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# THERMAL STABILITIES OF DIFFERENT POLYURETHANES AFTER HYDROLYTIC TREATMENT

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## Abstract

Different polyester urethanes and polyether urethanes were exposed to hydrolytic degradation at 70°C for up to 16 weeks. The dried samples were subsequently analysed in thermooxidation tests in the range 250–300°C by measuring the lifetime relating to 5% mass loss. The experimental results showed that polyether urethanes have lower thermal stabilities than those of polyester urethanes; the activation energies determined from the Arrhenius plot are around 65 and 80 kJ $mol^{-1}$, respectively. The activation energies of polyether urethanes did not change significantly as hydrolysis proceeded. In contrast, the polyester urethanes exhibited a progressive decrease in activation energy, which fell (after 16 weeks of hydrolysis) to the values characterizing polyether urethanes. The entropic parameter of the Arrhenius equation was also evaluated and related to the chemical composition of the as-received and hydrolysed polymers.

**Keywords:** hydrolysis, polyurethanes, thermal stability

## Introduction

Segmented polyurethanes (PURs) are a broad class of polymers consisting of hard (rigid) urethane segments and soft (flexible) segments which are mostly of polyester or polyether type. Their variable structures and properties make PURs suitable for a wide variety of applications. The type and length of the soft segments, which are joined by hard segments, determine whether a PUR is in the rubbery or the glassy state at room temperature. In the course of their service life, PURs may undergo hydrolysis, solvolysis, thermal degradation, thermooxidation, photooxidation, etc. [1]. PURs are frequently exposed to water, aqueous solutions, water dispersions, etc., which may initiate their partial hydrolysis, particularly at elevated temperatures [2–9]. In general the hydrolytic stability of PURs attracts attention because materials characterized by either high or controlled hydrolytic stability are required for diverse purposes.

In previous papers [10, 11], we studied the hydrolytic resistance of commercial polyester urethanes, i.e. Estanes 54600, 54610 and 54650, which can be re-

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garded as certain 'standards' of thermoplastic PURs in consequence of their large-scale applications. The tests were carried out in a basin with a great surplus of water to ensure identical conditions for all the test specimens. Moreover, we used samples with two different values of thickness in order to ascertain the effect of the sheet thickness on the hydrolysis rate, and produced changes in mechanical [10] and thermal [11] properties. The reduction in molar mass was manifested by a significant decrease in ultimate mechanical properties, i.e. tensile strength, strain at break and tensile energy to break. Interestingly the relative tensile strength was found to correlate well with the relative viscometric molar mass. The differences in hydrolysis resistance of the Estanes were ascribed to differences in the compositions of the soft segments.

A trend can currently be observed to synthetize generally applicable PURs with good hydrolytic and thermooxidative stability [12, 13] in order to prolong their service life and to preserve their mechanical properties. As mentioned before, the propensity of polyester urethanes to undergo hydrolysis is primarily associated with the hydrolytic instability of ester groups. The hydrolysis resistance of polyester urethanes is expected to rise if the accessibility of their ester groups to water is reduced. To implement a systematic analysis of the effects of various functional groups in polyester diols on the resulting hydrolytic stability, we prepared [14] a series of 14 model poly(ester urethane ureas) on a laboratory scale. Their hydrolyses were carried out in water at 70°C, as our earlier studies [10, 11] showed that the tests are sufficiently accelerated at 70°C and that the differences in hydrolytic stability can be observed in a reasonable period of time, e.g. within 10–30 days. However, the hydrolysis mechanisms may not be identical at 70°C and at ambient temperature. This study [14] has shown which diol compositions can be considered for PURs to achieve the highest or, alternatively, the lowest resistance to hydrolysis.

Thermal degradation of PURs begins at around 150°C by the dissociation of urethane groups to isocyanate and polyol (i.e. polyester or polyether) [1]. At about 210°C, the urethane linkage can no longer be detected and thermodegradation presumably proceeds via several possible mechanisms [1, 16, 17]. In the case of thermooxidation, the weak link is the ether, which means that polyether urethanes which usually resist hydrolysis are prone to oxidation [1]. At present, various tendencies can be observed in the synthesis of PURs: on the one hand, PURs with improved hydrolytic and thermooxidative stabilities are desired [12, 13], while on the other hand PURs with enhanced thermodegradability are sought to facilitate the disposal of polymer wastes [17].

