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## **Hydrolytic stability and mechanical properties of poly(ester urethanes)**

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### **SUMMARY:**

The effect of hydrolysis time at 70 °C on molar mass and mechanical properties of commercial poly(ester urethanes), i. e., Estanes 54600, 54610, and 54650, was analyzed. Kinetics of hydrolysis is plausibly described in terms of a first-order reaction with an average induction period of about 7 days. The resulting reduction of molar mass brought about a significant decrease in ultimate properties, particularly in stress at break and tensile energy to break, while elastic properties were affected much less. A quantitative correlation between relative changes in tensile strength and molar mass was attempted. Hydrolysis resistance of Estanes decreasing in the succession 54650 > 54600 > 54610 was related to their chemical composition.

### **ZUSAMMENFASSUNG:**

Der Einfluß der Hydrolysedauer bei 70 °C auf die Molmasse und die mechanischen Eigenschaften handelsüblicher Polyesterurethane (Estane 54600, 54610 und 54650) wurde untersucht. Die Kinetik der Hydrolyse läßt sich als Reaktion erster Ordnung mit einer mittleren Induktionsperiode von etwa 7 Tagen beschreiben. Die resultierende Molmassenabnahme verursacht eine signifikante Verschlechterung der Eigenschaften, insbesondere der Bruchdehnung und der Zugarbeit bis zum Bruch, während die elastischen Eigenschaften weit weniger beeinträchtigt wurden. Eine quantitative Beziehung zwischen der relativen Änderung der Zugfestigkeit und der Molmasse wird vorgeschlagen. Die in der Reihenfolge 54650 > 54600 > 54610 abnehmende Hydrolysebeständigkeit der Estane läßt sich mit Unterschieden in deren chemischer Zusammensetzung erklären.

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*Introduction*

Variability of the structure and properties of segmented polyurethanes (PURs) has predestined this broad class of polymers for a wide variety of applications. In the course of their service life, PURs may undergo hydrolysis, solvolysis, thermal degradation, thermooxidation, photooxidation, etc.<sup>1</sup>. Many PURs are exposed to water, aqueous solutions, aqueous dispersions, etc., which cause their partial hydrolysis, particularly at elevated temperatures<sup>1-9</sup>. Of the various bonds present in PURs, the most susceptible to hydrolysis is the ester bond which reverts to the carboxylic acid and alcohol. The produced acid catalyses the ester hydrolysis, which becomes an autocatalytic reaction<sup>1,7</sup>. To slow down the hydrolysis of polyester segments, polycarboimides are added to PURs which act as acid scavengers and suppress the autocatalytic effect<sup>1</sup>. Hydrolysis of the urethane group is by one order of magnitude slower<sup>1</sup>, so that its effect on molar mass decrease in poly(ester urethanes) is practically negligible. Kinetics of hydrolytic ageing of poly(ester urethane) elastomers in water was successfully treated as a pseudo-first-order reaction<sup>7</sup>. Though the percentage of hydrolysed ester groups is small, it accounts for a significant reduction of average molar mass and, consequently, for changes in all physical properties, which primarily hold for mechanical properties.

Elastic properties of a material represent average properties of the bulk, so that hardly any changes in these properties can be observed as long as the physical and/or chemical structure of a major part of the material has not been changed, e.g., due to crystallization, crosslinking, thermal degradation, etc. On the other hand, fracture processes are initiated by defects present in the structure, which primarily develop on the specimen surface. Hydrolysis, aging, thermooxidation, static and dynamic fatigue, etc., produce localized damage of structure, e.g., in places of irregularities occurring on molecular level<sup>10,11</sup>. The influence of such local defects on elastic properties is beyond the accuracy of standard methods, but they will markedly decrease ultimate properties. Thus, ultimate mechanical properties of polymer rank among the properties which are most sensitive to structure changes.

