**Full Paper:** A series of random poly(ester amide)s with different chemical compositions and derived from sebacoyl dichloride, 1,6-hexanediamine and 1,6-hexanediol was synthesized and characterized. In addition, a poly(ester amide) with equal ratio of 1,12-dodecanediamine and 1,12-dodecanediol units was prepared. All these poly(ester amide)s were obtained by interfacial polymerization with high yields. Thermal behavior, mechanical properties, crystallinity and degradability were studied and compared with the parent polyesters (6,10 and 12,10) and nylons (6,10 and 12,10). The new poly(ester amide)s were hydrolyzable, the degradation rate depending on the ester/amide ratio and the methylene content of the diol or diamine units. On the contrary, they were not degraded with proteolytic enzymes. This observation contrasts with the behavior of related poly(ester amide)s that include α-amino acid units in their composition.
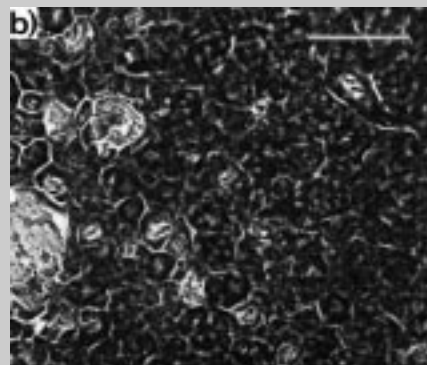
Scanning electron micrograph of a PEA1210(0.5) plate after 75 d of incubation under distilled water at 70 °C. Scale bar: 100 µm.

Study on the Degradability of Poly(ester amide)s Related to Nylons and Polyesters 6,10 or 12,10

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Introduction

There has recently been a growing interest in poly(ester amide)s due to their expected degradable, thermal and mechanical properties. Thus, ester bonds are highly hydrolyzable whereas amide groups may establish intermolecular hydrogen bonds that give good fiber-forming properties and increase the characteristic low melting temperature of polyesters.[1] The first works were carried out in 1979 and were based in the amide-ester interchange reaction produced when a polyamide/polyester mixture is heated at temperatures near 270 °C.[2] Since then, extensive work has been done to develop polymers with either a random or a sequential distribution of amide and ester groups.[3–11] Furthermore, different poly(ester amide)s have recently been commercialized (BAK®) with a wide range of applications due to their performance and processing facilities.[12]

Our recent investigations have been focused on the study of poly(ester amide)s derived from α-amino acids, since an enhanced susceptibility to enzymatic degradation is expected.[13–18] These polymers are defined by the repeat unit —NHCHRCOO(CH$_2$)$_n$OCOCHRNHCO(CH$_2$)$_m$CO—, and can be prepared by interfacial polymerization of an acid dichloride and a diamine containing two amino acid units linked to a diol by ester bonds. Several series derived from 1,6-hexanediol or 1,12-dodecanediol (n = 6 or 12) have been synthesized and characterized. The results indicate that these polymers are rapidly degraded by using proteolytic enzymes such as papain or proteinase K. Furthermore, high molecular weights can only be obtained when a hydrolytically stable dichloride, such as sebacoyl, is used in the interfacial polymerization.

For the sake of completeness, we decided to compare the degradation behavior of the above poly(ester amide)s to that of the related poly(ester amide)s (i.e., also derived from sebacoyl dichloride and 1,6-hexanediol or 1,12-dodecanediol) that do not contain α-amino acid units. Diamines with the same number of main chain atoms as the diols were employed to obtain the amide function and

to disrupt as little as possible the polymer sequence in a random polymerization. Note that isomorphous crystals may be formed when the amide and ester moieties are similar. Several works on the synthesis and degradability of this kind of polymers appear in the literature,[4–6] but they only concern adipoyl dichloride, 1,6-hexanediamine and 1,10-dodecanediol or 1,6-hexanediol derivatives, namely the study of polymers related to nylon 6,6.

