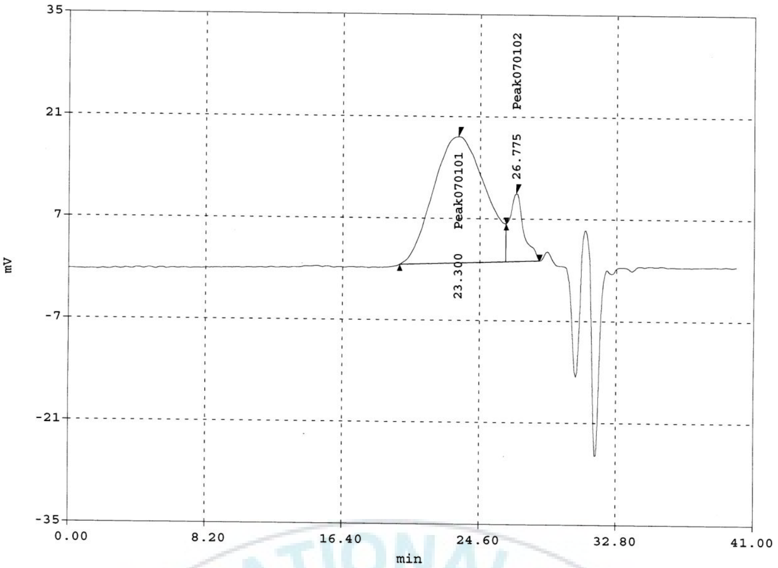
2b: Poly(ethyl urethane) acrylate oligomer : ^{1}H-NMR (acetone-d_6, ppm) 0.96-1.00 (m, 3H, $C\underline{H}_3$), 1.55-1.58 (m, 3H, $C\underline{H}_3CH_2$), 1.93 (s, 3H, $C\underline{H}_3$), 1.95-2.03, 2.59-2.65 and 2.72-2.80 (m, all kinds of CH_2 and CH), 3.24-3.30 (m, 2H, $NHC\underline{H}_2$), 4.08-4.13 (m, 2H, $CH_3C\underline{H}_2$), 4.40-4.46 (m, 2H, $CO_2C\underline{H}_2$), 5.71 (dd, 1H, J = 1.5 Hz and J = 15.0 Hz, $C{=}CH_2$, trans to methyl), 6.38 (dd, 1H, J = 1.2 Hz and J = 8.0 Hz, $C{=}CH_2$, cis to methyl), 8.20 (NH).

2c: Poly(2-ethylhexyl urethane) acrylate oligomer : ^{1}H-NMR (acetone-d_6, ppm) 0.96-1.06 (m, 3H, $C\underline{H}_3$), 1.93 (s, 3H, $C\underline{H}_3{-}C{=}CH_2$), 1.25-1.29, 1.57-1.65, 1.99-2.06, 2.25-2.29 and 2.72-2.79 (m, all kinds of CH_2 and CH), 3.20-3.29 (m, 2H, $NHC\underline{H}_2$), 4.41-4.45 (m, 2H, $CO_2C\underline{H}_2$), 5.80 (dd, 1H, J = 1.5 Hz and J = 15.0 Hz, $C{=}CH_2$, trans to methyl), 6.25 (dd, 1H, J = 1.2 Hz and J = 8.0 Hz, $C{=}CH_2$, cis to methyl), 8.18 (NH).

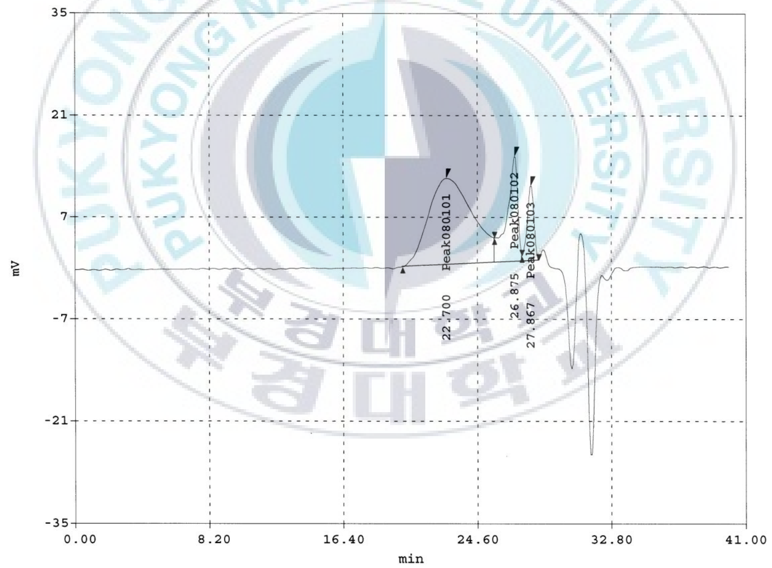
The protons of acrylic double bond exhibit three signals between 5.58 and 5.80 ppm in each spectrum. According to this result, we can confirm introduction of C=C bonds in the final structures of AUAOs for UV curing.

2.1.3. GPC Analysis

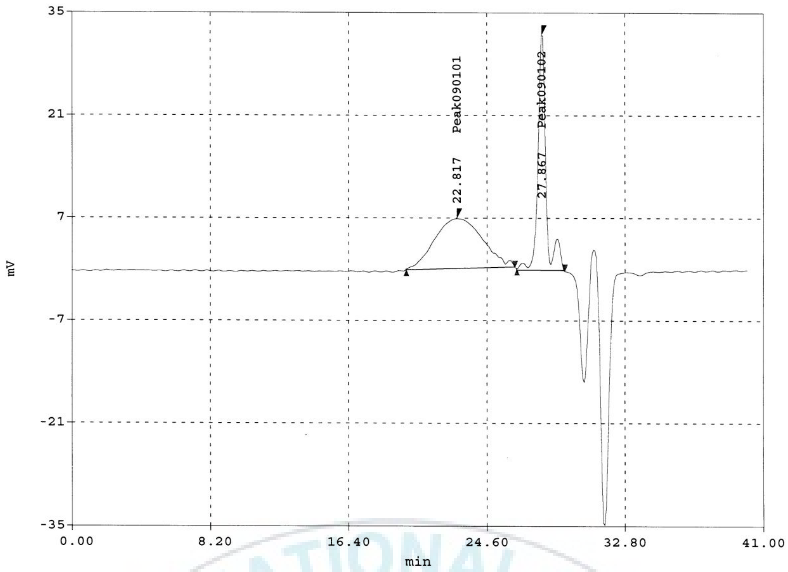
The molecular weight measurements were performed by GPC in a THF eluent with a calibration curve of polystyrene standards. For example, the number average molecular weight (M_n), weight average molecular weight (M_w), and molecular weight distribution (M_w/M_n) of MUAO were 2077, 3198, and 1.5, respectively. M_n, M_w, and M_w/M_n curve of AUAOs are shown in Fig. 1-3 and listed in Table 1-1.



