

# Hydrolytic Resistance of Model Poly(ether urethane ureas) and Poly(ester urethane ureas)

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Received 12 January 1998; accepted 22 February 1998

**ABSTRACT:** Poly(ester urethane ureas) (PesURUs) and poly(ether urethane ureas) (PetURUs) synthesized from diphenylmethane-4,4'-diisocyanate and poly(butylene adipate) diol, and poly(tetramethylene oxide) diol or poly(propylene oxide) diol, respectively, were hydrolyzed at 70°C for various periods up to 16 weeks. Differences in thermal and mechanical properties of as-received dry samples are correlated with the number and strength of hydrogen bonds formed between urea/urethane groups of hard segments and polyester or polyether groups of soft segments. Gel permeation chromatography measurements show that the molar mass of linear PesURUs markedly decreases with the hydrolysis time, whereas that of linear PetURUs remains almost unaffected. PesURU crosslinked by polymeric isocyanate has lower crystallinity, but shows somewhat better resistance to hydrolysis than its linear counterpart because of its more stable three-dimensional molecular structure. Water uptake at 37°C, dynamic mechanical thermal analysis, and differential scanning calorimetry thermograms determined for redried hydrolyzed specimens concurrently show that advancing hydrolysis accounts for decrease in the crystallinity (if any) of soft polyester segments, in the efficacy of hydrogen bonding and in crosslinking density. Experimental data indicate that hydrolytic resistance of PetURUs is primarily determined by (1) the hydrolytic stability of individual types of present groups, (2) steric hindrances affecting the access of water molecules to these groups, and (3) the hydrophilicity of backbones. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 577–586, 1998

**Key words:** poly(ether urethane ureas); poly(ester urethane ureas); hydrolysis; water uptake; dynamic mechanical properties

## INTRODUCTION

Segmented polyurethanes (PURs) consist of hard (rigid) urethane segments and soft (flexible) poly-

ester or polyether segments. Their variable structure and properties make PURs suitable for many kinds of applications. Depending on the type and length of soft segments, PURs can be in the rubbery or glassy state at room temperature. Various chemical and/or physical factors may modify PUR properties in the course of their service life (e.g., hydrolysis, solvolysis, thermal degradation, thermooxidation, photooxidation, etc.).<sup>1</sup> Exposure to water, water solutions, water dispersions, etc., can initiate (partial) hydrolysis of PURs, particularly at elevated temperatures.<sup>2–9</sup> In general, the

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Contract grant sponsor: Academy of Sciences of the Czech Republic; contract grant number: 12/96/K.

Contract grant sponsor: Brite Euram Project; contract grant number: 4045.

*Journal of Applied Polymer Science*, Vol. 70, 577–586 (1998)

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CCC 0021-8995/98/030577-10

hydrolytic stability of PURs attracts much attention because it is of primary importance for many applications.

Of the bonds present in poly(ester urethanes) (PesURs), the most susceptible to hydrolysis is the ester that reverts to the carboxylic acid and alcohol. Moreover, the produced acid catalyzes further ester hydrolysis, thus accounting for an autocatalytic effect.<sup>1,7</sup> Kinetics of the hydrolysis of PesURs was successfully treated as a pseudo-first-order reaction.<sup>7,10,11</sup> Although the percentage of hydrolyzed ester groups may be rather small, they are likely to account for a significant reduction of average molar mass and, consequently, deterioration of mechanical properties. To slow down the hydrolysis of polyester groups, polycarboimides can be added to PesURs that act as acid scavengers and suppress the autocatalytic effect.<sup>1</sup> As generally known, ether groups resist hydrolysis much better than ester groups, which make poly(ether urethanes) (PetURs) relatively much more stable in an aqueous environment.<sup>1,12-16</sup> The hydrolysis of urethane groups in hard segments is at least 1 order of magnitude slower than that of ester groups, so that it plays a secondary role in reducing the molar mass of PURs.<sup>1</sup> Another significant factor determining PURs hydrolytic stability is their hydrophilicity and permeability to water.<sup>13</sup> In general, the more hydrophilic the PUR, the larger the amount of sorbed water and the lower the hydrolytic resistance. As reported in former studies,<sup>11,17</sup> hydrolysis decreases the thermal stability of both PURs and PUR ureas, thus reducing their lifetimes.

On the other hand, special PURs are used in various medical applications as biodegradable materials.<sup>18,19</sup> Their water sorption and hydrolysis rate can be effectively controlled by selecting polyols used in the synthesis of soft segments. For instance, PesURs containing various polyester diols were found much more susceptible to the *in vitro* degradation than PetURs synthesized from polyether diols.<sup>19,20</sup> Thus, a high degradation rate was observed for PURs with poly(ethylene adipate)<sup>21</sup> or poly(diethylene glycol adipate)<sup>21</sup> or poly(alkylene tartrate).<sup>3</sup> Under moderately acidic conditions, PURs synthesized from aromatic diisocyanates are less stable than those containing aliphatic diisocyanates.<sup>9</sup>

To preserve the mechanical properties of PUR materials and to prolong their service life, a trend can be observed to synthesize materials with a good hydrolytic, as well as thermooxidative stability.<sup>22-24</sup> Hydrolysis of PesURs is primarily associated with the instability of ester bond, thus

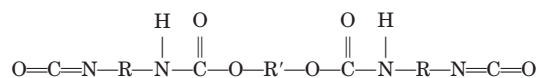
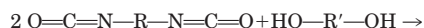
the hydrolysis resistance of PesURs is expected to be improved by reducing the accessibility of water to ester groups. A series of 14 model poly(ester urethane ureas) (PesURUs) was synthesized on a laboratory scale to implement a systematic analysis of the effects of various functional groups in polyester diols on the resulting hydrolytic stability.<sup>25</sup> Accelerated tests were conducted in water at 70°C up to 4 weeks, and the results showed which diol compositions determined the highest or, alternatively, the lowest resistance to hydrolysis of the various PesURUs.

