

Effect of Chemical Structure on the Properties of UV-cured Polyurethane Acrylates Films

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Abstract: The effect of compositions of isophorone diisocyanate (IPDI)/4,4'-diphenylmethane diisocyanate (MDI) and polypropylene oxide diol (PPG, M_n : 3000)/1,4-butane diol (BD) on the properties of UV-cured polyurethane acrylate films based on 2-hydroxyethyl acrylate (HEA) was examined. UV-curable polyurethane acrylates were formulated from the prepolymer, trimethylol propane triacrylate (TMPTA) as a reactive diluent, and 1-hydroxycyclohexyl ketone (Irgacure 184) as a photoinitiator. Dynamic mechanical thermal properties and elastic properties of UV-cured polyurethane acrylates was found to depend on the chemical composition of IPDI/MDI and PPG/BD. As the BD content increased, the tensile storage modulus of all series samples increased significantly. The storage modulus increased in the order of samples A (IPDI based samples) > samples B (IPDI/MDI (7/3 molar ratio) based samples) > samples C (IPDI/MDI (5/5 molar ratio) based samples) at the same composition. Two distinct loss modulus peaks for all samples are observed owing to the soft segment glass transition temperature (T_{gs}) and hard segment glass transition temperature (T_{gh}). The difference between T_{gs} and T_{gh} (ΔT_g) increases in the order of A > B > C at the same composition. In cycle test, the initial onset strain (%) was found to decrease with increasing BD content in PPG/BD and with increasing MDI content in IPDI/MDI.

Keywords: UV-cured polyurethane acrylate, Onset strain (%), Dynamic mechanical property, Strain-stress hysteresis

Introduction

Polyurethanes are a unique class of polymers, which have a wide range of applications because their properties can be readily tailored by the variation of their components[1-4]. Polyurethane acrylate resins are often used, in the liquid state, as precursor to produce three-dimensional networks, which gives as a final product a high-performance material in terms of hardness, flexibility and abrasive resistance. This behaviour is in keeping with the material requirements for various industrial sectors[5]. Polyurethane acrylates are composed of soft segments formed of polyol chains, hard segments formed from diisocyanate 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 these materials have mechanical properties inferior to those of thermoplastic polyurethanes 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 polyurethanes with the superior optical properties and weatherability of polyacrylates. Interest in UV-curable systems is notably demonstrated by the numerous studies published in this field over the passed 15 years[3,6-12].

In the meantime, UV curing saves energy and reduces or eliminates solvent emission compared to solvent-based system since most formulations are 100% reactive oligomers and

diluents[8]. This technique has been applied commercially in printing, photolithography, coatings, sealants and adhesives. The UV-curable system is typically composed of reactive polyurethane oligomer, reactive diluents, and photoinitiator [11,13-16].

The reactive polyurethane oligomer is the most important component in determining the ultimate physical properties of UV cured materials[17]. Typically it is a segmented copolymer, which consists of soft and hard segment units, tipped with acrylic functionality, such as 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) [4]. The soft segments generally consists of polyether or polyester polyol, whereas the hard segments are usually formed by the extension of diisocyanate with a chain extender of a low molecular diol or diamine. 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 dynamic mechanical properties of the polyurethane acrylates. Liquid reactive diluents miscible with the oligomer should be used to decrease the viscosity of the viscose oligomer in this systems.

The UV-curable system is formulated with three basic components including prepolymer diluent and photoinitiator. Generally, the reactive mixture of urethane acrylates 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. Segmented polyurethanes are two-phase systems, consisting of soft and hard phases. The soft segment in polyurethanes contributes to the high extension and elastic recovery, while the hard segment contributes high modulus and strength to the composite[18-21]. The segmented structure

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of polyurethanes is mainly characterized by hydrogen bonding between adjacent urethane groups. Hydrogen bonding causes relatively strong interactions, even when the hard segments are very short[22,23]. The polar nature of the hard urethane segments causes a strong mutual attraction leading to domain formation. On the other hand, the soft domains are created by interaction between the soft segments, give flexibility and elastomeric properties to the polyurethane acrylates, and present a relatively low softening temperature[24,25].

In this study, three kinds of urethane-acrylate prepolymers having different chemical composition were synthesized from isophorone diisocyanate (IPDI)/4,4'-diphenylmethane diisocyanate (MDI), polypropylene oxide diol (PPG, M_w : 3000)/1,4-butane diol (BD), 2-hydroxyethyl acrylate (HEA), and dibutyltin dilaurate as a catalyst. UV-curable polyurethane acrylates were formulated from the prepolymer, trimethylol propane triacrylate (TMPTA) as a reactive diluent, and 1-hydroxycyclohexyl ketone (Irgacure 184) as a photoinitiator. The different ratios of IPDI/MDI and BD/PPG were utilized, keeping the soft segment PPG (M_w : 3000) and reactive diluent TMPTA constant. The purpose of this work was to study the effects of the compositions in IPDI/MDI and BD/PPG on tensile strength and elastic recovery, and dynamic mechanical properties.