Experimental Part

Random poly(ester amide)s based on polyester 6,10 and nylon 6,10 (named as PEA610(x), x being the molar ratio CONH/(CONH + COO)) or polyester 12,10 and nylon 12,10 (PEA1210(x)) were synthesized by interfacial polymerization following the procedure outlined in Scheme 1. This method is similar to that previously reported by Castaldo et al.[4] for related derivatives based on polyester 10,6 and nylon 6,6. The synthesis involves two steps: first, a thermal esterification between the appropriate diol and an excess of sebacoyl dichloride to give a mixture of oligomers having terminal —COCl reactive groups, together with a variable amount of unreacted sebacoyl dichloride; second, an interfacial polyamidation between the mixture obtained in the former step and the stoichiometric amount of the appropriate diamine.

A general procedure to prepare the new poly(ester amides) defined by the theoretical molar ratio x is described as follows:

The diol (y mmol) was added under nitrogen to sebacoyl dichloride (y+x = 1.0 mmol). The mixture was heated up to 80 °C under stirring, kept at this temperature for 1 h until the hydrogen chloride evolution ceased and then dissolved in 125 mL of carbon tetrachloride. Thereafter, an aqueous solution of the diamine (x mmol, concentration 0.1 mmol/mL) and sodium hydroxide (2x mmol) was rapidly poured into a blender containing the former mixture. After 15 min of vigorous stirring, the precipitated polymer was collected on a glass filter, washed repeatedly with distilled water, acetone, carbon tetrachloride, methanol, and diethyl ether, and finally dried at 80 °C in vacuum overnight.

Polyesters 6,10 and 12,10 were synthesized from sebacic acid and an excess of 1,6-hexanediol or 1,12-dodecanediol (molar ratio 2.2/1), respectively, by thermal polycondensation in vacuum at 200 °C using titanium butoxyde as catalyst.

Nylons 6,10 and 12,10 were synthesized by interfacial polycondensation of sebacoyl dichloride and 1,6-hexamethylene diamine or 1,12-dodecamethylene diamine, respectively, according to the methods reported in the literature.[19, 20]

Intrinsic viscosities were determined with a Cannon-Ubbelohde microviscometer in dichloroacetic solutions at 25 ± 0.1 °C.

Infrared absorption spectra were recorded with a Perkin-Elmer 1600 FT-IR spectrometer in the 4000–500 cm^{-1} range from films obtained by evaporation of formic acid (poly-(ester amide)s and polyamides) or chloroform solutions (polyesters). NMR spectra of nylon 6,10 and PEA610 series were registered from deuterated formic acid solutions,
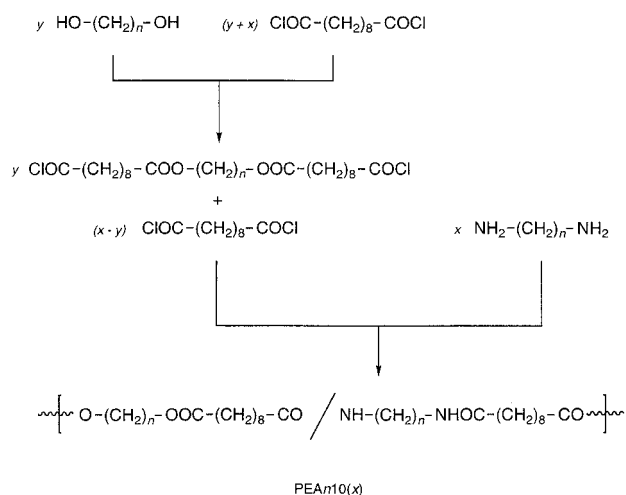
Scheme 1.

whereas those of 12,10 derivatives and polyester 6,10 were registered in CDCl$_3$/TFA mixtures and CDCl$_3$, respectively. Chemical shifts were calibrated using tetramethylsilane as an internal standard. A Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz was used for ^{1}H and ^{13}C NMR investigations, respectively.

Thermal analysis was performed by differential scanning calorimetry with a Mettler DSC-3, using indium metal for calibration. Thermogravimetric analysis was carried out with a Perkin Elmer TGA-6 thermobalance. Heating and cooling runs were always done at 20 °C/min under a flow of dry nitrogen.

Samples for mechanical and degradation studies were cut off from regular films (30 × 30 mm^2 of surface and 200 μm of thickness), which were prepared by melt pressing 200 mg of the appropriate polymer at a temperature 10 °C below fusion.

