Structured Polyurethanes for Oil Uptake

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ABSTRACT: In an attempt to develop a desirable resin formulation for spilled oil absorption, segmented polyurethanes of various types and lengths of hard and soft segments have been synthesized and tested for X-ray diffraction, thermal, mechanical, and dynamic mechanical properties in addition to oil and water absorptions. Significant oil absorption was obtained with ether type polyol of high molecular weight, especially with short hard segments of long-chain diamines. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2080–2087, 2005

Key words: polyurethanes; oil absorption; structure–property relations; XPS

INTRODUCTION

Ocean pollution by spilled oil has long been a serious environmental problem.[1] A number of treatments including mechanical, physical, and chemical ones have practically been made and partial success is reported.[2–4] Physical treatments generally make use of certain chemicals to disperse the spilled oil into small particles (dispersant), to coagulate the oil particles to prevent precipitation (gelling agent), and to preferentially absorb the oil using solid surfaces (absorbent). Dispersed or emulsified and coagulated oils are then mechanically collected using, for example, net and oil fences, although they can be decomposed by UV, wind, and insects. Each treatment has certain advantages and disadvantages and often they are used in combination.

Probably nonwoven polypropylene fabrics most often have been encountered as spilled oil absorbent.[5] However, on-time manufacturing and transportation of large volumes to the accident site have been practical disadvantages. Recently, on-site polyurethane (PU) foam has been proposed as an oil absorbent, i.e., highly reactive liquid reactants are transported to the site of spilled oil and reacted to form foams.[6–9] This on-site forming could be a most suitable on-time technology for spilled oil treatment.[10,11]

We consider here the effect of PU structure on oil and water absorption. That is, type and molecular weight of polyol, hard segment structure, length, and crosslinking have systematically been varied, and the effects of these variables on initial and equilibrium oil and water absorption have been studied. In addition, crystallization, thermal, mechanical, and dynamic mechanical properties have also been measured to investigate the basic structure–property relationships of segmented PUs.

EXPERIMENTAL

Materials

To prepare PUs of various chemical compositions, structures, and morphologies, a number of polyols, isocyanates, and extenders have been incorporated (Table I). Four types of polyol, viz., polypropylene glycol (PPG), poly(tetramethylene ether) glycol (PTMG), poly(tetramethylene adipate) glycol (PTAd), and poly(caprolactone) diol (PCL) with number average molecular weight M_n = 2000 (g/mol), four types of diisocyanates, viz., 4,4-diphenylmethane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI), and four types of chain extender, viz., ethylene glycol (EG), hexane glycol (HG), ethylene diamine (EA), and hexane diamine (HA) have been used to prepare PUs. Reagent grades of these materials were used as received. The effect of M_n of polyol was studied with PTMG of M_n = 1000, 1500, and 2000 (g/mol).

Synthesis

A 500-mL four-neck round-bottom flask equipped with a mechanical stirrer, thermometer, condenser

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TABLE I
Formulation for Polyurethane Synthesis

Run	PPG 2000	PEG 2000	PTMG 2000	PTAd 2000	PCL 2000	PTMG 1000	PTMG 1500	MDI	TDI	HDI	IPDI	EG	BG	HG	EA	HA
PPG	1							2					1			
PEG		1						2					1			
PTMG																
2000			1					2					1			
1000						1		2					1			
1500							1	2					1			
PTAd				1				2					1			
PCL					1			2					1			
PTB			1						2				1			
PHB			1							2			1			
PIPB			1								2		1			
PMB2			1					2					1			
PMB3			1					3					2			
PMB4			1					4					3			
PMEG			1					2				1				
PMHG			1					2							1	
PMEA			1					2						1		
PMHA			1					2								1

with a drying tube, and N_2 inlet was used to synthesis PU via the one-shot procedure in most cases in a constant temperature water bath: polyol, diisocyanate, and chain extender dissolved in dimethyl formamide were charged into the dried flask, with a solid content of about 30 wt % to control the viscosity. Temperature profile of the reaction was 50°C (30 min)–70°C (30 min)–90 °C (1 h). However, when hard segment length was extended NCO-terminated prepolymers were first prepared, followed by extension with BD and MDI as desired. Basic formulations are given in Table II.

