Preparation and Properties of UV Curable Polyurethane Acrylates

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ABSTRACT: UV curable polyurethane (PU) acrylates have been synthesized from polypropylene glycol (PPG), isophorone diisocyanate (IPDI), and three types of reactive diluents, i.e., 2-hydroxyethylacrylate (HEA), tripropylene glycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA). The effects of soft segment length, type and concentration of the reactive diluents on the mechanical and dynamic mechanical properties have been determined. When the soft segment length was short (750), the tensile strength (σt) decreased, and elongation at break (εb) generally increased with increasing HEA concentration, due to the inferior strength of HEA homopolymer and increased molecular weight between crosslinks (M). Initial modulus (E) and σt increased and elongation at break (εb) decreased with an increase in TPGDA concentration, and the effect was more pronounced as the soft segment length was decreased. Increase in hardness and σt by increasing the diluent concentration in PPG2000 based materials, was more pronounced with higher functionality diluent, due to the increased crosslinking density. The lower temperature glass transition peak of PU was not influenced by the TPGDA incorporation, whereas that of the higher temperature moved toward the higher temperature. This was interpreted in terms of compatibility of hard segments and acrylates due to their similar polarity and hydrogen bonding.

Introduction

UV curing saves energy, and reduces or eliminates solvent emission, compared to solvent based system, since most formulations are 100% reactive oligomers and diluents. This technique has commercially been applied in printings, thin film coatings and adhesives.1–2 Recently, UV curing has also been used in photolithography1 and polymer dispersed liquid crystal (PDLC).3 In photolithographic application, a UV beam is repeatedly projected onto photocurable resin along every layer of the sliced image of model, which creates a complex structure which is not possible with any conventional manufacturing method. In preparing the PDLC composite, UV curing modifies the polymer-liquid crystal interfaces, thereby, enhancing the electrooptic performance of the composite films.

UV curable system is typically composed of reactive urethane oligomers, reactive diluents and photoinitiators. Reactive urethane oligomer is the most important component in determining the ul-
imate physical properties of UV cured coatings. Typically, it is a segmented polyurethane oligomer reacted with acrylic functionality, such as 2-hydroxyethylacrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA). The microphase separation of the urethane segments, which is mainly governed by the soft segment length and type, is a key parameter to control the dynamic mechanical properties of the PU acrylates.\textsuperscript{4,9} The reactive diluents are acrylic monomers which are added to modify the properties and to reduce the viscosity of the precursor liquids. The acylated urethanes ideally combine high abrasion resistance, toughness, tear strength and good low temperature properties of PU with the superior optical properties and weatherability of polyacrylates.\textsuperscript{5,8} Generally, monofunctional acrylates lead to decreased modulus and increased ductility, whereas multifunctional acrylates such as tripolypropylene glycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA) and monofunctional N-vinylpyrrolidone (NVP) lead to the opposite.\textsuperscript{4} In addition, multifunctional diluents show higher response to radiation.

The reactive diluent phase is more compatible with the hard segments of PU, rather than the soft segments, mainly due to the similar polarity and hydrogen bonding formation between urethane NH and acrylate carbonyls. Following Cooper \textit{et al.}\textsuperscript{5} increasing the reactive diluent content permits the development of second, high glass transition temperature ($T_g$) phase, thereby leading to the increased modulus and strength. The effect of acrylate incorporation on phase behavior should depend on the phase morphology of PU prior to acrylate incorporation, and type of acrylate, i.e., the functionality and properties of the acrylate homopolymer. UV curing is induced by the incorporation of suitable ketone type initiator, in combination with proton donors, which produces free radicals upon exposure to UV.\textsuperscript{9}

Earlier works and potential applications of this technique have well been documented in books,\textsuperscript{50,11} patents,\textsuperscript{12,13} and reviews.\textsuperscript{44} A number of factors influence the physical properties of PU acrylates. Among others, the reactive diluents have most often been encountered.\textsuperscript{43,45,48} Soft segment type and length have also been extensively investigated.\textsuperscript{40,48}

Much less work has been devoted to the hard segment type.\textsuperscript{48}

This paper considers preparations and properties of UV curable PU acrylates. The NCO terminated PU prepolymers were synthesized from polypropylene glycol (PPG) and isophorone diisocyanate (IPDI),\textsuperscript{17} followed by tipping with HEA. Molecular weight of PPG has been varied from 400-3000, and the effects of PU soft segment length on the properties of PU acrylates were studied. In addition, three types of reactive diluents having mono-, di-, and trifunctionality were used in various concentrations. A total of 25 PU acrylates was synthesized and mechanical and dynamic mechanical properties of these materials have been studied in response to the structure.

