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Design and properties of UV cured polyurethane dispersions

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Abstract

UV curable polyurethane dispersions (UV-PUDs) having different prepolymer chain length, different types of capping agent (2,3-epoxy-1-propanol (glycidol) and 2-hydroxyethylacrylate (HEA)) and ionic center have been synthesized. Films based on polyurethane prepolymer were tack free prior to cure and showed high elongation at break over 200% as well as high hardness and modulus, especially when the terminal isocyanate groups were capped with glycidol.

Keywords: Polyurethane dispersion; UV-curing; Glycidol; High elongation; Tack free

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1. Introduction

Due mainly to their environmentally friendly nature and versatile structure–property relationships of polyurethane (PU), polyurethane dispersions (PUDs) are steadily expending their usages in coatings, adhesives, textile sizing, etc.

PUDs are typically prepared via prepolymer mixing process since their properties are easily tailor made [1,2]. In this process, the isocyanate terminated prepolymers are chain extended in aqueous media using typically tetramine providing PU with crosslinkings [3,4]. However, reactions within the particles which are dispersed in aqueous media do not occur stoichiometry leaving a certain amount of unreacted isocyanate groups which slowly react with moistures and cause property change with time in use. In addition, high molecular weight of prepolymer also poses limits on such coating properties as hardness and abrasion resistance of PUD cast films.

On the other hand, 100% UV cure system provides coatings with high hardness, high solvent and stain resistance, and high gloss due to the high crosslinking density [5]. However, high crosslinking density of UV cure system inevitably lacks flexibility and its formulation prior to cure is subject to tack due to its low average molecular weight. UV cure of polyurethane dispersion (UV-PUD) benefits from the advantages of both UV and PUD without suffering from any of their obvious disadvantages [6].

Epoxy is well known for its unique properties including high mechanical strength, high heat resistance and toughness for use in high performance applications [7]. However, it is too brittle to be utilized alone.

However, when the epoxy is incorporated with UV-PUDs such problem can be properly overcome with the excellent elasticity and high impact strength of PU segments [8,9].

In this study, we used a tetrafunctional pentaerythritol as the starting material to build up four armed polyurethane prepolymers of various molecular weight. The isocynate termini were caped with glycidol and/or hydroxy acrylate at various compositions. In this structure, molecular weight between crosslink (M_c) corresponds to one quarter of prepolymer molecular weight. Effect of prepolymer molecular weight, types of caping agent and ionic center have been studied in terms of dispersion characteristics, surface and physical properties of uncured and cured PUD cast films.

2. Experimental

Polytetramethylene ether glycol (PTMG; $M_n = 650$; Korea Polyols, Korea) were dried and degassed at 80 °C, 1–2 mmHg for 2 h before use. Dimethylol butanoic acid (DMBA; Aldrich), dimethylol propionic acid (DMPA; Aldrich) and pentaerythritol (Aldrich) were dried at 50 °C for 48 h. Extra pure grades of 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI;

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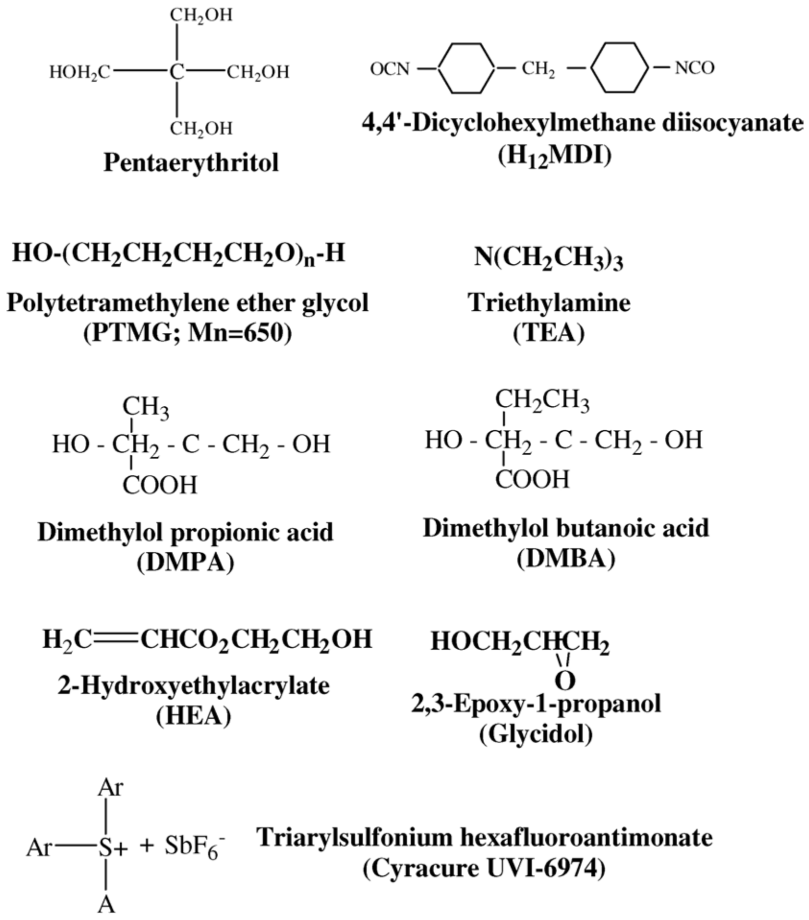


