

Poly(ester amide)s Derived from Tartaric and Succinic Acids: Changes in Structure and Properties upon Hydrolytic Degradation

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ABSTRACT: The changes in structure and properties taking place in a set of tartaric acid-based polyamides and poly(ester amide)s upon hydrolytic degradation were examined. Poly(hexamethylene 2,3-di-*O*-methyl-L-tartaramide)s, either pure or containing minor amounts of succinate ester groups ($\leq 10\%$), were exposed to humidity or incubated in buffered water at pH 7.4 and 37°C, and their thermal and mechanical properties were evaluated as a function of time. Both moisture uptake and hydrolysis induced a noticeable decay in the tensile properties of polymers. These effects were greatly enhanced by the presence of ester groups, whereas no large differences were noticed for changes in the enantiomeric composition. Variations in the glass transition temperatures and melting points appeared to be slight, whereas crystallinity clearly increased with incubation time. The latter effect was most apparent in poly(ester amide)s with a nearly racemic composition, in which a crystal-to-crystal transition was observed to take place upon degradation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 486–494, 2000

Key words: poly(ester amide)s; tartaric acid; succinic acid; hydrolytic degradation

INTRODUCTION

The investigation of nylons derived from carbohydrates is a subject of much current attention.^{1–3} These polymers offer a potential as advanced materials with novel properties without precedents among conventional nylons. The highly substituted nature of monosaccharides derivatives used as monomers confers to the resulting polymers an enhanced water affinity that can be adjusted by a convenient choice of the starting compounds. Furthermore, if an adequate method of synthesis is applied, stereoregular polymers displaying high

crystallinity and optical activity may be attained.^{4,5} An intelligent combination of such properties is expected to lead to nylons susceptible to biodegradation without much decaying of the good mechanical and thermal properties characteristic of this family of polymers.

In the last few years we have devoted substantial efforts to the study of polytartaramides,^{6–9} i.e., polyamides obtained from tartaric acid. Among the different classes of polytartaramides that have been explored, those obtained from 2,3-di-*O*-methyl-L-tartaric acid and 1,*n*-alkanediamines stand out because their stereoregularity, easy accessibility, and good overall properties.⁷ These polyamides are abbreviated as PnDMLT, and their general chemical structure is depicted in Figure 1. Extensive accounts on the synthesis, crystal structure, and properties of this family of polytartaramides have been recently reported.^{7,10,11}

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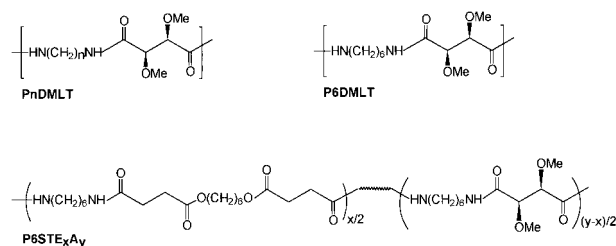


Figure 1 Chemical structures of polyamides and poly(ester amide)s investigated in this work.

P6DMLT is the polytartaramide that has been examined in most detail. This modified nylon 6,4 is highly crystalline, melts at 230°C, and may absorb up to 20% of water when exposed to a humid atmosphere. The hydrolytic degradability of P6DMLT has been measured for a variety of pHs and temperatures.¹² Although it degrades faster than its homologues P8DMLT and P12DMLT, its resistance to hydrolysis under physiological conditions, i.e., pH 7.4 and 37°, continues to be high with a weight loss of less than 10% of the initial sample after 1 year of incubation.

To render P6DMLT more degradable, minor amounts of ester linkages were incorporated into the chain in the form of disuccinate units.¹³ Poly(ester amide)s with the chemical structure shown in Figure 1 were prepared with contents in ester groups ranging from 1 to 20%. The acronym used for these poly(ester amide)s is P6STE_xA_y, where x and y stand for the content in ester and amide groups, respectively. As expected, the degradability of these modified P6DMLT steadily increased with the ester/amide ratio, whereas other properties such as water uptake, melting point (T_m), and glass transition temperature (T_g) were found to decay. No evaluation of mechanical properties was reported in that study.

In the present work we wish to report on the effects exerted by humidity, hydrolytic degradation, and sample preparation methods on the thermal and mechanical properties of P6DMLT and its derived poly(ester amide)s P6STE₃A₉₇ and P6STE₁₀A₉₀. In addition, a poly(ester amide) with a nearly racemic composition, namely *r*-P6STE₃A₉₇, was comparatively investigated, with the purpose of assessing the influence of configuration on degradability and concomitant changes in properties. The final aim of this study is to provide a survey of the behavior displayed by polytartaramides and poly(tartaraester amide)s when exposed to environment conditions close to those expected to exist during their potential uses like, for instance, biomaterials for temporary applications.