Dynamic-mechanical behavior was analyzed using a Rheometrics PL-DMT MK3 instrument. The work frequency was 1 Hz. After a rapid cooling, the dynamic spectrum was detected on heating the sample at 2 °C/min in the temperature range −150 to 150 °C. Complex modulus and tan δ were obtained and reported as function of the temperature. In this case, samples of 2.5 × 1 cm^2 were cut off from films with a thickness of 400 μm prepared by melt pressing.

Mechanical properties were determined with a Minimat instrument from Polymer Laboratories. Plate samples with a length of 30 mm, a width of 3 mm, and a thickness of 200 μm were used in stress-strain experiments, which were carried out at a deformation rate of 0.8 mm/min. Mechanical parameters were averaged from a minimum of ten measurements for each polymer sample.

Powder and fiber X-ray diffraction patterns were recorded in vacuum at room temperature. Calcite (dB = 3.035 Å) was used for calibration. A modified Statton camera (W. H. Warhus, Wilmington, DE) with a nickel-filtered radiation of 1.542 Å was used for these experiments.

Hydrolytic degradation assays were carried out at 37 °C in a pH 7.4 sodium phosphate buffer. Each plate of 1.5 cm × 1.5 cm × 200 μm was kept in bottles filled with 30 mL

of the buffer and sodium azide (0.03 wt.-%) to prevent microbial growth. After the immersion time, the retrieved samples were thoroughly rinsed with distilled water, dried to constant weight in vacuum, and stored over $CaCl_2$ before analysis. Hydrolysis was also studied under the accelerated conditions provided by distilled water at a temperature of 70 °C.

Enzymatic degradation studies were performed at 37 °C by using lipases from *Pseudomonas cepacea* or *Rizophus dele-mar*, and a proteolytic enzyme such as papain. The enzymatic media, 10 mL, consist of a sodium phosphate buffer (pH 6.0 for papain and 7.4 for the other enzymes) containing sodium azide (0.03 wt.-%), and the appropriate enzyme. In the case of papain, the solution also contains L-cysteine (0.034 M) and ethylenediaminetetraacetic disodium salt (0.030 M) for activation. All enzymatic solutions were renewed after every 72 h because of enzymatic activity loss. After the immersion time, the retrieved samples were washed and dried as indicated for hydrolytic experiments.

Mass loss, intrinsic viscosity, changes in NMR and IR spectra, and changes in the surface of polymer films were evaluated in these hydrolytic and enzymatic degradation studies.

Scanning electron microscopy was employed to examine the surface/cross-sectional morphology of samples before and after degradation. Gold coating was accomplished by using Balzers SCD-004 Sputter Coater. The SEM microphotographs were carried out by using a JEOL JSM-6400 instrument.

Results and Discussion

Synthesis and Characterization

The poly(ester amide)s studied in this work were obtained with yields in the 50–85% range, as shown in Table 1. The amide molar ratio (x) was kept in all polymerizations higher than 0.5, since otherwise a non negligible fraction of the oligomers obtained in the first synthesis step (Scheme 1) would have unreactive hydroxyl end groups, and consequently low molecular weight materials should be obtained. It is also worthy of note that a low degree of polymerization (p) should be expected in this first step, since it depends on the stoichiometric ratio ($q = (1-x)/1$) by the equation:

$$p = (1 + q)/(1-q) = (2-x)/x$$

Therefore, the final poly(ester amide)s must not contain blocks of polyester ($p = 1-3$ for x varying in the 1–0.5 range). On the contrary, it is possible that a block distribution of amide groups exists and also the occurrence of a homopolyamide fraction.

The intrinsic viscosities shown in Table 1 correspond to an average of three different polymerizations for each sample. These values indicate that molecular weights increase as ester ratio does so too, probably as a consequence of both the increasing solubility of polymers and

Table 1. Yields, intrinsic viscosities, and composition of the synthesized polymers.