Experimental

Materials

Isophorone diisocyanate (IPDI, Aldrich Chemical) and 4,4'-diphenylmethane diisocyanate (MDI) were used as received. The polypropylene glycol (PPG, Aldrich Chemical) with molecular weight of 3000 was dried under vacuum at 80°C for 6 hr. 1,4-buthandiol (BD), 2-hydroxyethyl acrylate (HEA, Aldrich Chemical) and trimethylol propane triacrylate (TMPTA, Aldrich Chemical) was used after dehydration with 4Å molecular sieve for one week. Dibutyltin dilaurate (DBT, Fluka chemical) and 1-hydroyl cyclohexyl ketone (Irgacure 184, Aldrich chemical) were used as-received.

Synthesis of UV-curable Polyurethane Acrylate Prepolymers

Segmented polyurethane acrylate were synthesis by bulk polymerization under dry by one-shot method. Stoichiometric amount of PPG, BD and IPDI (or MDI) 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 three hours until the theoretical isocyanate (NCO) value was reached. The reaction mixture was cooled down to 45°C to avoid thermal polymerization of vinyl group, and tipping of NCO-terminated prepolymer with HEA was continued until the NCO content reached zero as evidenced by disappearance of the IR peak of NCO (2270 cm^{-1}). The compositions of UV-

Table 1. Description of UV-curable polyurethane acrylates

Sample cord	Composition of prepolymer (mol%)		Diluent (wt%)
	IPDI/MDI/PPG3000/BD/HEA		TMPTA
A ^a -1	40.0/0.0/9.2/14.8/36.0		10.0
A -2	40.0/0.0/4.1/19.9/36.0		10.0
A -3	40.0/0.0/1.6/22.4/36.0		10.0
B ^b -1	28.0/12.0/9.2/14.8/36.0		10.0
B -2	28.0/12.0/4.1/19.9/36.0		10.0
B -3	28.0/12.0/1.6/22.4/36.0		10.0
C ^c -1	20.0/20.0/9.2/14.8/36.0		10.0
C -2	20.0/20.0/4.1/19.9/36.0		10.0
C -3	20.0/20.0/1.6/22.4/36.0		10.0

^a) A series were synthesized using IPDI as a diisocyanate.

^b) B series were synthesized using IPDI/MDI (7/3 mol/mol) as diisocyanates.

^c) C series were synthesized using IPDI/MDI (1/1 mol/mol) as diisocyanates.

curable polyurethane acrylate prepolymers are shown in Table 1.

Formulation and Curing

The UV-curable mixture were formulated from the viscous prepolymer (90 wt%), diluent (10 wt%) and photoinitiator Irgacure 184 (3 wt% based on prepolymer/diluent). The air bubbles entrapped during mixing were removed by applying vacuum at 60°C for 1 hr. The final UV-cured urethane acrylate films were prepared by casting the above-formulated mixture onto a glass plate at room temperature and cured using a medium pressure mercury lamp (80 W/cm). Radiation curing has been carried out with the UV light (365 nm) for 3 min. Film samples of about 0.6 mm in thickness were used.

Measurements

The spectra of UV-curable polyurethane acrylates were obtained over the frequency range of 4000-500 cm^{-1} at a resolution of 2 cm^{-1} using a Nicolet Impact 400D Fourier transform infrared spectrometer.

The dynamic mechanical properties of UV-cured films were measured at 5 Hz using DMTA Mk III (Rheometrics Scientific) with the heating rate of 4°C/min over a temperature range of -50 to 200°C.

Stress-strain measurements were made in simple extension on dumbbell specimens using a tensile tester (Tensilon AGS 500D, Simazu) at a cross-head speed of 2 mm/min. Tensile recovery test was carried out with a Tensilon AGS 500D on bumbbell specimens of 10×0.45 mm^2 cross-sectional area at room temperature. The samples were clamped in the tester and subjected to successive given elongations in the range of 10~40%. The number of cycling was 4 times. The cross-head speed was 2 mm/min, and the chart drive speed was 4 mm/min. The initial recovery onset strain (%) was taken as

the percentage of elongation at which the retraction curve return to zero stress at the outset. The final recoveries of samples (A-1, A-2, B-1, B-2, C-1, and C-2) were 100% at the given elongation in the cycle tests.