EXPERIMENTAL

A detailed account of the synthesis of the polymers investigated in this work has been published elsewhere.^{7,13} A selection of polymer data of relevance to the present study is provided in Table I.

Viscosities measurements were carried out on a microviscometer Cannon-Ubbelohde at $25 \pm 0.1^\circ\text{C}$ in dichloroacetic acid solutions within the 1.0–0.3 g dL⁻¹ range of concentrations. Size-exclusion chromatography (SEC) was performed on a 510 Waters Associates instrument fitted with two columns with respective exclusion limits at 10³ and 10⁴ nm and a refractive index detector. The (95 : 5) chloroform : *o*-chlorophenol mixture was used as the mobile phase, and molecular weights were estimated against polystyrene standards (Polysciences) using the Maxima 820 computer program. It should be stressed that molecular weights given in this work are only apparent, because no absolute measure-

Table I Selected Data of Polyamides and Poly(ester amide)s

Polymer ^a	[COO]/[CONH] ^b	$[\eta]$ (dL g ⁻¹) ^c	$M_w \cdot 10^{-3}$ ^d	PD ^d	T_m (°C) ^e	T_g (°C) ^e
P6DMLT	0/100	2.34	388	2.2	230	106
P6STE ₃ A ₉₇	3.1/96.9	0.81	63.4	3.6	226	92
P6STE ₁₀ A ₉₀	9.6/90.4	2.16	177	4.9	221	88
<i>r</i> -P6STE ₃ A ₉₇	2.7/97.3	1.75	110	3.5	214	90

^a Acronyms taken from previous published work (refs. 4 and 9).

^b Ester to amide groups ratio in the polytartaramide determined by ¹H NMR.

^c Intrinsic viscosity measured in DCA at $25 \pm 0.1^\circ\text{C}$.

^d Average-weight molecular weights and polydispersities determined by GPC.

^e Melting and glass temperatures determined by DSC.

ments were made. Hygroscopicities were evaluated by measuring the moisture sorption in films exposed to a 55% relative humidity atmosphere at room temperature. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris 1 apparatus calibrated with indium. Thermograms were recorded in the 20–300°C range from filmy samples of 5–10 mg weight at heating rates of 20°C min⁻¹. Glass temperatures were measured from samples that had been rapidly cooled from the melt. X-ray diffraction was performed on a modified Statton camera (W. H. Wharus, Willmington, DE) with nickel-filtered Cu-K_α radiation. Diffraction patterns were recorded on Kodak DEF-5 flat films, and they were calibrated with calcite ($d = 0.3035$ nm).

For degradation and mechanical properties testing, both films and filaments were used. Cast films were prepared from chloroform solutions at room temperature. The degree of crystallinity of the films was varied by adjusting the evaporation rate. Melt-pressing films were prepared by heating the polymer sample at a temperatures near above to its melting point under a pressure of 2 tons. Specimens were shaped according to ASTM D-882 standards, which is specifically designed for testing thin films. Slight modifications were made fit our sample availability and testing machine requirements. Film thickness was controlled to be in the range of 150–300 μm, and it was accurately measured by means of a magnetic induction Neurtek micrometer previously calibrated at 295 μm with a plastic sheet calibration standard. Strips with lateral dimensions of 30.0 × 3.0 mm were cut from films with a razor edge, and their dimensions were exactly determined (±1%) with a profile projector Nikon 6C. Continuous filaments were dry spun at room temperature from a chloroform solution in a laboratory extrusion machine Bradford University Research. Orientation was induced by suspending a constant weight from pieces of 40-cm length for 72 h. The degree of orientation achieved was estimated by X-ray diffraction. Test specimens were conditioned before testing either at room conditions or in an enclosed chamber at 55% relative humidity and 25°C.

For hydrolytic degradation experiments, strips were dipped in phosphate buffer at pH 7.4 at 37°C for periods of times ranging from 8 h to 70 days. After incubation, specimens were drawn and subjected to structural analysis and properties evaluation. Properties in the wet state were measured on specimens directly drawn from the incubation medium and drained with a cleaning tissue. For

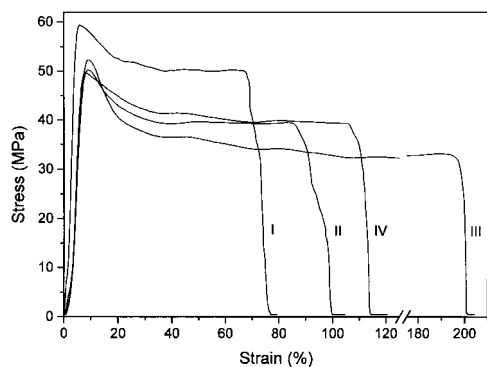
evaluation in the dry state, specimens were conditioned under vacuum to constant weight. Mechanical properties were measured at room temperature in tensile tests on a minitensiometer Miniature Materials Tester instrument of Polymer Laboratories Inc. Tests were carried out at a constant deformation rate of 1 mm min⁻¹ and using at least six specimens for each sample.