In general, studies of hydrolytic resistance of PURs and its effects on mechanical properties<sup>10,11,22,24</sup> are of extraordinary importance from a practical point of view. The objective of this article is to analyze the effects of hydrolysis time on molar mass, crystallinity, and dynamic mechanical properties of newly synthesized PesURUs and poly(ether urethane ureas) (PetURUs).

## EXPERIMENTAL

### Materials

Composition of the studied poly(urethane ureas) (PURUs) and the used abbreviations are reported in Table I. Hard segments consist of diphenylmethane-4,4'-diisocyanate (MDI), while soft segments are of polyester or polyether type. Polyester segments of two PesURUs (PU-PBA and PU-PBAc) consist of poly(butylene adipate) diol, whereas those of PetURUs were synthesized from poly(tetramethylene oxide) diol (PU-PTMEG) and poly(propylene oxide) diol (PU-PPG and PU-PPGc). Molar mass of used polyols ranged from 1000 to 2000. PUR elastomers were synthesized via prepolymers. In the first stage, an oligomer was prepared (average molar mass between 1000 and 3000) by the reaction of one part of a diol with up to 3.6 parts of the diisocyanate, e.g.:



In the second stage, an aliphatic diamine was used as extender to complete the reaction and to obtain an elastomer of suitable molar mass. Crosslinked polymers were synthesized by using either polymeric MDI (for PU-PPGc) or trifunctional poly(propylene oxide) triol<sup>8,26,27</sup> (for PU-PBAc). Sheets of PURUs with a thickness in the

**Table I** Composition of the Linear and Crosslinked (c) PURs Under Investigation

Name	Isocyanate (average functionality)	Polyol [average molar mass] (average functionality)	NCO/OH/NH <sub>2</sub> Ratio	Urethane Groups (wt %) Urea Groups (wt %)
PU-PTMEG	MDI (2)	Poly(tetramethylene-oxide) diol [1000] (2)	2.55 /1/1.35	6.2 8.4
PU-PPG	MDI (2)	Poly(propylene oxide) diol [2000] (2)	3 /1/1.8	3.8 6.8
PU-PPGc	MDI (2)	Poly(propylene oxide) diol [2000] + poly(propylene oxide) triol [2200] (2.6)	2 /1/0.9	5.2 4.3
PU-PBA	MDI (2)	Poly(butylene adipate) diol [2000] (2)	3.6 /1/2.34	3.5 8.2
PU-PBAc	MDI + polymeric MDI (2.24)	Poly(butylene adipate) diol [2000](2)	3.6 /1/2.34	3.5 8.2

All of the prepolymers were extended with an aliphatic diamine.

range 0.7–1.2 mm were cast from the reaction mixture after addition of processing aids based on dioctyl phthalate (a solvent-free process); test specimens of required dimensions were cut for hydrolytic treatment and subsequent characterization. The materials, synthesized by Morton International S.p.A (Mozzate, Como, Italy) and processed by Chiorino S.p.A. (Biella, Italy), are mainly intended for usage in the conveyor belt production.

### Methods

Hydrolytic stability of all tested PURUs was investigated under identical conditions [i.e., test specimens were stored at 70°C for 4, 8, 12, and 16 weeks in a great surplus of distilled water (~ 20 L for all studied specimens of total weight of ~ 10 g; 0.5 g of PURU per L of water)]. In the course of hydrolysis, specimens were periodically taken out of the bath, water was wiped away from their surface, and they were weighed to evaluate the water uptake (expressed as an average value for three test pieces). As soon as a preselected hydrolysis period had elapsed, the specimens were removed from the bath and kept at room temperature for 1 week. Before any subsequent measurement, they were dried for ~ 3 days at 50°C in vacuum until a constant mass was achieved. Afterward, one specimen of each PURU (as-received or hydrolyzed) was immersed in distilled water at 37°C, periodically taken out, wiped, and the

water uptake was determined by the weight change.

The weight average molar mass,  $\bar{M}_w$ , of each studied PURU was determined as a function of the hydrolysis time by gel permeation chromatography (GPC). Measurements were performed with an apparatus consisting of an isocratic pump (Spectra Physics, P1500), a refraction index indicator (Shodex RI71), and a chromatography column (Shodex KD 80M). All linear samples were dissolved in *N,N*-dimethyl formamide (the concentration of polymers was ~ 0.4 wt %). Analyses were conducted at a flow rate of 1 ml min<sup>-1</sup>; calibration was performed with polystyrene standards having molar masses in the range from 5,000 to 400,000.

A differential scanning calorimeter Mettler DSC 30 was used to detect the glass transition temperature,  $T_g$ , of amorphous parts and the melting temperature,  $T_m$ , of crystalline domains (if any) of PURUs. The conditions of differential scanning calorimetry (DSC) measurements were as follows: specimen weight, ~ 20 mg; temperature interval, -100 to 100°C; heating rate, 10°C min<sup>-1</sup>; and nitrogen flux, 100 mL min<sup>-1</sup>.