While the ester is the weak link in water hydrolysis, thermal degradation of PURs begins at about 160 °C by dissociation of urethane groups to the isocyanate and polyol and at higher temperatures it proceeds via several possible mechanisms<sup>1,12,13</sup>. In the case of thermooxidation, the weak link is the ether, as polyether segments are particularly prone to oxidation<sup>1</sup>. Thus a natural trend is to synthesize polyurethanes with hydrolytic as well as thermooxidative

stability<sup>14-16</sup> in order to preserve their mechanical properties during their service life. On the other hand, easily thermodegradable polyurethanes, e.g. those having azo groups in the main chains, are believed to facilitate the disposal of polymer wastes<sup>17</sup>.

Hydrolytic stability of similar poly(ester urethanes) was tested<sup>5</sup> earlier in water at 70 °C up to 8 weeks, but test specimens were kept in test tubes in a relatively small amount of water. As the acid products of PUR hydrolysis accelerate the hydrolysis, the conditions were not unique for all samples. Therefore, we have carried out the hydrolysis of all specimens simultaneously in a great surplus of water. The objective of this communication was to analyse the effect of the hydrolysis time on molar mass and mechanical properties of Estanes 54600, 54610, and 54650, which can be viewed as certain "standards" of thermoplastic polyester PURs due to their large-scale applications. The samples were used in two different values of thickness in order to ascertain the effect of sheet thickness on the hydrolysis rate and produced changes in mechanical properties. This paper is a part of our work<sup>18</sup> encompassing also the effect of hydrolysis time on thermal and thermooxidative stability of Estanes.

## *Experimental*

### *Materials*

The studied poly(ester urethanes) are produced by Goodrich and commercially available under the tradenames Estane 54600, 54610, and 54650. The <sup>1</sup>H- and <sup>13</sup>C-NMR analysis<sup>19</sup> has shown that the fraction of hard segments consisting of diphenylmethane-4,4'-diisocyanate (MDI) diminishes with the product number; at the same time, the molar mass of soft segments rises. The soft segments of Estanes 54600 and 54610 consist of adipic acid and 1,4-butanediol, while those of Estane 54650 contain adipic acid and 1,6-hexanediol. The chain extender is identical in all species, i.e. 1,4-butanediol.

### *Test specimens*

Specimens of a dumbbell shape were cut from the sheets 0.3 and 1.5 mm thick of Estanes processed by Chiorino, Biella, Italy. The gauge length and width were 45 and 6 mm, respectively. The total length of test specimens was 115 mm, the width of the gripped parts was 25 mm. These dimensions of test specimens were selected intentionally to prevent the specimen slippage in grips during tensile testing.

### *Hydrolysis*

As the hydrolysis stability of Estanes was to be compared under identical conditions, test specimens were stored at 70 °C for 1, 2, 4, and 8 weeks in a great surplus of distilled water (about 30 L for specimens of total weight of about 290 g, i. e., 10 g of PUR per 1 L of water). After the exposure, the specimens were dried for three days at about 50 °C and then kept for more than one week under room conditions in order to equalize the content of sorbed water in all specimens (including as-prepared samples). The specimens were then weighed to assess the extract due to the hydrolysis.

Despite a great water surplus, the products of PUR hydrolysis were decreasing the pH value of the bath with the rising time of hydrolysis. The observed time dependence of pH was as follows (the time of hydrolysis in weeks is given as the first number): 1/6.40; 2/6.03; 3/5.77; 4/5.60; 5/5.50; 6/5.32; 7/5.17; 8/5.04. It is to be noted that though the series of hydrolysed specimens were taken out after 1, 2, and 4 weeks, the decrease in pH proceeded, obviously due to accelerated hydrolysis of the remaining specimens.

### *Intrinsic viscosity*

Intrinsic viscosity  $[\eta]$  of PURs was determined at 25.0 °C by using an Ubbelohde viscometer (type I). Solutions of various concentrations of PUR in N,N-dimethyl formamide were prepared by diluting the initial solution containing about 160 mg of a PUR in 25 ml of solvent.

### *Mechanical properties*

Testing of tensile properties was carried out with the aid of an Instron Tester 4502. Cross-head speed was 450 mm/min, which corresponds to a strain rate equal to 1000 %/min (the standard test method ASTM D882-88 for tensile properties of thin plastic sheetings recommends a strain rate of 1000 %/min for materials marked with a strain at break exceeding 100%). For each sample and a given time of hydrolysis, 6 test specimens were measured.

