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Comparision of the Properties of UV-cured Polyurethane Acrylates Containing Different Diisocyanates and Low Molecular Weight Diols

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Abstract: UV-curable polyurethane acrylate prepolymers were prepared from diisocyanates [isophorone diisocyanate (IPDI), 2,4-toluene diisocyanate (TDI), or 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI)], diols [ethylene glycol (EG), 1,4-butane diol (BD), or 1,6-hexane diol (HD)], polypropylene glycol as a polyol. UV-curable mixtures were formulated from the prepolymer (90 wt%), reactive diluent monomer trimethylol propane triacrylate (10 wt%), and photoinitiator 1-hydroxycyclohexyl ketone (3 wt% based on prepolymer/diluent). The effects of different diisocyanates/low molecular weigh diol on the dynamic mechanical thermal properties and elastic recovery of UV-cured polyurethane acrylate films were examined. The tensile storage modulus increased a little in the order of EG > BD > HD at the same diisocyanate. Two loss modulus peaks for all samples are observed owing to the glass transition of soft segments (T_{gs}) and the glass transition temperature of hard segments (T_{gh}). For the same diisocyanate, T_{gs} decreased, however, T_{gh} increased, in the order of HD > BD > EG. The elastic recovery also increased in the order of HD > BD > EG at the same diisocyanate. In case of same diols, T_{gh} increased in the order of H_{12}MDI > TDI > IPDI significantly. The ultimate elongation and elastic recovery increased in the order of TDI > IPDI > H_{12}MDI at the same diol.

Keywords: UV-curable polyurethane acrylate, Dynamic mechanical property, Strain-stress hysteresis

Introduction

The UV-curable Polyurethane acrylate system is typically composed of reactive polyurethane acrylate oligomer, reactive diluenets and photoinitiator. UV curing saves energy and reduces or eliminates solvent emission compared to solvent-based system since most formulations are 100% reactive oligomers and diluents[1]. This technique has been applied commercially in printing, photolithography, coatings, sealants and adhesives. The reactive polyurethane oligomer is one of the most important components in determining the ultimate physical properties of UV cured materials[2]. Generally, the reactive mixture of polyurethane acrylate oligomer tipped with acrylic functionality is combined with reactive diluent, which are added to make harder products and/or to reduce the viscosity of the precursor liquid to obtain better processability[3-6]. Therefore, UV-cured polyurethane acrylates are composed of soft segments formed of polyol chains, hard segments formed from diisocyanates and low molecular diol, and acrylic structure unit formed from HEA (or hydroxyl ethyl methacrylate (HEMA)) and reactive acrylate monomers.

Researches in UV-curable polyurethane acrylates have shown that materials have mechanical properties inferior to those of thermoplastic polyurethane with very similar composition owing to the high cross-link density in UV-curables, in particular, their ultimate extension is low (less than 100%). However, in general, polyurethane acrylates have the potential to combine the high abrasion resistance, toughness, tear strength, and good low temperature properties of polyurethane with the superior optical properties and weatherability of polyacrylates[7-11].

Segmented polyurethane is a two-phase system consisting of soft and hard phases. The microphase separation of the urethane segments, which is governed mainly by the soft segment length and type, is a key parameter to control the mechanical properties of the polyurethane acrylates. The soft segment in polyurethane contributes to the high extension and elastic recovery, while hard segments contributes high modulus and strength to the composition[12-14,2]. The polar nature of the hard urethane segments causes a strong mutual attraction leading to hard domain formation. On the other hand, the soft domains are created by interaction between the soft segments, give flexibility and elastomeric properties to the polyruethane acrylates, and present a reactively low softening temperature[15-17].

In this study, we used three kinds of diols such as EG, BD, and HD, which have different chain length. Aliphatic IPDI and HMDI having different cyclic structure and aromatic TDI were used to prepare polyurethane acrylate oligomer. Studies have been made on the effects of structures of diisocyanates/low molecular weight diol on the dynamic thermal properties and elastic recovery of UV-cured polyurethane acrylate films.

Experimental

Materials

Polypropylene glycol (PPG, M_w=3500, Aldrich chemical) were dried at 80°C and 0.1 mmHg for several hours until no bubbling was observed. Isophorone diisocyanate (IPDI, Aldrich

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chemical), 2,4-toluene diisocyanate (TDI, Aldrich chemical), 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI, Aldrich chemical), and trimethylol propane triacrylate (TMPTA, Aldrich chemical) were kept dry with a molecular sieve (4 Å) for one week. Ethylene glycol (EG), 1,4-butane diol (BD), or 1,6-hexane diol (HD) were used as received. Dibutyltin dilaurate (DBT, Fluka chemical) and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Aldrich chemical) were used without futher purification.