Dynamic mechanical tests were conducted in the tensile mode by a dynamic mechanical thermal analyzer (DMTA, model MKII, by Polymer Laboratories) under the following conditions: sample size, 20 mm × 5 mm × (0.7–1.2) mm; temperature interval, -100 to 100°C; heating

**Table II**  $T_g$ , Heat of Fusion ( $\Delta H_m$ ), and Melting Temperature ( $T_m$ ) After Various Hydrolysis Periods Found in the First and Second DSC Scans

Hydrolysis Time (weeks)	PU-PTMEG		PU-PPG		PU-PPGc	
	$T_g$ I° Scan (°C)	$T_g$ II° Scan (°C)	$T_g$ I° Scan (°C)	$T_g$ II° Scan (°C)	$T_g$ I° Scan (°C)	$T_g$ II° Scan (°C)
0	ND	ND	-46	-47	-43	-43
8	ND	ND	-44	-44	-42	-42
12	ND	ND	-46	-46	-41	-41
16	ND	ND	-46	-46	-42	-41

Hydrolysis Time (weeks)	PU-PBA			PU-PBAc				
	$T_g$ I° Scan (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$T_m$ (°C)	$T_g$ II° Scan (°C)	$T_g$ I° Scan (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$T_m$ (°C)	$T_g$ II° Scan (°C)
0	-41	34	56	-44	-43	18	46	-45
8	-39	37	54	-49	-49	25	43	-45
12	-32	32	47	-43	-46	26	43	-46
16	-38	32	46	-37	-43	7	45	-41

ND, not detectable.

rate, 3°C min<sup>-1</sup>; displacement, 64  $\mu$ m; applied force, 0.1N; and frequency, 1 Hz.

## RESULTS AND DISCUSSION

### As-Received Materials

Properties of PURUs listed in Table I are affected by their structure [linear or crosslinked (c)] and the type of soft segments [i.e., polyether (PU-PTMEG, PU-PPG, and PU-PPGc) or polyester (PU-PBA and PU-PBAc)]. PURs derived from ether diols are amorphous, whereas polyester-based polymers are semicrystalline materials, as revealed by DSC results reported in Table II. As can be seen, all the PURUs show the  $T_g$  of the soft segments in the range from -46 to -41°C, in good agreement with the data reported by other authors.<sup>28</sup> Linear PU-PBA has crystallinity about twice as high as the crosslinked counterpart, as evidenced by the  $\Delta H_m$  values reported in Table II.

Table III reveals significant differences in both the storage and loss moduli of PURUs in the dry state. In particular, a marked difference exists between “soft” (PU-PPG and PU-PPGc) and “stiff” (PU-PTMEG, PU-PBA, and PU-PBAc) polymers with dynamic storage moduli of  $\sim$  6 MPa and 100–140 MPa, respectively. To explain this obser-

vation, we can refer to several studies<sup>28–34</sup> that have concluded that PURUs are extensively hydrogen-bonded: the donor is the N—H group of urethane or urea groups, whereas the acceptor is either the ester carbonyl or the ether oxygen of the soft segments. Lower steric hindrances in the tetramethylene-oxide units of PU-PTMEG with respect to those in the propylene-oxide units (PU-PPG and PU-PPGc) could lead to stronger hydrogen bonding. Moreover, urea groups have two N—H bonds so that higher density of hydrogen bonds can be expected to affect the properties of PURUs. Taking into account the total amount of the initial OH and NH groups, the weight percentage of urethane-urea groups (see Table I) is 14.6 wt % (PU-PTMEG), 11.7 wt % (PU-PBA and PU-PBAc), to 10.6 wt % (PU-PPG), and 9.5 wt % (PU-PPGc). Thus, the differences in stiffness of PURUs in the dry state (Table III) can be ascribed to (1) the hydrogen bond capability (acceptor and donor contributions) of hard segments and (2) the crystallinity of polyester segments (Table II).

### Hydrolysis of PURUs

According to GPC measurements, linear PetURUs (PU-PTMEG and PU-PPG) show an excellent hydrolytic stability, because their molar masses do not appreciably decrease even after 16

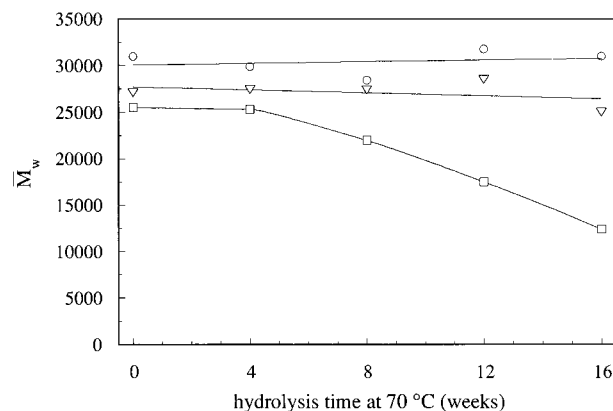
**Table III DMTA Data and Water Uptake at 37°C and Redried Specimens After Various Hydrolysis Times**