**Experimental**

PPG was dried and degassed at 80 °C, 1-2 mmHg until no bubbling was observed. Extra pure grade of IPDI (Scholven), dibutyltin dilaurate (DBT), benzophenone and N-methyl-3-aminopropanolamine (MDEA) were used without further purification.

PPG and IPDI (1:2 by mole) were charged into a 500 mL round bottom, separable flask equipped with a mechanical stirrer, thermometer and condenser with a drying tube. Approximately 300 ppm of DBT was added. The urethane forming reaction proceeded at 90 °C for over 1h and the progress of reaction was determined using a standard di-n-butylamine back titration method.\textsuperscript{46} Upon obtaining the theoretical NCO value, the reaction mixture was cooled down to 40 °C and HEA was added drop-wise. Reaction of NCO-terminated prepolymer with HEA was done for 3 h below 45 °C, and 30 min at 60 °C. The progress of reaction was also detected by measuring the NCO value.

The mixtures of urethane acrylates, 1.5 wt% benzophenone (initiator), 1.5 wt% MDEA (accelerator), and reactive diluents were heated slightly above ambient temperature to ensure homogeneous mixing, followed by casting them on a glass plate. Films were about 1 mm in thickness for tensile specimens, and 0.3-0.4 mm for dynamic mechanical test. The samples were irradiated from one side using a 80W-UV(365 nm) lamp for 30 s.
## Table 1. Tensile Properties and Hardness of UV-cured Urethane Acrylates

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Tensile modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Stress at break (MPa)</th>
<th>Hardness (Shore A)</th>
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<tr>
<td>P400-0</td>
<td>11.25</td>
<td>38.22</td>
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<td>P400-H10</td>
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<td>12.38</td>
<td>30.96</td>
<td>-</td>
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<td>23.94</td>
<td>22.31</td>
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<td>P750-0</td>
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<td>110.2</td>
<td>5.30</td>
<td>72.5</td>
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<tr>
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<tr>
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<td>25.0</td>
<td>4.06</td>
<td>85</td>
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</table>

Tensile tests at room temperature were performed following the ASTM D-1822 using a tensile tester (Tinius Olsen 1000), at a crosshead speed of 5 mm/m, and an average of at least five measurements was taken to report. Dynamic mechanical tests were performed using a Rheovibron (Orientec, DDV 01-FP) at 11 Hz.

## Results and Discussion

Hardness and tensile properties (initial modulus ($E$), breaking stress ($\sigma_b$), and elongation at break ($\epsilon_b$) of the UV-cured PU acrylates are given in Table 1. Sample designation code includes the molecular weight of PPG, the type (H=HEA, T=TPGDA, TM=TMPTA) and wt% of diluent. For example, P2000-T40 indicates a PU of a 2000 molecular weight PPG and 40 wt% TPGDA.

Figure 1 shows $\sigma_b$ and $\epsilon_b$ of P400-H series as a function of HEA concentration. 0% diluent i. e.,

![Figure 1. Tensile strength and elongation at break vs. HEA content of P400-HEA series.](image)

P400-0 is the NCO terminated PU oligomer which is simply reacted with HEA and cured by UV. It is
seen that $\sigma$ decreases almost linearly, and $\epsilon$ increases after a shallow minimum at 10% HEA. Since the PU acrylates of this series are phase mixed because soft segment length is short (400), the decrease of $\sigma$ with HEA is caused by the relatively weak strength of homopolymer $\text{HEA}_{100}$ and decreased crosslinking density. The decrease of $\epsilon$ at low HEA concentration is perhaps a dilution effect, and the increase is due to the increased molecular weight between crosslinks ($M_c$), since HEA gives linear extensions.

Figure 2 shows the stress-strain curves of P750-T series. PUs in this series are also phase mixed due to their insufficient molecular weight of PPG.\cite{Lee96}

With increasing TPGDA content, $E$ and $\sigma$ increase and $\epsilon$ decreases. TPGDA based PU acrylates seem to have a higher degree of crosslinking. An increase in hardness with TPGDA is also in line with the increased crosslinkings (Table I).

Figures 3 and 4 show the stress-strain behavior of P1000-T and P3000-T series. The former is phase mixed, and the latter is presumably phase separated from the dynamic mechanical measurements to follow. In both series, $E$ and $\sigma$ were increased and $\epsilon$ was decreased with diluent concentration. One interesting fact is, however, that $\epsilon$ of P1000 series drops sharply from over 70 (0% TPGDA) to about 30%, regardless of the diluent concentration. On the other hand, $\epsilon$ of P3000 series decreases smoothly with increased TPGDA concentration, and it is higher as compared with P1000 series at the same TPGDA concentration.