TABLE II
Materials Used

	Materials	Supplier
Diisocyanate	MDI 4,4′-diphenylmethane diisocyanate	Aldrich
Polyols	PTMG	
	Poly(tetramethylene ether) glycol	Dongsung Chemical
	$M_n = 2000$	
	PPG	
	Poly(propylene glycol)	Aldrich
	$M_n = 2000$	
	PEG	
	Poly(ethylene glycol)	Aldrich
	$M_n = 2000$	
	PTAd	
	Poly(tetramethylene adipate) diol	Dongsung Chemical
	$M_n = 2000$	
	PCL	
	Poly(hexamethylene carbonate) diol	Aldrich
	$M_n = 2000$	
Chain extenders	EG	Aldrich
	Ethylene glycol	
	HG	
	Hexane glycol	
	BG	
	Butane glycol	Aldrich
	EA	
	Ethylene diamine	
	HA	
	Hexane diamine	

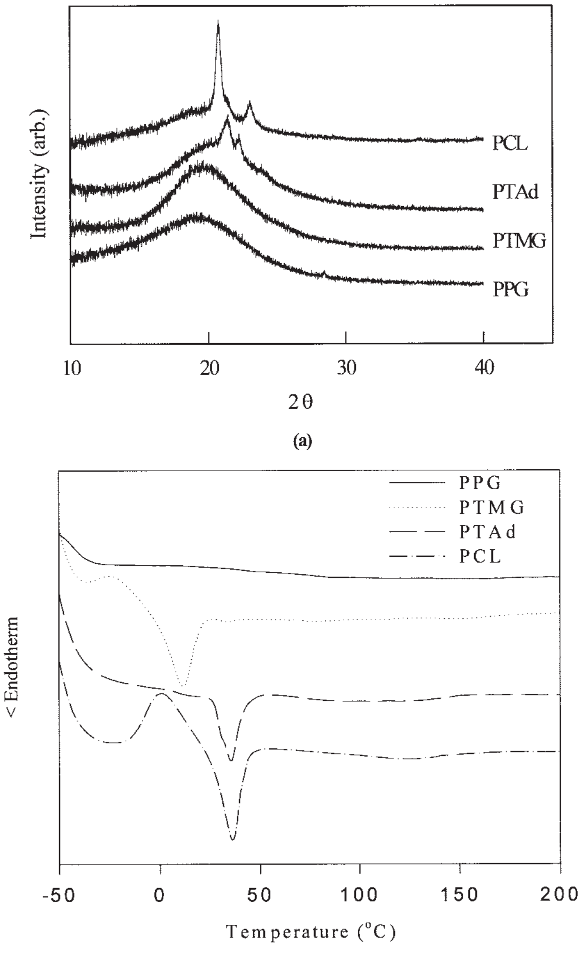

Figure 1 XRD profiles (a) and DSC thermograms (b) of PUs for various types of polyol.

Film casting

Films were cast on a glass plate (10 × 6 cm^2) and dried overnight at 100 °C in an oven, followed by 30 °C under vacuum.

X-ray diffraction (XRD) profiles

XRD profiles of the solution cast films were measured using a Rigaku (Model D/max-2400) with CuKα (30 kV, 20 mA) for $2\theta = 4–40°$ at room temperature.

Thermal properties

Thermal properties of the samples were measured by differential scanning calorimetry (Seiko DSC 220). Samples were first heated to 250 °C and cooled down to −50 °C. DSC thermograms were recorded during the second heating cycle at 20 °C/min from −50 to 250 °C.

Mechanical properties

Room temperature tensile properties of the solution cast film were measured using a Tinius Olsen tensile tester at a crosshead speed of 500 mm/min, and an average of at least five measurements was calculated.

Dynamic mechanical properties

Dynamic mechanical tests were performed with a Rheovibron (Orientec DDV-01FP) from −80 to 200 °C at 3 °C/min and 11 Hz.

Water and oil swell

Sorption of water and oil (light oil) was measured at 20 °C using a 2 × 3 × 0.03 cm specimen, and the