Fig. 1. Structures of materials used to prepare UV-PUD.

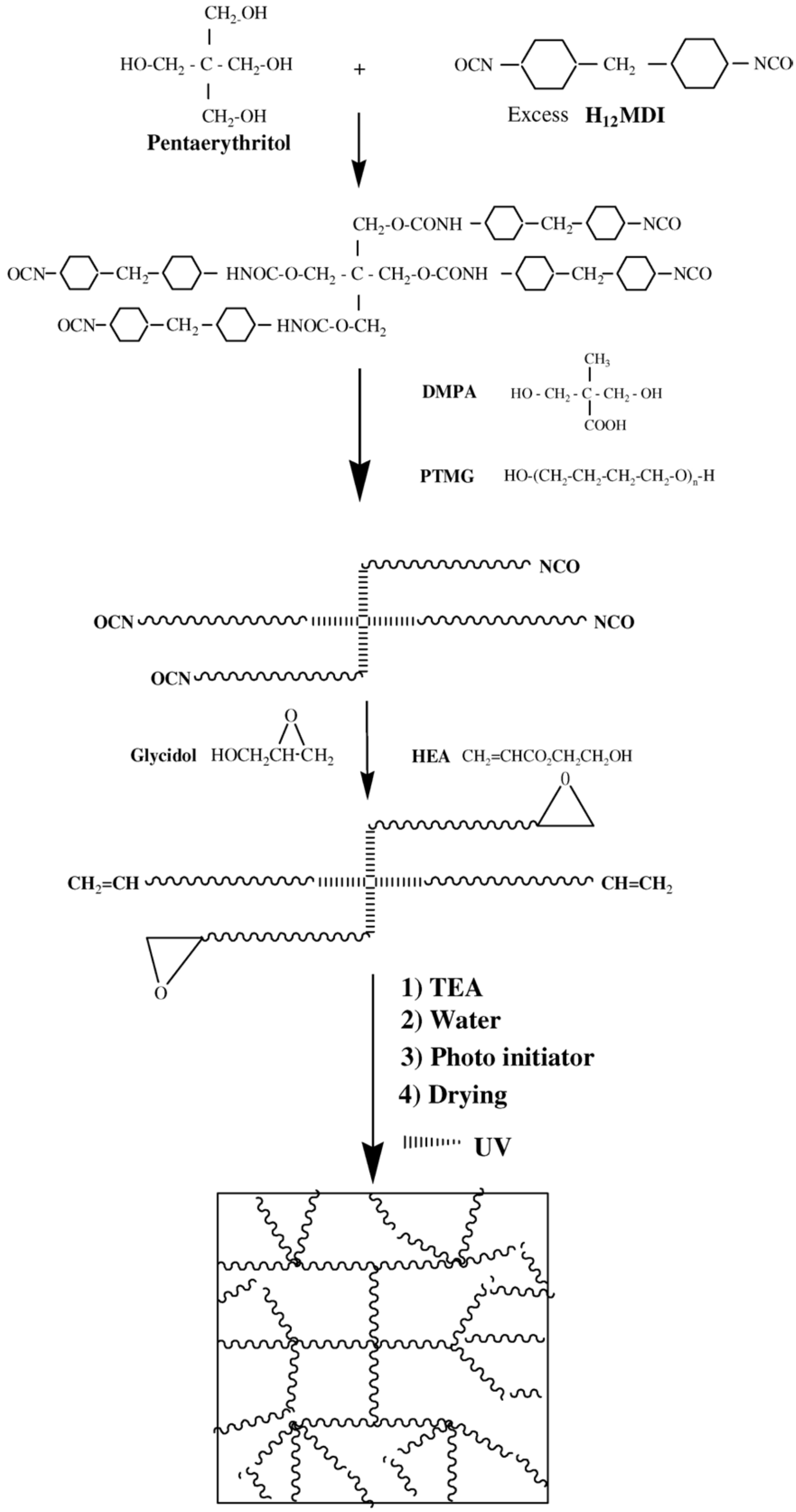
Bayer), 2,3-epoxy-1-propanol (Glycidol; Aldrich), dibutyltin dilaurate (DBTDL; Aldrich), 2-hydroxyethylacrylate (HEA; Aldrich) and triarylsulfonium hexafluoroantimonate (Cyracure UVI-6974; Union Carbide) were used as received. Triethylamine (TEA; Aldrich) was dried over 4 °C molecular sieves before use. Chemical structures of these materials are shown in Fig. 1 whereas basic formulations and procedure to prepare UV-PUD are respectively given in Table 1 and Scheme 1.