RESULTS AND DISCUSSION

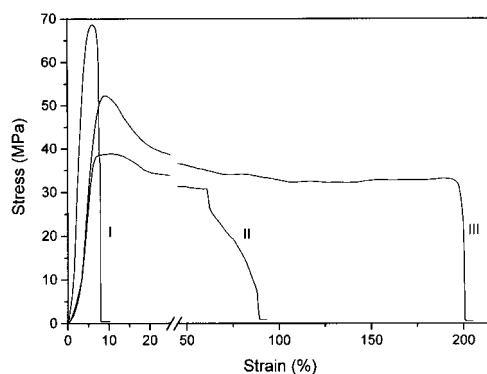
Undegraded Samples

Stress–strain curves obtained from strips of polymer films prepared by casting and dried to constant weight are shown in Figure 2(a). A tensile behavior characteristic of semicrystalline plastic exhibiting well-defined yielding at about 10% strain and plastic flowing at almost constant stress was observed for the all four cases. Data provided by these curves (Table II) reveal that the mechanical strength of the polyamide P6DMLT is significantly depressed by the incorporation of ester groups in the chain, even at the very low contents used in this work. Comparison of data obtained for P6STE₃A₉₇ optically pure and for the racemic polymer *r*-P6STE₃A₉₇ indicates that the configuration of the tartaric units seems to have little influence on the mechanical behavior of dried polyamides. This is a largely expected result because previous studies carried out on the crystal structure of P6DMLT have revealed that changes in the enantiomeric composition of this polymer have not influence on crystallinity provided that samples are crystallized under favorable conditions.^{7,8}

As a first stage in the characterization of the mechanical behavior of polytartaramides, the influence of the procedure used for the preparation of the specimen was evaluated. As it is illustrated in Figure 2(b) for the representative case of P6STE₁₀A₉₀, drastic variations in the stress–strain profiles were observed, depending on the method used to generate the films. Films prepared by melt pressing exhibited higher modulus but they were unable to show cold flow. On the contrary, films prepared by casting displayed comparatively lower yielding strength. In general, stronger samples were obtained at slower solvent evaporation rates, an effect that, according to X-ray diffraction, can be associated to differences in crystallinity, as will be shown in the following section. However, an incongruent be-



(a)



(b)

Figure 2 Stress–strain curves of polytartaramides obtained from strip specimens cut from films and dried to constant weight. (a) Influence of the polymer (films prepared by casting): I) P6DMLT, II) P6STE₃A₉₇, III) P6STE₁₀A₉₀, IV) *r*-P6STE₃A₉₇. (b) Influence of crystallinity (P6STE₁₀A₉₀): I) Film prepared by melt-pressing (high crystallinity), II) film prepared by casting at high evaporation rate (nearly amorphous), III) film prepared by casting at low evaporation rate (medium crystallinity).

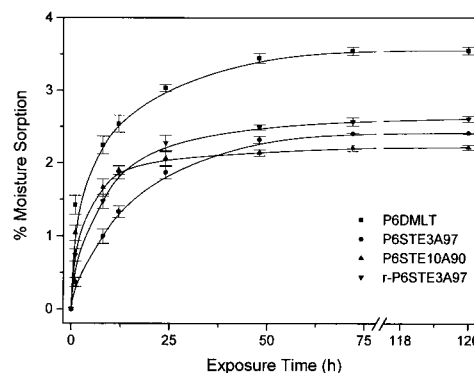


Figure 3 Moisture uptake of polymers exposed to 55% R.H. at 25°C as a function of time.

havior was found regarding the toughness of the polymer with longer elongations at break being observed for higher crystalline samples. Such results may be explained by taking into account the uneven thickness of films obtained at high evaporation rates, with necks being responsible for the unexpectedly early failing.