### *Results and discussion*

Relative changes in molar mass  $M_v$  can be calculated by using the Mark-Houwink equation in the following form:

$$M_{vh}/M_{v0} = ([\eta]_h/[\eta]_0)^{1/a} \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity, indices  $h$  and  $0$  denote the values after the hydrolysis time  $t_h$  and the initial values for  $t_h = 0$ , respectively; exponent  $a = 0.64$  has been reported<sup>20</sup> for poly(ester urethanes) dissolved in  $N,N'$ -dimethyl formamide. The hydrolysis of ester linkages has been plausibly described<sup>7</sup> in terms of a first-order reaction. Each cleavage of the backbones leads to the generation of a new molecule. Thus,

$$dn/dt = d_p [d(1/M)/dt] = k t_h \quad (2)$$

where  $n$  is the number of moles of macromolecules in a volume unit,  $d_p$  is the polymer density, and  $k$  is the first-order rate constant. Integration of Eq. (2) and its combination with Eq. (1) give

$$\ln(M_{vh}/M_{v0}) = \ln([\eta]_h/[\eta]_0)^{1/a} = -k (t_h - t_i) \quad (3)$$

where  $t_i$  is the induction period of hydrolysis. The data for all Estanes obey this dependence quite well (Fig. 1); the induction period ranges between 5 and 9 days. The difference in sample thickness does not seem to have any pronounced effect on the hydrolysis rate. Since the dependences are close to one another, it is obvious that the hydrolysis of the specimens proceeds in an

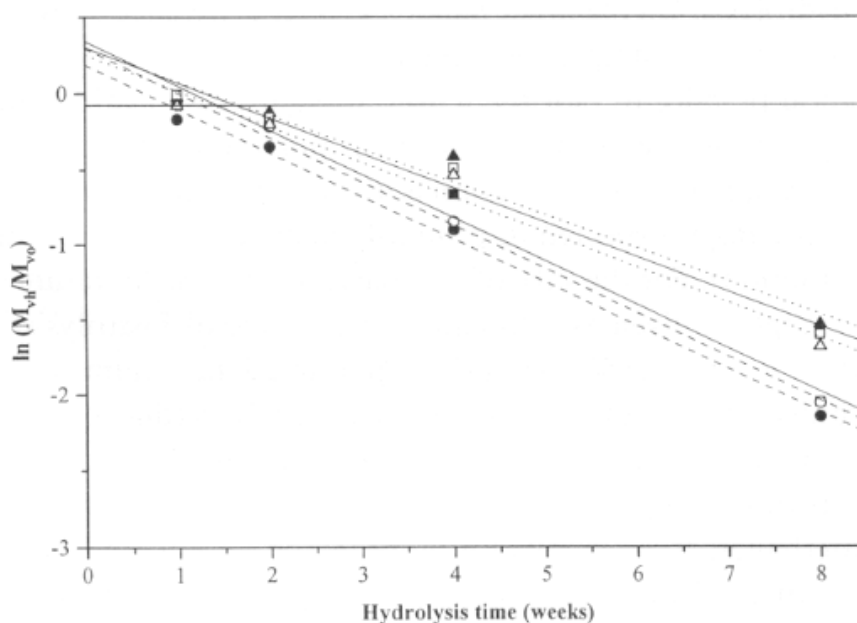


Fig. 1. Effect of hydrolysis time on the decrease in relative molar mass of Estanes; symbols used:  
 Estane samples 1.5 mm: (■) 54600; (●) 54610; (▲) 54650;  
 Estane samples 0.3 mm: (□) 54600; (○) 54610; (△) 54650.

analogous manner, even though the as-prepared samples differ in  $[\eta]_0$  and  $M_{v0}$ . As can be seen,  $M_{vh}$ s drop after 8 weeks of hydrolysis to 20–10% of the initial values.