Results and Discussion

Identification of Reactions

The preparation process of UV-cured polyurethane acrylate film samples in this study can be represented by the Scheme 1. The reaction of capping and curing were 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} was still remained after capping reaction of 1 hour (see Figure 1(a)), but the band completely disappeared after capping reaction of six hours indicating the completion of capping (see Figure 1(b)). In general, 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. The characteristic C=C absorption of urethane acrylate at 1635 cm^{-1} was used to determine the completion of curing in this study. Figure 1(c) shows that the band disappeared after UV irradiation for

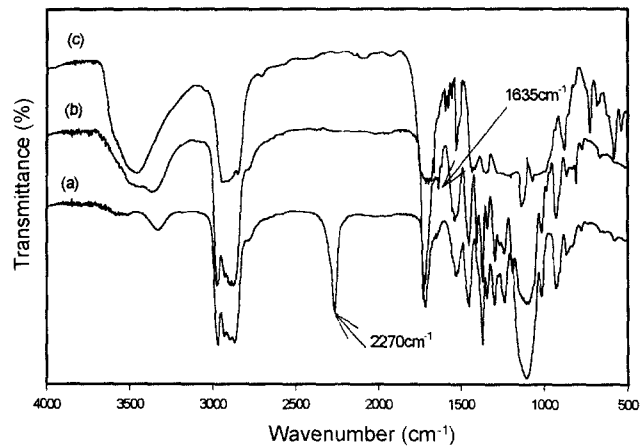
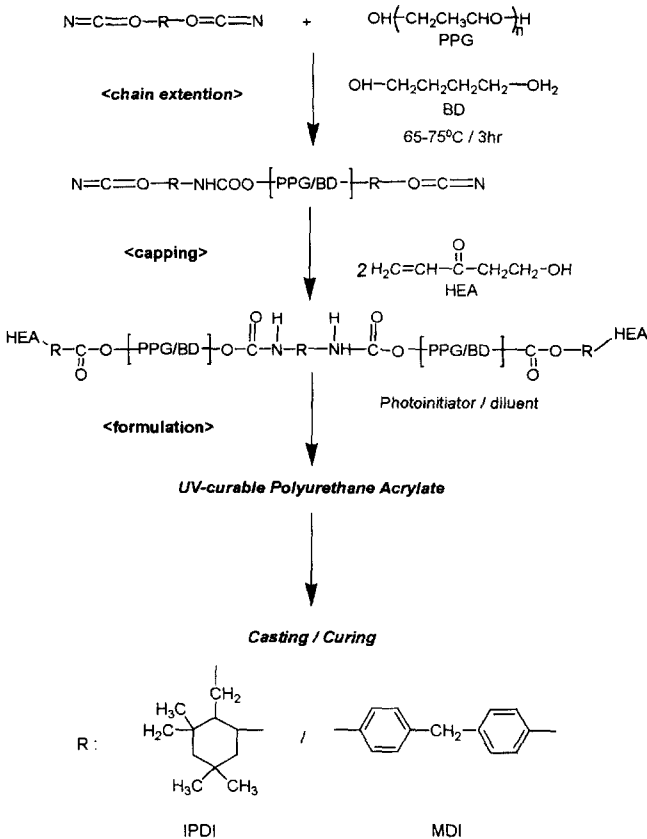


Figure 1. Infrared spectra of sample A-2 after capping reaction for (a) 1 hr and (b) 7 hrs, and after curing reaction for (c) 3 min.



Scheme 1. Preparation process of UV-cured polyurethane acrylate film samples.