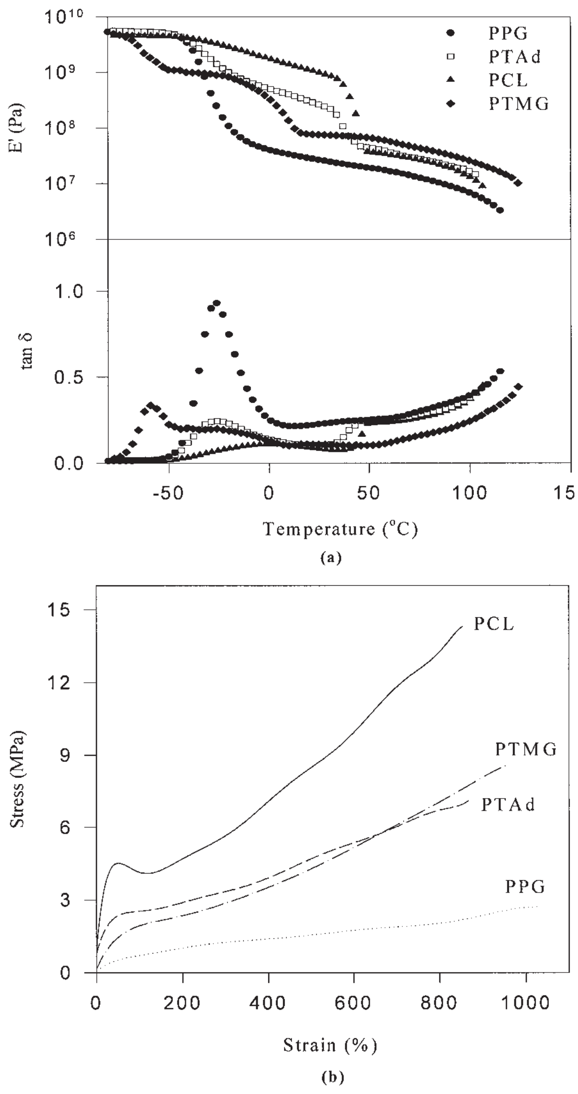

Figure 2 Dynamic mechanical (a) and tensile properties of PUs for various types of polyol.

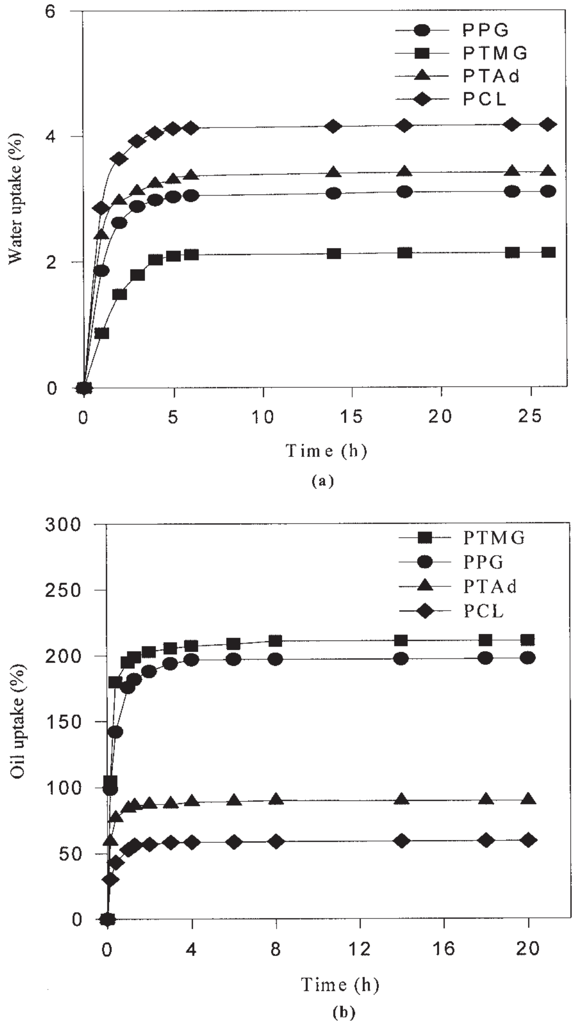

Figure 3 Water (a) and oil (b) uptake of PUs for various types of polyol.

uptake precent swell was calculated using the equation

$$\% \text{ Swell} = \frac{(W - W_0)}{W_0} \times 100,$$

where W_0 and W are the weight of dried and swelled samples, respectively.

RESULTS AND DISCUSSION

Effect of polyol type

In this series of structural design, four types of polyol, viz. PCL, PTAd, PTMG, and PPG (M_n = 2000) were combined with MDI and BD to prepare PUs. PUs from PCL2000 and PTAd2000 show sharp (clearer with PCL) XRD profiles (Fig. 1a), indicative of soft segment crystallization, whereas those from PTMG and PPG simply show an amorphous shoulder at around $2\theta = 18–20°$.

DSC thermograms (Fig. 1b) also show sharp melting endotherms for PCL (36 °C) and PTAd (35 °C) PUs. PCL gives a slightly higher peak temperature and relatively large peak area compared with PTAd. PTMG PU also shows a sharp melting peak at around 11 °C. It seems that the PCL, PTAd, and PTMG based soft segments are crystallizable and the degree of crystallinity is in the increasing order of PTMG < PTAd < PCL. DSC is more sensitive to define crystallinity of a PU than XRD.