(a) GPC curve of MUAO.



(b) GPC curve of EUAO.



(c) GPC curve of 2-EHUAO

Fig. 1-3. Molecular weight of AUAOs measured by GPC; (a) MUAO, (b) EUAO, and (c) 2-EHUAO.

Table 1-1. Molecular weight of AUAOs.

#	Sample	M_n	M_p	M_w	M_z	M_{z+1}	M_v	PD	IV
1	MUAO	2077	2786	3198	4607	6136	N/A	1.53962	N/A
2	EUAO	2580	3701	3582	4706	5832	N/A	1.38811	N/A
3	2-EHUAO	2634	3503	3871	5384	7075	N/A	1.46960	N/A

2.2. Thermal behavior analysis on AUAOs

2.2.1. DSC Analysis

In Fig. 1-4 (a), T_g of MUAO using DSC scanned from -50 ℃ to 50 ℃ shows the lower value of T_g than that of the previous material [23]. Reported T_g value of HTPMA was about -25 ℃, but that of MUAO containing urethane groups was measured as -34 ℃. T_g is very important factor to prepare polymer by UV curing. After UV curing, oligomers having low T_g are easily processed by lower cost and energy. Because such advantage was obtained, the data was valuable although only one reagent was used newly in this research.

Fig. 1-4 (b) and (c) show T_g values of EUAO and 2-EHUAO determined from the DSC. T_g of synthesized materials were as follows; EUAO was -13.13 ℃, and 2-EHUAO was -9.17 ℃. Generally, polar groups have a high cohesive force and participate in intermolecular hydrogen bonding and restrict the rotation of polymer segment. This results in a higher hardness and smaller elongation at break [33]. However, the increase of the length of the methylene groups in the branches was caused that T_g of EUAO is lower than that of 2-EHUAO, while 2-EHUAO has longer branches and the same molar ratio of monomer compared with EUAO. From this result, we can confirm that the length of the branches affected their thermal property more than effect of hydrogen bonding.

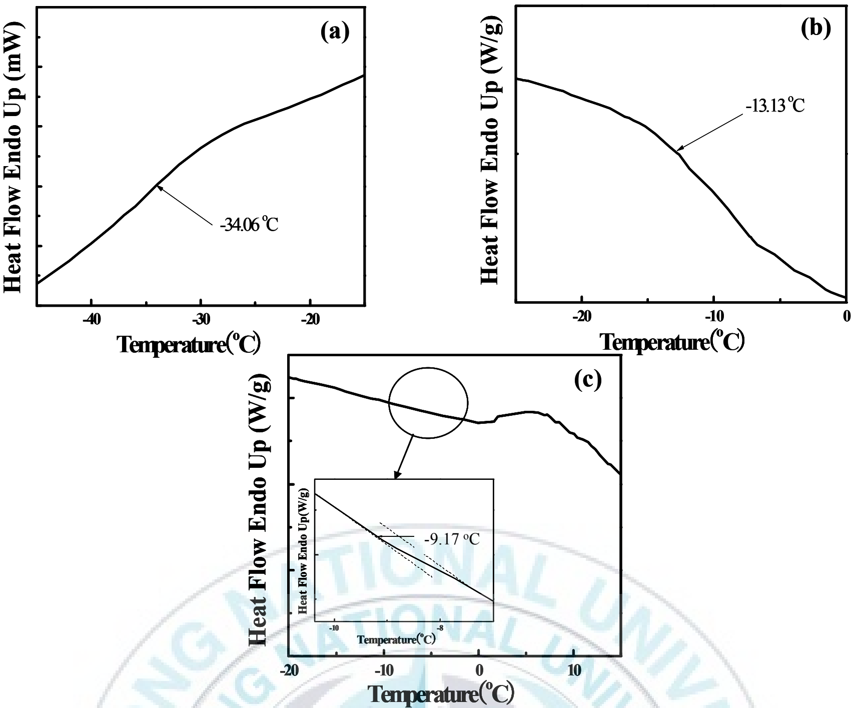
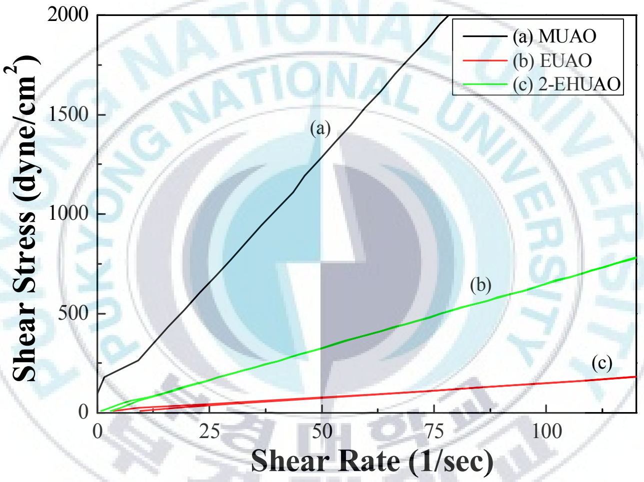


Fig. 1-4. The glass transition temperature (T_g) for: (a) MUAO (b) EUAO, and (c) 2-EHUAO.

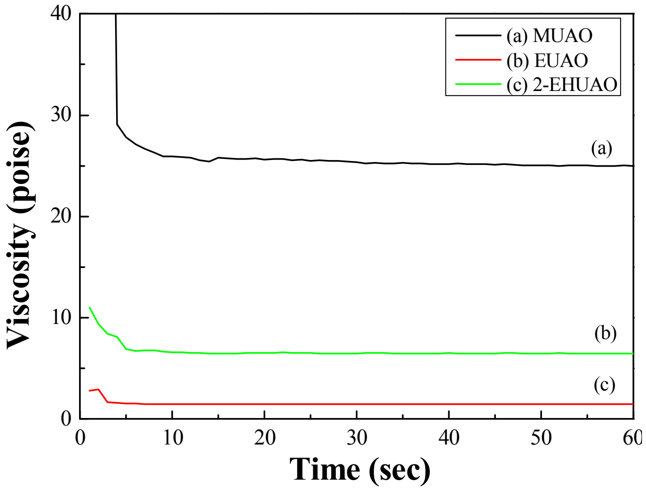
2.3. Rheological behavior analysis on the AUAOs

2.3.1. Rheometer Analysis

The rheological property is very important factor determining the processibility and end-use property of a polymer material. The chain structure of a polymer determines its rheological properties [34]. Fig. 1-5 shows that shear stress (dyne/cm^2) increased with the increase of the shear rate (1/sec) and the viscosity of AUAOs was constant to the measuring time at 25 ℃. 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 [35,36]. Rheological behavior of EUAO and 2-EHUAO appears as two types. The stress-strain curves have the point to some capacity for the orientation on the extension of these polymers [37]. Even if both of reactants had the same amount of monomer in this study, 2-EHUAO had to have the higher viscosity because of stereochemical effect of different kinds of alkyl groups. However, we identified that the rheological property was more affected by hydrogen bonds than their structure. Also when phenoxyethyl acrylate was used as a reactive diluent, the lower viscosity was obtained than using 2-ethylhexyl acrylate [38,39].