The influence of humidity on the stress–strain behavior was then investigated. In the first place, the hygroscopicity of the polymers was evaluated by exposing sheet specimens to a 55% R.H. environment at the temperature of 25°C. Moisture sorption vs. exposure time curves are presented in Figure 3, which reveals that water uptake diminishes when the ester content increases, and that variations with differences in configuration are not significant. It should be noticed that, as logically anticipated, values attained here are much lower than those previously reported for the powdered samples of the same polymers exposed to 100% R.H. The effect of humidity on the tensile properties is illustrated in Figure 4(a), where stress–strain curves obtained for P6DMLT strips

Table II Influence of Humidity on the Tensile Properties of Polytartaramides^a

Polymer	σ_Y (MPa)		E (MPa)		ϵ_{\max} (%)	
	Dry ^b	Wet ^c	Dry ^b	Wet ^c	Dry ^b	Wet ^c
P6DMLT	63	43	1800	1300	60	130
P6STE ₃ A ₉₇	49	39	1400	900	90	140
P6STE ₁₀ A ₉₀	51	35	1300	700	200	290
<i>r</i> -P6STE ₃ A ₉₇	54	28	1250	650	110	200

^a Averaged data taken from eight strip specimens.

^b Samples dried to constant weight.

^c Samples conditioned in an atmosphere of 55% RH at 25°C for 24 hours.

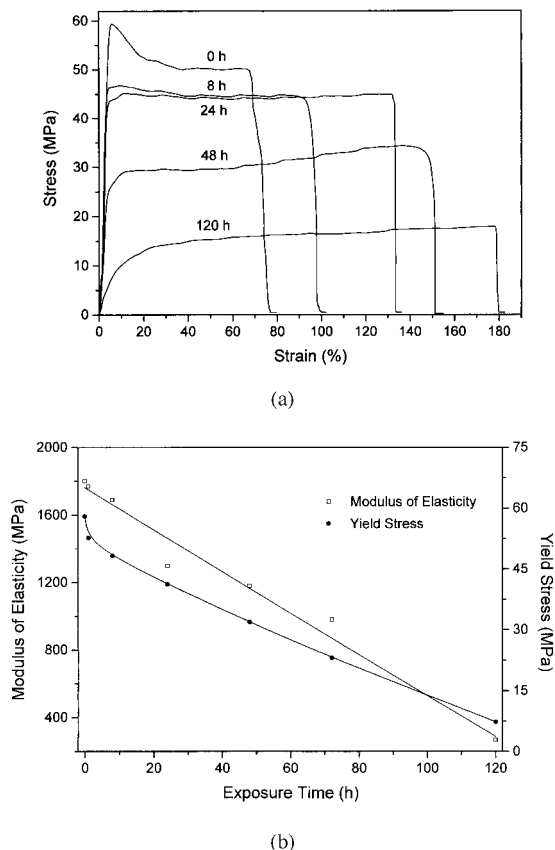


Figure 4 Change in tensile properties of polyamide P6DMLT exposed to a humid (55% R.H.) atmosphere. (a) Stress–strain curves at the indicated exposure times. (b) Modulus and yield stress decay with exposure time.

exposed to a 55% R.H. atmosphere for increasingly longer times are compared. The plasticizing action of water is clearly manifested in the decrease of both the yield stress (σ_y) and elastic modulus (E) and in the increase of the elongation at break that are observed with exposure time. The steadily decay undergone by E and σ_y is vividly illustrated in Figure 4(b). A similar trend was observed for poly(ester amide)s, their basic parameters measured under humid and dried conditions being those given in Table II.

Degraded Samples

The degradability of the four poly(ester amide)s was assessed using the same specimens that were then used for structure and properties evaluation. The decay of the average number molecular weight with degradation time for polymers immersed in pH 7.4 buffer at 37°C is shown in

Figure 5. A significant decrease of the polymer size is detected for P6STE₁₀A₉₀, whereas P6DMLT appears to be the most reluctant to hydrolysis. The behavior displayed by P6STE₃A₉₇ was intermediate and independent on configuration. The number of main chain bonds split per polymer chain calculated as $[M_n(0)/M_n(d)] - 1$ is between 1 and 0.5 at the end of the incubation time, indicating that an important fraction of chains remains unbroken.

Influence of Composition

The evolution of mechanical behavior with degradation was followed by tensile tests on both dry and wet films of polyamides differing in composition. Results are compared in Table III showing a decrease in the mechanical parameters at a rate that increases with the content in ester groups. Figure 6(a) illustrates the decay for the elastic modulus. After three weeks of incubation, P6STE₃A₉₇ and P6STE₁₀A₉₀ samples were so much eroded that so no further measuring was feasible.

The influence on degradation of the technique used for the preparation of the specimen was explored for the representative case of P6STE₁₀A₉₀. Comparative tensile tests were carried out with strips cut from cast or melt-pressed films as well as with a continuous filament made by dry spinning. The variation of the elastic modulus with degradation for the three cases is plotted in Figure 6(b). Significant differences were found among them, with the crystalline specimen prepared by melt pressing giving the weakest response. The great sensitivity displayed by the spun polymer is surely due to the high specific surface inherent to the shape of this specimen.