A 500 ml round-bottom, four-necked separable flask with a mechanical stirrer, thermometer and condenser with drying tube and N_2 inlet was used as reactor. The reaction was carried out in a constant temperature oil bath. Pentaerythritol and molar excess of H_{12}MDI were charged into the dried flask and stirred at 80 °C for about 2 h to obtain star shaped prepolymer with NCO termini. DMPA and PTMG were subsequently added and reacted to build up urethane segments of desired molecular weight. This NCO-terminated prepolymers were caped with

Table 1
Basic formulation to prepare UV-PUD (unit in mole)

Run	Pentaerythritol	M_c[a]	M_p[b]	PTMG	H_{12}MDI	Ionic center		TEA	Glycidol	HEA
						DMBA	DMPA			
B8-0	1	2000	8000	5	11	2	0	2	0	4
P8-0		2000	8000	5	11		2	2		4
P16-0		4000	16000	12	20	0	4	4	0	4
P24-0		6000	24000	21	32	7	7	4		
P8-25		2000	8000	5	11	0–	2	2	1	3
P8-50									2	2
P8-75									3	1
P8-100									4	0

[a] Molecular weight between crosslinks.
[b] Prepolymer molecular weight.



Scheme 1. Reaction route to prepare UV-PUD.

glycidol and/or HEA, and the reactions were monitored by FT-IR measurements. When the absorption peak of NCO group at 2270 cm^{-1} disappeared, prepolymers were cooled down to 50 °C and a neutralizing agent (TEA) was added and stirred for the next 1 h while maintaining the temperature at 50 °C. PUDs were obtained by adding water to the mixture using a tubing pump. The resulting product was a stable dispersion with a solid content of about 30%. To this 3 wt.% of photoinitiator (Cyracure

UVI-6974) was added before the dispersion was cast and dried for UV cure.

Average particle size was measured with an electrophonetic light scattering spectrophotometer (Otsuka Electronics; ELS-8000). Films were prepared by casting the dispersion onto Teflon plate, followed by drying at 30 °C for 24 h. The resulting films were then heated overnight in an oven at 50 °C under 2–3 mmHg. Samples were irradiated from one side using an 8W-UV (365 nm) lamp for 4 min at room temperature [10]. To measure the tack, a weak pressure (50 g/cm^2) has been applied to the surface of uncured film for 30 s. Film is called tack free when the surfaces were separated without leaving any defect on them. Shore A hardness was measured using an indentation hardness tester according to ASTM D2240-75. Contact angle of the dispersion cast film with water drop at room temperature was measured using an Erma (G-1).

Tensile properties were measured with a universal testing machine (Tinius Olsen 1000) at a crosshead of 500 mm/min using specimens prepared according to ASTM D-1822. Tests were made at room temperature and at least five runs were made to report the average. Dynamic mechanical tests were preformed with a Dynamic Mechanical Thermal Analyzer (Rheometric Scientific; DMTA MK-IV) at 10 Hz, 4 °C/min and 0.025 strain over a temperature range from −60 to 100 °C. For thermogravimetric analysis (TA Instruments; TGA Q50), 5 mg of sample was put in an alumina crucible and heated at 20 °C/min under N_2 atmosphere.

