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자외선 경화 Polyurethane Acrylate의 물성에 미치는 분자구조의 영향

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Effect of Molecular Structure on Properties of a Series of UV-cured Polyurethane Acrylates

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요 약 : 프리폴리머의 형태와 프리폴리머/희석제의 조성이 자외선경화 폴리우레탄 아크릴레이트의 물성에 미치는 영향을 검토하였다. 일련의 자외선경화 폴리우레탄 아크릴레이트 프리폴리머는 hexamethylene diisocyanate(HMDI), polyols(polypropylene oxide diol(PPG) or polytetramethylene ether glycol(PTMG))/glycerine(GL), 2-hydroxyethyl acrylate(HEA)로부터 촉매인 dibutyl tin dilaurate을 사용하여 합성하였다. 자외선경화 폴리우레탄 아크릴레이트는 프리폴리머, 반응성 monomer인 희석제 trimethylolpropane triacrylate(TMPTA) 및 광개시제인 benzophenone(BP)으로 부터 만들어졌다. 자외선경화 폴리우레탄 아크릴레이트의 gel content(%)는 1초의 자외선 조사에 의해 90%이상의 값을 나타내었으며, GL과 TMPTA의 함량의 증가에 따라 동적 저장탄성율은 증가하였으며, 시료 A의 글라스 전이온도는 GL의 함량의 증가에 따라 고온으로 이동하였다. 희석제인 TMPTA는 글라스 전이온도에 기인하는 loss modulus 및 loss tan δ 피크의 온도에는 거의 영향을 미치지 않았다.

Abstract : The effect of prepolymer type and overall composition of the perpolymer/diluent on the properties of UV-cured polyurethane acrylate as a function of temperature are studied. A series of UV-curable polyurethane acrylate prepolymers were synthesized from hexamethylene diisocyanate HMDI), polyols(polypropylene oxide diol(PPG) or polytetramethylene ether glycol(PTMG))/glycerine(GL), 2-hydroxyethyl acrylate(HEA), and dibutyl tin dilaurate as a catalyst. UV-curable polyurethane acrylates were formulated from prepolymer, reactive monomer, TMPTA as a diluent and photoinitiator benzophenone. The gel content of the UV-cured polyurethane acrylates reached to near 90% within 1 sec. The storage modulus increase with increasing GL and TMPTA contents. The glass transition of sample A shifted to higher temperature as the content of GL was increased. The diluent TMPTA did not affect the temperature of loss modulus and loss tan δ peaks attributed to the glass transition of polyurethane chain significantly.

INTRODUCTION

In recent years, the number of applications that use radiation curing have remarkably increased. The inherent advantage of UV/EB curing(no solvents, no heat and no postcure) are covered with in areas of new applications. Special attention has been paid to the process to utilize the coatings by UV/EB irradiation. Some of the first oligomers employed for commercial radiation cure applications were unsaturated polymers.[1,2] In general, the cure rates are slow due to the relatively unreactive nature of the unsaturated polymer internal double bond.

In response to industrial demands for higher cure speed(enhanced productivitys), acrylated oligomers were developed. Of the common unsaturation types, acrylate exhibits the most rapid UV, free-radical cure response in the following order : acrylate>methacrylate>allyl>vinyl. UV cured acrylated products, based primarily on urethane and epoxy backbones, filled a wide range of application needs. The UV curable polyurethane acrylates[3,4] have been used widely as the coating materials and the binder resins because of their rapid cure speed and eminent properties.

UV-curable polyurethane acrylates have been intensively studied for optical fiber coating.[5,6] Generally, the materials have the potential to combine the high abrasion resistance, toughness, tear strength,[7,8] and good low temperature properties of polyurethanes with the superior optical properties and weatherability of polyacrylates.

Generally, UV-curable polyurethane acrylate prepolymers were synthesized from polyol, isocyanates and hydroxy acrylates and the UV curable coating materials were formulated with the three basic components including prepolymers, diluent (reactive monomer), and photo-initiator. The reactive prepolymer polyurethane tipped with acrylic functionality was combined with reactive diluents (mono or multifunctional monomers), which were added to control the properties of cured material and to reduce the viscosity of the liquid precusor mixture to provide better processibility.