(a) Shear stress versus shear rate for AUAOs.



(b) Viscosity of AUAOs.

Fig. 1-5. Shear stress versus shear rate and viscosity for AUAOs in 20 wt% of phenoxyethyl acrylate as a diluent at 25 ℃.

3. Conclusion

Poly(alkyl urethane) acrylate oligomers were synthesized from 2-mercaptoethanol (2-MEOH), alkyl (methyl, ethyl, and 2-ethylhexyl) acrylate, 2,2´-azobisisobutyronitrile (AIBN, initiator), and 2-isocyanatoethyl methacrylate for the UV curing. And 2-isocyanatoethyl methacrylate was used to obtain the hydrophilicity of the molecule due to the formation of urethane group and the unsaturated C=C groups of the molecular backbone was introduced for the UV curing. The structure, thermal property, and rheological behavior were characterized with FT-IR, NMR, GPC, DSC, and rheometer. Poly(alkyl urethane) acrylate oligomers had the lower T_g and viscosity than those reported in the previous study [23]. It means that synthesized oligomers were suitable to do UV curing compared with single hydroxyl-terminated polyacrylate oligomers. Therefore, lower T_g and viscosity of the reactants are better for the production efficiency. Also, because urethane groups are contained in the structure of AUAOs, they have more advantages than those without urethane group as excellent physical and mechanical properties, such as adhesion on substrates, flexibility and impact strength.

Part II. Photo-Polymerizaion of Poly(Alkyl Urethane) Acrylate Oligomers Using Hyperbrenched Polymer by UV Irradiation for Curable Coating

1. Experiment

1.1. Materials

Seven prepolymers were used. These are poly(alkyl urethane) acrylate oligomers (AUAOs) (R = methyl, ethyl, and 2-ethylhexyl) [40], epoxy urethane acrylate oligomer (EUA) [33], and hyperbranched urethane acrylate oligomers (HUA, HUA-s, HUA-p) [18]. Fig. 2-1 and 2-2 show the structures of used prepolymers. Irgacure 184 (3 wt%) as a photoinitiator was purchased from Ciba Specialty Chemicals. 2(2-Ethoxyethoxy) ethyl acrylate and cyclic trimethylolpropane formal acrylate were obtained from Sartomer Company, Inc. and used without any further purification. All solvents (HPLC grade) were purchased from Junsei Chemical Co. and Sigma-Aldrich Co. and they were used without further purification.

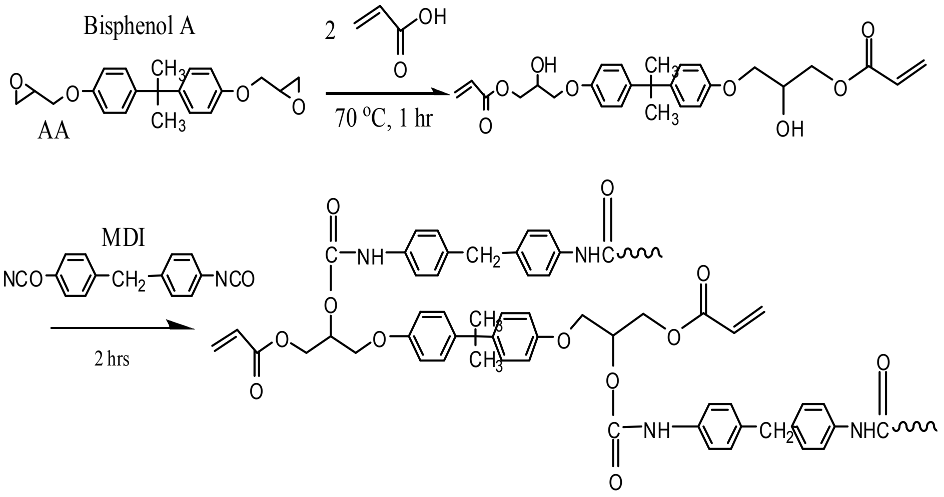


Fig. 2-1. Synthetic scheme and structure of epoxy urethane acrylate oligomer (EUA).

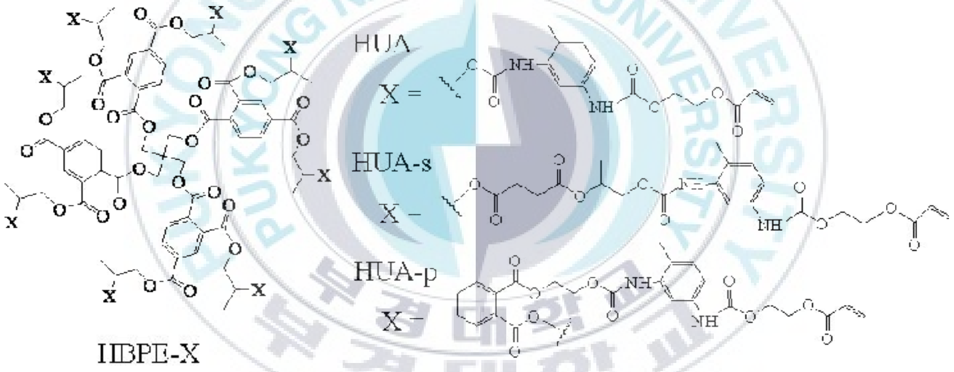


Fig. 2-2. Structures of hyperbranched urethane acrylate oligomers (HUA); HUA[1], HUA-s[2], HUA-p[3].