Dynamic mechanical analysis (Fig. 2a) shows a single transition for PPG (−25 °C) and PCL (+42 °C), double transitions for PTAd (−25 °C, 42 °C) and PTMG PU (−60 °C, 20 °C). For PTAd and PTMG PUs, the lower and higher transition temperatures should, respectively, correspond to the T_g and T_m of soft segments. Single transitions for PPG should correspond to its soft segment T_g and that for PCL to its T_m. It is suggested that the almost amorphous nature of PPG

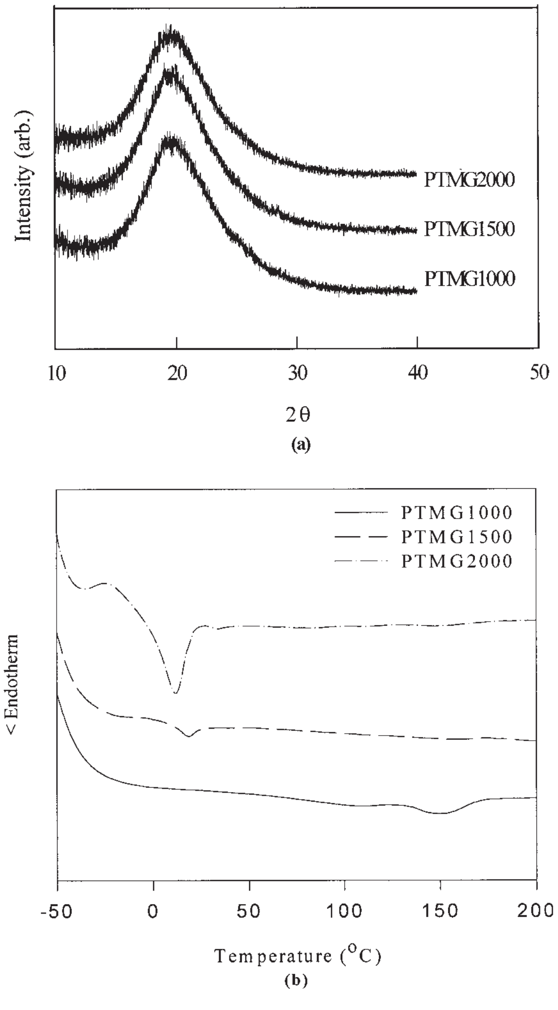

Figure 4 XRD profiles (a) and DSC thermograms (b) of PUs for various M_n of PTMG.

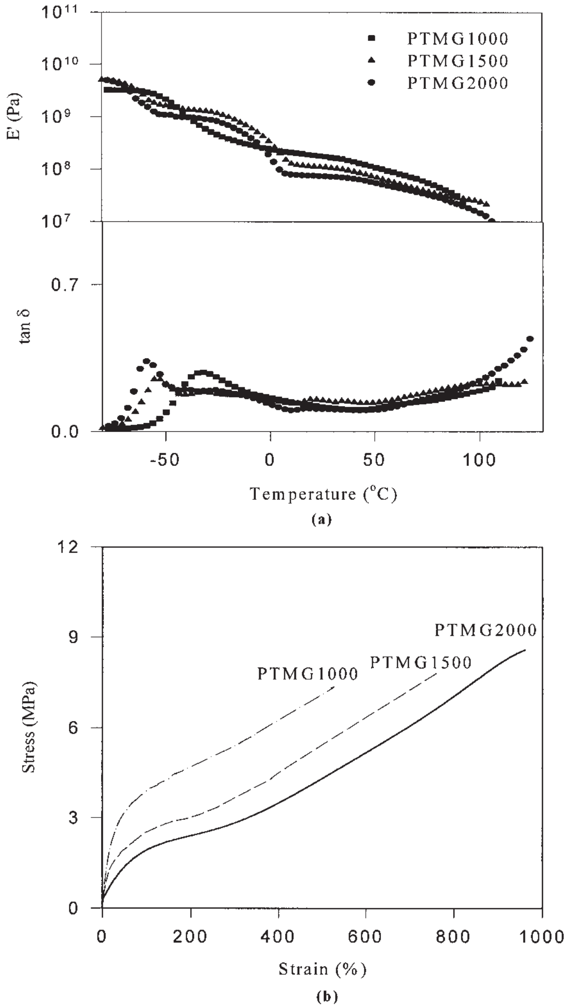

Figure 5 Dynamic mechanical (a) and tensile (b) properties of PUs for various M_n of PTMG.

soft segments and the high crystallinity of PCL soft segments, respectively, give single transitions corresponding to glass transition and soft segment melting. On the other hand, the less perfect crystalline structures of PTAd and PTMG soft segments showed both T_g for the amorphous domains and T_m for the crystalline domains.