In this study, a series of UV-curable polyurethane acrylate prepolymers were synthesized from hexamethylene diisocyanate(HMDI), polyols(polypropylene oxide diol(PPG) or polytetramethylene ether glycol(PTMG))/glycerine(GL), 2-hydroxyethyl type and overall composition of the perpolymer/diluent(trimethylolpropane triacrylate(TMPTA) ; trifunctional reactive monomer) on the properties of UV-cured polyurethane acrylate films were investigated.

EXPERIMENTAL

Materials. HMDI(Aldrich Chemical) was used as received. PTMG(Mw 1,000, Korea Polyol Co.) and GL(Aldrich Chemical) were degassed before use at 80℃ for 6 h under vacuum. HEA(Aldrich Chemical) and the diluent TMPTA(Wako Chemical) were kept dry with a molecular sieve(4Å) before use for 1 week. Dibutyl tin dilaurate(Fluka Chemical) and benzophenone(BP, Fisher Chemical) were used without further purification.

Syntheses of Urethane Acrylate Prepolymers. HMDI based urethane acrylate prepolymers was synthesized by adding dehydrated HEA dropwisely to HMDI under a nitrogen atmosphere. The reaction temperature was kept below 45℃ to avoid thermal polymerization of vinyl groups. When the temperature of the HMDI/HEA mixture began to drop, dehydrated polyols were added along with dibutyltin dilaurate catalyst(0.3 wt%). The mixture was agitated for 3 h and heated to 70℃ to complete the reaction. Then, the UV-curable liquid mixtures were formulated from the above viscous prepolymers(oligomers) by adding the 3 wt% of photoinitiator BP and the required amount of selected diluent prior to curing. The air bubbles entrapped during mixing were removed by applying vacuum at 30℃ for 30 min and kept under vacuum at 60℃ for 3 h.

UV Curing. The final UV-cured urethane acrylates films were prepared by casting the above formulated product onto a glass plate at room tempe-

rature and cured using a medium-pressure mercury lamp(80 W/cm). UV radiation curing has been carried out with the UV light of 365 nm of main wavelength. The thickness of the cast film was about 300μm.

Measurements. Infra-red spectra of urethane acrylate prepolymers were taken before and after UV irradiation using a FTIR spectrophotometer. Changes in the absorption peaks at 1635 cm^{-1}, assigned to the C=C stretching of TMPTA and HEA terminated prepolymer, were observed. The gel content of the cured samples was determined by Soxhlet extraction using toluene for 24 h. The insoluble portions were dried under vacuum for about 2 days and weighed to determine the gel content. The gel content of the cured film samples was determined from the difference in weight before and after the extraction experiment as follows : gel content(%)=$W/W_0 \times 100$, where W_0 and W are sample weights before and after extraction, respectively. Several runs were made for each sample, and average values were taken. The dynamic mechanical properties were obtained using a Rheovibron DDV-II(Toyo Baldwin Co.) at 11 Hz with a heating rate of 2℃/min. The temperature range was −120 ℃ to 150℃. Film samples of about 0.3 mm(thick)×0.4 cm(wide)×4 cm(long) were used.

RESULTS AND DISCUSSION

A series of polyurethane acrylate prepolymers from HMDI, PTMG/PPG/GL and HEA with dibutyl tin dilaurate as a catalyst were prepared. UV-curable coating materials were formulated from the prepolymers and TMPTA with BP as a photoinitiator. The effects of the composition of reactive urethane acrylate prepolymers/diluents(reactive monomers) on the properties of the UV-cured polyurethane acrylates have been investigated. A description of each of the materials prepared in this study is given in Table 1.

The curing of the urethane acrylate prepolymers/diluent was analyzed by FTIR. Fig. 1 shows typical IR spectra of B-1 before and after UV irradiation for 5s. To certify the curing of acrylates, generally, the absorbance bands of acrylate at 1635 cm^{-1}, 1410 cm^{-1}, and 810 cm^{-1} are used. The urethane acrylate has a sharp C=C absorption band at 1635 cm^{-1} before UV irradiation, but the band wasn't nearly detectable after irradiation. And the