HUA[1] : hyperbranched urethane acrylate oligomer
HUA-s[2] : hyperbranched urethane acrylate oligomer - succinic
HUA-p[3] : hyperbranched urethane acrylate oligomer – phthalic anhydride

1.2. UV Curable Formulations

UV curable resins are most commonly based on acrylates as the reactive functional group. Substituting a new component in a basic formulation and comparing the properties of new material to those of original formulation usually make improvements [43]. The various components such as synthesized AUAOs, EUA, and HUA, diluent, and photoinitiator were mixed in different ratios and the formulations tested for their efficacy. According to control of amount of AUAOs and diluent, standard component was separated two kinds of type such as permanent and removal adhesive. Glass transition temperature (T_g) of final adhesive was controlled with Fox equation (Eq. 2-1) from -50 ^{o}C to 10 ^{o}C.

$$1/T_g\ (\mathrm{K}) = \omega_1/T_{g1} + \omega_2/T_{g2} + \omega_3/T_{g3} + \ldots + \omega_n/T_{gn}$$

$$\omega_1 + \omega_2 + \omega_3 + \ldots + \omega_n = 1,\ \omega : \text{weight fraction}$$

Eq. 2-1. Fox equation for selection of standard component.

Poly(methyl urethane) acrylate oligomer (MUAO) and poly(ethyl urethane) acrylate oligomer (EUAO) were used as a main oligomer. And 2(2-ethoxyethoxy) ethyl acrylate (2-EEEA) was used as a reactive diluent. Experiment was implemented separating two parts such as -50 ~ -30 ^{o}C of low T_g component and -30 ~ -10 ^{o}C of high T_g component. Table 2-1 shows T_g and viscosity according to the components.

Table 2-1. T_g and viscosity according to the components for permanent and removal adhesive; (a) low T_g component and (b) high T_g component.

Sample Name	LT-1	LT-2	LT-3	LT-4	LT-5	LT-6	LT-7	LT-8
[1]EUAO	75	75	50	25	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]2-EEEA	50	75	75	50	100	150	150	150
T_g (℃)	-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

(a) Low T_g component for permanent adhesive.

Sample Name	HT-1	HT-2	HT-3	HT-4	HT-5
EUAO	100	100	100	100	100
2-EEEA	50	40	30	20	10
[5]CTFA	0	10	20	30	40
T_g (℃)	-28.4	-24.3	-20.1	-15.8	-11.4
Viscosity (cps)×1000	4.1	4.1	4.1	4.2	4.2

(b) High T_g component for removal adhesive.

[1] Poly(ethyl urethane) acrylate oligomer (EUAO)

[2] Poly(methyl urethane) acrylate oligomer (MUAO)

[3] Poly(2-ethylhexyl urethane) acrylate oligomer (2-EHUAO)

[4] 2(2-ethoxyethoxy) ethyl acrylate (2-EEEA)

[5] Cyclic trimethylolpropane formal acrylate (CTFA)

1.3. Preparation of Process for UV Curing

Various components were mixed with Irgacure 184 (3 wt%), then drawn on a 25 µm of polyethylene terephthalate film (PET) with an applicator of 20 μm^{-1} (permanent type) and 10 μm^{-1} (removal type) gap, respectively, then exposed to obtain a cured film to an UV lamp (mercury and metal halide, 220/380V, 3 P, 50/60 Hz, 120 w/cm, made by JEIL UV Co., Ltd., Korea) at 60 m/s of line speed and distance from light source was 10 cm.

1.3.1. Selection of Light Source and Arrangement

A permanent type of LT-6 and LT-7 and a removal type of HT-1 and HT-2 were tested for selection of arrangement of light source. Fig. 2-3 shows a UV curer including four of UV lamps and carrier belt. Used UV lamps were consisted of two mercury lamp (300 and 365 nm) and two metal halide lamp (265 ~ 420 nm). Their arrangement was selected as Table 2-2. Because arrangement of metal halide lamp at first position radiating continuously 265~420 nm of wavelength affected high inside cure efficiency.

Table 2-2. Arrangement of UV lamps consisted of metal halide and mercury lamps.

Name	Lamp 1	Lamp 2	Lamp 3	Lamp 4
1	[1]MH	[2]HPM	[1]MH	[2]HPM

[1]MH : Metal Halide Lamp, [2]HMP : High Pressure Mercury Lamp.

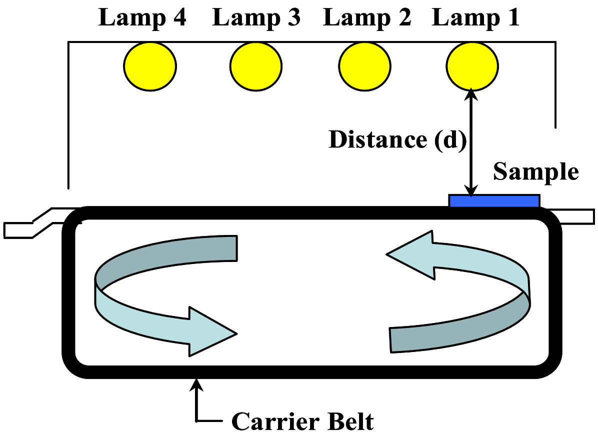


Fig. 2-3. UV curor.

1.3.2. Selection of Line Speed and Distance between Light Source and Materials

To maximize UV dose is to optimize UV cure rate because UV cure rate is in proportion to radiated energy to substrate. These UV dose can be expressed as following equation.

$$\text{Dose } (\mu\text{W}\bullet\text{sec/cm}^2) = \text{Intensity } (\mu\text{W/cm}^2) \times \text{Time (sec)}$$

Eq. 2-2. Equation of UV dose for calculation of cure rate.

From this equation and experiment, line speed was selected as 30 m/min. And distance between light source and material was settled as 4 cm.

1.4. Characterization

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). UV curing was performed with UV curor (LICHTZEN CO., LTD., Jeil UV Testing Curer). After 48 hrs from UV curing, formulations' adhesiveness was identified with ball tack tester according to KSA 1107. Their heat resistance was obtained by checking temperature when sample was detached from SUS304 plate as 0.1 mm. And test for gel content was performed UV cured sample (10 cm × 10 cm) was dipped in toluene for 24 hrs at 25 ℃. Then, ratio of its changed weight was calculated after drying completely in 120 ℃ of dry oven.

2. Results and discussion

2.1. Physical properties of standard components

2.1.1. Physical properties of low T_g component for permanent adhesive

Fig. 2-4 shows adhesiveness and ball tack of low T_g component for permanent adhesive. We can know that from Fig. 2-4 according to the decrease of T_g, ball tack was increased. On the other hands, adhesiveness of LT-7 had maximum value. Low T_g led to the increase of flexibility and tack, but cohesive force was decreased. As a result, adhesiveness for T_g was maximum.