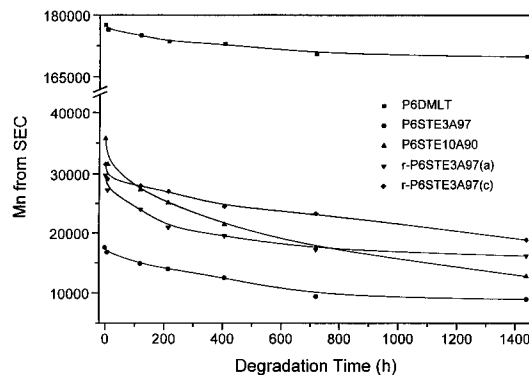


Figure 5 Variation of molecular weight with degradation time.

Table III Changes in Tensile Properties of Polytartaramides with Degradation Time^a

Time (weeks)	P6DMLT						P6STE ₃ A ₉₇						P6STE ₁₀ A ₉₀					
	σ_Y (MPa)		E (MPa)		ϵ_{max} (%)		σ_Y (MPa)		E (MPa)		ϵ_{max} (%)		σ_Y (MPa)		E (MPa)		ϵ_{max} (%)	
	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
0	77	18	1970	114	36	114	49	9	1520	123	11	30	70	9	1650	73	11	102
1	78	17	1920	125	33	125	31	4	1180	120	4	10	34	6	1210	68	3	1
3	76	14	1670	125	31	133	3	0.3	270	16	0.8	2	1	0.9	120	18	0.9	0.2
8	62	11	1310	80	19	80	—	—	—	—	—	—	—	—	—	—	—	—

^a D and W refer to dry and wet samples, respectively.

Influence of Configuration

To estimate the influence of tacticity on properties under degradation, the behavior of polymer *r*-P6STE₃A₉₇ was examined, and results were compared with those obtained for the optically

pure isomer. Because the degree of crystallinity displayed by racemic polytartaramides is known to be highly dependent on crystallization conditions,^{7,8} crystalline and amorphous samples were prepared by casting at low and high rates of solvent evaporation, respectively. The powder X-ray diffraction patterns produced by such samples are shown in Figure 7(c) and (d). The degrees of ordering displayed by these samples are according to what should be anticipated from the respective methods used for preparation. The pattern obtained from optically pure P6STE₃A₉₇ [Fig. 7(a)] turns to be identical to that arising from the slowly crystallized racemic polymer [Fig. 7(c)]. On the other hand, the sample prepared by press melting [Fig. 7(b)] showed the best-defined ring pattern indicative of maximum crystallinity. A closely comparative inspection of Figure 7(b) and (c) revealed that a different crystal structure is adopted in each case; the two crystal forms can be preliminary called form I characterized by spacings at 0.59 and 0.35 nm and form II, with characteristic spacings at 0.64 and 0.32 nm, respectively. The diffraction pattern produced by form I is identical to that reported for polytartaramide P6DMLT,⁸ which was described as a triclinic lattice of parameters $a = 0.500$ nm, $b = 0.684$ nm, $c = 1.320$ nm, $\alpha = 61.5^\circ$, $\beta = 90.0^\circ$, $\gamma = 111.6^\circ$. Therefore, it is reasonable to assume that this will also be the crystal structure of form I of *r*-P6STE₃A₉₇. It should be noted that the prominent spacings appearing in the X-ray diagrams at ~ 1.15 and 0.46 nm are common to forms I and II, indicating that differences between these forms are presumably restricted to the lateral packing of the chains.

Changes in structure, thermal, and mechanical properties upon degradation were measured for

