

Preparation and Properties of UV-Curable Polyurethane Acrylates

B. K. KIM,^{1*} K. H. LEE,² and H. D. KIM¹

¹Department of Textile Engineering and ²Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

SYNOPSIS

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), tripropyleneglycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA). The effects of soft segment length, type, and concentration of reactive diluent on the mechanical and dynamic mechanical properties have been determined. When the soft segment length was short (750) tensile strength (σ_b) decreased, and elongation at break (ϵ_b) generally increased with increasing HEA concentration, due respectively to the inferior strength of HEA homopolymer, and increased molecular weight between crosslinks (M_c). Initial modulus (E) and σ_b increased and elongation at break (ϵ_b) decreased with the increase of TPGDA concentration, and the effect was more pronounced as the soft segment length decreased. The hardness and σ_b increase with diluent concentration in PPG 2000-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 the higher temperature one moved toward still higher temperature. This was interpreted in terms of possible compatibility of hard segments and acrylates due to their similar polarity and hydrogen bonding. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

UV curing saves energy, and reduces or eliminates solvent emission, compared to solvent-based systems, since most formulations are 100% reactive oligomers and diluents. This technique has been applied commercially in printing, thin film coatings, and adhesives.^{1,2} Recently, UV curing has also been used in photolithography³ and for polymer-dispersed liquid crystal (PDLC).³ In photolithographic applications, a UV beam is repeatedly projected onto photocurable resin along every layer of the sliced image of model, and creates³ a complex structure, which is not possible with any conventional manufacturing method. In preparing the PDLC composite, UV curing modifies the polymer-liquid crys-

tal interfaces, thereby enhancing the electrooptic performance of the composite films.

A 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 ultimate physical properties of UV cured coatings. Typically it is segmented polyurethane oligomer tipped 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.⁴⁻⁷

The reactive diluents are acrylic monomers that are added to modify the properties and to reduce the viscosity of the precursor liquids. The acrylated urethanes ideally combine the high abrasion resistance, toughness, tear strength, and good low temperature properties of PU with the superior optical

* To whom correspondence should be addressed.

properties and weatherability of polyacrylates.^{4,8,9} Generally monofunctional acrylates lead to decreased modulus and increased ductility, whereas multifunctional acrylates such as tripropyleneglycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA) and monofunctional *N*-vinylpyrrolidone (NVP) lead to the opposite.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, due mainly to the similar polarity and hydrogen bonding formation between urethane NH and acrylate carbonyls. Following Koshiba et al.,⁵ increasing the reactive diluent content permits the development of a 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 produce free radicals upon exposure to UV.¹⁰

Earlier works and potential applications of this technique have been well documented in books,^{11,12} patents,^{13,14} and reviews.⁴⁻⁶ A number of factors influence the physical properties of PU acrylates. Among others, the reactive diluents have most often been encountered.^{4,5,15,16} Soft segment type and length have also been extensively investigated.^{5,6,17} Much less work has been devoted to the hard segment type.^{5,17}

This paper considers preparation and properties of UV curable PU acrylates. The NCO terminated PU prepolymers were synthesized from polypropylene glycol (PPG) and isophorone diisocyanate (IPDI),¹⁸ followed by tipping with HEA. Molecular weight of PPG was varied from 400 to 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 were synthesized, and mechanical and dynamic mechanical properties of these materials were studied in response to the structure.

EXPERIMENTAL

PPG was dried and degassed at 80°C, 1–2 mm Hg until no bubbling was observed. Extra pure grade of

IPDI (Scholven), dibutyltin dilaurate (DBT), benzophenone, and *N*-methyldiethanolamine (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 drying tube. Approximately 300 ppm of DBT was added. The urethane forming reaction proceeded at 90°C for over 1 h, and the progress of reaction was determined using a standard di-*n*-butylamine back titration method.¹⁹ Upon obtaining the theoretical NCO value, the reaction mixture was cooled down to 40°C and HEA was added dropwise. Tipping of NCO-terminated prepolymer with HEA was done for 3 h below 45°C, and 30 m at 60°C. The progress of reaction was also detected by measuring the NCO value.

The mixture of urethane acrylates, 1.5 wt % benzophenone (initiator), 1.5 wt % MDEA (accelerator), and reactive diluents was heated slightly above ambient temperature to ensure homogeneous mixing, followed by casting 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 an 80 W UV (365 nm) lamp for 30 s.