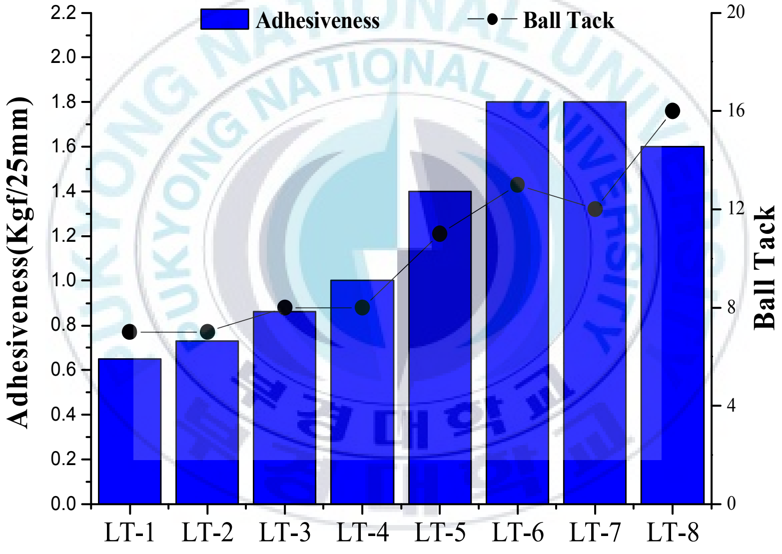


Fig. 2-4. Adhesiveness and ball tack of low T_g component for permanent adhesive.

Heat resistance of low T_g component for permanent adhesive appears in Fig. 2-5. Result of heat resistance test shows similarity with cohesive force analysis by adhesiveness test. As shown Fig. 2-5, heat resistance of LT-4 and LT-5 was the highest, but that of LT-1 and LT-2 was low. It can be found that adhesive having too high T_g has high cohesive force, but its flexibility is decreased drastically. So, this phenomenon occurred as a result of the decrease of adhesion area and adhesiveness.

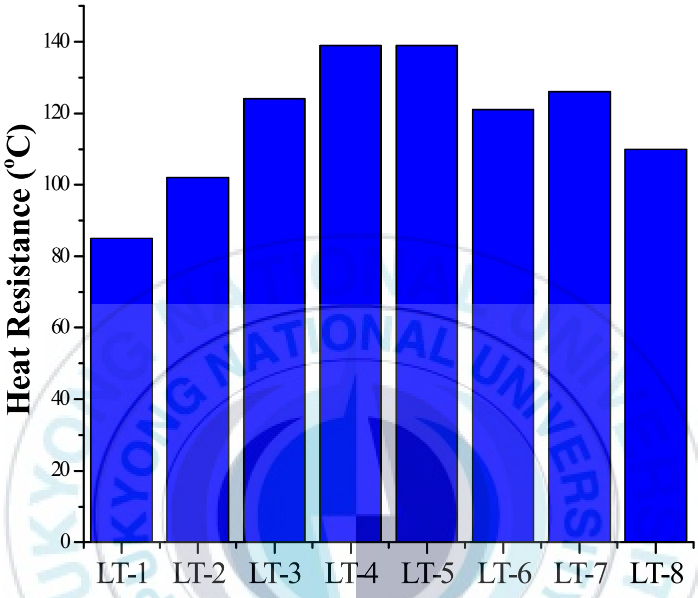


Fig. 2-5. Heat resistance of low T_g component for permanent adhesive.

2.1.2. Physical properties of high T_g component for removal adhesive

Fig. 2-6 and 2-7 show adhesiveness, ball tack, and heat resistance of high T_g component for removal adhesive. Adhesiveness and ball tack was decreased according to the increase of T_g like as low T_g component. In case of HT-4 and HT-5, to obtain their ball tack was impossible because it was lower than lowest value to be measured by ball tack tester.

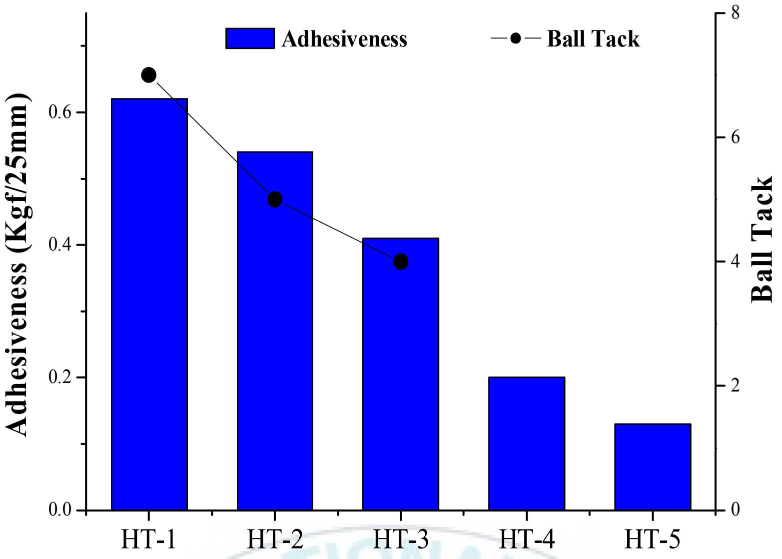


Fig. 2-6. Adhesiveness and ball tack of high T_g component for removal adhesive.

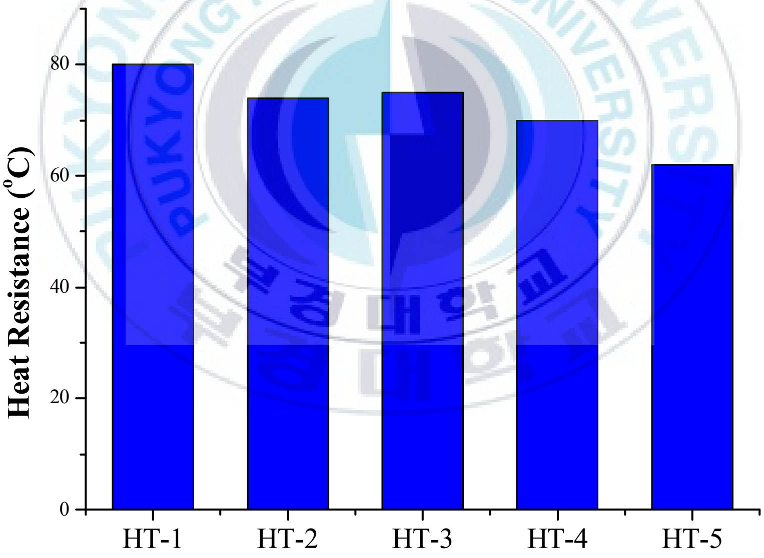


Fig. 2-7. Heat resistance of high T_g component for removal adhesive.