The values of “initial” Young’s modulus (determined at very small strains) are not given in this paper due to the low accuracy of tensile measurements of low-modulus elastomers like Estanes. Instead, the 20% secant modulus (i.e. the slope between the zero point and 20% of strain) is presented in Fig. 2a as a function of hydrolysis time. This modulus is somewhat lower (by 10–20%) than the Young’s modulus, but it has been proven to be a reproducible quantity. The secant modulus at 100% strain equals to the stress required for achieving the double length of a test specimen (Fig. 2b); however, as soon as the strain at break becomes lower than 100%, this modulus is no longer available. Figs. 2a and 2b qualitatively indicate the proportionality between the moduli and the content of hard segments in Estanes.

As can be seen, the 20% secant modulus of tested species drops during the first week of hydrolysis; in the interval 1 week  $< t_h < 4$  weeks it does not change significantly, thus indicating that the elastic properties have been preserved; after 8 weeks of hydrolysis, Estane 54610 has lost a great part of its stiffness. In all cases the thinner samples display lower values of the 20% secant modulus, except for 54650, where the differences are very small. Neither does the 100% secant modulus show any pronounced dependence on the time of hydrolysis. On the other hand, a greater difference between moduli of “thick” and “thin” samples was detected.

It is common practice to plot the tensile strength,  $\sigma_{bh}$ , against the time of hydrolysis,  $t_h$ , to visualize the deterioration of polyurethane materials. It is to be noted, however, that such correlation is difficult to analyse in a quantitative manner, because  $\sigma_{bh}$  is expected to primarily depend on the molar mass  $M_{vh}$  (and its distribution). For the sake of comparison with the literature data<sup>4,5,8</sup>, the tensile strength is given as a function of the time of hydrolysis in Fig. 3. The strength of Estane 54650 passes through a small maximum, which can be hardly attributed to an “optimum degree” of hydrolysis (due to the induction period, the initial changes in molar mass are small), so that different explanation is to be sought. A similar dependence was observed earlier<sup>5</sup> for other polyurethanes. It is obvious for all tested polyurethanes that the detrimental effect of the hydrolysis becomes more pronounced after 2 weeks of exposition when the molar mass is perceptibly decreased. The initial values of thinner samples are higher than those of thicker samples, which can be tentatively attributed to higher orientation of macromolecules in thinner