Simultaneous studies of the hydrolytic and thermal stabilities of PURs are rather rare [10–12, 18], though both characteristics are of extraordinary importance from a practical point of view. Moreover, few data are available on how the hydrolysis may affect the thermooxidative stabilities of PURs [11]. The objective of this communication is to analyse the effect of the hydrolysis time on the

resistance to thermooxidation of newly synthetized polyester urethanes and polyether urethanes. The samples synthetized by Morton International S.p.A. (Como, Italy) are mainly intended for usage in conveyor belt production.

## Experimental

### *Materials*

The compositions of the studied PURs, synthetized by Morton International S.p.A. (Mozzate, Como, Italy) and processed by Chiorino S.p.A. (Biella, Italy), are reported in Table 1. The hard segments consist of diphenylmethane-4,4'-diisocyanate (MDI), while the soft segments are of either polyester or polyether type. Polyester segments of two polyester urethanes (PU-PBA and PU-PBAc) consist of poly(butylene adipate) diol, while those of polyether urethanes are synthetized from poly(tetramethylene oxide) diol (PU-PTMEG) and poly(propylene oxide) diol (PU-PPG and PU-PPGc). The molar masses of the polyols used ranged from 1000 to 2000. Polyurethane elastomers were synthetized via prepolymers. Crosslinked polymers were obtained by using either polymeric MDI (for PU-PPGc) or trifunctional poly(propylene oxide) triol [8, 19, 20] (for PU-PBAc). PU sheets (thickness range 0.7 to 1.2 mm) were cast from the reaction mixture (after the addition of processing aids based on DOP) prepared by a solvent-free technology. Test specimens were cut to the required sizes for hydrolytic treatment and subsequent characterization.

**Table 1** Composition of the linear and crosslinked (c) PURs under investigation. All the prepolymers were extended with an aliphatic diamine

| Name | Isocyanate | | Polyol | |
|---|---|---|---|---|
| | (average functionality) | % by wt | (average functionality) | % by wt |
| PU-PTMG | diphenylmethane-4,4'diisocyanate (MDI) | | poly(tetramethylene-oxide) diol | |
| | (2) | 34.1 | (2) | 53.5 |
| PU-PPG | diphenylmethane-4,4'diisocyanate (MDI) | | poly(propylene-oxide) diol | |
| | (2) | 24.5 | (2) | 65.4 |
| PU-PPGc | diphenylmethane-4,4'diisocyanate (MDI) | | poly(propylene-oxide) diol + poly(propylene-oxide) triol | |
| | (2) | 20.4 | (2.6) | 73.3 |
| PU-PBA | diphenylmethane-4,4'diisocyanate (MDI) | | poly(butylene-adipate) diol | |
| | (2) | 27.3 | (2) | 60.6 |
| PU-PBAc | diphenylmethane-4,4'diisocyanate (MDI) + polymeric MDI | | poly(butylene-adipate) diol | |
| | (2.24) | 27.9 | (2) | 60.0 |

### *Methods*

As the hydrolysis stabilities of all tested PURs should be investigated under identical conditions, test specimens were stored at 70°C for 4, 8, 12 or 16 weeks in a great surplus of distilled water (about 20 l for specimens with a total mass of about 10 g, i.e. 0.5 g of PUR per liter of water). After a period of hydrolysis, the specimens were removed from the water bath and kept at room temperature for 1 week. Before measurements, they were dried in vacuum for 3 days at 50°C until constant mass was achieved.

A Mettler TG50 thermogravimeter was used to evaluate the effect of the hydrolysis time on the thermooxidation of the PURs. The lifetimes up to 5% mass loss were determined in air (flux: 200 ml $min^{-1}$) at several temperatures in the interval 250–300°C.

## Results and discussion

The molar masses of soluble PURs were determined by GPC and will be reported elsewhere [21]. Both linear polyether urethanes exhibited excellent hydrolytic stability because their molar masses were not appreciably decreased even after 16 weeks of immersion in water. As expected, the molar mass of the linear polyester urethane (PU-PBA) dropped considerably with the hydrolysis time. The effect of hydrolytic treatment on thermal stability was studied on dried samples by using a procedure previously defined [11]. It is evident that the polyester urethanes have initial lifetimes (150–190 min) about 2–3 times longer than those of the polyether urethanes (40–90 min), because the ether bond is particularly prone to oxidation [11]. Specifically, polytetramethylene oxide chains were found to be more stable than polypropylene oxide chains.