The higher value of $\epsilon$ of P3000 series is mainly due to the higher soft segment content of this material. However, phase separation of P3000 series should also contribute to the higher $\epsilon$ of these materials. Following Koshiba et al., who studied the effect of diluent on PU acrylates from poly(tetramethylene) glycol (PTMG) and either IPDI or toluene diisocyanate (TDI), $\epsilon$ depends on the phase separation of the materials, i.e., $\epsilon$ could increase in phase separated materials, but should decrease in phase mixed materials with increasing diluent concentration.

It is noted that $E$ and $\sigma$, enhancement by adding...
and increasing the diluent concentration was much greater with longer soft segment length. That is, for P750 series, $E$ and $\sigma_t$ increase about 7 and 2 times as TPGDA increases from 0 to 60%. However, $E$ and $\sigma_t$ increase over 16 and 4 times for P1000 series, and more for P2000 series. This is primarily because the $E$ and $\sigma_t$ without any diluent was sufficiently lower with longer soft segment length.

Effect of TPGDA on hardness of the PU acrylates having different soft segment lengths (Figure 5) shows similar tendency with tensile modulus and strength. That is, hardening effect is also more pronounced with the PU of higher molecular weight PPG. As TPGDA concentration was increased the difference becomes smaller, indicating that the effect of diluent polymer becomes dominant.

Effects of types of the diluents on hardness, and tensile properties were studied for P2000, and the results are shown in Figures 6 to 8. Regardless of diluent type, hardness increases with diluent concentration. However, the effect is more pronounced with di- and triacrylate. This is in part due to the higher glass transition temperature ($T_g$) of these multifunctional diluent homopolymers, however, is mainly due to the higher cross-linkability of di- and triacrylates. As the con-
properties of HEA-tipped PU oligomers with different PPG molecular weight. Regardless of PPG molecular weight, rubbery plateau is well defined, and the value increases with the increase of temperature and decreases with the increase of PPG molecular weight. Such well defined rubbery plateau is seldom obtained with segmented PU alone.\textsuperscript{29}

In PUs rubbery plateau is well defined only when the phase separated hard segments effectively act as physical crosslinks for the soft domains, or when PUs are chemically crosslinked with multifunctional chain extender such as triethylentetramine.\textsuperscript{28} It seems that the basic structure-property relationships of PU work for these PU acrylates. UV curing of reactive urethane oligomers without diluent, makes chain extension with vinyl monomer, such as HEA or HEMA, and provides the PUs with crosslinkings, rather than the conventional linear extension of PU pre-polymers with butanediol. Properties pertinent to crosslinking are thus introduced. HEA provides the PUs with chemical crosslinks, where $M_r$ is inversely proportional to the PPG molecular weight (Figure 9a).

Regardless of the PPG molecular weight, a single tan $\delta$ peak is observed (Figure 9b). The tan $\delta$ peak temperatures for P1000-0, P2000-0, and P3000-0 are about +12, -46, and -54 °C, respectively. The tan $\delta$ peak temperature increases as the soft segment length was decreases. The incremental peak temperature change resulting from the difference in soft segment length is larger for the low molecular weight PPG. The change of peak temperature is 58 °C when PPG molecular weight changed form 1000 to 2000, and it is 8 °C when the PPG molecular weight changed form 2000 to 3000. Essentially identical dependence of soft segment $T_g$ on soft segment length has been reported by Lin et al.\textsuperscript{29} in PPG-isocyanatoethyl methacrylate (IEM), and by Cooper et al.\textsuperscript{28} in polamine-IEM system. Following Cooper et al., the soft segment may become purer at a fast rate, and the soft segment end groups that are immobilized in the hard segment phase are a much larger percentage with lower molecular weight polyol.

The soft segment content in P1000-0, P2000-0, and P3000-0 are about 63, 77, 84%, respectively. In segmented PUs, soft segment-hard segment

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hard segment glass transition may not occur due to the insignificant amount of this segment, which is not unusual in segmented PUs. Also, the peak temperature of P3000-0 at around -54°C closely correspond to the $T_g$ of pure PPG, indicative of phase separation. The larger increase in $T_g$ with P1000-0, as compared to P2000-0, seems due to the combined effects of increased crosslinking density and increased degree of phase mixing which is driven by the increased hard segment fraction.

Dynamic mechanical properties of the PU acrylates with varying TPGDA content have been studied with P3000-T series (Figure 10). Regardless of the TPGDA concentration, well defined rubbery plateau is obtained with the value increasing as TPGDA concentration increases. With the addition and increase of TPGDA, two peaks are obtained. The lower peak position is essentially the same with P3000-0, indicating that the soft segment of PU is not influenced by the reactive diluent. On the other hand, the higher temperature peak moves toward the higher temperature, and the peak area increases with increasing TPGDA. This is attributed to compatibility of TPGDA with hard segment of PU, and the compatibility is due to the similar polarity and hydrogen bonding between the urethane hydrogens and acrylate carbonyls, which is also observed in PU ionomer acrylates as well as in PU acrylates.

References

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