Water swell was measured by emerging a film in water at room temperature for 11 h and %swell was calculated by the following equation:

$$\%\text{swell} = \frac{W - W_o}{W_o} \times 100 \quad (1)$$

where W_o is the weight of dried film and W is weight after water absorption. Gel content was measured by immersing the films (W) in toluene for 48 h. Films were then throughly dried (W_o) and %gel was calculated according to %gel = $((W_o - W)/W_o) \times 100$. To determine the yellowing films were exposed to the UV (80 W × 5 m/min × 20 times) and color change (ΔE) was determined. Solvent resistance to methyl ethyl ketone (MEK) was determined by brushing the films with MEK 200 times.

3. Results and discussion

Particle size of dispersion primary depends on several factors such as hydrophilicity which is mainly governed by the ionic group content and prepolymer molecular weight which primarily contributes to viscosity. Particle size also depends on the main chain flexibility and the location of ionic group. Generally, flexible chains with ionic groups in soft segment give finer dispersion since migration of ionic groups to the surface during dispersion is more feasible due to the easier conformational change of soft segment [11].

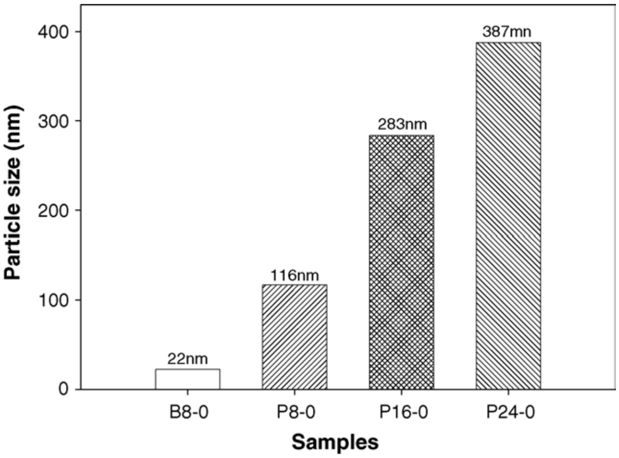


Fig. 2. Particle size of dispersion vs. prepolymer molecular weight.

Fig. 2 shows that particle size of the dispersion monotonically increases with the increase in prepolymer molecular weight which is primarily related to the increased viscosity of prepolymer. Since the ionic content of the prepolymer was kept at constant (4.0%) higher prepolymer viscosity should primarily be responsible for the larger dispersion size.

Notably DMBA (B8-0) gives much finer dispersion than DMPA (P8-0) although their molecular structures do not support the result. That is, DMBA has larger alkyl pendant group which reduces main chain flexibility and hydrophilicity as well. Therefore, it is believed that larger pendant group provides the carboxylic group with greater steric hinderance to the attack of isocyanate groups leaving more carboxylic groups available for subsequent ionization.

Physical properties of the uncured and UV cured dispersion cast films are shown in Table 2. Contact angle of the film with water drop increased with increasing prepolymer molecular weight. On the other hand, contact angle decreased with increasing glycidol content due to the polarity of epoxy group. Regardless of the type of formulation, all of the prepolymer dispersions were tack free before cure due to the larger prepolymer molecular weight (8000–24,000). Tack is a property to form a connection of measurable strength to a substrate under usually slight pressure after short contact time [12,13]. Therefore, tack needs viscous flow of materials near the surface during the short contact time which becomes difficult with high molecular weight polymer [14]. Tack free prior to cure is an important property for such application as resilient flooring since its coated surface can be embossed without sticking to the embossing roll [6].

Prior to cure, most of the dispersion cast films were transparent implying that the prepolymers are amorphous where soft and hard segments are well mixed to form homogeneous morphology. With high glycidol content (P8-75 and P8-100) light yellowing was noted before cure and this film upon curing gave color change larger than 1 ($\Delta > E1$).