Table 1. Description of UV Curable Polyurethane Acrylates

Sample designation	Composition of prepolymer (mole ratio)	Diluent (wt%)	Tg* (℃)
	HEA/HMDI/PPG/GL		TMPTA
A-1	1.0/1.0/0.5/0.00	20	−40, 46
A-2	1.0/1.0/0.4/0.07	20	−36, 50
A-3	1.0/1.0/0.3/0.13	20	−27, 57
	HEA/HMDI/PTMG/GL		TMPTA
B-1	1.0/1.0/0.5/0.00	20	−67, 42
B-2	1.0/1.0/0.4/0.07	20	−68, 32
B-3	1.0/1.0/0.3/0.13	20	−67, 36
	HEA/HMDI/PPG/GL		TMPTA
C-1	1.0/1.0/0.4/0.07	10	−36, 50
C-2	1.0/1.0/0.4/0.07	20	−36, 50
C-3	1.0/1.0/0.4/0.07	30	−43, 49
	HEA/HMDI/PTMG/GL		TMPTA
D-1	1.0/1.0/0.2/0.2	10	−61, 27
D-2	1.0/1.0/0.2/0.2	20	−60, 26
D-3	1.0/1.0/0.2/0.2	30	−60, 28

* Main glass transition temperature determined by loss modulus(E″)

absorption band at 1410 cm^{-1} remained a trace, and a small absorption band at 810 cm^{-1} remained after UV irradiation. It is assumed that remained small peaks are presumably due to the C=C group of acrylate remained unreacted in the cured polymer. The N=C=O stretching band near 2270 cm^{-1} was used to monitor the extent of the reaction between isocyanate and the hydroxyl group. The band was no longer detectable after UV irradiation. The result in Fig. 1 indicates that UV radiation curing and the reaction between isocyanate and hydroxy group had been mostly performed.

The degree of cure of the polyurethane acrylates after exposure to UV was measured in terms of gel content. Fig. 2 illustrates the change in gel content as a function of curing time for samples A-2 and B-2. It is seen that there are dramatic increases in gel content up to near 90% within 1s, but thereafter there are very small gains in gel contents with further increasing the irradiation time, and the gel content could reach about 97% regardless of the polyol type used. It is generally accepted that a gel content of 90~96% indicates a complete cure of the coatings.

Generally, polyurethane acrylates possess a two phase microstructure, i. e., a diisocyanate/short or stiff chain diol rich hard segment and a flexible

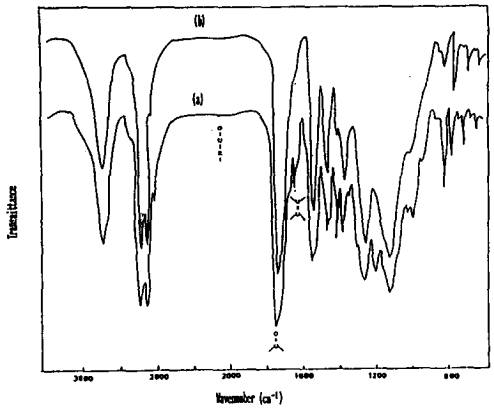

Fig. 1. Infrared spectra of prepolymer(HMDI/HEA/PTMG/GL)/diluent(TMPTA)(80/20 wt%) before(a) and UV curing(b).

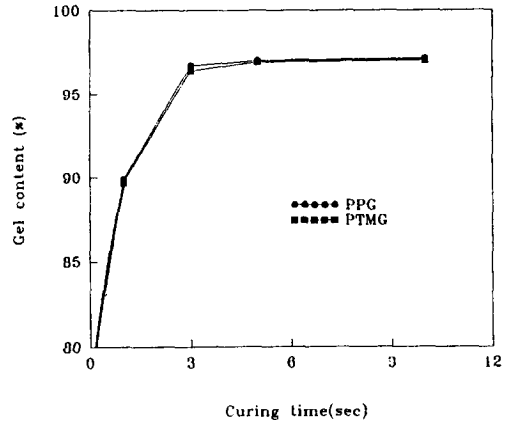

Fig. 2. Gel content of cured film with curing time for sample A-2 and B-2(prepolymer(HMDI/HEA/PPG/GL)/diluent(TMPTA)(80/20 wt%) prepolymer (HMDI/HEA/PTMG/GL)/diluent(TMPTA)(80/20 wt %).

long chain diol rich soft segment. The microstructures of cured polyurethane acrylates were investigated through the measurement of dynamic mechanical properties. The effect of the structure of prepolymer containing two different polyols and formulation of prepolymer and diluent on the dynamic thermal mechanical properties of UV-cured polyurethane acrylate films were investigated. The storage modulus(E'), loss modulus(E"), and loss factor(tan δ) obtained at 11 Hz are shown in Figs 3~15.