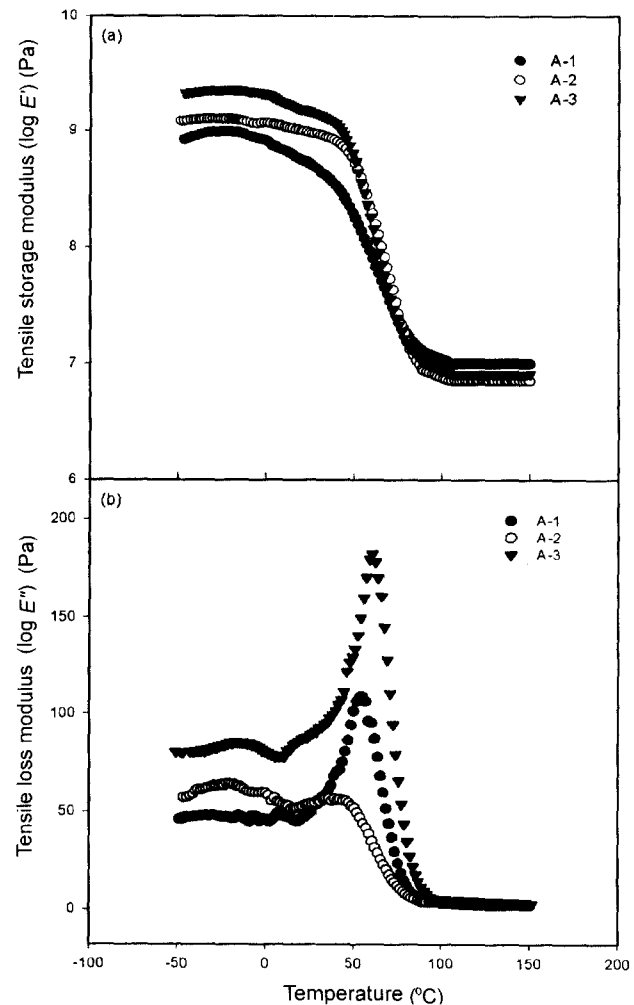


Figure 2. Dynamic mechanical properties of polyurethane acrylate A series: (a) tensile storage modulus $\log E'$, (b) tensile loss modulus $\log E''$.

5 minutes indicating the completion of curing.

Dynamic Thermal Mechanical Properties

Figures 2, 3, and 4 shows the dynamic mechanical properties of IPDI based A series film samples, IPDI/MDI (7/3 molar ratio) based B series film samples, and IPDI/MDI (5/5 molar ratio) based C series film samples, respectively. For the temperature range of $-50\sim 150^{\circ}\text{C}$, the storage modulus of all series increased with increasing of hard segment component (BD) content in PPG/BD. When we compared the magnitude of storage modulus among A, B, and C film samples, the storage modulus increased in the order of $A > B > C$ at the same composition. This may be due to the increase of irregularity in the order of $C > B > A$

caused by mixing of IPDI and MDI.

Soft segment phase is more likely to be separated with hard segment phase in the case of polyurethane acrylates based on high molecular weight polyol such as PPG (M_w : 3,000). This leads to the existence of two glass transition regions. Two distinct loss $\tan\delta$ peaks for all samples are observed owing to the T_{gs} and T_{gh} transitions (see Figures 2~4). The smaller peaks at lower temperature are attributed to the glass transition of soft segments (T_{gs}), and the larger peaks at higher temperature are due to the glass transition temperature of hard segments (T_{gh}). As the BD content of all samples increased, the T_{gh} shifted to higher temperature significantly, however, T_{gs} shifted to lower temperature slightly. This suggests that the phase separation of soft/hard segments increased with increasing hard segment component BD content. The difference (ΔT_g) between T_{gs} and T_{gh}

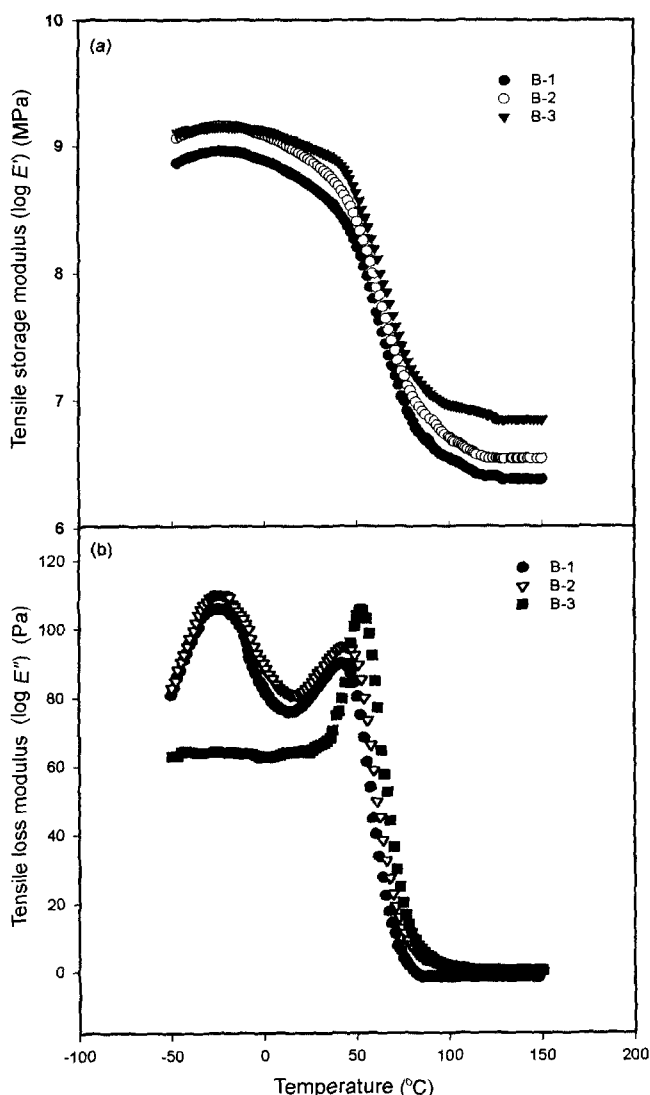


Figure 3. Dynamic mechanical properties of polyurethane acrylate B series: (a) tensile storage modulus $\log E'$, (b) tensile loss modulus $\log E''$.