Hardness of the cured films significantly decreased with increasing prepolymer molecular weight due to the increased crosslinking density. Hardness increased with glycidol content although the increase is small. For elastomers hardness generally shows a linear relationship with elastic modulus which is inversely proportional to the M_c [15]. Gel fraction of the polymer in toluene slightly decreased with increasing prepolymer molecular weight due to the decreased crosslinking density, and increased as glycidol content increased. It seems that hardness

Table 2
Physical properties of uncured and UV-PUD

Run	Particle size (nm)	Uncured film		Cured film				
		Tack	Hazy	Yellowing resistance, ΔE	Solvent resistance	Gel (%)	Contact angle (°)	Hardness (Shore A)
B8-0	22	Free	○	<1	○			
P8-0	116	Free	○	<1	○	89.7	56	82
P16-0	283	Free	○	<1	○	88.3	66	45
P24-0	387	Free	○	<1	○	87.2	68	6
P8-25	127	Free	○	<1	○	90.7	52	92
P8-50	146	Free	○	<1	○	94.2	48	92.9
P8-75	132	Free	Δ	>1	○	95.1	40	94.3
P8-100	138	Free	Δ	>1	○	95.7	29	96.3

is much more sensitive to the crosslinking density than the gel fraction.

Solvent resistance to MEK is satisfactory for all of the formulations. This indicates that solvent resistance of PUD improves dramatically with UV cure. Water swell (Fig. 3) increases with increasing prepolymer molecular weight due to the decreased crosslinking density, and decreases with the increase in glycidol content due to the rigidity as noted from the hardness and dynamic modulus to follow.

Dynamic mechanical properties of the UV cured films as a function of prepolymer molecular weight are shown in Fig. 4 where the modulus, especially in rubbery region increases as the molecular weight of prepolymer decreases. This implies that our elastomers follow the Gaussian statistics given by:

$$G_N^o = \frac{\rho RT}{M_c} \tag{2}$$

where G_N^o is rubbery modulus, ρ the density, T the absolute temperature and R is the gas constant [15].

Generally, a single $\tan\delta$ peak is seen, especially at smaller prepolymer molecular weight implying that these segmented PUs are generally phase mixed. The peak temperature moves toward the higher temperature as the prepolymer molecular weight decreases. This is an effect of crosslinking on the glass transition temperature (T_g). The least square plot of T_g (°C) against $1/M_c$ (Eq. (3)) gave a straight line with $C_1 = -5.51$ and $C_2 = 1.37 \times 10^5$ [16].

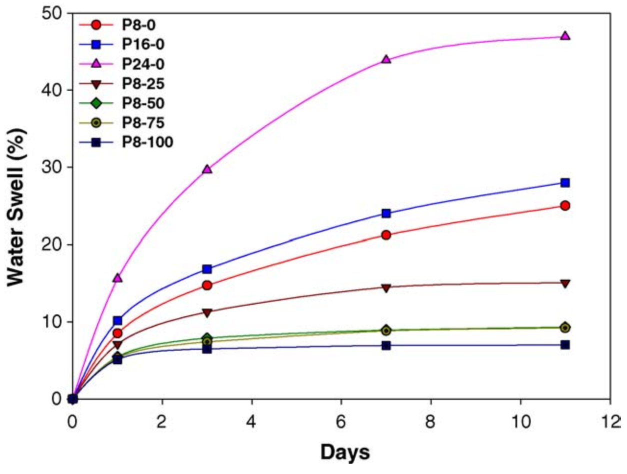


Fig. 3. Water swell of UV-PUD.