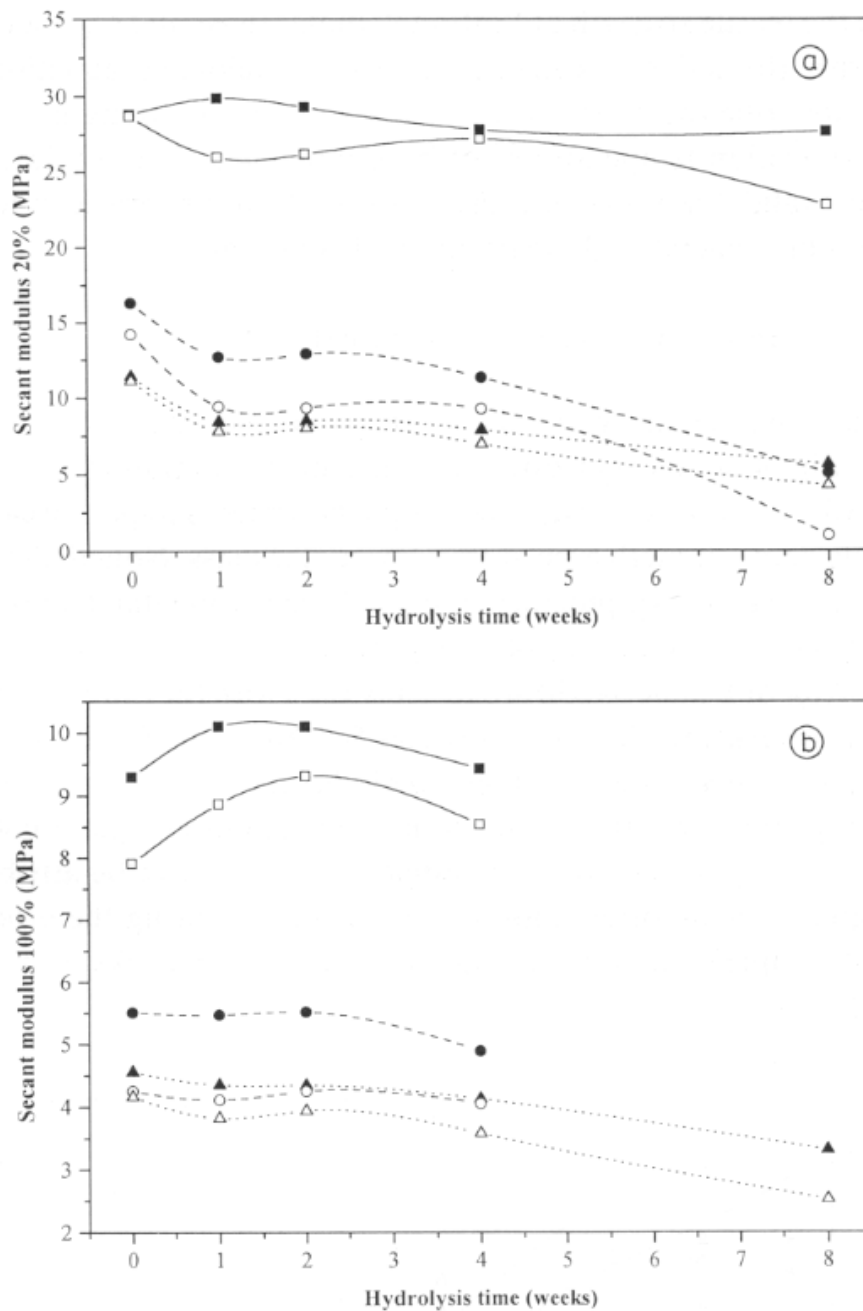


Fig. 2. Effect of hydrolysis time on the secant modulus of Estanes at (a) 20% and (b) 100% strain; symbols as in Fig. 1.

sheets during processing. However, after 8 weeks of hydrolysis the situation has been reversed, thus evidencing faster hydrolysis of thinner species.

The following equation was proposed<sup>11, 21</sup> to encompass the effect of molar mass on tensile strength:

$$\sigma_b = \sigma_b^\infty - C_1/M \quad (4)$$

where  $\sigma_b^\infty$  is the tensile strength at “infinite” molar mass and  $C_1$  is a constant evaluated with the aid of experimental data. Analogous equations were proposed to describe the effect of molar mass on tensile strength of fibers<sup>22</sup> or on glass transition temperature<sup>23</sup> of homopolymers. Though Eq. (4) has been found<sup>21</sup> valid for polymeric materials undergoing brittle fracture, it seems to be quite general<sup>11</sup>. By rearranging it we obtain

$$(\sigma_{b0} - \sigma_{bh})/\sigma_{b0} = (C_1/M_{vo}\sigma_{b0})(M_{vo}/M_{vh} - 1) \quad (5)$$

where  $\sigma_{b0}$  and  $\sigma_{bh}$  characterize the as-received and hydrolysed samples, respectively. Fig. 4 shows that experimental data fit a straight line up to 4 weeks of hydrolysis; afterwards, the slope becomes smaller because the samples retain some strength even at very low molar mass. Nonetheless, it can be said that in the region of practical interest the experimental data on tensile strength of Estanes obey Eq. (5) plausibly well.

Strain at break of Estane 54650 appreciably rises with the time of hydrolysis (Fig. 5) up to 4 weeks, while that of Estanes 54600 or 54610 only slightly increases within 2 weeks. Beyond these periods, the strain at break of all specimens drops rapidly with the time of hydrolysis. Lower extensibility — as well as higher strength (Fig. 3) — of thinner specimens can be attributed to a higher degree of chain orientation in thinner sheets during the processing. The effect of sample thickness on strain at break after 8 weeks of hydrolysis is very small.