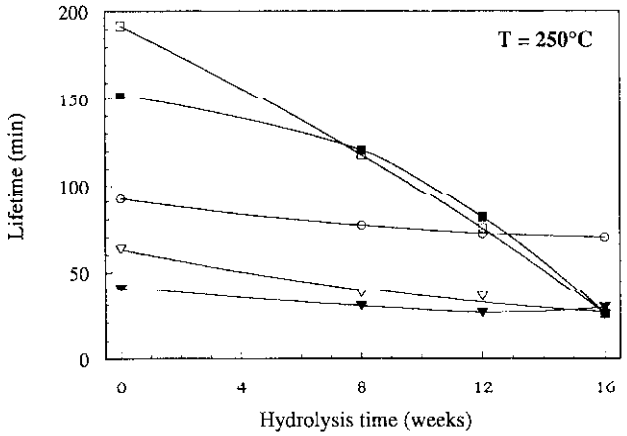


**Fig. 1** Effect of hydrolysis time on thermooxidative lifetime (5% mass loss) at a temperature of 250°C for ○ – PU-PTMEG, ▽ – PU-PPG, ▼ – PU-PPGc, ⊔– PU-PBA, ■ – PU-PBAc

The lower thermal stability of the crosslinked polyether urethane (PU-PPGc) has to be related to the higher percentage of polyol with respect to the corresponding linear PU-PPG, i.e. 73.3% *vs.* 65.4% (Table 1). Figure 1 depicts the effect of the hydrolysis time on the thermooxidative lifetime at 250°C. As the hydrolysis proceeds, the lifetimes of the polyester urethanes at 250°C underwent a strong decrease, reaching a value of about 35 min after 16 weeks of hydrolysis, in consequence of the progressive formation of carboxylic group, which have a lower thermal stability than that of ester groups. On the other hand, the lifetimes of the polyether urethanes remained almost constant over the whole interval of hydrolysis after 16 weeks of immersion in water, PU-PTMG exhibited the highest lifetime at 250°C, about 80 min. At higher temperatures, the degradation kinetics is accelerated and the differences between the various materials become smaller (Fig. 2).

The thermogravimetric data of all the studied PURs in the range 250–300°C fit quite well the Arrhenius plot which is usually [11, 15, 22] used to describe the effect of temperature on the lifetimes of samples exposed to thermal degradation. In the reported figures, the thermal data on polymers hydrolysed for 4 weeks have been excluded, as they were very close to those on the initial materials. Figure 2a shows that very slight differences can be observed between the original PU-PTMG and the hydrolysed ones after 16 weeks, with some exception. The best-fit lines are very close to each other and have almost the same slope. The other polyether urethanes, PU-PPG and PU-PPGc, exhibited a more evident effect of hydrolysis on thermal stability over the whole temperature range, which is observed as a decrease in lifetime with increasing immersion time in water (Fig. 2b and 2c). As expected, the polyester urethanes showed more differentiated behaviour as far as the effects of both hydrolysis time and thermooxidation temperature on the observed lifetimes are concerned (Figs 2d and 2e).

Finally, by comparing Figs 2, we can see that the lifetimes of polyether urethanes decrease by about one order of magnitude if the temperature rises from 250 to 300°C, whereas those of polyester urethanes drop by about two orders of magnitude. Assuming that the degradation kinetics obeys an Arrhenius-type equation, we can define

$$\log \text{ lifetime} = A + \frac{E_{act}}{RT} \tag{1}$$

where $A$ is a constant encompassing steric and entropic effects, $E_{act}$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature.