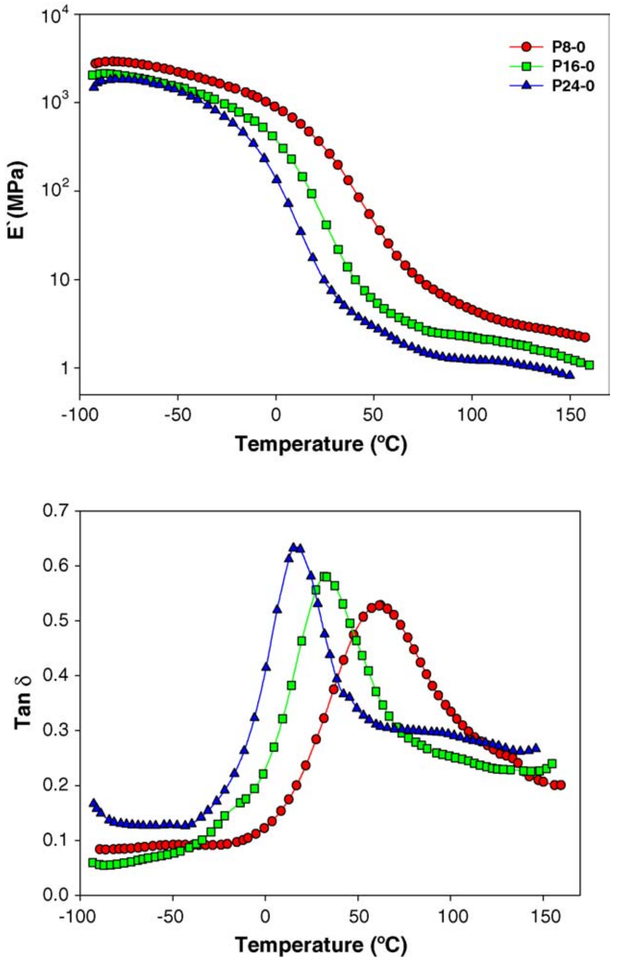


Fig. 4. Dynamic mechanical properties of UV-PUD vs. prepolymer molecular weight.

$$T_g = C_1 + \frac{C_2}{M_c} \tag{3}$$

It should also be mentioned that at high M_c (6000) a second peak which in fact is a mere shoulder is also seen at about 100 °C.

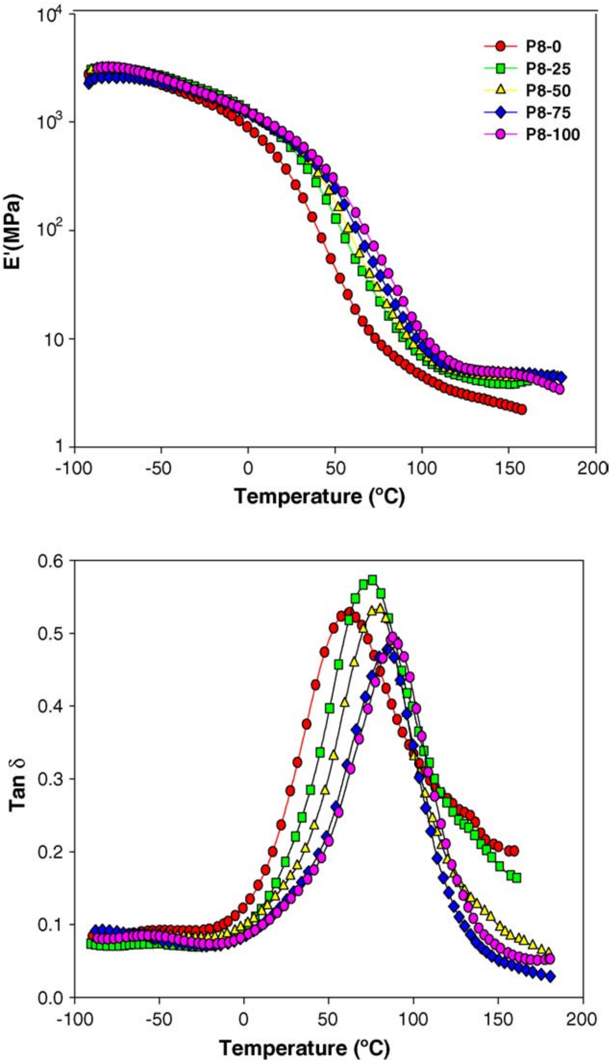


Fig. 5. Dynamic mechanical properties of UV-PUD vs. glycidol content.

This indicates that soft and hard segments of polyurethane tend to phase separate when the chain length becomes large. Modulus and tan δ peak temperature of the cured film also increase as glycidol content increases due to the rigidity of epoxy group (Fig. 5).

Temperature at which the value of rubbery modulus changes significantly is often considered to indicate the limit of thermal stability of the polyurethane elastomers [17]. Such limit is not seen from our dynamic data probably due to the crosslinked structure of the cured films. On the other hand, TGA measurements (Fig. 6) show that degradation temperature of urethane group at around 300 °C as well as that of soft segment at around 400 °C has been increased with the addition and increasing amount of glycidol owing to its high thermal stability.