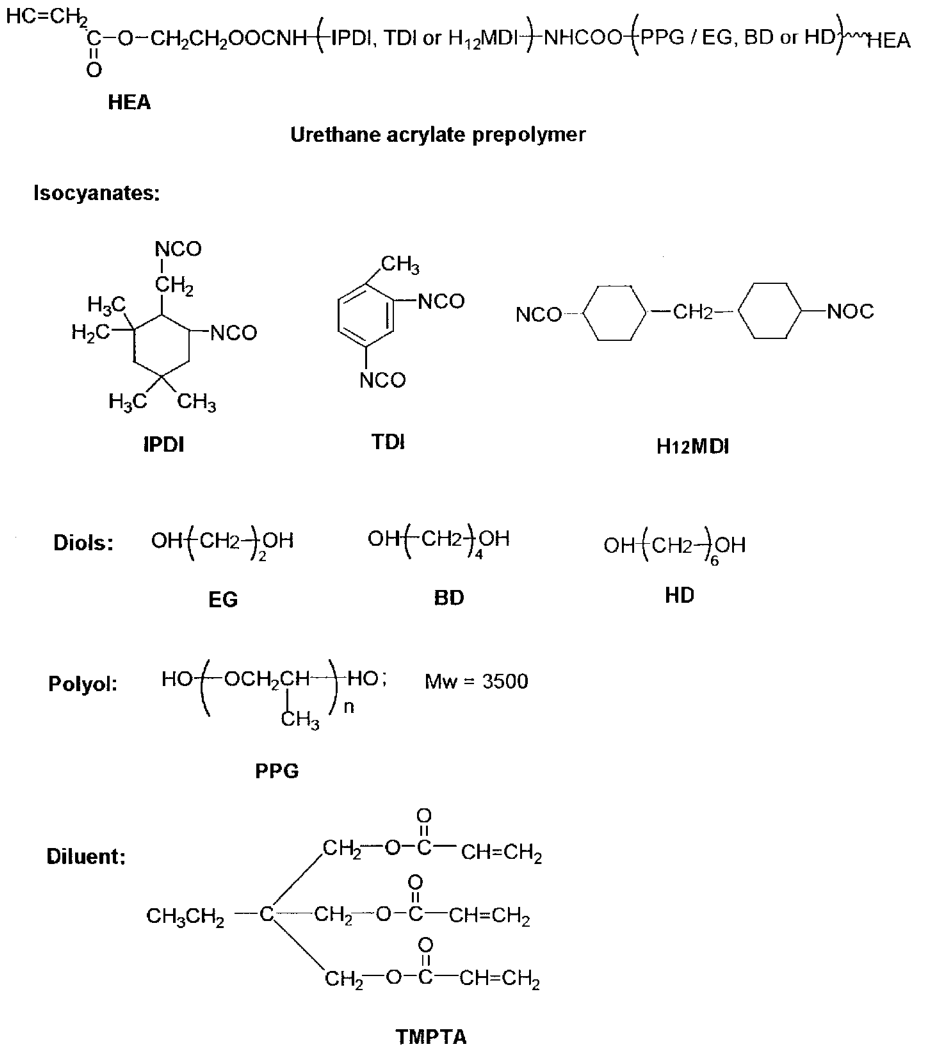
Synthesis of Polyurethane Acrylate Prepolymer

Molar excess of diisocyanate (IPDI, TDI, or H_{12}MDI), PPG (M_w=3500), and chain extender (EG, BD, or HD) were charged into a round-bottom 4-neck 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 65°C for over 3 h. Upon obtaining the theoretical NCO value, the reaction mixture was cooled down to 40°C and HEA was added dropwise. Capping of NCO-terminated prepolymer with HEA was done below 45°C for 3 h until the NCO-content reached zero as evidenced by the disappearance of the IR peak of NCO. The hard segment content of prepolymer prepared in this study were about 50 wt%.

Formulation and Curing of UV-curable Polyurethane Acrylate

By adding reactive diluents and photoinitiator Irgacure 184 (3 wt%) to urethane acrylate prepolymer, UV-curable polyurethane acrylates was formulated. To entrapping the air bubble during mixing, vacuum was applied at 60°C for three hours.

The final UV-cured polyurethane acrylate films were prepared by casting the above-formulated product onto a glass plate at room temperature and cured using a medium pressure mercury lamp (80 W/cm) for 30s. Film were about



Scheme 1. The chemical structures of polyurethane acrylate prepolymer, isocyanates, diols, and TMPTA.

1mm in thickness for tensile specimens, and 0.3-0.4 mm for dynamic mechanical test. Radiation curing has been carried out with the UV light of 365 nm of main wavelength.

Measurements

FTIR Spectra: Thin films for infrared studies were prepared by casting on KBr pellet. Infrared spectra were obtained with computerized Nicolet Impact 400D Fourier transform infrared spectrometer. For each sample, 2 scans at 2 cm^{-1} resolution were collected in the transmittance mode.