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

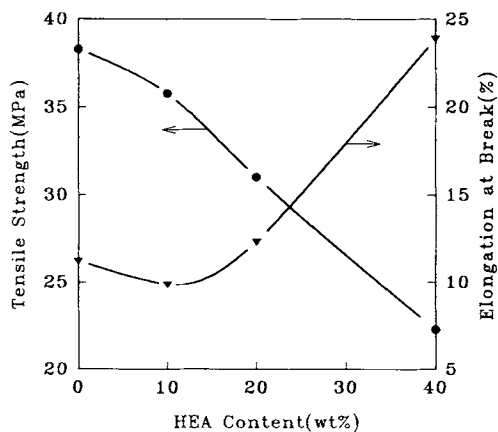
Hardness and tensile properties [initial modulus (E), break stress (σ_b), and elongation at break (ϵ_b)] of the UV-cured PU acrylates are given in Table I. Sample designation code includes molecular weight of PPG, the type (H = HEA, T = TPGDA, TM = TMPTA) and wt % of diluent. For example, P2000-T40 indicates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

Figure 1 shows σ_b and ϵ_b of P400-H series as a function of HEA concentration. Zero percent diluent, i.e., P400-0, is the NCO terminated PU oligomer that is simply tipped with HEA and cured by UV. It is seen that σ_b decreases almost linearly, and ϵ_b 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 σ_b with HEA is caused by the relatively

Table I Sample Designation, Tensile Properties, and Hardness of UV-cured Urethane Acrylates

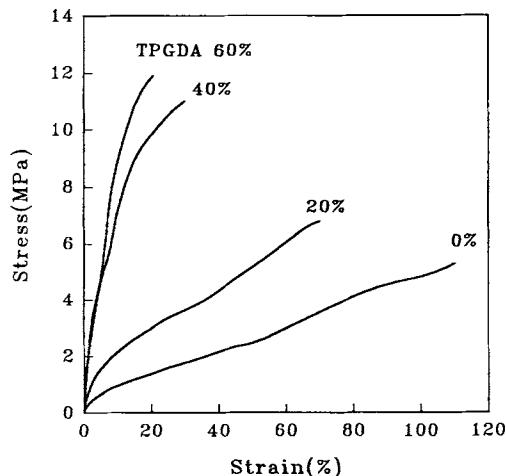
Sample Designation	Tensile Modulus (kg/cm ²)	Elongation at Break (%)	Stress at Break (kg/cm ²)	Hardness (Shore A)
P400-0		11.25	390.90	—
P400-H10		9.90	365.15	—
P400-H20		12.38	316.65	—
P400-H40		23.94	227.7	—
P750-0	188.24	110.2	53.99	72.5
P750-T20	442.92	69.95	69.20	79.5
P750-T40	1186.20	29.9	112.28	88
P750-T60	1336.00	20.5	121.4	92
P1000-0	38.89	73.75	15.00	57
P1000-T20	304.00	26.675	28.48	71
P1000-T40	418.72	26.675	39.23	85
P1000-T60	644.08	26.675	60.34	91
P2000-0		60.25	10.78	50
P2000-H20		67.75	12.0	53
P2000-H40		72.3	13.0	60
P2000-H60		87.5	13.76	62
P2000-T20		55.00	13.85	66
P2000-T40		44.80	24.29	80
P2000-T60		21.75	32.00	90
P2000-TM20		32.35	22.89	80
P2000-TM40		21.71	41.56	91
P3000-0	24.0	69.45	6.8	47
P3000-T20	38.87	60.83	14.08	59.5
P3000-T40	126.32	38.58	24.56	74
P3000-T60	468.52	25.0	41.44	85

weak strength of homopolymer HEA^{20,21} and decreased crosslinking density. The reason for the decrease of ϵ_b at low HEA concentration is not clear, however, its increase at high HEA concentrations is due perhaps to the increased molecular weight


Figure 1 Tensile strength and elongation at break vs. HEA content of P400-HEA series.

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


Figure 2 Stress-strain behavior of P750-TPGDA series with various TPGDA concentrations.