The dynamic mechanical properties of the UV cured films for samples A-1, A-2 and A-3 were determined as a function of temperature(as shown in Figs. 3, 4 and 5). Over the temperature range of −40℃ and 60℃, the higher the content of GL, the higher the value of E'(Fig. 3). As shown in Figs. 4 and 5, in the temperature range examined, several relaxation peaks which varied with composition of the polyurethane acrylates are observed owing to the multiple microstructures. These multi-microstructures are no doubt due to the complex nature of polyurethane acrylate segments comprised of two kinds of polyol. A detailed assignment of these multiple relaxations will not be attempted. With increasing GL content, the main relaxation

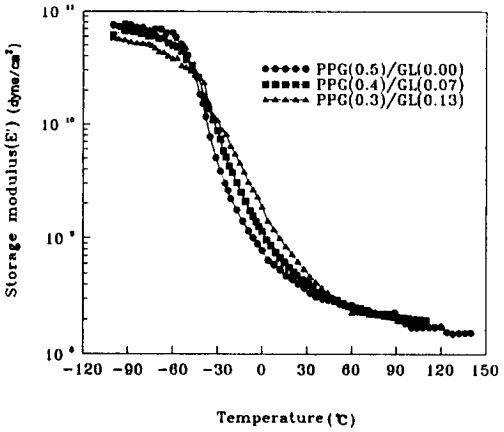

Fig. 3. Effect of PPG/GL composition of E′ with temperature for sample A(prepolymer(HMDI/HEA/PPG/GL)/diluent(TMPTA)(80/20 wt%).

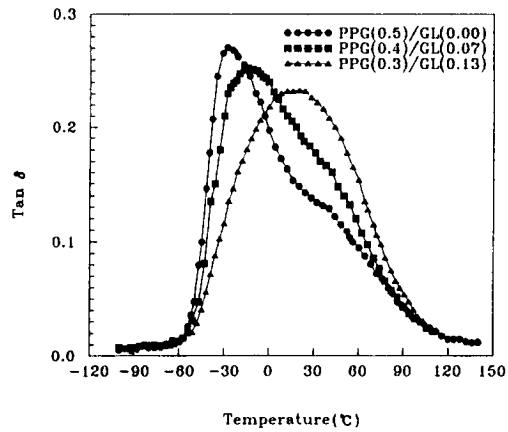

Fig. 5. Effect of PPG/GL composition on tan δ with temperature for sample A(prepolymer(HMDI/HEA/PPG/GL)/diluent(TMPTA)(80/20 wt%).

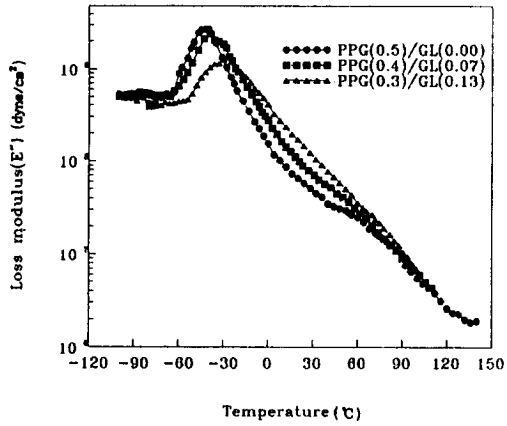

Fig. 4. Effect of PPG/GL composition on E″ with temperature for sample A(prepolymer(HMDI/HEA/PPG/GL)/diluent(TMPTA)(80/20 wt%).