Dynamic Mechanical Measurement: The dynamic mechanical properties of UV-cured films were measured at 10 Hz using DMTA MK III (Rheometric scientific) with a heating rate 4°C/min over a temperature range of –50 to 150°C.

Tensile and Stress Hysteresis Measurement: Tensile measurement was made in simple extension on dumbell specimens using a Tensilon AGS 500D at cross-head speed of 2 mm/min.

Results and Discussion

Identification of Reactions

The chemical structures of polyurethane acrylate prepolymer, isocyanates, diols, polyol and diluent TMPTA are shown in Scheme 1. The reaction of capping and curing was identified by infrared spectroscopy. IR spectra of polyurethane acrylate with reaction time of capping were taken to confirm the completion of capping. The NCO stretching band near 2270 cm^{-1} still remained after capping reaction of 1 hour indicating the completion of capping (see Figure 1(b)). Generally, the infrared absorbance bands of acrylates at 1635 cm^{-1}, 1410 cm^{-1}, and 810 cm^{-1} are used to certify the curing of acrylates[18]. The characteristic C=C band of urethane acrylate at 1635 cm^{-1} was used to determine the completion of curing in this work. Figure 1(c) is shown that the band disappeared after UV irradiation for 5 minutes indicating the completion of curing.

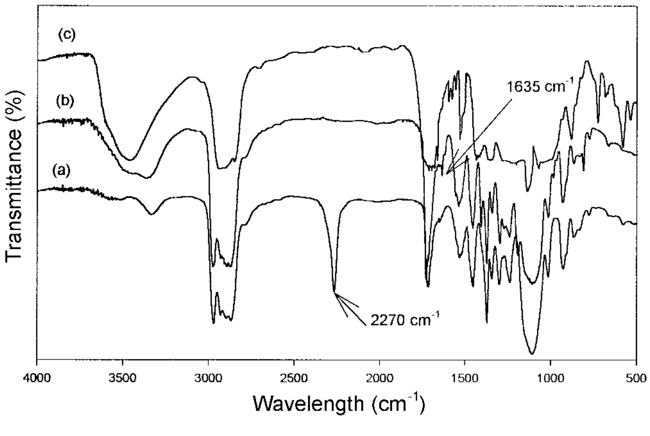


Figure 1. Infrared spectra of sample I-BD after capping reaction for (a) 1 hr and (b) 6 hrs, and after curing reaction for (c) 3 min.

Dynamic Thermal Mechanical Properties

The dynamic storage modulus, loss modulus and loss factor (tan δ) for three series samples are shown in Figures 2, 3, and 4, respectively. The storage modulus at 20°C increased a little in the order of EG > BD > HD at the same diisocyanate (see Table 2). This may be due to the decrease of chain length of chain extender diol. The effect of diisocyanate type on the storage modulus is not significant compared to the effect of chain extender diol type on the modulus. Generally, soft segment phase is likely to be separated with hard