Hydrolysis Time (weeks)	$E'$ $T = 25^\circ\text{C}$ (MPa)	$E''$ Peak Temperature ( $^\circ\text{C}$ )	$E''$ Peak Value (MPa)	$\tan \delta$ Peak Temperature ( $^\circ\text{C}$ )	$\tan \delta$ Peak Value	Water Uptake After 4 Weeks (wt %)
PU-PTMEG						
0	138	-39	168	ND	<0.17	$4.5 \pm 0.1$
8	134	-44	108	ND	<0.17	$11.3 \pm 0.5$
12	104	-25	76	ND	<0.17	$11.6 \pm 0.1$
16	80	-27	70	ND	<0.17	$9.4 \pm 0.5$
PU-PPG						
0	6	-42	350	-27	0.56	$5.9 \pm 0.2$
8	6	-43	274	-28	0.54	$9.2 \pm 0.9$
12	6	-35	297	-21	0.53	$10.2 \pm 1.0$
16	6	-34	310	-21	0.54	$9.9 \pm 0.7$
PU-PPGc						
0	5	-43	359	-29	0.72	$1.0 \pm 0.1$
8	5	-41	275	-28	0.67	$2.1 \pm 0.2$
12	3	-30	200	-17	0.69	$2.2 \pm 0.4$
16	3	-32	214	-20	0.72	$2.4 \pm 0.1$
PU-PBA						
0	100	-46	135	-38	0.26	$0.4 \pm 0.2$
8	NM	NM	NM	NM	NM	$2.8 \pm 0.7^a$
PU-PBAc						
0	125	-42	139	-29	0.16	$4.8 \pm 0.9$
8	71	-46	190	-34	0.27	$4.3 \pm 0.2$
12	NM	NM	NM	NM	NM	$12.1 \pm 1.4^a$

ND, not detectable; NM, not measured.

<sup>a</sup> Water uptake after 1 week at 37°C.

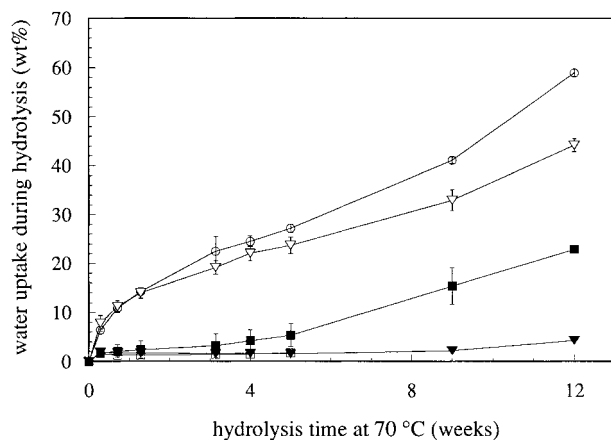
weeks of hydrolysis (Fig. 1); on the other hand, molar mass of a linear PesURU (PU-PBA) profoundly drops with the hydrolysis time. It is interesting to observe that—similar to a previous



**Figure 1** Weight average molar mass,  $\bar{M}_w$ , of soluble PURs determined by GPC for various hydrolysis times. (○) PU-PTMEG; (▽) PU-PPG; (□) PU-PBA.

study on three commercial PesURs (Estanes by Goodrich)<sup>10,11</sup>—an induction period of  $\sim 4$  weeks can be observed, during which the PesURUs do not show any noticeable drop in molar mass.

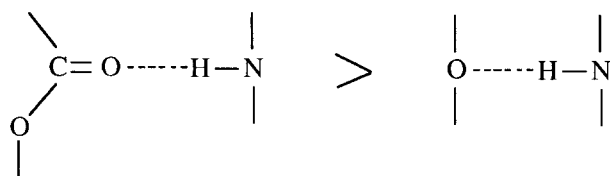
Water uptake during hydrolysis (Fig. 2) is helpful for the analysis of the hydrolytic resistance of PURUs. As expected, amorphous linear PetURUs show the highest water uptake (59.0 wt % and 44.2 wt % for PU-PTMEG and PU-PPG after 12 weeks, respectively) due to the highly hydrophilic character of the polyether soft segments. Lower sorption of PU-PPG, in comparison with PU-PTMEG, can be attributed to the steric hindrance represented by the side methyl group in the poly(propylene oxide) units.<sup>35</sup> On the other hand, amorphous crosslinked PU-PPGc absorbed a water amount much lower (2.3 wt % after 9 weeks) than the corresponding linear PetURUs, obviously due to the presence of a polymer network and the lower percentage of urethane-urea groups. In fact, as reported in Table I, PU-PTMEG or PU-PPG contain 6.2–8.4 wt % or 3.8–6.8



**Figure 2** Water uptake versus hydrolysis time in water at 70°C for (○) PU-PTMEG, (▽) PU-PPG, (▼) PU-PPGc, (□) PU-PBA, and (■) PU-PBAc.

wt % of urethane-urea groups, whereas PU-PPGc contains only 5.2–4.3 wt %. Although PU-PPGc has a higher content of poly(propylene oxide) units than PU-PPG (12.6 mmol g<sup>-1</sup> vs. 11.3 mmol g<sup>-1</sup>), the crosslinked structure brings about the water sorption of this polymer to be less than one-half that found for PU-PPG. In fact, as the diol (average molar mass: 2000) and the triol (average molar mass: 2200) represent 40 and 60%, respectively, of the polymer composition, the average length of linear segments in PU-PPGc is 914 with respect to 2000 in PU-PPG.

Figure 2 reveals that the water uptake of linear PU-PBA is practically negligible with respect to linear PetURUs (i.e., 1.5 wt % vs. 24.5 wt % or 22.1 wt % after 4 weeks); thus, we can presume that the structure of PU-PBA is still tightly packed at 70°C,<sup>31</sup> which is also evidenced by the relatively high storage modulus (50 MPa) of the as-received PU-PBA at this temperature (Table III). Moreover, hydrogen bonds possibly formed between NH and newly available ester groups of the molten soft segments could also contribute to the preservation of a long-range ordered structure and hence low water uptake. The stability of hydrogen bonds decreases in the order:



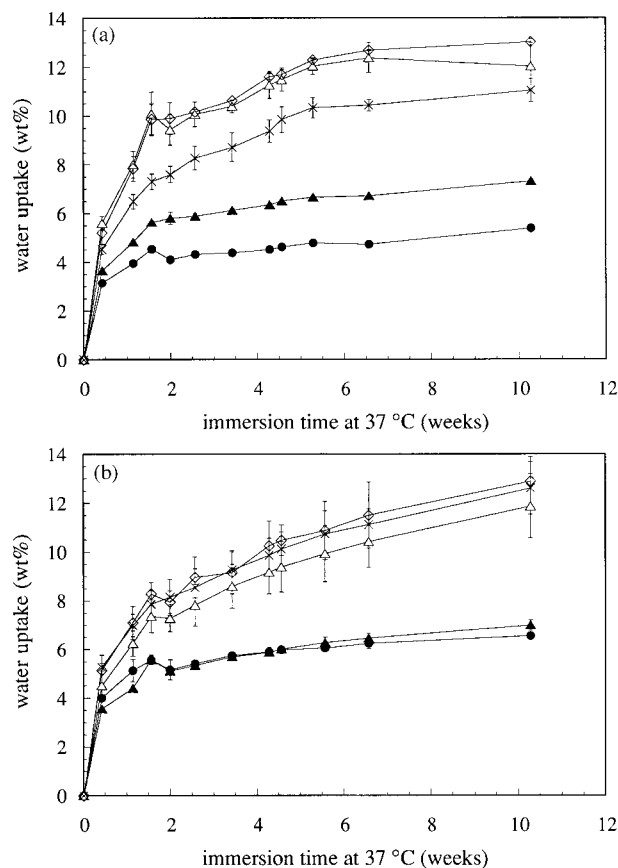
as evaluated with the Hoftyzer–Van Krevelen method,<sup>36</sup> for which the group contributions to hydrogen bonding energy are 7,000 J mol<sup>-1</sup> and

3,000 J mol<sup>-1</sup> for ester and ether groups, respectively. This effect and the lower hydrophilicity of ester certainly contribute to the lower water uptake of PU-PBA, in comparison with PU-PTMEG. After 5 weeks of hydrolysis, PU-PBA was partially fragmented, which prevented further measurements of water uptake. On the contrary, the crosslinking of PesURU resulted in a lower crystallinity and in a reduction of backbone mobility; hence, a lower percentage of intermolecular hydrogen bonds. The melting enthalpy or melting temperature was found two times or 10° lower than those of linear PU-PBA (Table II). Thus, regardless the relative high urethane-urea weight percentage equal to 11.7 wt % (the same as the corresponding linear PU-PBA), the less compact structure of PU-PBAc is likely to facilitate the water uptake that reached 15.4 wt % after 9 weeks. In the case of PU-PBAc, two of three test pieces hydrolyzed at 70°C became fragmented after the ninth week.

#### Water Uptake at 37°C

As-received and hydrolyzed specimens (previously dried to a constant mass) were swollen in water at 37°C to collect information on the changes in PURU structure produced by hydrolysis at 70°C. Linear PetURUs show a significant water uptake at 37°C, which holds for both as-received and hydrolyzed samples [Fig. 3(a,b) and Table III]. Specimens exposed to a long hydrolysis show almost two time higher uptake than as-received ones. The water sorption of PU-PTMEG hydrolyzed for 0, 4, and 8 or 12 weeks reaches after 4 weeks (at 37°C) 4.5 wt %, 6.4 wt %, and ~ 12 wt %, respectively [Fig. 3(a)]. Similar behaviour can be observed for PU-PPG: after 4 weeks at 37°C, the water sorption of the predried specimens amounts to 5.9 wt %, 9.2 wt %, and 10.3 wt % after 0, 8, and 12 weeks of hydrolysis, respectively [Figure 3(b)]. Small changes in the structure and molar mass of hard domains, which are probably beyond the sensitivity of the GPC measurements, are likely reasons for the dependence visualized in Figure 3(a,b). As expected, a relatively low water uptake after 4 weeks at 37°C is found for PU-PPGc (Table III). However, the ratio between the water uptake after 4 weeks at 37°C of samples hydrolyzed for 16 weeks and as-received material is about the same (2–2.5%) for all of the PetURUs. This fact indicates that the structural changes produced during the hydrolysis of linear and crosslinked PetURUs are similar.

As-received linear PU-PBA shows a low level of water uptake at 37°C (0.4 wt % after 4 weeks), in