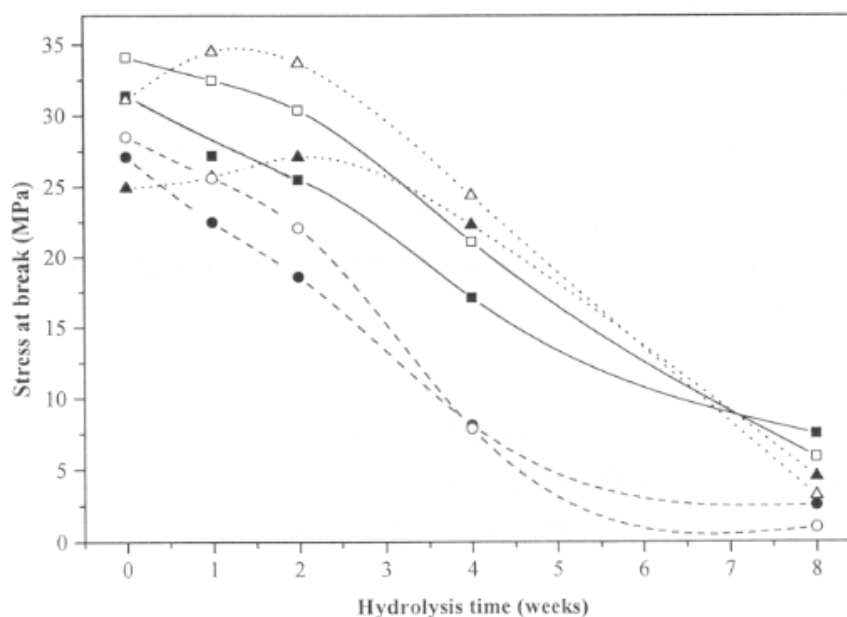


Fig. 3. Effect of hydrolysis time on the tensile strength; symbols as in Fig. 1.



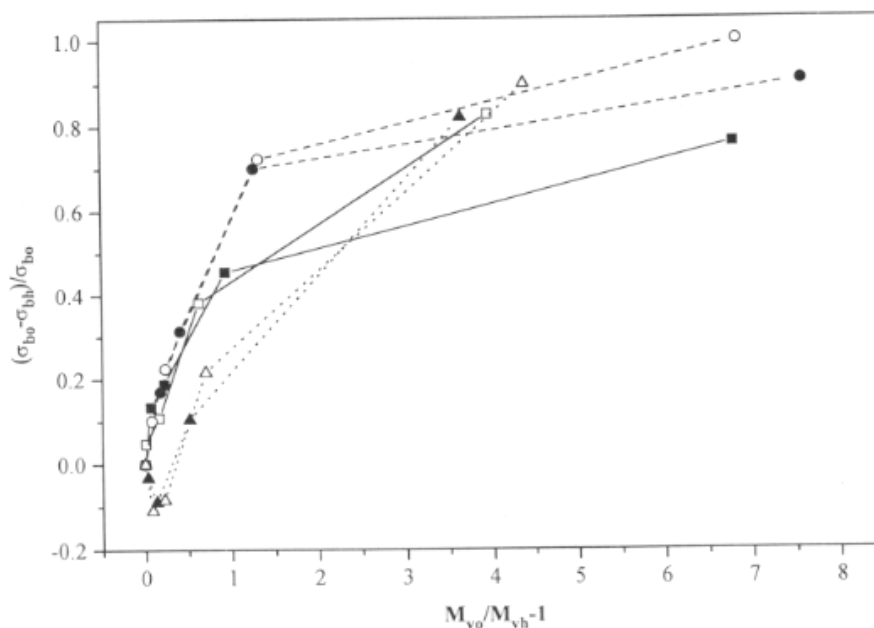


Fig. 4. Effect of relative molar mass on tensile strength; symbols as in Fig. 1.

Though there is virtually no change in the molar mass of Estanes after 1 week of hydrolysis (Fig. 1), some changes in mechanical properties can be observed: a significant decrease in modulus (Fig. 2a) and a small increase in tensile strength (Fig. 3) and /or strain at break (Fig. 5). Therefore, a tentative explanation of these changes has to link to structural changes caused by the storage in water at 70°C. As we have reported<sup>18</sup> earlier, the soft polyester segments in all Estanes show a partial crystallinity, which is manifested in thermograms by an endotherm peak located between 70–80°C. The peak area is drastically reduced after one week of hydrolysis and the peak disappears after two weeks of hydrolysis. Thus, it seems likely that crystalline domains are melted during the storage in water at 70°C so that the hydrolytic cleavage is evenly distributed in the whole bulk of the specimens. Due to partial hydrolysis of polyester segments, the crystalline domains are not reconstituted after cooling the specimens down to room temperature or during drying (annealing) at about 50°C. Hence, decrease in or elimination of crystallinity may lead to lower modulus and higher extensibility of Estanes. However, as soon as the decrease in molar mass becomes significant at longer hydrolysis periods, all mechanical properties of the hydrolysed specimens deteriorate.