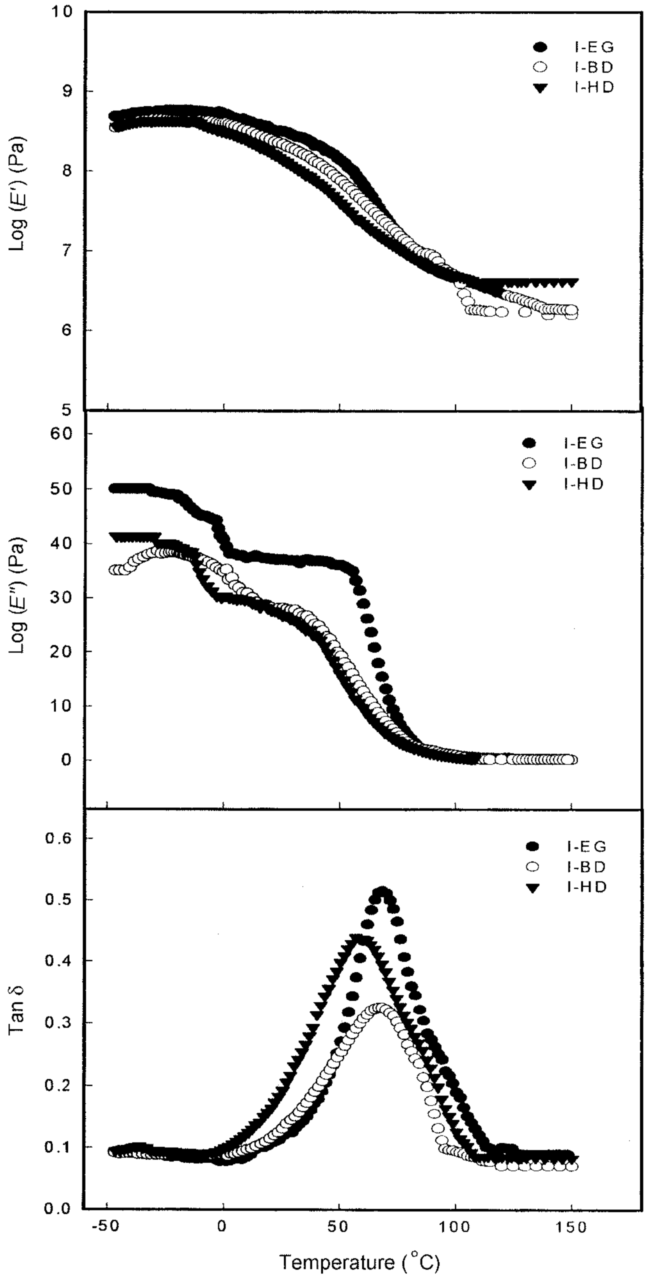


Figure 2. Dynamic mechanical properties of polyurethane acrylate A series.

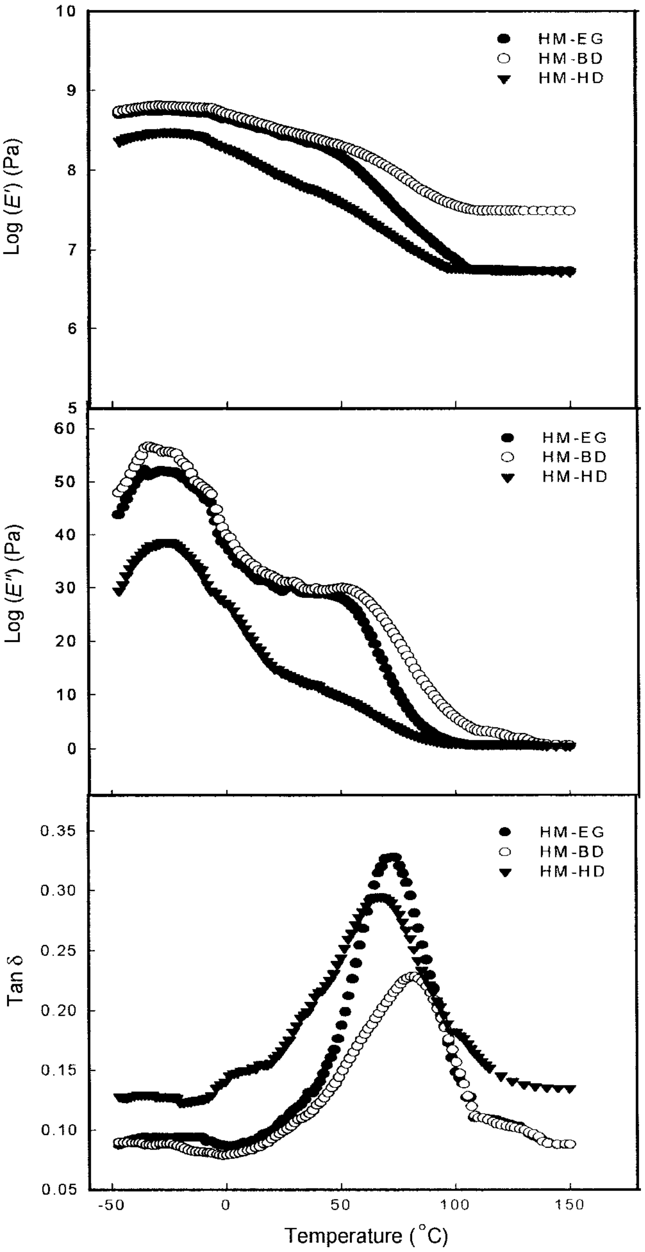


Figure 3. Dynamic mechanical properties of polyurethane acrylate B series.