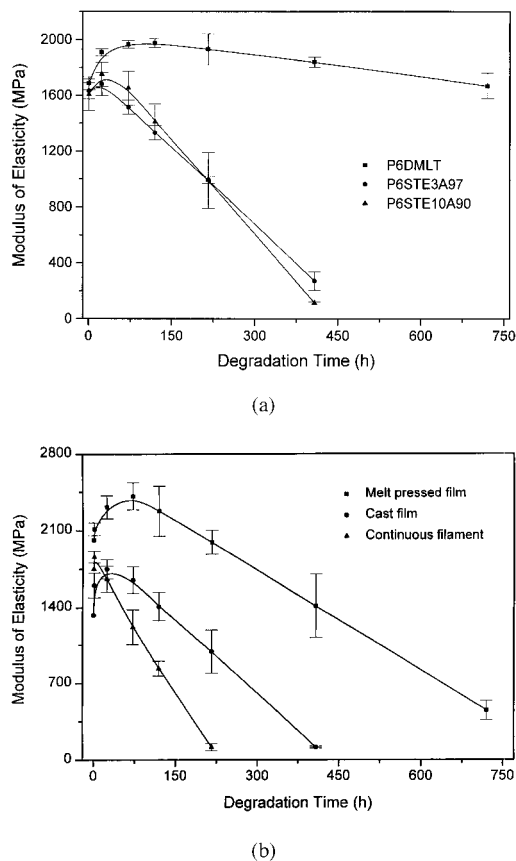


Figure 6 (a) Modulus decay with degradation time for the indicated polymers. (b) Influence of specimen characteristics on the stress-strain behavior of poly(ester amide) P6STE₁₀A₉₀.

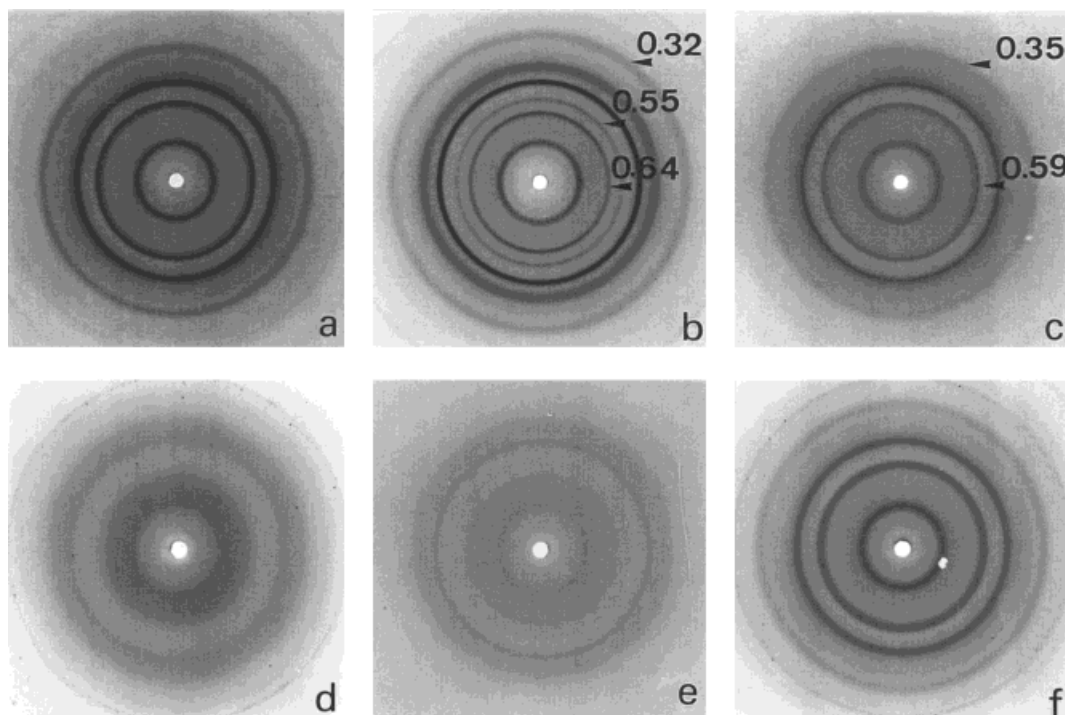


Figure 7 Powder X-ray diffraction patterns of polyamide P6STE₃A₉₇ films prepared and treated as indicated: (a) optically pure polymer, casting from chloroform, undegraded (form II). (b–f) Racemic polymer *r*-P6STE₃A₉₇: (b) melt-pressing, undegraded (form I); (c) casting at low evaporation rate, undegraded (form II); (d) casting at high evaporation rate, undegraded (amorphous); (e) like (d), and degraded for 1 week (form I); (f) like (d) and degraded for 8 weeks (form II).

the crystalline and the amorphous samples, and results are compared in Table IV. DSC traces reveal that the amorphous sample undergoes extensive cold crystallization at temperatures far below the melting point of the polymer. DSC thermograms recorded at heating for increasing times

of degradation are compared in Figure 8. Differences between heats of crystallization and fusion diminish with degradation, revealing that no “crystallizable” phase remains after 8 weeks of incubation. Such changes in thermal behavior are accompanied by variations in the corresponding

Table IV Changes in Remaining Weight and Thermal and Tensile Properties of *r*-P6STE₃A₉₇ with Degradation Time^a

Time (w)	Weight (%)		DSC						Tensile Properties					
			<i>T_g</i> (°C)		<i>T_m</i> (°C)		ΔH_m (cal g ⁻¹)		σ_y (MPa)		<i>E</i> (MPa)		ϵ_{max} (%)	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
0	—	—	49	48	207	209	5.5	5.8	44	54	900	1250	150	110
1	86	91	49	49	208	213	6.1	7.1	53	65	1480	1820	30	10
4	82	88	49	51	210	213	6.4	8.2	11	387	240	1060	1.2	3
8	80	87	49	48	212	211	7.3	9.8	—	6	—	130	—	1

^a I: “amorphous” sample prepared by casting at high solvent evaporation rate. II: polycrystalline sample prepared by casting at very low solvent evaporation rate.