Stress–strain measurements (Fig. 2b) show that the four PUs types are all highly elastic with elongation at break over 800%. This is mainly due to high soft segment content. Notably, PCL PU depicts a sharp positive yield, necking, and subsequent strain hardening, which are typical of semicrystalline polymers. On the other hand, PPG PU shows a behavior typical of amorphous polymers with no yield.

Water uptake, both initially and at equilibrium (Fig. 3a), increases as follows: PTMG < PPG < PTAd < PCL. Water uptake by lactone and ester type polyols is greater than that for the ether type polyols. It is expected that sorption of water molecules by crystalline domains is difficult compared with the amorphous domains. However, the results obtained indicate that at constant hard segment content, hydrophilicity of PU governs water uptake. It should be noted that equilibrium water absorption is limited to just a few percentages, regardless of the polyol type.

Oil absorption (Fig. 3b) changes in an ascending order PCL < PTAd < PPG < PTMG, contrary to the water absorption, again implying that hydrophobicity of PU governs the level of oil uptake. It is noted that absorption reaches equilibrium in approximately 2 h for oil and 4 to 5 h for water, mainly due to the hydrophobic nature of the segmented PUs, regardless of the soft segment type. The equilibrium oil absorption is approximately 100 times that of water absorption, indicating that these PUs preferentially absorb oil. It should also be mentioned that soft segment crystallinity is not important for both water and oil absorption, probably due to the low crystallinity degree of the polyols.

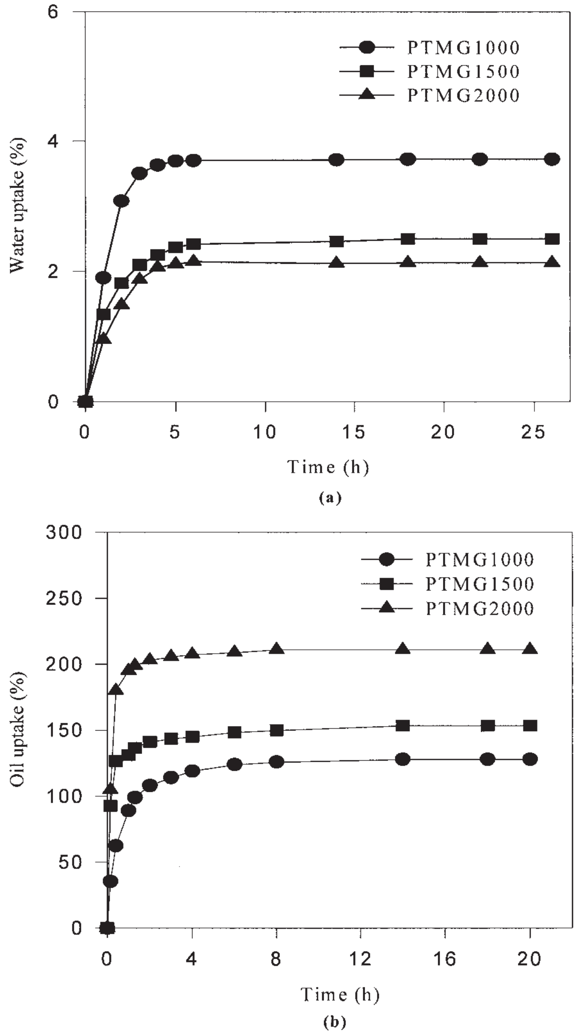

Figure 6 Water (a) and oil (b) uptake of PUs for various *Mn* of PTMG.