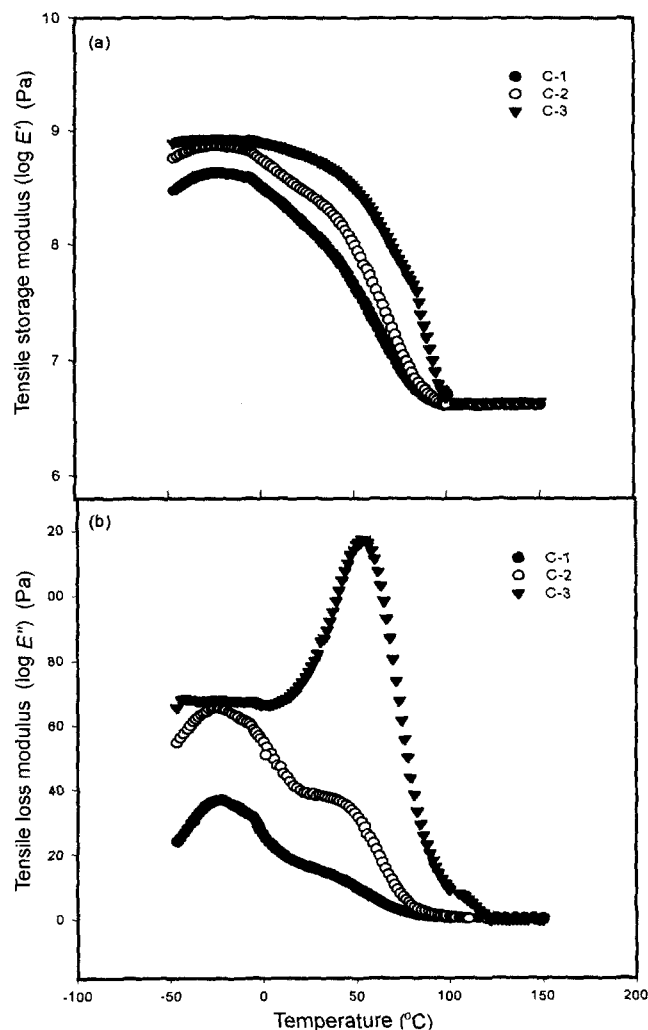


Figure 4. Dynamic mechanical properties of polyurethane acrylate C series: (a) tensile storage modulus $\log E'$, (b) tensile loss modulus $\log E''$.

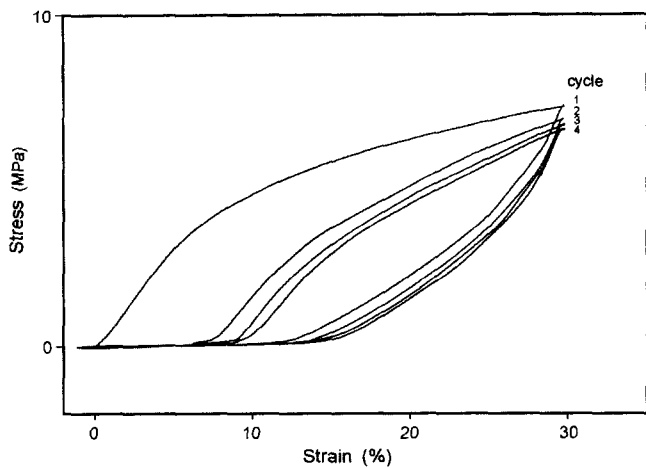


Figure 5. Hysteresis of sample A-1 at successive given elongation 30%.