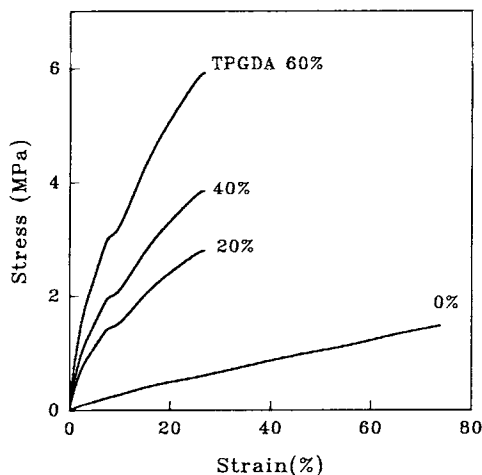


Figure 3 Stress-strain behavior of P1000-TPGDA series with various TPGDA concentrations.

to their lower molecular weight of PPG.^{5,22,23} With increasing TPGDA, E and σ_b increase and ϵ_b decreases. TPGDA-based PU acrylates seem to have a higher degree of crosslinking. Increase in hardness with TPGDA is also in line with the increased crosslinkings (Table I).

Figures 3 and 4 show stress-strain behavior of the P1000-T and P3000-T series. The former is phase mixed, and the latter is presumably phase separated from the dynamic mechanical measurements discussed later. In both series, E and σ_b increase and ϵ_b decreases with diluent concentration. Of interest is the observation that the ϵ_b of the P1000 series drops sharply from over 70 (0% TPGDA) to about 30%, regardless of the diluent concentration. On the other hand, ϵ_b of the P3000 series decreases smoothly with increasing TPGDA concentration, and it is higher compared with the P1000 series at the same TPGDA concentration. The higher value of ϵ_b of the P3000 series is mainly due to the higher soft segment content of this materials. However, phase separation of the P3000 series should also contribute to the higher ϵ_b of these materials. Following Koshiba et al.⁵ who studied the effect of diluent on PU acrylates from poly(tetramethylene glycol) (PTMG) and either IPDI or toluene diisocyanate (TDI), ϵ_b depends on the phase separation of the materials, i.e., ϵ_b could increase in phase-separated materials, but should decrease in phase-mixed materials with increasing diluent concentration.

It is noted that E and σ_b enhancement, by adding and increasing the diluent concentration, was much greater with the longer soft segment length. That is, for the P750 series, E and σ_b increase about 7 and 2 times as TPGDA increases from 0 to 60%. How-

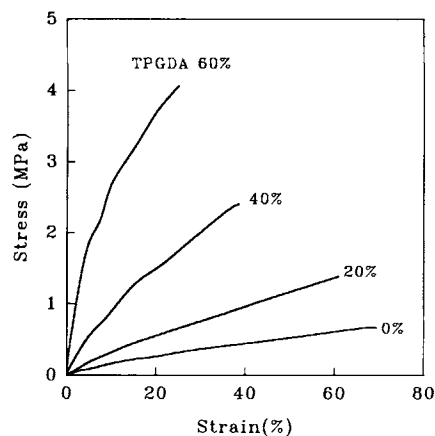


Figure 4 Stress-strain behavior of P3000-TPGDA series with various TPGDA concentrations.

ever, E and σ_b increase over 16 and 4 times for the P1000 series, and still more for the P2000 series. This is primarily because the E and σ_b without any diluent were significantly lower with the longer soft segment length.

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

Effects of different types of diluent 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

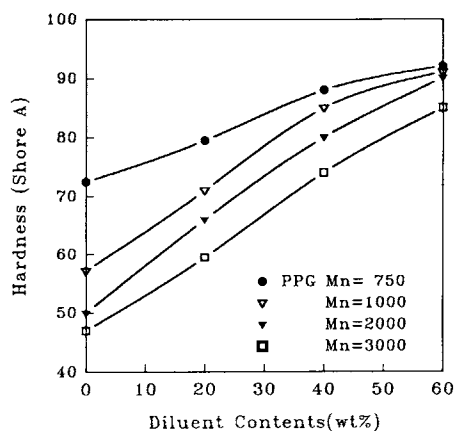


Figure 5 Hardness vs. TPGDA concentration for various molecular weight of PPG-based PU acrylates.