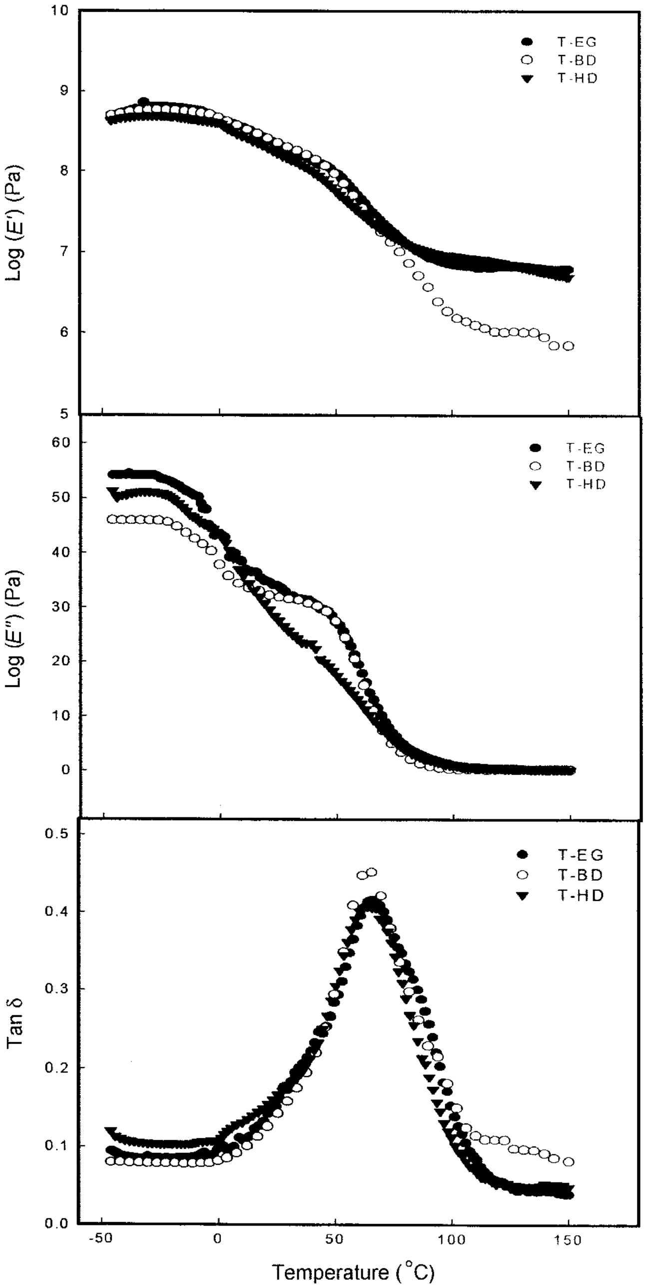


Figure 4. Dynamic mechanical properties of polyurethane acrylate C series.

segment phase in the case of polyurethane acrylate based on the high molecular weight polyol. The fixed composition of high molecular weight PPG (M_w=3500) was used to prepare UV- curable polyurethane acrylate prepolymer in this study. Two loss modulus peaks for all samples prepared here were observed indicating the occurrence of phase separation. The smaller peak at lower temperature is attributed to the glass transition of soft segments, T_{gs}, and the large peak at higher temperature is due to the glass transition temperature of hard segments, T_{gh}. The two glass transition temperatures (soft segment T_{gs} and hard segment T_{gh}) obtained from loss modulus peak are shown in Figure 5 and Table 2. For the same diisocyanate, the T_{gh} increased, on the contrary, the T_{gs} decreased, in the order of HD > BD > EG. Consequently, ΔT ($T_{gh} - T_{gs}$) increased in the order of HD > BD > EG. This indicated that the phase separation between soft and hard segments increased in the order of HD > BD > EG. This may be ascribed to the chain length of diol. The effect of increased chain length of diol on the properties of UV-curable polyurethane acrylate film has not been documented systematically. The reason why the T_g changes in the order

Table 1. Description of UV-curable polyurethane acrylates

Sample designation	Composition of prepolymer (mole ratio)	Diluent (wt%)
series A a)	IPDI/PPG/HEA/Chain extender	
I-EG	2/0.27/1.6/0.93	10
I-BD	2/0.26/1.6/0.94	10
I-HD	2/0.27/1.6/0.94	10
series B b)	H_{12}MDI/PPG/HEA/Chain extender	
H-EG	2/0.28/1.6/0.93	10
H-BD	2/0.28/1.6/0.92	10
H-HD	2/0.29/1.6/0.91	10
series C c)	TDI/PPG/HEA/Chain extender	
T-EG	2/0.23/1.6/0.98	10
T-BD	2/0.24/1.6/0.97	10
T-HD	2/0.24/1.6/0.97	10

a) A series were synthesized using IPDI as a diisocyanate.
b) B series were synthesized using H_{12}MDI as a diisocyanate.
c) C series were synthesized using TDI as a diisocyanate.

of HD > BD > EG is not clear at the present moment. More detailed studies should be made. In case of same diol, the T_{gh} increased in the order of H_{12}MDI > TDI > IPDI significantly. While the T_{gs} decreased a little in the order of TDI > H_{12}MDI > IPDP. It should be remarked, however, that the effect of different isocyanates is not significant when compared to the effect of diol types on the T_{gs}. The 2,4-TDI has a rigid aromatic asymmetric structure. As shown in the Scheme 1, H_{12}MDI has a cyclic aliphatic symmetric structure, but IPDI has a cyclic aliphatic asymmetric structure. Theses changes of T_{gh} and T_{gs} with isocyanate type may be due to the rigidity and symmetric of isocyanate structure. Especially the higher T_{gh} of H_{12}MDI based sample may be attributed to the rigid symmetric structure of H_{12}MDI.