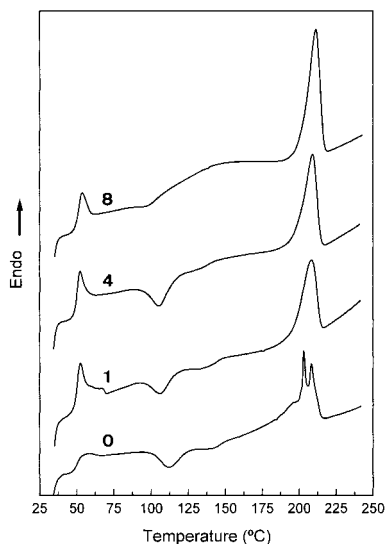


Figure 8 DSC curves of *r*-P6STE₃A₉₇ films prepared by casting at high evaporation rates and incubated for the indicated number of weeks.

diffraction patterns, indicative that crystallinity increases with degradation [Fig. 7(e) and (f)]. Furthermore a detailed degradation comparison of successive diffractograms indicates changes in spacings and intensities consistent with the occurrence of a crystal transition during the later stages of the degradation process. This is clearly illustrated in Figure 9, where X-ray spacings are plotted

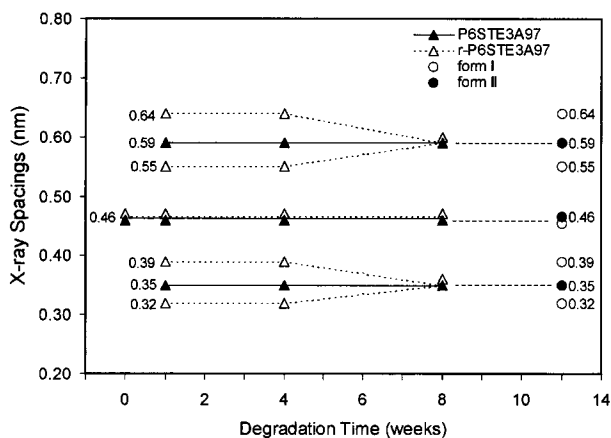
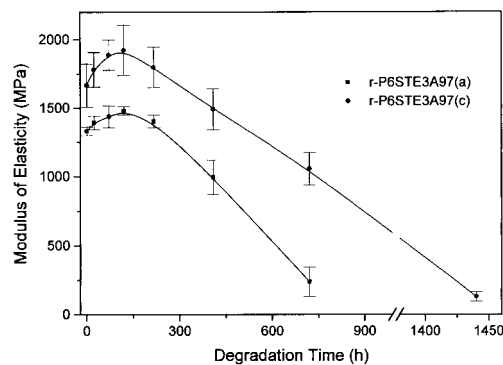
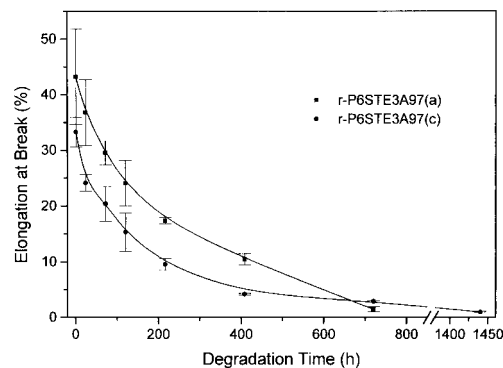


Figure 9 Variation in the X-ray spacings of characteristic reflections of racemic and optically pure forms of poly(ester amide) P6STE₃A₉₇ with degradation time. The strong reflection with a spacing about 1.15 nm remains unchanged and has not been represented. The only reflection appearing in the initial amorphous samples has a spacing of 0.46 nm. Spacings identifying forms I and II are displayed on the right.