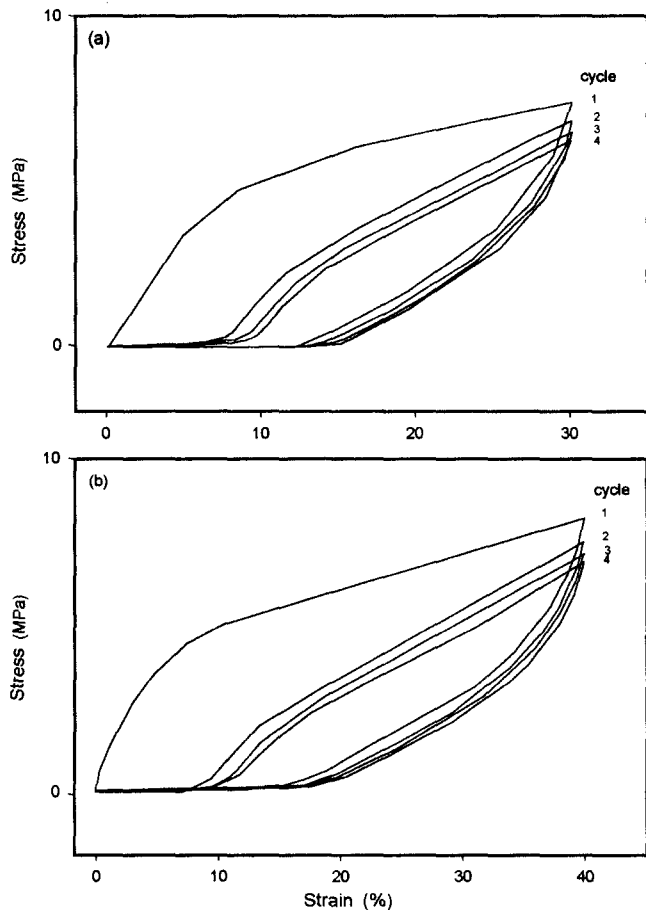


Figure 6. Hysteresis of sample B-1 at successive given elongations (a) 30% and (b) 40%.

increases in the order of $A > B > C$. This implies that phase mixing increased in the order of $C > B > A$. This also may be due to the mixture structure of IPDI/MDI.

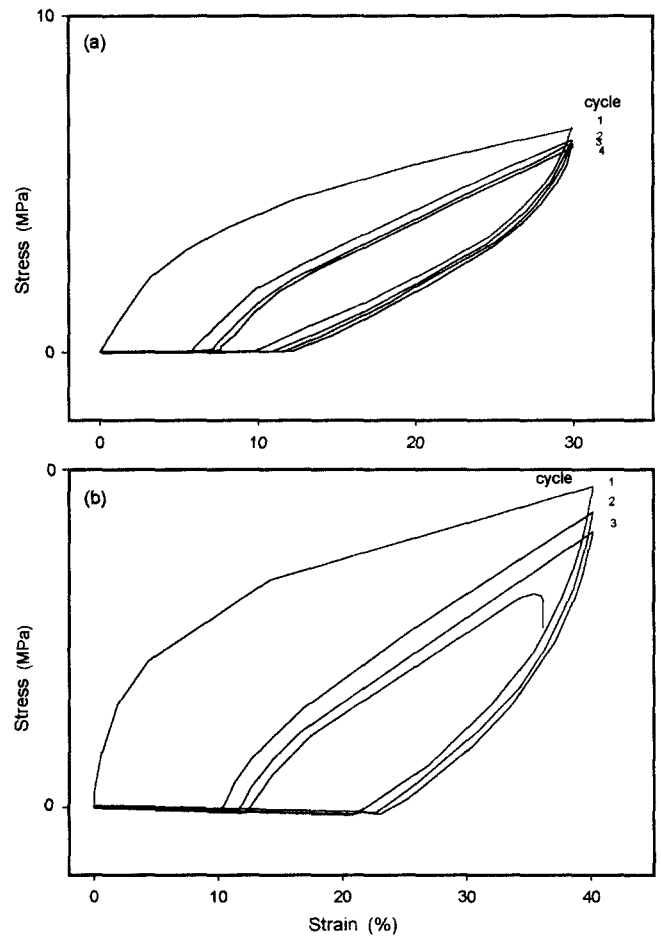


Figure 7. Hysteresis of sample C-1 at successive given elongations (a) 30% and (b) 40%.