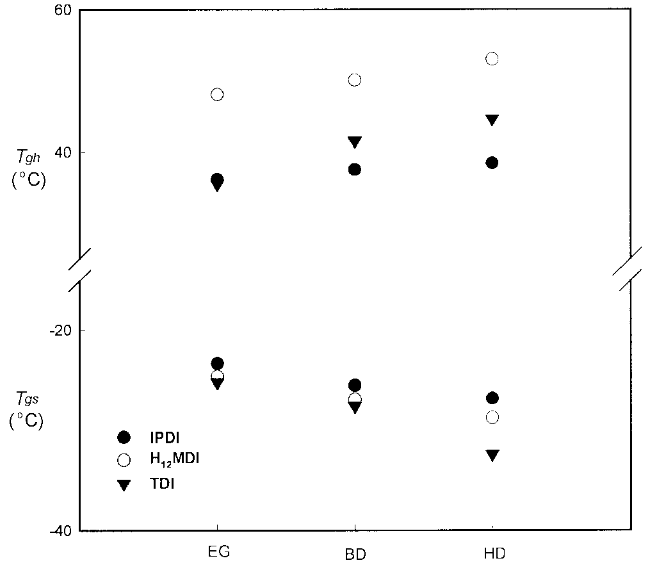


Figure 5. Effect of diol/diisocyanate on the glass transition temperature.

Table 2. Properties of UV-cured polyurethane acrulate film

Sample cord	T_{gs} a) (°C)	T_{gh} b) (°C)	ΔT_g (°C)	Tensile strengh at break (MPa)	Ultimate elongation (%)	Sorage Modulus (MPa)	Oneset stran (%)				Recovery d) (%)			
							1 st	2 nd	3 rd	4 th	1 st	2 nd	3 rd	4 th
Series A							Elogation c) (%): 35 (%)							
I-EG	−23.4	36.1	59.5	14.1	37.4	852	15.7	16.8	17.4	18.1	55	52	50	48
I-BD	−25.6	37.5	63.1	6.2	79.6	839	13.0	14.1	14.7	15.0	63	60	58	55
I-HD	−26.9	38.4	65.3	3.2	42.9	823	12.5	13.4	14.2	14.9	64	62	59	57
Series B							Elogation c) (%): 20 (%)							
H-EG	−24.7	48.1	72.8	20.9	27.9	850	9.0	9.4	10.0	10.8	55	53	50	46
H-BD	−27.0	50.1	77.1	16.1	18.4	846	4.2	4.6	4.9	5.2	58	54	51	48
H-HD	−28.8	53.0	81.8	7.5	29.6	797	8.2	8.6	9.0	9.5	59	57	55	53
Series C							Elogation c) (%): 40 (%)							
T-EG	−25.3	35.5	60.8	17.6	49.9	842	15.3	17.0	17.5	18.2	62	58	56	55
T-BD	−27.6	41.6	68.2	17.3	54.6	838	13.9	14.4	15.1	16.3	65	64	62	59
T-HD	−32.4	44.7	77.1	14.7	57.6	828	12.4	13.3	14.8	15.4	69	67	63	62

a) Transition temperature (T_{gs}) of soft segment determinaed from loss modulus (log *E'*) by DMTA.
b) Transition temperature (T_{gh}) of soft segment determinaed from loss modulus (log *E''*) by DMTA.
c) Successive given elogation in cycle test.
d) $\text{Recovery (\%)} = \dfrac{\text{G−oneset strain}}{\text{Given elongation}} \times 100$