(a)



(b)

Figure 10 Changes in tensile properties of *r*-P6STE₃A₉₇ upon degradation. Two samples, one amorphous (a) and the other crystalline (c), are compared. (a) Elastic modulus, (b) elongation at break.

against degradation time for racemic and optically pure P6STE₃A₉₇ samples, both of which were initially in the amorphous state. Both polymers crystallized after 1 week of incubation, but they take up different crystal structures and behave differently upon further degradation. The optically pure P6STE₃A₉₇ adopted the structure of form II, which was retained throughout the whole degradation process. On the contrary, *r*-P6STE₃A₉₇ preferred the form I present in samples crystallized from the melt, and it changed into form II after 8 weeks of incubation.

Tensile tests performed for both types of samples show a trend similar to that found for the optically active polymers, which is characterized by a steady decay in mechanical strength with degradation time. Changes in the elastic modulus and elongation at break for the two samples are graphically compared in Figure 10. These plots bring into evidence the higher sensitivity to degradation displayed by the amorphous sample in

agreement with its less compact structure. It seems that influence of crystallinity on mechanical behavior is important at the very early degradation stages, whereas the depressing effects of water like plasticizer and hydrolytic reagent become the predominant at later stages.

CONCLUSION

In this work a study of the evolution of properties and structure of polytartaramides with moisture uptake and hydrolytic degradation is carried out for the first time. The influence of both the incorporation of minor amounts of ester groups in the polytartaramide chain and the configuration of the polymer on hydrolytic degradation have been also examined. The study included an evaluation of the extent in which results are affected by specimen factors such as shape and crystallinity. Main conclusions derived from this study are the following: (a) Polytartaramide P6DMLT in the dry state is a strong polymer with high elastic modulus, ultimate strength, and extensive yielding under constant stress. The incorporation of succinate moieties in amounts below 10% entails a considerable reduction in the mechanical resistance of the polyamide. Configurational changes have not important additional effects on properties. The stress-strain curves appear to be extremely sensitive to conditions used in the preparation of the specimen. (b) Exposure of polytartaramides to humidity promotes a notable decay in their tensile properties with modulus falling up to near 50%. Such effect increases with the ester content being maximum for the polymer having racemic composition. (c) The hydrolytic degradation of polytartaramides at pH 7.4 and 37°C causes a rapidly decay in the initial mechanical properties. In the case of poly(tartaraester amide)s, degradation leads to the complete erosion of the material in less than 8 weeks of incubation. Although results are highly influenced by sample processing, the overall trend is maintained whichever are the extrinsic specimen characteristics. (d) Noticeable differences were found

in the degradation of polyamide *r*-P6STE₃A₉₇, depending on the crystallinity of the specimen; whereas crystalline samples behave like optically pure P6STE₃A₉₇, amorphous samples degraded much faster showing a remarkable increasing in crystallinity. A structural crystal-crystal transition seems to happen during degradation of *r*-P6STE₃A₉₇; this observation needs further support, both theoretical and experimental.

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REFERENCES

1. Thiem, J.; Bachmann, F. *Trends Polym Sci* 1994, 2, 425.
2. Gonsalves, K. E.; Mungara, P. M. *Trends Polym Sci* 1996, 4, 25.
3. Bou, J. J.; Rodríguez-Galán, A.; Muñoz-Guerra, S. In *Encyclopedia of Polymer Materials*; CRC Press Inc., Boac Raton, FL, 1996, p. 561, vol. 1.
4. Kiely, D. E.; Chen, L.; Lin, T.-H. *J Am Chem Soc* 1994, 116, 571.
5. Molina, I.; Bueno, M.; Galbis, J. A. *J Polym Sci Chem Ed* 1995, 28, 3766.
6. Rodríguez-Galán, A.; Bou, J. J.; Muñoz-Guerra, N. *J Polym Sci Polym Chem Ed* 1992, 30, 713.
7. Bou, J. J.; Rodríguez-Galán, A.; Muñoz-Guerra, S. *Macromolecules* 1993, 26, 5664.
8. Bou, J. J.; Iribarren, I.; Muñoz-Guerra, S. *Macromolecules* 1994, 27, 5263.
9. Bou, J. J.; Muñoz-Guerra, S. *Polymer* 1995, 36, 181.
10. Regaño, C.; Martínez de Ilarduya, A.; Iribarren, I.; Rodríguez-Galán, A.; Galbis, J. A.; Muñoz-Guerra, S. *Macromolecules* 1996, 29, 8404.
11. Iribarren, I.; Aleán, C.; Regaño, N. xxxx; Martínez de Ilarduya, A.; Bou, J. J.; Muñoz-Guerra, S. *Macromolecules* 1996, 29, 8449.
12. Ruiz-Donaire, P.; Bou, J. J.; Muñoz Guerra, S.; Rodríguez-Galán, S. *J Appl Polym Sci* 1995, 58, 41.
13. Alla, A.; Rodríguez-Galán, A.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. *Polymer* 1994, 38, 4935.