2.1.3. Selection of standard components for UV curable adhesives

From measured physical properties including adhesiveness, ball tack, and heat resistance, we can choose the standard components for permanent and removal type of UV curable adhesives. LT-6 was selected as a permanent type of standard component. And HT-1 was chosen as a removal type of standard component.

2.2. Physical properties of components added multifunctional oligomers (MFOs)

In order to prepare high performance adhesives, blending was tried using difunctional epoxy urethane acrylate oligomer (EUA), octafunctional hyperbrenched urethane acrylate oligomer (HUA, HUA-s, and HUA-p), and tackifier. Then, tackifier was C-9 hydrocarbon.

2.2.1. Physical properties of components added multifunctional oligomers for permanent adhesive

For improvement of heat resistance and gel content of permanent adhesive, MFOs were added to LT-6. Then, their influence on adhesion properties and heat resistance were shown in Fig. 2-8 and Table 2-3. As shown in Fig. 2-8, case of EUA was decreased smoothly because it was difunctional oligomer compared with octafunctional HUA. Component containing 0.8 ~ 1.0 part of addition and 2 part of EUA for all MFOs was selected for permanent adhesive.

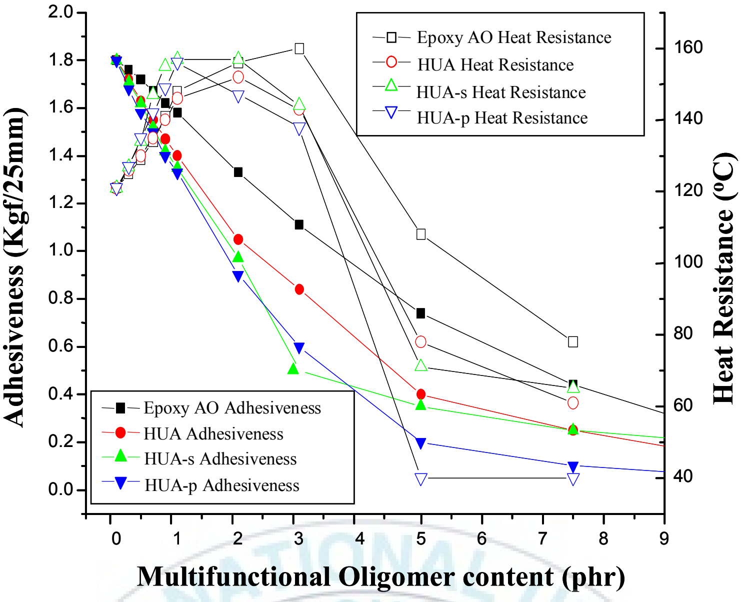


Fig. 2-8. Adhesiveness and heat resistance curves of LT-6 according to the content of multifunctional oligomers.

Table 2-3. Adhesiveness and heat resistance of LT-6 according to the content of multifunctional oligomers for permanent adhesive.

A	Epoxy AO		HUA		HUA-s		HUA-p	
	B	C	B	C	B	C	B	C
0	1.8	121	1.8	121	1.8	121	1.8	121
0.4	1.72	129	1.63	130	1.62	134	1.58	135
0.8	1.62	141	1.47	140	1.42	155	1.4	149
1	1.58	148	1.4	146	**1.35**	**157**	**1.33**	**156**
2	**1.33**	**156**	1.05	152	0.97	157	0.9	147
3	1.11	160	0.84	143	0.5	144	0.6	138
5	0.74	108	0.4	78	0.35	71	0.2	40

A : Content (ratio), B : Adhesiveness, C : Heat resistance.

Modification of physical properties was tried by addition of C-9 hydrocarbon as a tackifier. Several components including MFOs and tackifier appear in Table 2-4.

Table 2-4. Components including LT-6, multifunctional oligomers, and tackifier for permanent adhesive.

Sample Name	LT-6	EpoxyAO	HUA-s	HUA-p	C-9
PC-1	100	2			5
PC-2	100	2			10
PC-3	100	2			15
PC-4	100		1		5
PC-5	100		1		10
PC-6	100		1		15
PC-7	100			1	5
PC-8	100			1	10
PC-9	100			1	15

From Fig. 2-9 we can confirm that adhesiveness of PC-1 and PC-4 was 1.54 and 1.56 Kgf/25mm. Therefore, their heat resistance was obtained as 152 and 154 °C. Accordingly, final permanent component for UV curable adhesive was selected as PC-1 and PC-4.

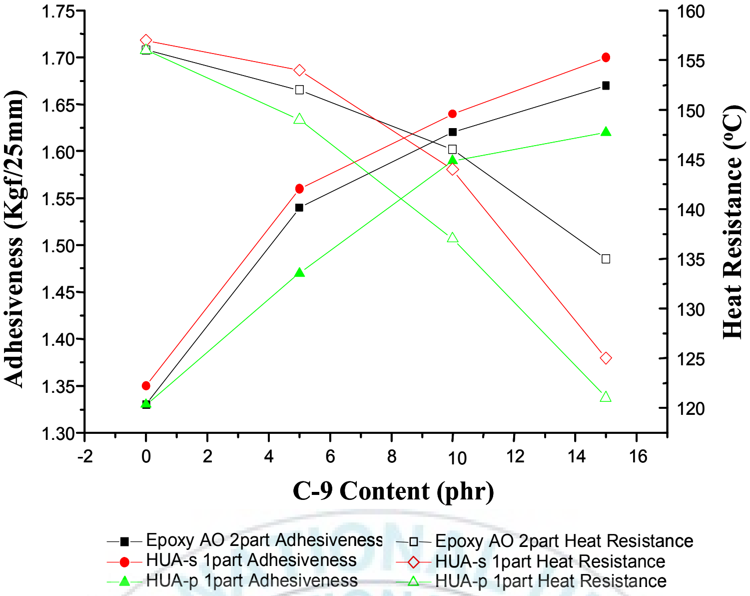


Fig. 2-9. Adhesiveness and heat resistance curves of permanent adhesive according to the content of C-9 as a tackifier.

2.2.2. Physical properties of components added MFOs for removal adhesive.

In order to prepare removal type of UV curable adhesive, blending was tried using HT-1 as a standard component, MFOs, and C-9 hydrocarbon as a tackifier. Several components appear in Table 2-5, and their adhesiveness and heat resistance are shown in Fig. 2-10.

Table 2-5. Components including HT-1, multifunctional oligomers, and tackifier for removal adhesive.