Tensile energy to break which rises with increasing strength and extensibility passes through a maximum at about  $t_h = 2$  weeks (Fig. 6) for Estane 54650 while the other species show more or less constant values. At  $t_h > 2$  weeks, tensile energy to break falls down for all Estanes. Thus we can see that ultimate

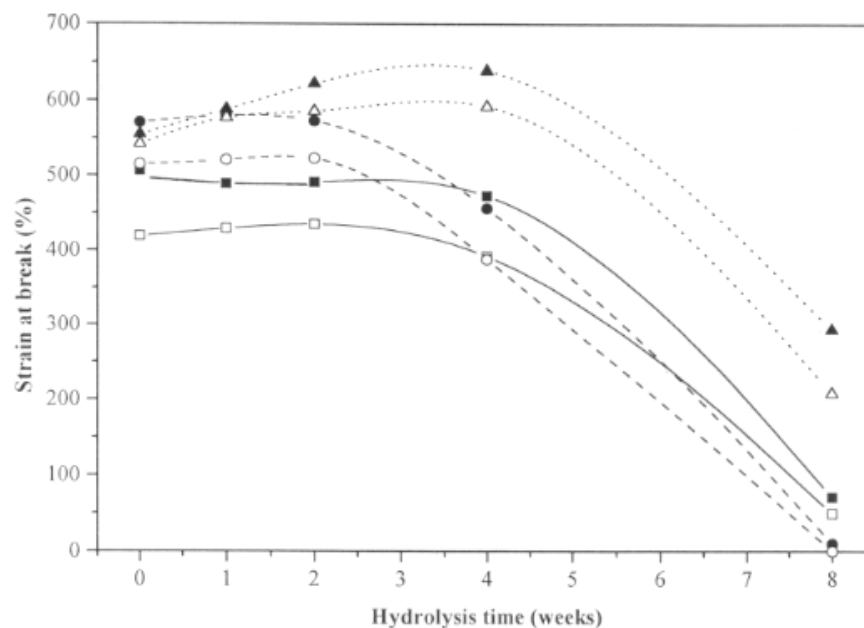


Fig. 5. Effect of hydrolysis time on strain at break; symbols as in Fig. 1.

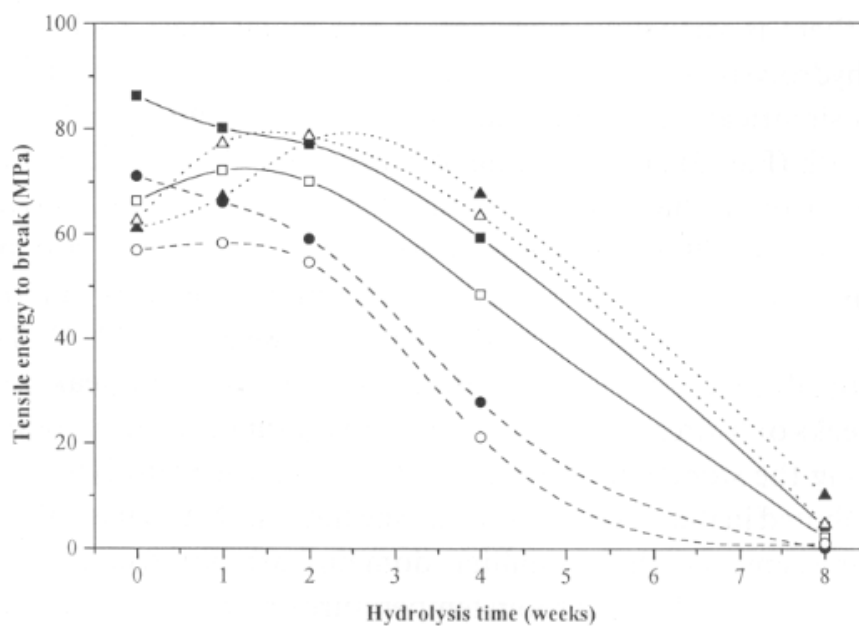


Fig. 6. Effect of hydrolysis time on the tensile energy to break; symbols as in Fig. 1.