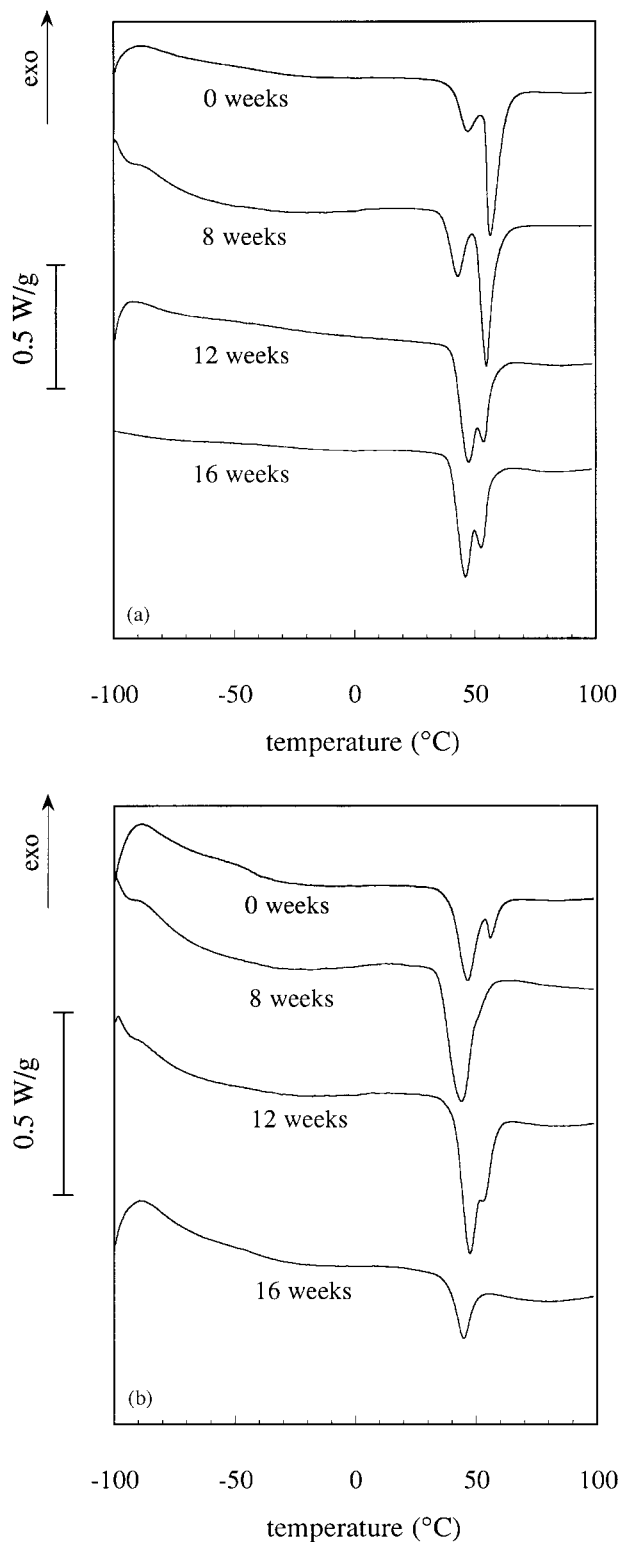
**Figure 3** Water uptake versus immersion time in water at 37°C for (a) PU-PTMEG and (b) PU-PPG. Hydrolysis time (weeks): (●) 0, (▲) 4, (△) 8, (◇) 12, and (×) 16.

comparison with PetURUs. Nevertheless, the samples hydrolyzed for 4 and 8 weeks display an increasing water uptake to 1.6 wt % and 2.8 wt %, respectively. This behavior can be explained by considering that, despite the slow increase in crystallinity (Table II), hydrolysis results in a higher number of hydrophilic groups originating from ester cleavage. On the other hand, the presence of crosslinks in PU-PBAc results in a lower crystallinity content (see Table II) and, consequently, a higher water uptake that reaches 4.8 wt % after 4 weeks at 37°C for the as-received specimen. In hydrolyzed materials, a double effect can be distinguished: (1) in the initial stages of hydrolysis, the increase in crystallinity prevails, which leads to a reduction in the water uptake achieved after 4 weeks at 37°C (2.7 wt % and 4.3 wt % for specimens hydrolyzed for 4 and 8 weeks respectively); and (2) in later stages, the proceeding cleavage of ester bonds enhances the hydrophilic character of the materials. For instance, redried specimens of PU-PBAc hydrolyzed for 8 and 12 weeks reach 3.2 wt % and 12.1 wt % of

water uptake, respectively, after only 1 week of immersion at 37°C. Analysis of materials hydrolyzed for longer periods could not be done because of their partial fragmentation and integrity loss.