Sample Name	HT-1	Epoxy AO	HUA-s	HUA-p	C-9
RC-1	100	2			5
RC-2	100	2			10
RC-3	100	2			15
RC-4	100	2			20
RC-5	100		1		5
RC-6	100		1		10
RC-7	100		1		15
RC-8	100		1		20
RC-9	100			1	5
RC-10	100			1	10
RC-11	100			1	15
RC-12	100			1	20

From Fig. 2-10 we can confirm that adhesiveness of RC-3 was 0.8 Kgf/25mm. Therefore, its heat resistance was obtained as 153 ^{o}C. Accordingly, final permanent component for UV curable adhesive was selected as RC-3.

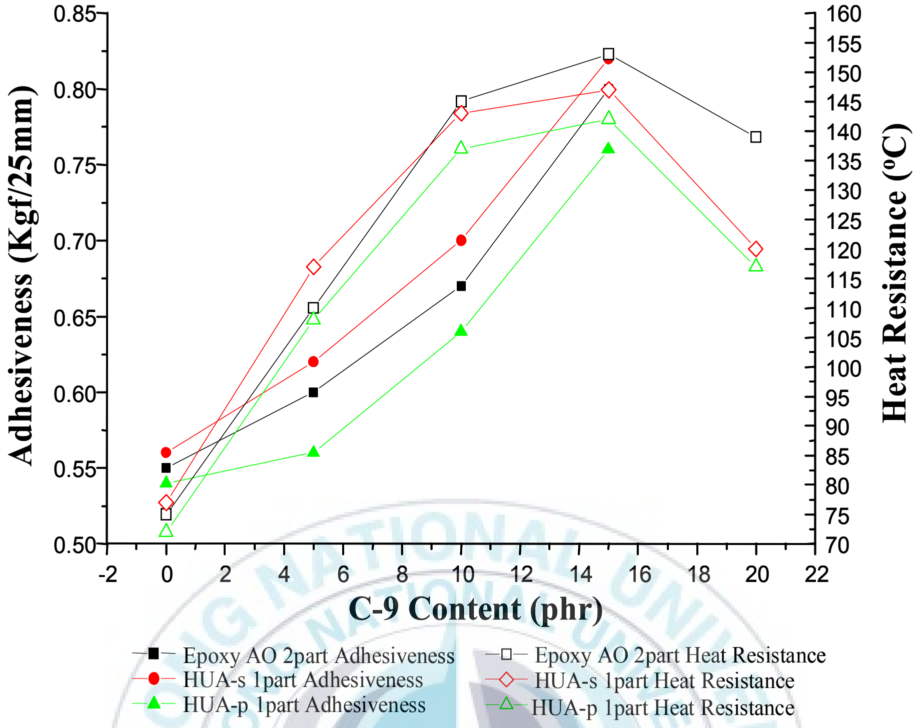


Fig. 2-10. Adhesiveness and heat resistance curves of removal adhesive according to the content of C-9 as a tackifier.

2.3. Final formulations.

Final formulation of permanent type of adhesive was selected as PC-1 and PC-4. And that of removal type of adhesive was chosen as RC-3. Their gel content and ball tack are shown in Fig. 2-11.

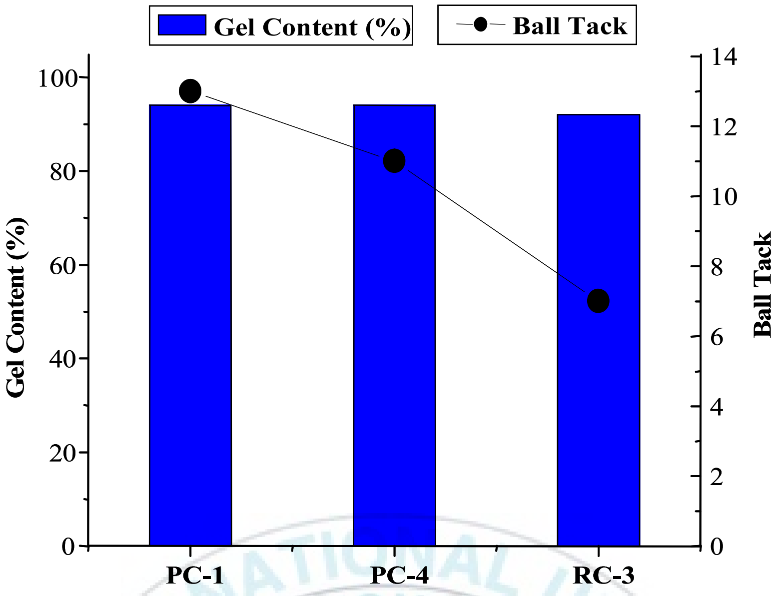


Fig. 2-11. Gel content and ball tack of permanent and removal type of adhesives.

3. Conclusion

AUAOs were blended with epoxy urethane acrylate oligomers (EUA) and hyperbranched urethane acrylate oligomers (HUA, HUA-s, and HUA-p). Then, photopolymerized by UV irradiation. Each oligomer was blended and photopolymerized by UV light, and their thermal resistance, ball tack, gel content were confirmed by peeling tester and ball tack tester. Photopolymerized permanent and removal materials can be used for UV curable coatings, inks and adhesives.

III. Summary

Growing concern for environmental protection has driven industry toward the use of solvent-free polymerization system, where UV-radiation curing has become a viable alternative to conventional thermal curing of solvent-containing polymer formulations. This solvent-free technology is now commonly used in various industrial applications to achieve an ultrafast hardening of protective coatings, printing inks, adhesives, varnishes and composites.

Three types of poly(alkyl urethane) acrylate oligomers such as poly(methyl urethane) acrylate oligomer (MUAO), poly(ethyl urethane) acrylate oligomer (EUAO), and poly(2-ethylhexyl urethane) acrylate oligomer (2-EHUAO) were synthesized from single hydroxyl-terminated polyacrylate oligomers in this research. And each oligomer was blended with epoxy urethane acrylate oligomers (EUA) and hyperbranched urethane acrylate oligomers (HUA, HUA-s, and HUA-p), and then, photopolymerized by UV irradiation.

The poly(alkyl urethane) acrylate oligomers were obtained by the reaction of hydroxyl-terminated poly(alkyl) acrylate oligomer and 2-isocyanatoethyl acrylate. Synthesis of poly(alkyl) acrylate oligomers were done with 2-mercaptoethanol (2-MEOH), alkyl (methyl, ethyl, 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, GPC, and DSC. Each oligomer was blended and photopolymerized by UV irradiation, and their thermal resistance, ball tack, and gel content were confirmed by peeling tester and ball tack tester. Photopolymerized poly(alkyl urethane) oligomers can be used for UV curable coatings, inks, and adhesives.

IV. References

[1] Tey JN, Soutar AM, Priyadarshi A, Mhaisalkar SG, Hew KM. *J Appl Polym Sci* 2007;**103**:1985.