Elastic Behavior of UV-cured Polyurethane Acrylate Films

Figures 5, 6, and 7 represents the stress-strain hysteresis curves of typical UV-cured polyurethane acrylate film samples A-1, B-1, and C-1 for a successive given elongations 30% and 40%, and Figures 8~10 represents stress-strain hysteresis curves of A-2, B-2, and C-2 for a successive elongations 10% and 20% in cycle tests of 4 runs. The initial onset strain (%) of these samples was taken as the percentage of elongation at which the retraction curve returns to zero stress firstly. Generally, UV-curable polyurethane acrylate materials are used as coatings. When a considerable force is given to coating materials, the large deformation of these materials is not desirable and the deformation should recover instantly. The initial onset strain (%) of these samples at successive given elongations are shown in Table 2. The lower value of initial onset (%) means higher elastic recovery for samples. The initial onset of sample A, B, and C series decreased with increasing hard segment component BD content in PPG/BD (see Table 2 and Figures 5~10). However, samples A-1, A-2, B-1, B-2, C-1, and C-2 eventually

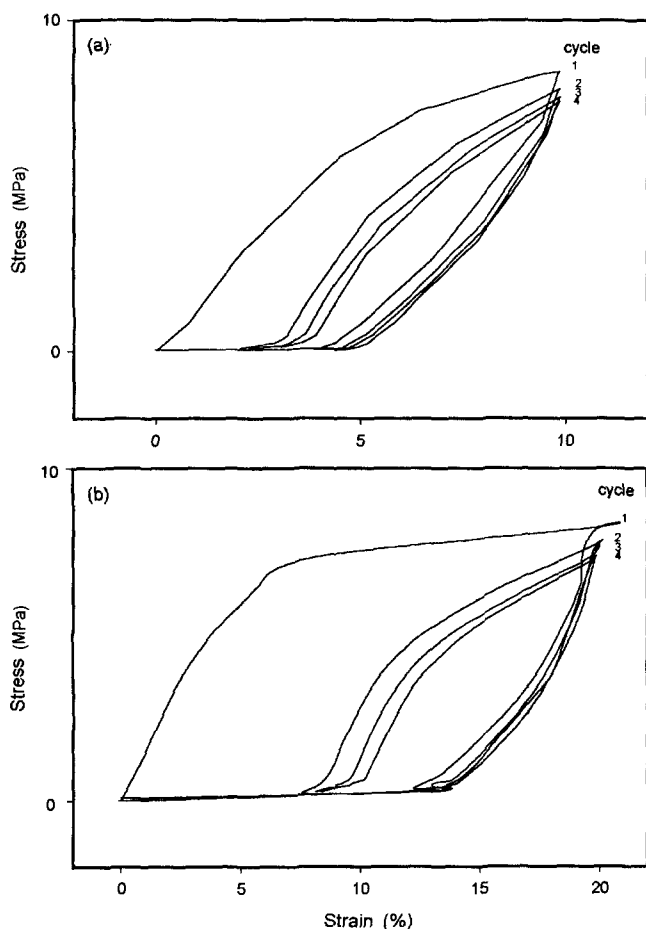


Figure 8. Hysteresis of sample A-2 at successive given elongations (a) 10% and (b) 20%.

recovered to original point in the all cycle tests in this study. As the number of run in cycle increased, the initial onset (%) increased and the required stress decreased, gradually. But the stress-strain hysteresis curves for A-3, B-3, and C-3 were not obtained, because the elongation at break of these samples was too small to measure hysteresis curves. For A, B and C series samples, as the hard segment component BD content in PPG/BD increased, the initial onset (%) decreased respectively, however, the maximum elongation at break decreased. In the case of samples A-1, B-1, and C-1 containing lower BD content, the initial onset (%) decreased in the order of A-1 > B-1 > C-1. Therefore the elastic recovery was found to increase in the order of A-1 > B-1 > C-1. However, in the case of higher BD content, the initial onset (%) decreased in the order of C-2 > B-2 > A-2. This means the elastic recovery increased in the order of C-2 > B-2 > A-2.