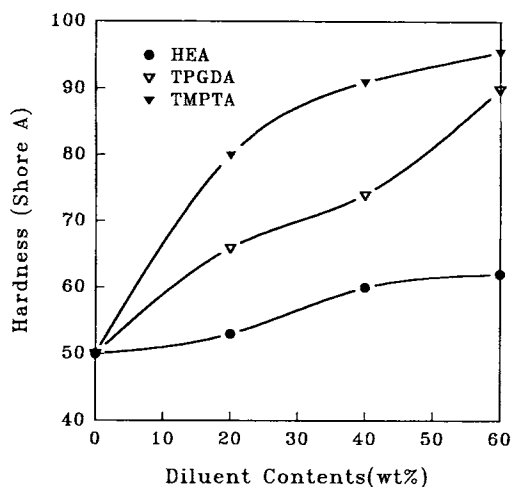


Figure 6 Effect of type and concentration of the reactive diluent on hardness of P2000-based PU acrylates.

higher glass transition temperature (T_g) of these multifunctional diluent homopolymers. However, it is mainly due to the higher crosslinkability of di- and triacrylates. As the concentration of diluent increases from 0 to 60%, σ_b increase over four times with TMPTA and three times with TPGDA, and marginally with HEA. Though marginal, the increase of σ_b with HEA in the P2000 series contrasts with the decreased σ_b with HEA in the P400 series (Fig. 1). This indicates that the strengthening effect of diluent, regardless of its functionality, is more pronounced with longer soft segments. ϵ_b decreases with di- and triacrylates and increases with HEA. This is mainly because M_c decreases with TPGDA and TMPTA, and increases with HEA.

Figure 9(a) and (b) shows the dynamic mechanical properties of HEA-tipped PU oligomers with different PPG molecular weight. Regardless of PPG molecular weight, the rubbery plateau is well defined, increasing slightly with the increase of temperature, and decreases with the increase of PPG molecular weight. Such a well-defined rubbery plateau is seldom obtained with segmented PU alone.²⁴ In PUs the rubbery plateau is well defined only when the phase-separated hard segments effectively act as physical crosslinks, or when the PUs are chemically crosslinked with a multifunctional chain extender such as triethylenetetramine.²⁵ Basic structure-property relationships of PU hold true for these PU acrylates. UV curing of reactive urethane oligomers having HEA or HEMA termini corresponds to the chain extension with HEA or HEMA, and provides the PUs with crosslinkings, rather than the conventional linear extension of PU prepolymers with butandiol. Properties pertinent to crosslinking are thus

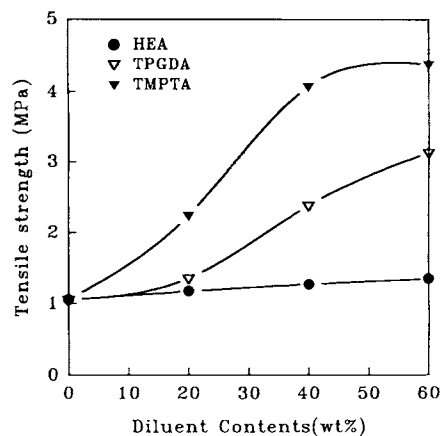


Figure 7 Effect of type and concentration of the reactive diluent on tensile strength of P2000-based PU acrylates.

introduced. HEA provides the PUs with chemical crosslinks, where M_c is inversely proportional to the PPG molecular weight [Fig. 9(a)].

Regardless of the PPG molecular weight, a single $\tan \delta$ peak is defined [Fig. 9(b)]. 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 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 changes from 1000 to 2000, and it is 8°C when the molecular weight changes from 2000 to 3000. Essentially identical dependence of soft segment T_g on soft segment length has been reported by Lin et al.²⁶ in PPG-isocyanatoethyl methacrylate

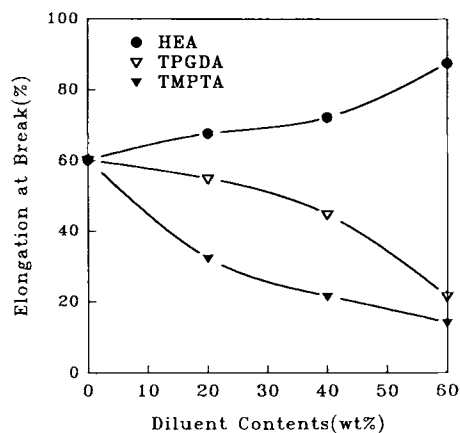


Figure 8 Effect of type and concentration of the reactive diluent on elongation at break of P2000-based PU acrylates.