[2] Wei YY, Luo YW, Li BF, Li BG. *J Zhejiang Univ SCI* 2004;**5**:906.

[3] Lange. *J Polym Eng Sci* 1999;**39**:1651.

[4] Kloosterboer JG, Lijten GFCM. *Polymer* 1990;**31**:95.

[5] Kloosterboer JG, Lijten GFCM. *A C S Symp Ser* 1988;**367**:409.

[6] Radhakrishnan S, Pethrick RA. *J Appl Polym Sci* 1994;**51**:863.

[7] Radhakrishnan S, Hayward D, Mackinnon AJ, Pethrick RA. *J Polym Eng Sci* 1995;**35**:184.

[8] Khan SA, Plitz IM, Frantz RA. *Rheol Acta* 1992;**31**:151.

[9] Cook WD. *Polymer* 1992;**33**:2152.

[10] Cook WD. *J Polym Sci Pol Chem* 1993;**31**:1053.

[11] Fournier J, Williams J, Holmes PA. *Macromolecules* 1997;**30**:2042.

[12] Decker C, Masson F, Schwalm R. *Macromol Mater Eng* 2003;**288**:17.

[13] Studer K, Decker C, Beck E, Schwalm R. *Eur Polym J* 2005;**41**:157

[14] Ha CS, Jung SJ, Kim ES, Kim WS, Lee SJ. *J Appl Polym Sci* 1996;**62**:1011.

[15] Lee BH, Kim HJ. *Polym Degrad Stabil* 2006;**91**:1025.

[16] Czech P, Okrasa L, Mechin F, Boiteux G, Ulanski J. *Polymer* 2006;**47**:7207.

[17] Takeichi T, Suefuji K, Inoue K. *J Polym Sci Pol Chem* 2002;**40**:3497.

[18] Xu G, Shi W. *Prog Org Coat* 2005;**52**:110.

[19] Hepburn C. *Polyurethane Elastomers* 2nd Ed. London and New York: Elsevier, 1993.

[20] Nabeth B, Corniglion I, Pascault JP. *J Polym Sci Pt B-Polym Phys* 1996;**34**:401.

[21] Alger M. *Polymer Science Dictionary* 2nd Ed. London: Chapman & Hall,

1997.

[22] Li S, Vatanparast R, Vuorimaa E, Lemmetyinen H. *J Polym Sci Pt B-Polym Phys* 2000;**38**:2213.

[23] Vásquez-garcía SR, Salgado-Delgado R, Trejo-O'Reilly JA, Martínez E, Castaňo VM. *Int J Polym Mater* 2004;**53**:735.

[24] Gang FC, Frank NJ. *Macromolecules* 1991;**24**:151.

[25] O'Brien JL, Gornick F. *J Am Chem Soc* 1995;**77**:4757.

[26] Lee MY, Park WH, Lenz RW. *Polymer* 2000;**41**:1703.

[27] Yousi Z, Jinquan G, Lizhong D, Ronghua P. *Eur Polym J* 1997;**33**:579.

[28] Takacs E, Emmi SS, Wojnarovits. *Radiat Phys Chem* 1999;**55**:621.

[29] Lim D, Kolinsky M. *J Polym Sci* 1958;**29**:579.

[30] Brandrup J, Innergut EH. *Polymer Handbook* 3rd Ed. Canada: John Wiley & Sons, Inc., 1989.

[31] Hu T, Chen S, Tian Y, Pojman JA, Chen L. *J Polym Sci Pol Chem* 2006;**44**:3018.

[32] Jena KK, Chattopadhyay DK, Raju KVSN. *Eur Polym J* 2007;**43**:1825.

[33] Oprea S, Vlad S, Stanciu A, Macoveanu M. *Eur Polym J* 2000;**36**:373.

[34] Asif A, Shi W, Shen X, Nie K. *Polymer* 2005;**46**:11066.

[35] Minoura Y, Yamashita S, Okamoto H, Matsuo T, Izawa M, Kohmoto S. *J Appl Polym Sci* 1978;**22**:1817.

[36] Minoura Y, Yamashita S, Okamoto H, Matsuo T, Izawa M, Kohmoto S. *J Appl Polym Sci* 1978;**22**:3101.

[37] Kultys A, Podkoscielny W, Pikus S. *J Polym Sci Pol Chem* 1999;**37**:4140.

[38] Kim HD, Lee DJ. *Jornal of the Korean Fiber Society* 1998;**35**:739.

[39] Lee DJ, Choi JY, Kim HD. *Jornal of the Korean Fiber Society* 1999;**36**:798.

[40] Park MN, Kang YS, Oh SW, Ahn BH, Moon MJ. *Surf Rev Lett* 2007;**14**:713.

V. Korean Summary

점착제는 테이프나 라벨이라고 하는 쉽게 접할 수 있는 제품에서 반도체 등의 분야까지 폭넓게 사용되고 있어 현대인의 생활공간 곳곳에 침투해 있다고 해도 과언이 아닐 것이다. 최근에는 환경문제에 대한 관심이 급증하면서 점착제를 무공해화 하는 대체가 시도되고 있다. 이에 UV 경화형 점착제는 UV 경화 시스템의 이점으로 인해 용제계 점착제를 대신할 훌륭한 무용제형 대체품으로 인정받고 있다. 용제/물을 사용하지 않고 무공해이며 높은 생산성과 에너지 저소비로 인한 경제성이 보장되고 치밀한 장비의 구성과 작은 작업공간만을 필요로 한다. 거기다 향상된 점착 물성과 높은 내약품성, 내열성, Tack, 내가소성을 가진다. 이러한 장점들을 가진 UV 경화형 점착제가 주목을 받고 있지만 현재까지의 UV 경화 기술의 응용은 진행되지 않았고 그에 따른 실용화에 이른 것은 거의 없는 실정이다.

이에 본 연구에서는 점착제에서 사용 가능한 유리전이온도를 가지면서 UV 경화가 가능한 아크릴계 올리고머를 합성하고, 기존 연구되었던 Hyperbranched urethane acrylate oligomer (HUA)와 Epoxy urethane acrylate oligomer (EUA)를 이용하여 내열성, 내용제성이 우수하면서 점착력과 tack 의 실용화 가능한 물성을 가지는 상온 코팅 가능한 UV 경화형 점착제 (영구형, 재박리형)를 연구•개발하였다. 합성시 구조분석 및 물성측정은 FT-IR, FT-NMR, rheometer, GPC, DSC 로 수행되었고 각기 다른 올리고머를 블렌딩하여 기본 조성 선정한 후 UV light 로 광경화한 영구형, 재박리형 점착제의 물성측정은 peeling tester, ball tack tester 등으로 이루어졌다.