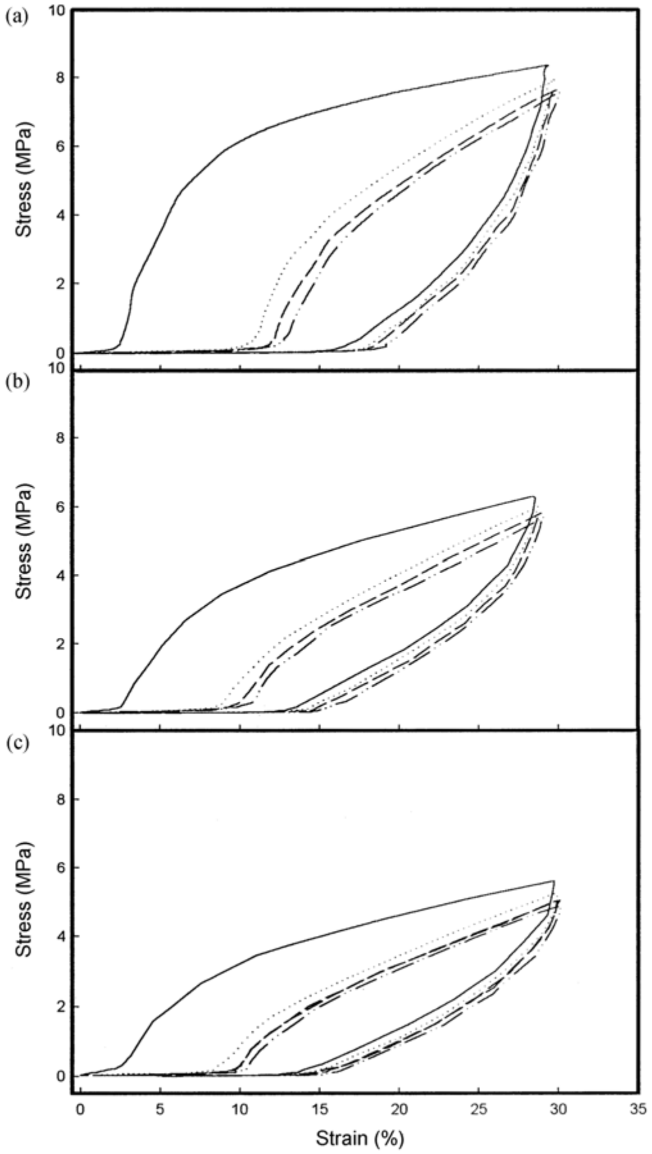


Figure 6. Stress hysteresis of (a) I-EG, (b) I-BD, and (c) I-HD.

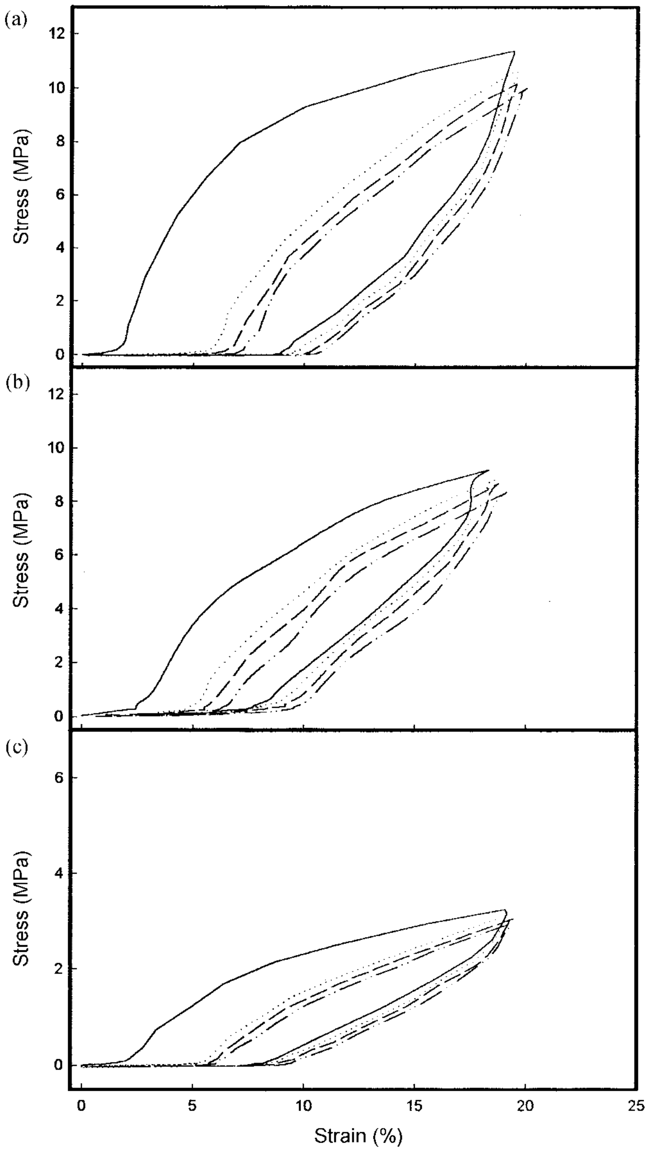


Figure 7. Stress hysteresis of (a) H-EG, (b) H-BD, and (c) H-HD.