### DSC and DMTA Measurements

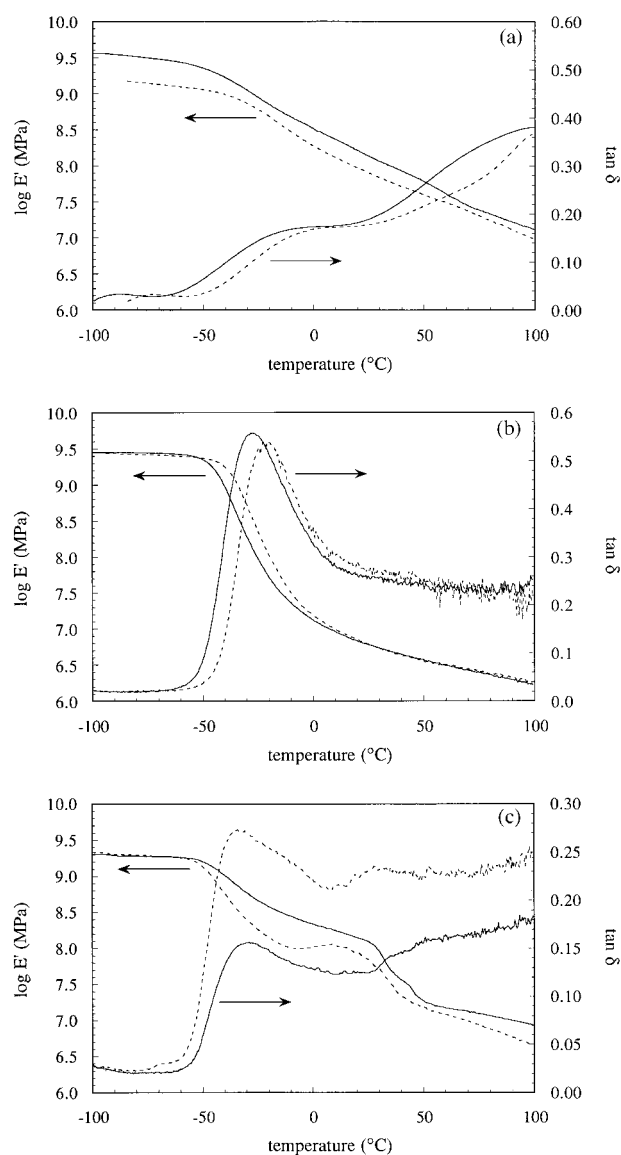
PetURUs show DSC thermograms (not reported) typical of amorphous polymers; however, DSC analysis reveals no significant difference in  $T_g$ s (Table II) of hydrolyzed samples. Slightly higher  $T_g$ s of PesURUs in comparison with those of PetURUs are attributable to the semicrystalline character of the hard segments, and the higher polarity<sup>37</sup> and lower flexibility of the soft segments.  $T_g$  of PU-PTMEG is not detectable in DSC thermograms, probably because the transition extends over a wide interval, as confirmed by the DMTA measurement reported in Figure 5(a), which shows that the loss factor ( $\tan \delta$ ) does not exhibit any clear peak. In contrast, as hydrolysis proceeds, PesURUs show differences in their DSC thermograms: the melting peaks of the polyester phase shift to lower temperatures and decrease in intensity [Fig. 4(a,b)]. In the case of linear PU-PBA, two melting peaks are observed at 46–47°C and 54–56°C, which are attributable to less and more stable compact crystalline structures, respectively. The intensity of the higher temperature peak decreases with hydrolysis time, whereas the intensity of the lower temperature peak increases. The total melting heat,  $\Delta H_m$ , initially increased from 34 to 37 J g<sup>-1</sup> after 8 weeks of hydrolysis and then decreased to ~ 32 J g<sup>-1</sup> after 16 weeks of hydrolysis. We can presume that hydrolysis initially promotes crystallization by increasing the chain mobility and afterwards—when the linear polyester segments fall below a critical length—reduces the crystallinity and the order in the crystalline structures that are then characterized by lower melting heat and temperature. In particular, the higher the terminal group content (due to the ester cleavage), the lower the ability to crystallize due to the increased concentration of defects. A small shift of the  $T_g$  of PU-PBA toward higher temperatures with advancing hydrolysis of PU-PBA is probably a combined effect of molar mass decrease and crystallinity increase. Although crosslinked PU-PBAc has a lower crystallinity than its linear counterpart, they show similar behavior: at first, the melting heat increases from 18 J g<sup>-1</sup> to ~ 25 J g<sup>-1</sup> after 8–12 weeks and then drops to 7 J g<sup>-1</sup> after 16 weeks of hydrolysis (Table II). Moreover, the melting peak at higher temperatures shows



**Figure 4** DSC thermograms of (a) PU-PBA and (b) PU-PBAc at various hydrolysis times.

lower intensity than that of the linear PU-PBA, probably due to the fact that the reduced mobility of the crosslinked chains impedes their crystallization.

All PetURUs preserved their integrity so that dynamic mechanical measurements were possible even after 16 weeks of hydrolysis (Table III). DMTA thermograms of as-received and hydrolyzed (16 weeks) PU-PTMG and PU-PPG are reported in Figure 5(a,b); crosslinked and linear PU-PPG exhibited similar DMTA thermograms. Although the storage modulus at 25°C shows a slight decrease with the period of hydrolysis, the loss factor peak corresponding to the glass transition moves toward higher temperatures ( $\sim 8$ – $10^\circ\text{C}$  after 16 weeks of hydrolysis). This result is not corroborated by the DSC measurements probably because DSC is a technique less sensitive



**Figure 5** DMTA thermograms of (a) PU-PTMEG, (b) PU-PPG, and (c) PU-PBAc. Hydrolysis time: (—) 0 week; (---) 16 weeks [8 weeks in (c)].



than DMTA to changes in molecular mobility. The effect of the hydrolysis period on  $T_g$  measured by DMTA may be explained by increasing interaction between the soft and hard segments, because it is believed<sup>38</sup> that the penetration of hard segments into the soft ones rises with the temperature and time of hydrolysis.

Linear [Fig. 5(c)] and crosslinked as-received PesPURUs showed similar thermograms. Nevertheless, PU-PBA was hydrolyzed so rapidly that, after 8 weeks of exposure in water at 70°C, the test pieces lost their mechanical integrity (DMTA measurements were no longer possible). A somewhat better hydrolytic stability of PU-PBAc made possible the DMTA measurements after 8 weeks of treatment. In this case, the molar mass reduction of the hydrolyzed samples leads to a decrease in the tensile storage modulus (from 125 to 71 MPa, at room temperature) and to an increase in the loss modulus peak (from 139 to 190 MPa). It is interesting to note that the presence of two distinct crystalline structures suggested by the DSC results [see Fig. 4(a)] is confirmed in Figure 5(c) by a double-step shape of the storage modulus as a function of the temperature in the melting region (temperature range: 25–50°C).

## CONCLUSIONS

Hydrolytic stability of PetURUs and PesURUs at 70°C (up to 16 weeks of exposure) can be related to their chemical composition, structure (linear or crosslinked), crystallinity, and hydrogen bonding capability. According to GPC measurements, linear PetURUs show excellent hydrolytic stability because their molar masses do not appreciably decrease even after 16 weeks of hydrolysis, whereas the molar mass of linear PesURU profoundly drops with hydrolysis time. Changes in structure due to the hydrolysis markedly increased the subsequent water uptake at 37°C measured with redried specimens. In particular, the observed differences in water uptake for hydrolyzed PetURUs are tentatively ascribed to modified capacity of hydrogen bonding, hydrolysis of ester groups, and reduction of crystallinity (if any). Also, the dynamic mechanical properties of both PetURUs and PesURUs adequately reflect structural changes produced during the hydrolysis process, with a progressive decrease of the storage modulus.