The $E_{act}$ values and their standard deviations were calculated from the slope of the best-fitting linear regression. Figure 3 clearly indicates the higher stability of the polyester urethanes (activation energy about 80 kJ mol$^{-1}$) with respect to the polyether urethanes (activation energy below 70 kJ mol$^{-1}$). It should be noted that $E_{act}$ for polyester urethanes is much higher than that for polyether urethanes,

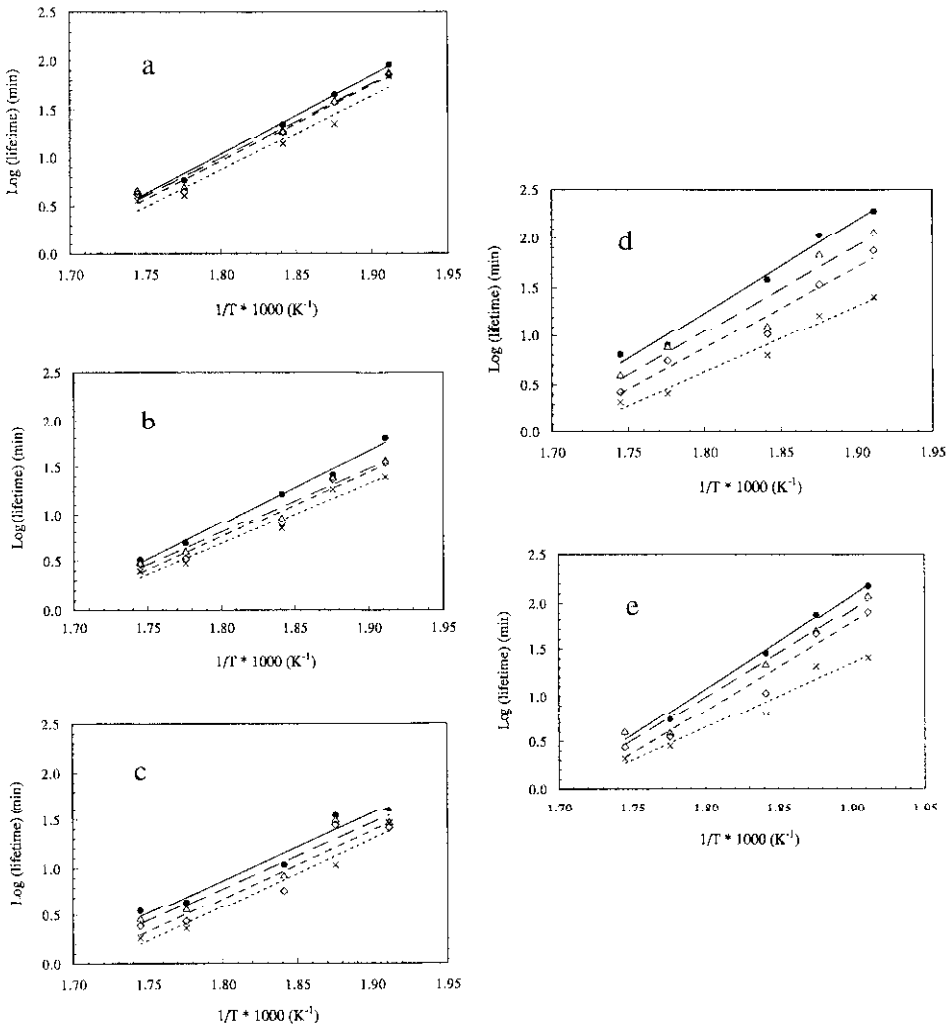


**Fig. 2** Arrhenius plots of the lifetimes *vs.* the reciprocal absolute temperature at different hydrolysis times: • 0, Δ 8, ◊ 12 and x 16 weeks for a) PU PTMG, b) PU PPG, c) PU-PPGc, d) PU-PBA, e) PU-PBAc

and shows a tendency to decrease to the level of that for polyether urethanes as the hydrolysis proceeds. This latter result could be related to the catalytic effects of the increased number of hydroxyl and carboxyl groups produced during the hydrolysis, which are active in the thermooxidation process. The formation of a network has a beneficial effect on the resistance to thermal oxidation, as documented by crosslinked polyester PU-PBAc, which also shows the highest activa-