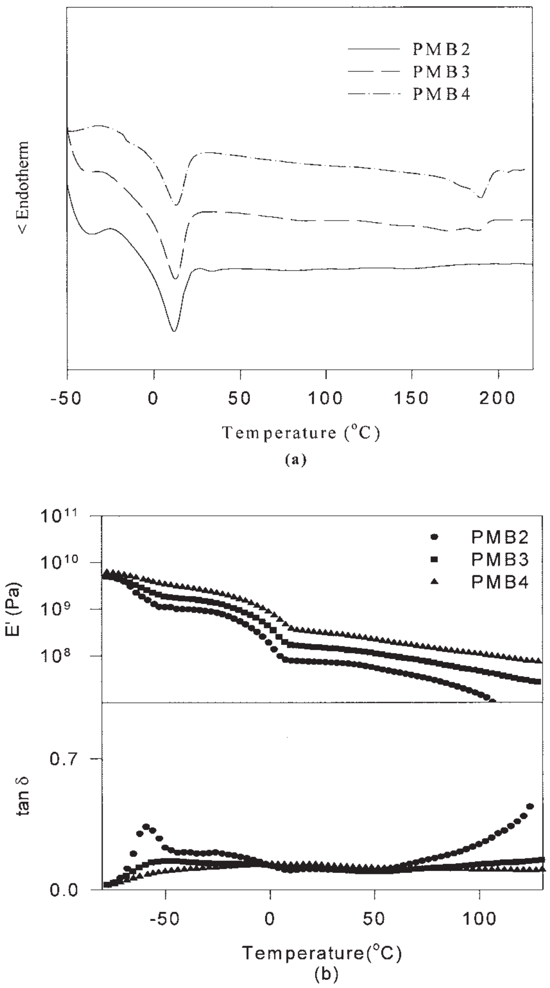

Figure 7 DSC thermograms (a) and dynamic mechanical (b) properties of PUs for various hard segment lengths.

Effect of polyol molecular weight

Since PTMG gave the largest oil absorption level among the four types of polyols, the effect of molecular weight of polyol was studied for the PTMG–MDI–BD series.

Regardless of molecular weight, XRD profiles simply show amorphous shoulders at around $2\theta = 18^{\circ}$ (Fig. 4a). On the other hand, DSC thermograms (Fig. 4b) show sharp melting peaks at 11 °C for PTMG2000 and 18 °C for PTMG1500 and a broad endotherm at 150 °C for PTMG1000. Soft segment and hard segment phase separation is increased with the soft segment length. Thus, for the higher molecular weight polyols, soft segments are well phase-separated and crystallized. With PTMG1000, microphase separation is less complete, and hence the soft segment crystallization process is hindered by the hard segments dissolved in the soft segment domain. However, due to the increased hard segment fraction, hard segment crystallization is favored, with PTMG1000 showing a broad shoulder at about 150 °C.

Owing to the greater phase separation with increasing M_n of polyol, PTMG2000 and PTMG1500, respectively, gave two transitions at about −60 (PTMG2000) and −55 °C (PTMG1500), and 20 °C (for both), whereas PTMG1000 showed a single transition at about −30 °C (Fig. 5a). The lower transition for PTMG2000 and PTMG1500 corresponds to the T_g of the phase separated soft segments and the high transition to the melting of soft segments. It is evident that melting transition is not observed for PTMG1000 PU by the storage modulus as well as by tanδ curves. A single T_g for PTMG1000 again confirms that soft segments and hard segments are mixed on a molecular scale.

Regarding the tensile properties (Fig. 5b), initial modulus increases, yielding becomes clearer, and the elongation at break decreases with decreasing M_n of polyol. This is primarily caused by the increased ri-

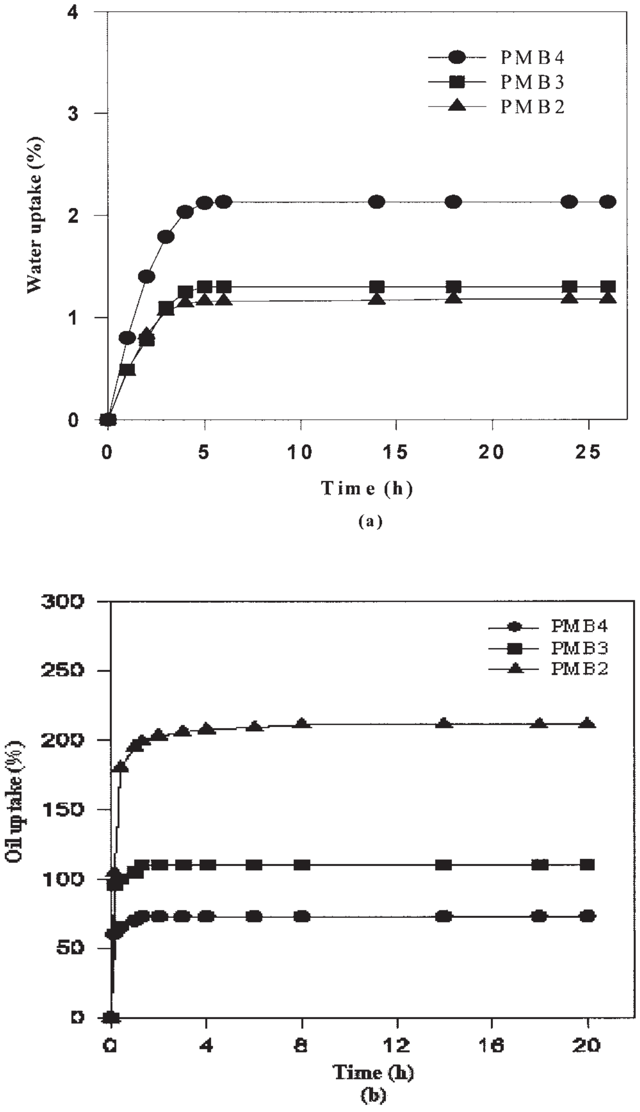

Figure 8 Water (a) and oil (b) uptake of PUs for various hard segment lengths.