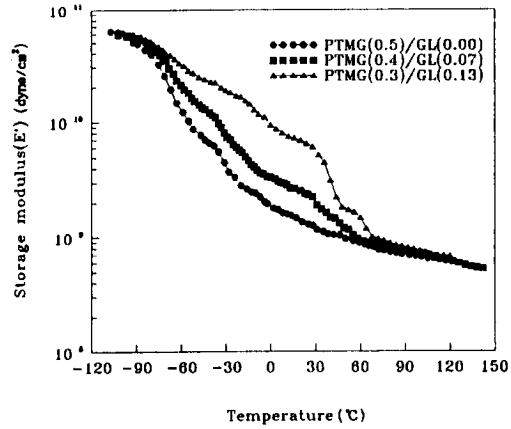

Fig. 6. Effect of PTMG/GL composition on E′ with temperature for sample B(prepolymer(HMDI/HEA/PTMG/GL)/diluent(TMPTA)(80/20 wt%).

peak assigned to the glass transition temperature shifted to higher temperature as shown in Figs 4 and 5. These behaviors may be due to higher functionality of GL than that of PPG.

The dynamic mechanical properties of samples B-1, B-2 and B-3 with temperature are shown in Figs 6, 7 and 8. The storage modulus increase with increasing GL content as shown in Fig. 6. In the temperature range examined several relaxation peaks are also observed due to the multiple microstructure discussed above. However, the marked trend in position of relaxation peak temperature with composition of PTMG/GL were not observed as shown in Figs 7 and 8.

Figs 9~14 show the effect of diluent(TMPTA) content on the dynamic mechanical behavior as a function of temperature for samples C and D. The effect of the diluent contents on the storage modulus are shown in Figs 9 and 12. As the diluent contents increases, the value of storage modulus, E′, increases. The increase of storage modulus may be due to the high functionality of TMPTA(tri-func-

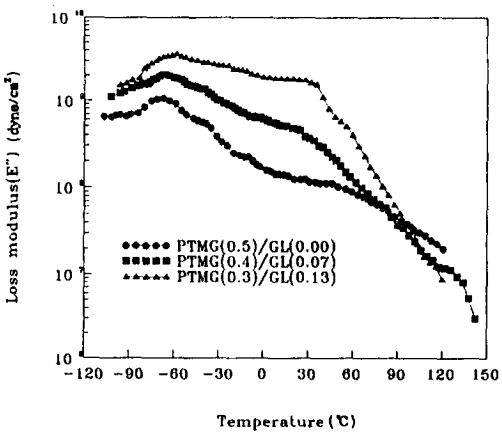

Fig. 7. Effect of PTMG/GL composition on E″ with temperature for sample B(prepolymer(HMDI/HEA/PTMG/GL)/diluent(TMPTA)(80/20 wt%).

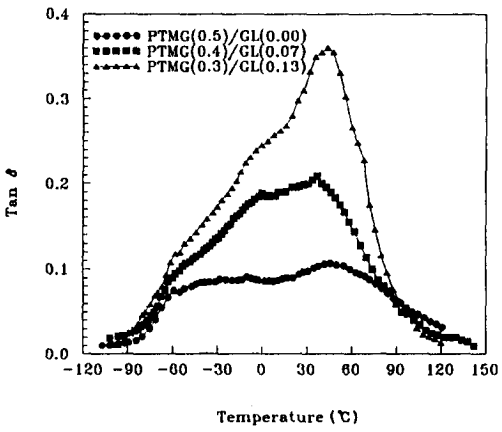

Fig. 8. Effect of PTMG/GL composition on tan δ with temperature for sample B(prepolymer(HMDI/HEA/PTMG/GL)/diluent(TMPTA)(80/20 wt%).

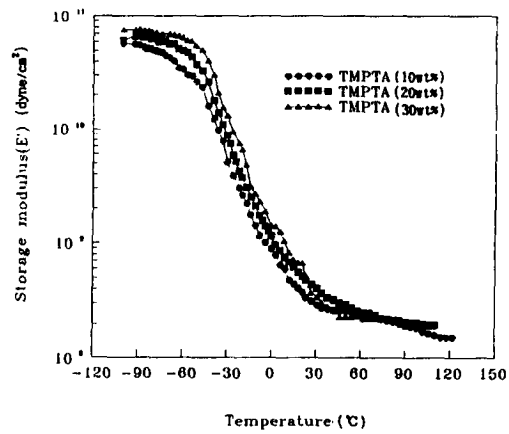

Fig. 9. Effect of diluent(TMPTA) content on E′ with temperature for sample C(prepolymer(HMDI/HEA/PPG/GL)/TMPTA).