Conclusions

UV-curable polyurethane acrylate prepolymers were

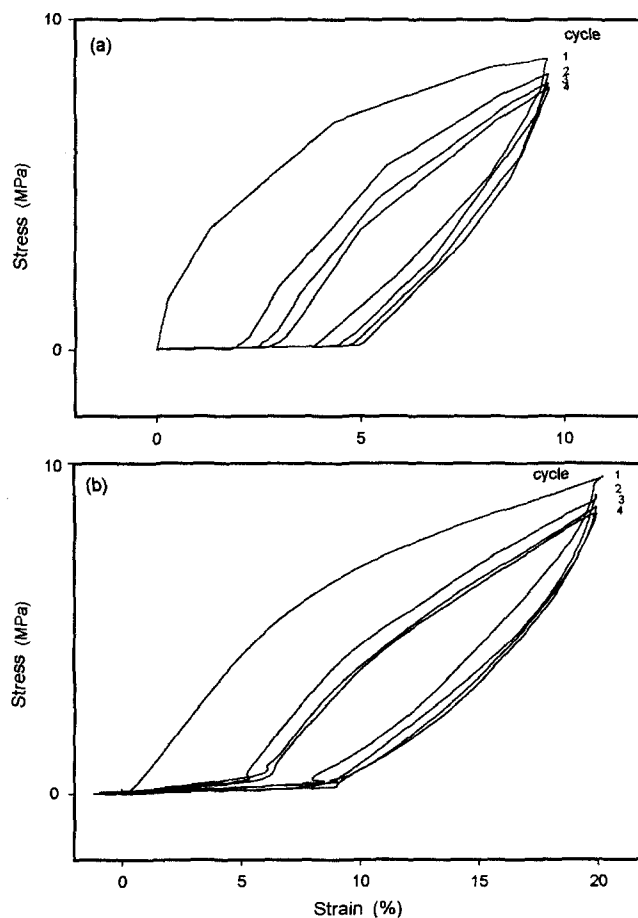


Figure 9. Hysteresis of sample B-2 at successive given elongations (a) 10% and (b) 20%.

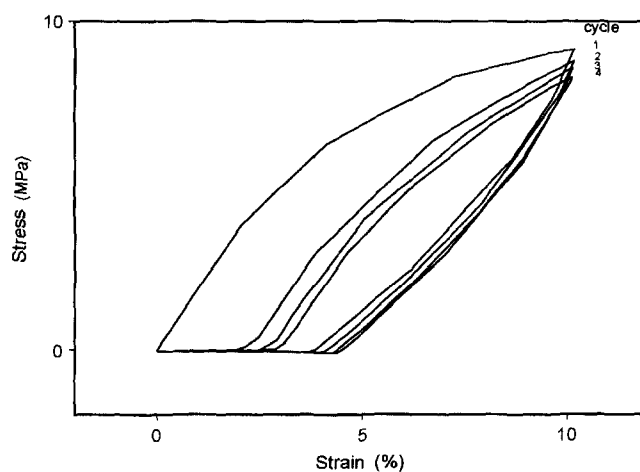


Figure 10. Hysteresis of sample C-2 at successive given elongation in 10%.

synthesized from IPDI, MDI, BD, PPG 3000, HEA and DBT as a catalyst. UV-curable polyurethane acrylates were

Table 2. Properties of UV-cured polyurethane acrylate films

Sample cord	$T_{gs}^a)$ (°C)	$T_{gh}^b)$ (°C)	ΔT_g (°C)	Tensile strength at break (MPa)	Elongation at break (%)	Tensile Modulus (MPa)	Initial onset strain (%) / Elongation(c) (%)	
A-1	-21.0	45.7	66.7	7.3	33.5	15.0	9.9/30.0	break/40.0
A-2	-22.5	53.5	76.0	10.2	20.0	119.0	4.0/10.0	12.0/20.0
A-3	-25.0	54.0	79.0	26.0	7.8	321.0	-	-
B-1	-23.0	42.1	65.1	7.2	72.0	27.5	11.5/30.0	17.4/40.0
B-2	-25.5	49.7	75.2	13.0	46.0	150.5	3.8/10.0	7.6/20.0
B-3	-26.0	51.7	77.2	27.0	17.0	525.0	-	-
C-1	-24.1	41.0	65.1	8.0	60.0	42.0	12.5/30.0	21.3/40.0
C-2	-26.0	48.0	74.0	31.0	12.5	620.0	3.7/10.0	break/20.0
C-3	-26.4	50.2	76.6	32.0	1.5	-	-	-

^{a)}Transition temperature (T_{gs}) of soft segment determined from loss modulus ($\log E''$) by DMTA.

^{b)}Transition temperature (T_{gh}) of hard segment determined from loss modulus ($\log E''$) by DMTA.

^{c)}Successive given elongation in cycle test.

formulated from prepolymer, TMPTA as a diluent and photoinitiator Irgacure 184. Effects of BD content in PPG/BD and MDI in IPDI/MDI on dynamic thermal mechanical and tensile recovery properties of UV-cured polyurethane acrylate films were investigated. As the BD content increased, For samples A (IPDI based samples), samples B (IPDI/MDI (7/3 molar ratio) based samples), and samples C (IPD/MDI (5/5 molar ratio) based samples), the tensile storage modulus increased with increasing BD content. The tensile storage modulus increased in the order of A > B > C at the same composition. Two distinct loss modulus peaks for all samples are observed owing to the soft segment glass transition temperature (T_{gs}) and hard segment glass transition temperature (T_{gh}). The difference between T_{gs} and T_{gh} (ΔT_g) increases in the order of A > B > C at the same composition. In cycle test, the initial onset strain (%) was found to decrease with increasing BD content in PPG/BD and with increasing MDI content in IPDI/MDI.

Acknowledgements

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