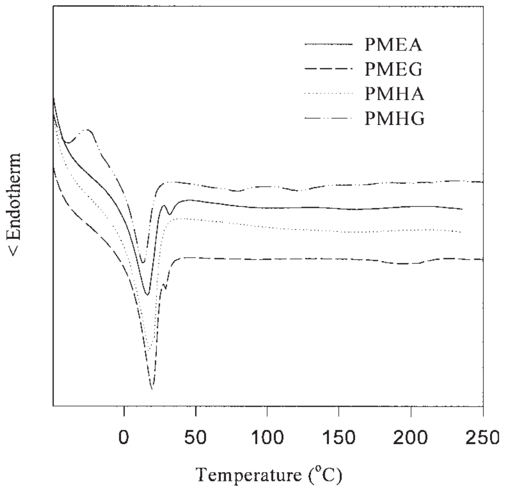

Figure 9 DSC thermograms of PUs for various types of chain extender.

gidity of the PUs due to the increased hard segment fraction, whereas the small crystallinity increase with M_n does not contribute significantly.

Water uptake (Fig. 6a) was small and insensitive to the M_n of polyol. However, the equilibrium water sorption increased with decreasing M_n of polyol due to the increased hydrophilic urethane group density. The small equilibrium water uptake (<4%) favors the use of these PUs for waterproof uses. On the other hand, the equilibrium oil absorption decreased from 200 to 140%, and the absorption rate decreased to half as the M_n of the PTMG decreased from 2000 to 1000 (Fig. 6b).

Effect of hard segment length

The effect of hard segment length was studied with the PTMG2000–MDI–BD series where the length of the hard block (MDI–BD) was varied from 1 to 3 repeat units. Regardless of the hard segment length, a Bragg peak for the hard segments was not observed.

DSC thermograms (Fig. 7a) showed soft segment melting at about 11 °C. As the length of hard segment increased, a melting peak of the hard segments appeared at about 190 °C, implying that at least two hard segment repeat units are necessary for hard segment crystallization.

By increasing the hard segment length, the rubbery modulus as well as the glassy modulus increases, and the soft segment T_g (below −50 °C) becomes weak and broad and shifts toward higher temperatures due to the decreased soft segment fraction and increased phase mixing (Fig. 7b). Water uptake increased up to 2% (Fig. 8a) and oil absorption decreased to about 1/3 (Fig. 8b) with increasing hard segment length.

Effect of chain extender type

Four types of chain extenders, viz., EG, HG, EA, and HA, have been incorporated, with PTMG1000 and MDI. XRD profiles of these PUs simply showing amorphous shoulders at about $2\theta = 18^\circ$ (not shown).

DSC thermograms showed endothermic peaks at 12 °C for HG, 19 °C for EG, and above 20 °C for EA and HA extended PUs (Fig. 9). The long aliphatic chains of HG augment hard segment miscibility with the aliphatic soft segments, and greater hard segment cohesion among urea groups augments soft segment and hard segment phase separation.

As expected, amine (EA, HA) extension gives an approximately one order of magnitude higher modulus plateau (G_N°) than glycol (EG, HG) extension due to the greater specific cohesion of urea groups in comparison with the urethane groups (Fig. 10a). The shorter extenders (EG, EA) result in higher rubbery moduli.