properties of Estanes remain fairly well preserved up to 2 weeks of hydrolysis, but further continuation of hydrolysis causes essential drops of all ultimate properties (Fig. 3–6) and increase in the extract (Fig. 7).

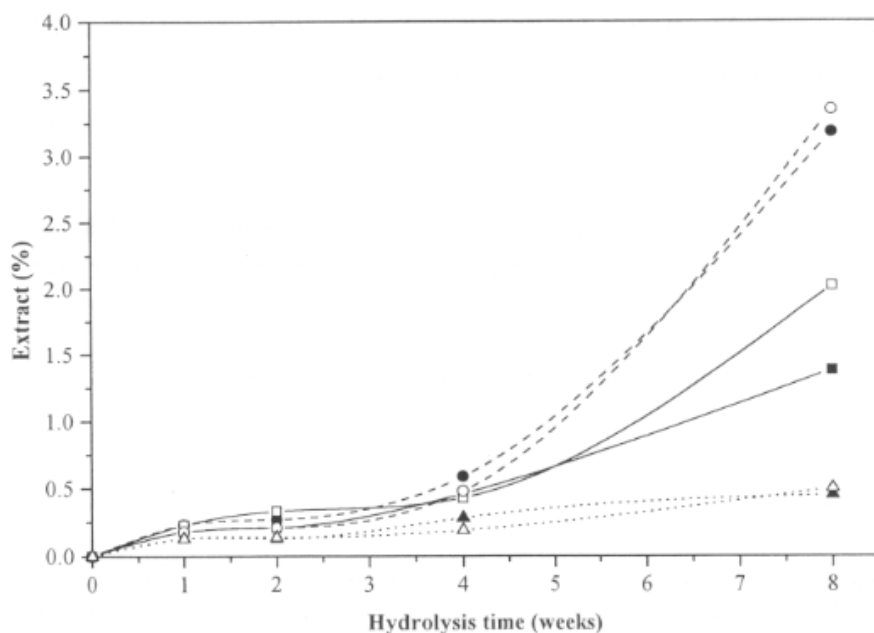


Fig. 7. Effect of hydrolysis time on the water extract; symbols as in Fig. 1.

### Conclusions

Mechanical properties of Estanes 54600, 54610, and 54650, which rank among poly(ester urethanes), are appreciably affected by prior hydrolysis at 70°C. The kinetics of the hydrolysis can be plausibly described in terms of a first-order reaction; the observed induction period is about 7 days, which means that short expositions to water do not cause any perceptible changes in molar mass. However, decrease in or elimination of the crystallinity of polyester segments brings about a drop in modulus and a small increase in extensibility. Reduction of molar mass induced by hydrolysis lasting longer than two weeks accounts for a decrease in ultimate properties, i. e., (i) tensile strength, (ii) strain at break, and (iii) tensile energy to break. The relative tensile strength was found to correlate well with the relative molar mass of hydrolysed samples. The obtained mechanical and extract data clearly evidence the differences in the hydrolysis stability of Estanes. Despite the lowest content of hard segments (which are much less susceptible to hydrolysis than ester groups), Estane 54650 shows superior resistance to hydrolysis which can be ascribed to the fact that 1,6-hexanediol increases the hydrophobicity of the soft segments. The reason why Estane 54610 displays lower hydrolysis stability than Estane 54600 is likely to consist in higher fraction of soft segments and, consequently, of ester groups exposed to hydrolysis. Even though the effect of sample thickness is not essential, stress at break, strain

at break, and tensile energy to break indicate that structure degradation is relatively deeper (or faster) in thinner samples, which evidences that the damage of structure caused by hydrolysis proceeds from the surface to the interior of the test specimens.

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