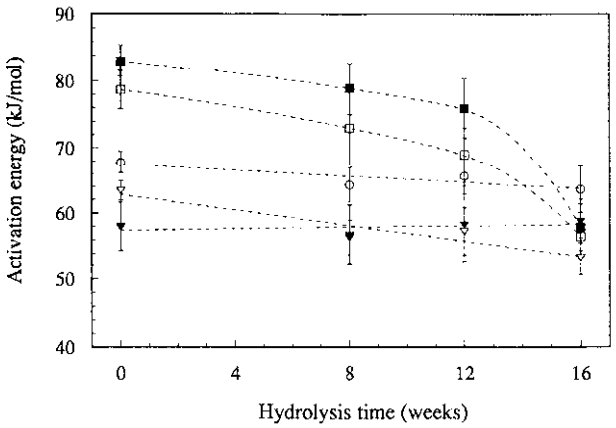


**Fig. 3** Effect of the hydrolysis time on the activation energy of thermooxidation for o – PU-PTMEG, ▽ – PU-PPG, ▼– PU-PPGc, □– PU-PBA and ■– PU-BAc

tion enthalpies after hydrolysis (up to 12 weeks). On the other hand, a sharp reduction in $E_{act}$ to about 60 kJ mol$^{-1}$ was found for both polyester urethanes after 16 weeks of hydrolysis. However, the Estane polyester urethanes previously tested as reference materials [11] displayed a slight increase in $E_{act}$ (about 3–9%) after 8 weeks of hydrolysis (their initial values affected by the composition were in the range 60–76 kJ mol$^{-1}$), whereas PU-PBA and PU-PBAc after the same hydrolysis time exhibited a reduction in $E_{act}$ in the range 6–7%. Polyether urethanes display higher hydrolytic stability but lower thermal stability (lower activation energy), which is virtually uneffected by the hydrolysis time.

**Table 2** Effect of hydrolysis time on the $A$ parameter of the Arrhenius equation

| Name | Time of hydrolysis/week | | | |
|---|---|---|---|---|
| | 0 | 8 | 12 | 16 |
| PU-PTMG | −13.6±0.7 | −12.9±1.2 | −13.2±1.2 | −12.9±1.2 |
| PU-PPG | −12.8±0.7 | −11.4±1.2 | −11.7±1.6 | −10.9±1.3 |
| PU-PPGc | −11.7±1.6 | −11.5±2.0 | −12.0±2.6 | −12.1±1.4 |
| PU-PBA | −13.8±1.3 | −14.8±2.5 | −14.1±1.7 | −11.6±1.2 |
| PU-PBAc | −16.9±1.0 | −15.9±1.7 | −15.8±2.0 | −11.9±1.5 |

The parameter $A$ of the Arrhenius equation, which formally represents the log (lifetime) at infinite temperature, provides interesting information on the tendency of various materials to undergo thermooxidation reactions. Table 2, summarizing the variation in $A$ after different hydrolysis times makes it evident that the polyether urethanes have $A$ values that are much higher than those for the

polyester urethanes (2–4 units on a log scale) and are almost independent of the hydrolysis time (the variation in $A$ is in the range of the standard deviation). On the other hand, both polyester urethanes display a progressive increase in the parameter $A$ (and hence a tendency for the intrinsic reactivity to decrease) after hydrolytic treatment. For PU-PBA and PU-PBAc, the effect of the increase in $A$ is compensated by the decrease in activation energy. An opposite trend was previously found for the Estane polymers [11], for which the parameter $A$ was decreased more than 10 times after 8 weeks of hydrolysis. In the case of the polyester urethanes presented in this study, the hydrolysis makes the thermal degradation faster. The kinetics is dominated by the activation energy decrease, though the parameter $A$ relating to the intrinsic reactivity to extents depending on steric and entropic factors.

## Conclusions

This paper shows how hydrolytic treatment at 70°C affects the thermal stabilities of different PURs as a function of their chemical compositions. The polyether urethanes under study do not show any appreciable decrease in molar mass within the period of 16 weeks of hydrolysis. On the other hand, the observed reduction in molar mass of polyester urethanes (induced by the hydrolysis) accounts for the decrease in the thermal stability evaluated as the thermooxidation lifetimes up to 5% mass loss at elevated temperatures. The temperature dependences of the lifetimes follow the Arrhenius plot for all species studied; the activation energies of polyether urethanes is lower (because of lower thermal stability) than those of polyester urethanes, but do not decrease with the duration of hydrolytic treatment, evidencing their hydrolytic stability. At the same time, the parameter $A$ of the polyester urethanes was found to increase as the hydrolysis proceeds, making the steric and entropic factors less favourable for thermal degradation.

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