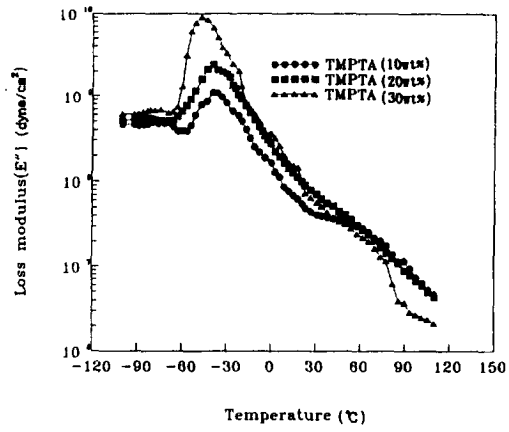

Fig. 10. Effect of diluent(TMPTA) content on E″ with temperature for sample C(prepolymer(HMDI/HEA/PPG/GL)/TMPTA).

tional acrylate monomer). However, the TMPTA affected the temperatures of loss modulus(E″) and loss tan δ peaks assigned to the glass transition of polyurethane chain insignificantly as shown in Figs. 10, 11, 13 and 14. This indicates that the diluent(TMPTA) component was not included in polyurethane segments. Thus, the TMPTA did not affect on the glass transition temperature of polyurethane chain significantly.

Fig. 15 shows the effect of two different polyols (PPG and PTMG) on E′ at the same composition of polyurethane acrylate. The storage modulus of the sample A containing PPG decreases more rapidly with temperature than that of the sample B containing PTMG with temperature. In the lower temperature range, the storage modulus of sample A is higher than that of sample B while the composition is the same. However, in the higher temperature range, the storage modulus of sample B is higher than that of sample A. This result may be due to the different structural feature between PPG and PTMG.

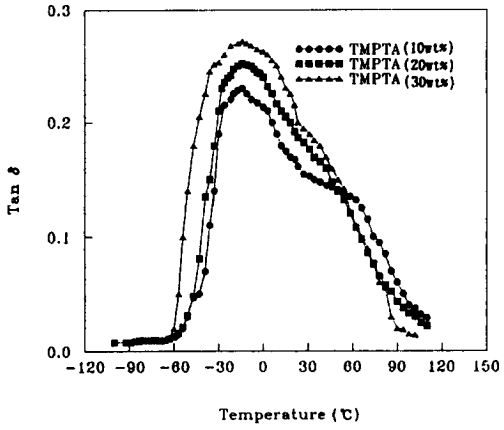

Fig. 11. Effect of diluent(TMPTA) content on tan δ with temperature for sample C(prepolymer(HMDI/HEA/PPG/GL)/TMPTA).

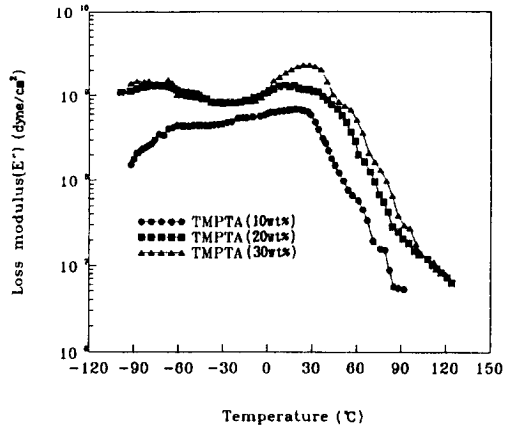

Fig. 13. Effect of diluent(TMPTA) content on E″ with temperature for sample D(prepolymer(HMDI/HEA/PTMG/GL)/TMPTA).

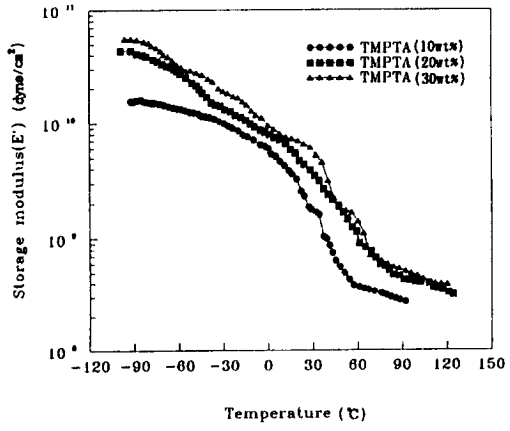

Fig. 12. Effect of diluent(TMPTA) content on E′ with temperature for sample D(prepolymer(HMDI/HEA/PTMG/GL)/TMPTA).