Tensile behavior of the cured film is shown in Figs. 7 and 8 where initial modulus increases and elongation at break decreases with the decrease in prepolymer molecular weight and increase in glycidol content. It is worth to note that elongation at break of the UV cured film is at least over about 200% which is not possible for conventional UV cure and this is a great advantage of UV-PUD. High elongation of UV cured film is of an essential property for coating of article to be processed by thermoforming like crash pad. Regardless of the type of formulation, strain hardening is noted as a response to the crosslinked structure.

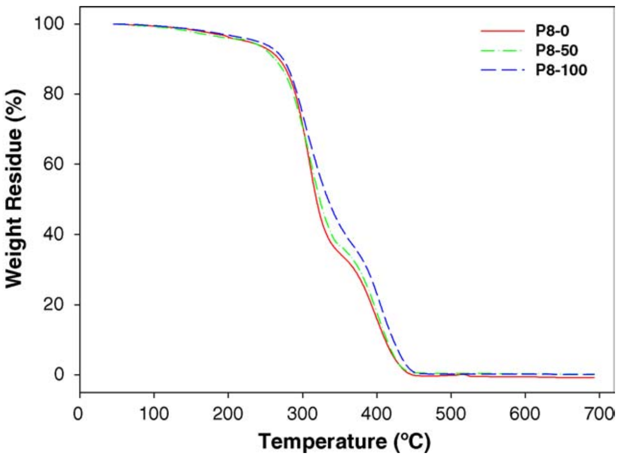


Fig. 6. Thermogravimetric Analysis of UV-PUD vs. glycidol content.

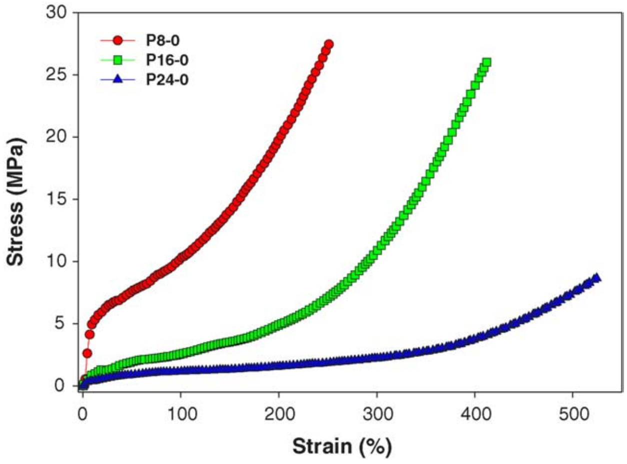


Fig. 7. Tensile behavior of UV-PUD vs. prepolymer molecular weight.

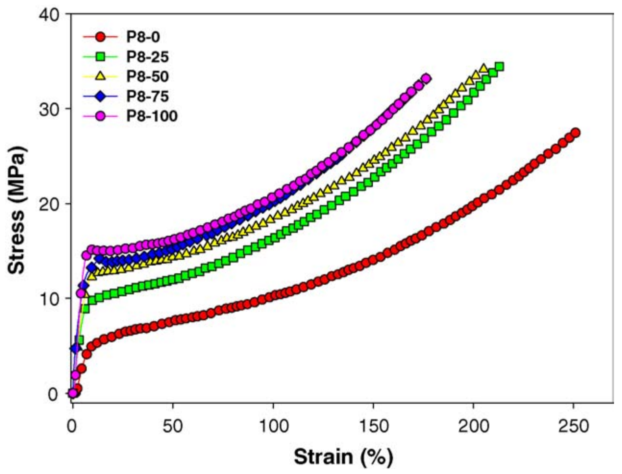


Fig. 8. Tensile behavior of UV-PUD vs. glycidol content.

4. Conclusions

UV-PUDs of various structures have been designed and synthesized based on the different molecular weight between crosslinks (M_c), type of caping agents and ionic center. DMBA as compared with DMPA gave much finer dispersion due presumably to the greater steric hindrance of large pendant group against the attack of isocyanate groups to the carboxylic groups.

Soft and hard segments of UV-PUDs were generally phase mixed. However, a tendency of phase separation was noted when the M_c becomes large.

UV-PUDs properly combined the advantages of UV cure and PU dispersion giving rise to tack free prior to cure, high hardness, high modulus, high solvent resistance and low water swell especially with high glycidol content while keeping the elongation at break high over 200%.

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