Elastic Behavior of UV-cured Polyurethane Acrylate Films

Figures 6, 7, and 8 represent the elastic behaviors of UV-cured polyurethane acrylate films. The ultimate elongation, initial onset strain and elastic recovery percentage of all samples at successive given elongations are shown in Table 2. We found that all samples prepared here eventually recovered to original point in the four cycle test. It was also found that the higher the given elongation, the higher the elastic recovery. The elastic recovery percentage decreased with increasing the number of cycle. The ultimate elongation and elastic recovery increased in the order of TDI > IPDI > H_{12}MDI at the same diol. The TDI based samples had the highest given elongation (40%) to give the best elastic behavior in four successive cycle test. While the H_{12}MDI based samples have the lowest given elongation (20%) and the poorest elasticity. The higher values of the ultimate elongation and elastic recovery of TDI based samples may be due to the rigid asymmetric structure of TDI. In general, the rigid asymmetric structure may disturb the molecular order materials. So the higher elongation and elastic properties of TDI based samples may be attributed to the rigid asymmetric structure. The elastic recovery percentage also increased in the order of HD > BD > EG at the same diisocyanate. This also may be due to the chain length of chain extender diol. Generally, the explanations of theses type of trends has based on change in either molecular polarizability or conformational effects resulting from the lengthening of the alkylene group and passing from even to odd terminal chain length. However, the nature of this

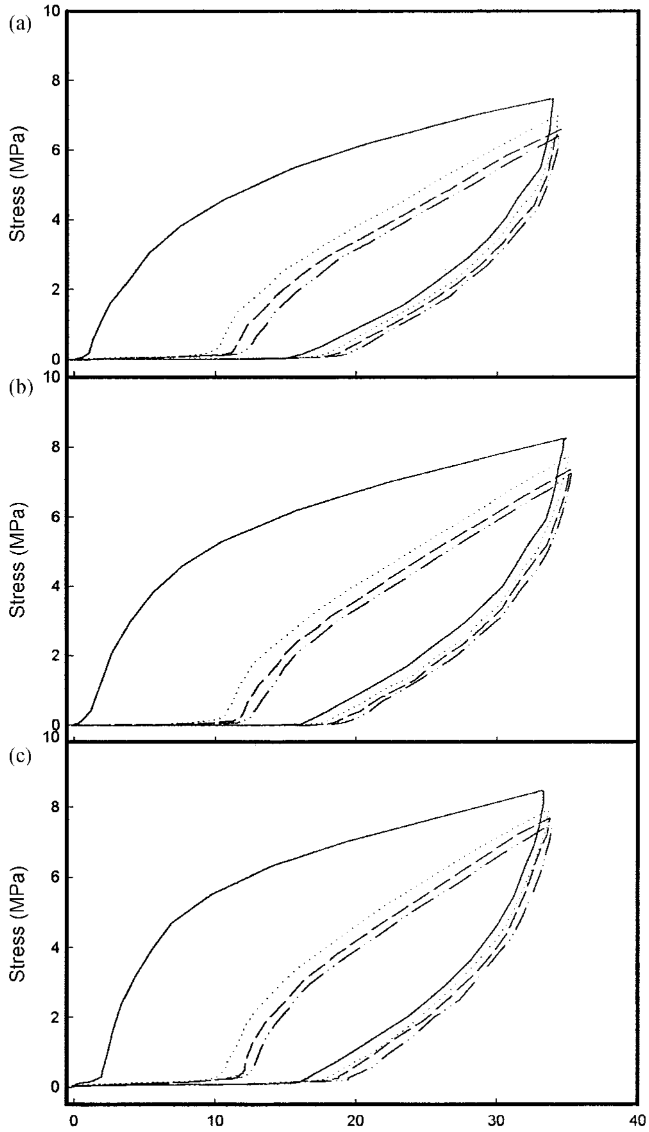


Figure 8. Stress hysteresis of (a) T-EG, (b) T-BD, and (c) T-HD.

phenomenon is also poorly understood.

Conclusions

Three different kinds of UV-curable polyurethane acrylate prepolymer were prepared from diisocyanates [IPDI, TDI, and $H_{12}MDI$], diols [EG, BD, and HD], polypropylene glycol [PPG] as a polyol. UV-curable mixtures were formulated from the prepolymer (90 wt%), reactive diluent monomer trimethylol propane triacrylate (TMPTA) (10 wt%), and photoinitiator 1-hydroxycyclohexyl ketone (Irgacure 184) (3 wt% based on prepolymer/diluent). Studies have been made on the effects of structures of diisocyanates/low molecular weight diol on the dynamic mechanical thermal properties and elastic recovery of UV-curable polyurethane acrylates films.

The number of methylene unit of diol increased in the order of HD > BD > EG. The tensile storage modulus increased a little in the order if EG > BD > HD at the same diisocyanate. Two loss modulus peaks for all samples are observed owing to the glass transition of soft segments and the glass transition temperature of hard segments. For the same diisocyanate, T_{gs} decreased, however, T_{gs} increased, in the order of HD > BD > EG. In case of same diol, T_{gh} increased in the order of $H_{12}MDI$ > TDI > IPDI significantly. The ultimate elongation elastic recovery increased in the order of TDI > IPDI > $H_{12}MDI$ at the same diol. The higher values of the ultimate elongation and elastic recovery of TDI based samples may be due to the rigid asymmetric structure of TDI. The elastic recovery were found to increase in order of HD > BD > EG at the same diisocyanate.

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