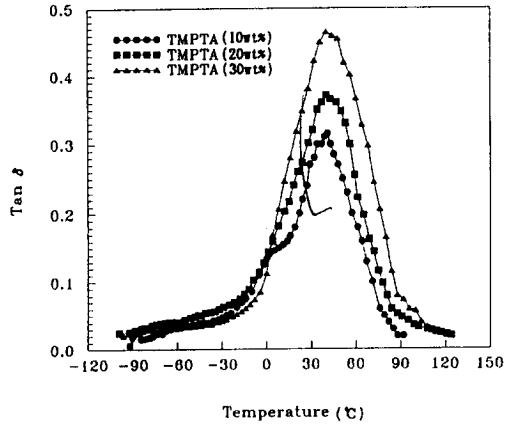

Fig. 14. Effect of diluent(TMPTA) content on tan δ with temperature for sample D(prepolymer(HMDI/HEA/PTMG/GL)/TMPTA).

CONCLUDING REMARKS

A series of UV-curable polyurethane acrylate prepolymers were synthesized from HMDI, polyol (PPG or PTMG)/GL, HEA, and dibutyl tin dilaurate as a catalyst. UV-curable polyurethane acrylate were formulated from prepolymer, reactive monomer, TMPTA as a diluent and photoinitiator benzophenone. The effect of prepolymer type and overall composition of the prepolymer/diluent on the properties of UV-cured polyurethane acrylate are as follows :

1. The gel content of the UV-curable urethane acrylates reached to near 90% within 1 sec.
2. The storage modulus increased with increasing GL and TMPTA contents.
3. The glass transition of sample A shifted to higher temperature as the content of GL was increased.
4. The diluent TMPTA did not affect the temperature of loss modulus and loss tan δ peaks assigned to the glass transition of polyurethane chain

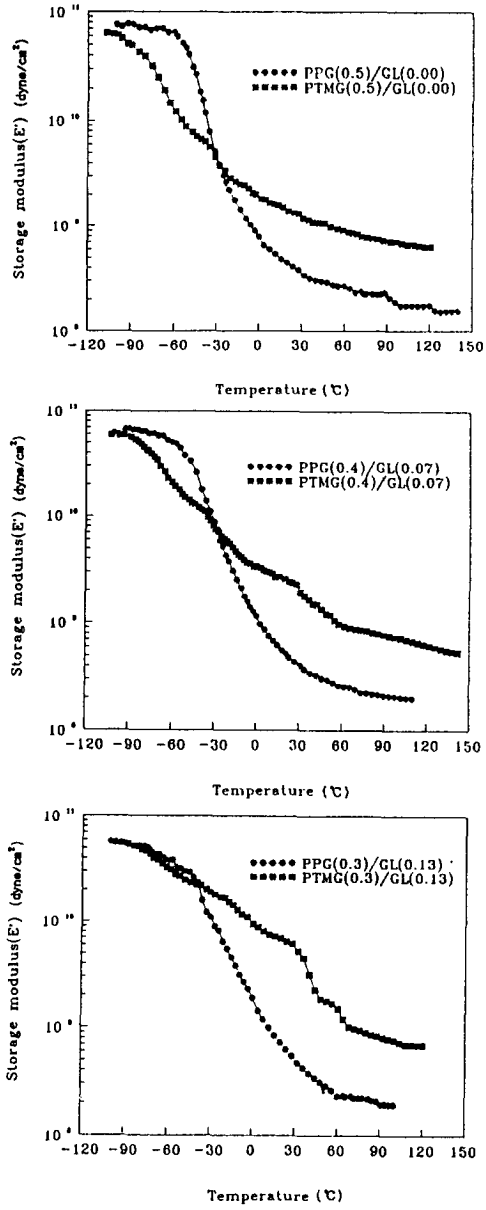

Fig. 15. Effect of PPG/GL, PTMG/GL composition on E′ with temperature for samples : A(prepolymer (HMDI/HEA/PPG/GL)/diluent(TMPTA)(80/20 wt %)), B(prepolymer(HMDI/HEA/PTMG/GL)/diluent (TMPTA)(80/20 wt%)).

significantly.

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