The authors thank Ms. C. Gavazza for her assistance with experimental measurements. Morton Interna-

tional S.p.A. (Mozzate, Italy) and Chiorino S.p.A. (Biella, Italy) are kindly acknowledged for providing materials.

## REFERENCES

1. V. Gajevski, in *33rd Annual Polyurethane Technical Marketing Conference*, 1990, p. 506.
2. A. Singh and L. Weissbein, *J. Polym. Sci. A-1*, **4**, 2551 (1966).
3. G. Magnus, R. A. Dunleavy, and F. E. Critchfield, *Rubber Chem. Technol.*, **39**, 1328 (1966).
4. Z. T. Ossefort and F. B. Testroet, *Rubber Chem. Technol.*, **39**, 1308 (1966).
5. C. S. Schollenberger and F. D. Steward, *Angew. Makromol. Chem.*, **29/30**, 413 (1973).
6. B. Masar, P. Cefelin, T. E. Lipatova, L. A. Bakalo, and G. G. Lugovskaya, *J. Polym. Sci., Polym. Symp.*, **66**, 259 (1979).
7. D. W. Brown, R. E. Lowry, and L. E. Smith, *Macromolecules*, **13**, 248 (1980).
8. G. Oertel, *Polyurethane Handbook*, Hanser Publishing, Munich, 1985.
9. T. M. Chapman, *J. Polym. Sci. A: Polym. Chem.*, **27**, 1993 (1989).
10. A. Pegoretti, J. Kolarik, and A. Penati, *Angew. Makromol. Chem.*, **220**, 49 (1994).
11. A. Pegoretti, A. Penati, and J. Kolarik, *J. Thermal Anal.*, **41**, 1441 (1994).
12. C. S. Schollenberger, in *Handbook of Elastomers*, A. K. Bhowmick and H. L. Stephens, Eds., Marcel Dekker, Inc., New York, 1988, Chap. 11.
13. J. W. Boretos, in *Biocompatibility of Clinical Implant Materials*, Vol. II, D. F. Williams, Ed., CRC Press, Boca Raton, FL, 1982, Chap. 6.
14. R. D. Deanin, in *High Performance Biomaterials*, M. Szycher, Ed., Technomic Publishing Co., Lancaster, PA, 1991.
15. C. Eisenbach, M. Baumgartner, and C. Günter, in *Advances in Elastomers and Rubber Elasticity*, J. Lal and J. E. Mark, Eds., Plenum Press, New York, 1986, p. 51.
16. E. Pechhold, G. Pruckmayr, and I. M. Robinson, *Rubber Chem. Technol.*, **53**, 1032 (1980).
17. L. Fambri, A. Pegoretti, J. Kolarik, C. Gavazza, and A. Penati, *J. Thermal Anal.*, **52**, 789 (1998).
18. H. C. Bamford and I. P. Middleton, *Plast. Rub. Process. Appl.*, **7**, 137 (1987).
19. M. D. Lelah and S. L. Cooper, Eds., *Polyurethanes in Medicine*, CRC Press, Boca Raton, FL, 1986, p. 205.
20. R. T. Darby and A. M. Kaplan, *Appl. Microbiol.*, **6**, 900 (1968).
21. W. Meckel, W. Goyert, and W. Wieder, in *Thermoplastic Elastomers*, N. R. Legge, G. Holden, and H. E. Schroeder, Eds., Hanser Publishing, Munich, 1987, Chap. 2.

22. T. M. Chapman, D. M. Rakiewicz-Nemeth, J. Swestock, and R. Benrashid, *J. Polym. Sci. A: Polym. Phys.*, **28**, 1473 (1990).
23. P. A. Gunatillake, G. F. Meijs, E. Rizzardo, R. C. Chatelier, S. J. McCarthy, A. Brandwood, and K. Schindhelm, *J. Appl. Polym. Sci.*, **46**, 319 (1992).
24. K. Tamareselvy, K. Venkatarao, and H. Kothandaraman, *J. Polym. Sci. A: Polym. Chem.*, **28**, 2679 (1990).
25. L. Fambri, A. Penati, and J. Kolarik, *Angew. Makromol. Chem.*, **228**, 201 (1995).
26. J. M. Buist and H. Gudgeon, *Advances in Polyurethanes Technology*, MacLaren & Sons, Ltd., London, 1968.
27. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology*, Interscience, New York, 1962.
28. P. C. S. Sung, C. B. Hu, and C. S. Wu, *Macromolecules*, **13**, 111 (1980).
29. T. Tanaka, T. Yokoyama, and Y. Yamaguchi, *J. Polym. Sci.*, **A1**, 2137 (1968).
30. R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
31. R. W. Seymour, A. E. Allegrezza, and S. L. Cooper, *Macromolecules*, **6**, 896 (1973).
32. H. Hishihara, I. Kimura, K. Saito, and H. Ono, *J. Macromol. Sci. Phys.*, **B10**, 591 (1974).
33. V. W. Srichatrapimuk and S. L. Cooper, *J. Macromol. Sci. Phys.*, **B15**, 267 (1978).
34. C. M. Brunette, S. L. Hsu, and W. J. MacKnight, *Macromolecules*, **15**, 71 (1982).
35. N. Shoenfeldt, *Surface Active Ethylene Oxide Adducts*, Pergamon Press, Oxford, 1969.
36. D. W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, The Netherlands, 3rd ed., 1990, p. 213.
37. R. W. Seymour, G. M. Estes, and S. L. Cooper, *Macromolecules*, **3**, 579 (1970).
38. G. L. Wilkes and J. A. Emerson, *J. Appl. Phys.*, **47**, 4261 (1976).