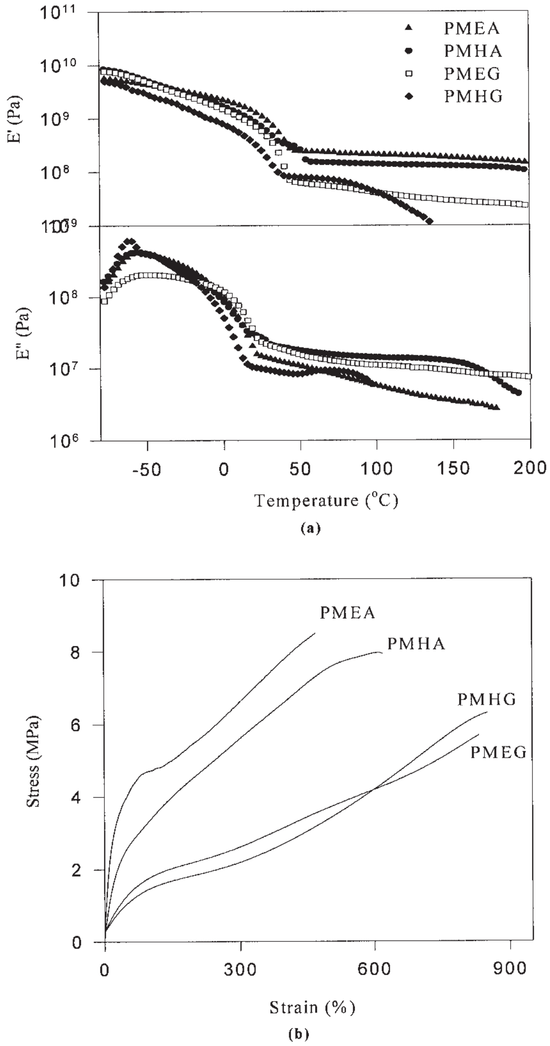

Figure 10 Dynamic mechanical (a) and tensile (b) properties of PUs for various types of chain extender.

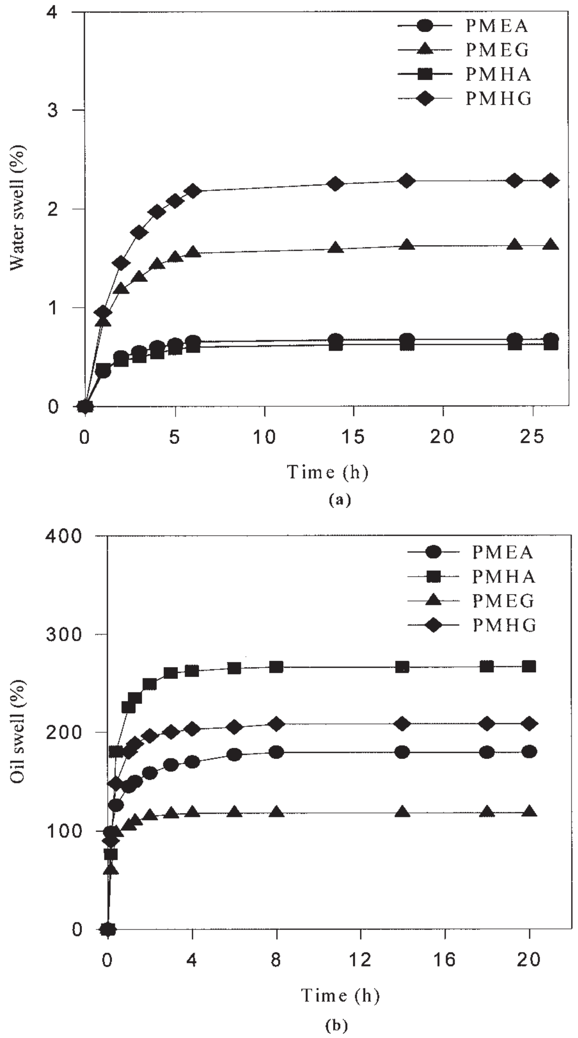

Figure 11 Water (a) and oil (b) uptake of PUs for various types of chain extender.

Regarding the tensile properties, the short extenders (EG, EA) give greater initial modulus and yield strength, whereas amine extension, compared with glycol extension, give greater initial modulus, yield strength, and tensile strength associated with a smaller elongation at break (Fig. 10b).

Equilibrium water uptake of amine extension is about half of the glycol extension, and the longer extender gives less water absorption due to greater hydrophobicity (Fig. 11a). Long-chain amine extension gives smaller water uptake and greater oil swell (Fig. 11b). For effective oil absorption, the long-chain diamine (HA) should be preferred as a chain extender.

CONCLUSIONS

Based on the structure–oil absorption experiments of segmented polyurethanes, the following can be concluded.

Oil absorption increased in the following ascending order PCL < PTAd $\ll$ PPG < PTMG PUs and with increasing molecular weight of polyol, contrary to water absorption. This implies that hydrophobicity governs oil absorption of the studied segmented polyurethanes.

Oil absorption decreased with increasing length of the hard segments, due to the increased number of hydrophilic urethane groups.

Diamine extension resulted in greater oil absorption levels for polyurethanes compared with glycol extension, implying that urea groups are favored over urethane groups for oil absorption. Oil absorption was further increased as the aliphatic chain of diamine became longer.

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