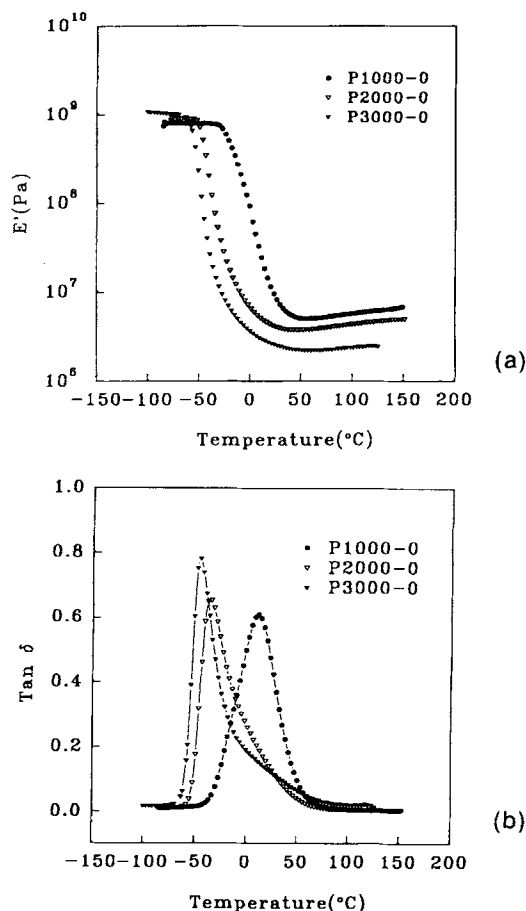


Figure 9 Dynamic mechanical properties of PPG-based PU acrylates without diluent: (a) storage modulus, (b) $\tan \delta$.

(IEM), and by Yu et al.⁶ in a polyamine-IEM system. Following Yu 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 contents in P1000-0, P2000-0, and P3000-0 are about 63, 77, and 84%, respectively. In segmented PUs, soft segment-hard segment phase separation is increased with the increase of soft segment fraction. The P2000-0 and P3000-0 are most likely phase separated.^{9,22,25} However, the single $\tan \delta$ peak [Fig. 9(b)] apparently indicates that these materials are phase mixed. Phase separation may have been prevented by the crosslinks between the HEA termini of PU.²⁷ The crosslinks are clear from the well-defined rubbery plateau, which shows higher values with shorter soft segment length, qualitatively obeying the ideal rubber elasticity. Alternatively, 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 corresponds 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 to be due to the combined effects of increased crosslinking density and increased degree of phase mixing which is driven by the increased hard fraction.

Dynamic mechanical properties of the PU acrylates with varying TPGDA content have been studied with the P3000-T series (Fig. 10). Regardless of the TPGDA concentration, a 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 as 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 still higher temperature with increasing TPGDA

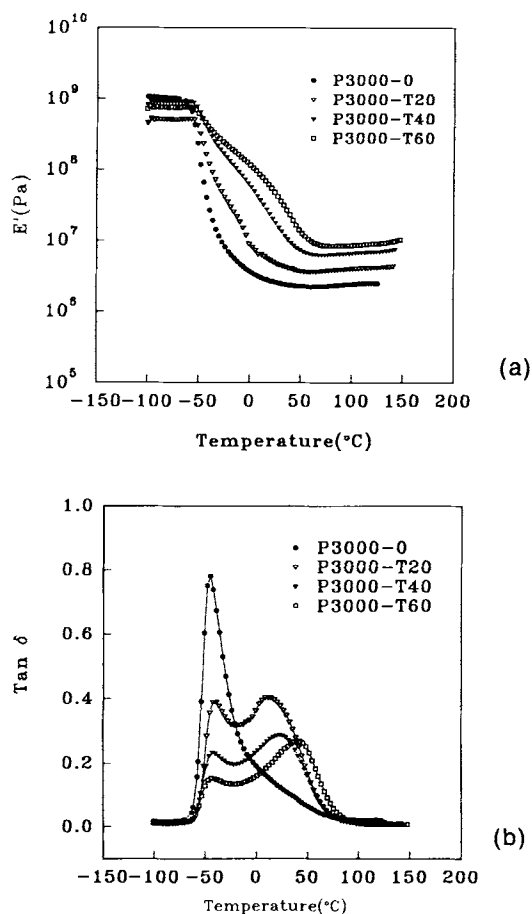


Figure 10 Dynamic mechanical properties of PPG 3000-based PU acrylates with varying TPGDA concentration: (a) storage modulus, (b) $\tan \delta$.

content, and the peak area decreases with increasing TPGDA. This is attributed to compatibility of TPGDA with hard segments of PU, due to the similar polarity and hydrogen bonding between the urethane hydrogens and acrylate carbonyls.

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