Polymer	Yield	$[\eta]^{a)}$	$x^{b)}$
	%	$dL \cdot g^{-1}$	
Nylon 6,10	50	0.45	1
PEA610(0.9)	55	0.51	0.91
PEA610(0.8)	62	0.67	0.86
PEA610(0.65)	85	0.73	0.70
PEA610(0.5)	60	0.82	0.65
Polyester 6,10	83	1.00	0
Nylon 12,10	59	0.67	1
PEA1210(0.5)	58	0.85	0.49
Polyester 12,10	70	1.10	0

[a] Intrinsic viscosity measured in dichloroacetic acid at 25 °C.
[b] Molar ratio CONH/(CONH + COO) as calculated from ^{1}H NMR spectroscopy.
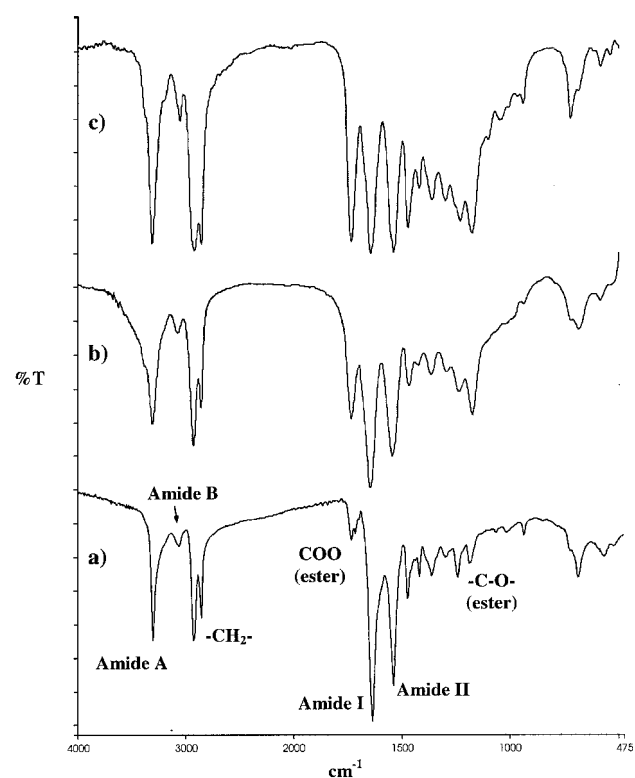

Figure 1. Infrared spectra of PEA610(0.9) (a), PE610(0.5) (b), and PEA1210(0.5) (c) samples.

the higher degree of polymerization of the oligomers prepared in the thermal polycondensation step ($p = 3$ for $x = 0.5$). Note also that the related polyesters have the highest molecular weights.

The infrared and NMR spectra of the polymers were fully consistent with the anticipated chemical constitution. Table 2 summarizes the main spectroscopic data, whereas representative spectra are shown in Figure 1 and 2. The infrared absorbances characteristic of ester groups (at ≈ 1734 cm^{-1} (C=O stretching) and in the 1 237–1 173 cm^{-1} range (C—O symmetry and anti-symmetry stretch-

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Table 2. Main spectroscopic data of the polymers studied in this work.

Infrared spectroscopy[a]	Amide A	Amide B	CH$_2$ (stretching)	OC=O (stretching)	Amide I	Amide II	C—O (stretching)
Nylon 6,10	3 302	3 063	2 927, 2 854	–	1 630	1 537	–
PEA610(0.9)	3 305	3 060	2 931, 2 855	1 732	1 635	1 539	1 241, 1 188
PEA610(0.8)	3 306	3 057	2 932, 2 855	1 733	1 635	1 540	1 240, 1 178
PEA610(0.65)	3 308	3 063	2 933, 2 857	1 732	1 635	1 539	1 240, 1 178
PEA610(0.5)	3 309	3 073	2 930, 2 858	1 734	1 644	1 542	1 235, 1 174
Polyester 6,10	–	–	2 930, 2 857	1 732	–	–	1 222, 1 177
Nylon 12,10	3 309	3 052	2 920, 2 850	–	1 634	1 536	–
PEA1210(0.5)	3 314	3 117	2 919, 2 852	1 716	1 638	1 540	1 204, 1 146
Polyester 12,10	–	–	2 919, 2 852	1 732	–	–	1 223, 1 180

^{1}H and ^{13}C NMR spectroscopy[b]	CONH ^{13}C	COO ^{13}C	OCH_2 ^{1}H	OCH_2 ^{13}C	NHCH_2 ^{1}H	NHCH_2 ^{13}C	NHCOCH_2 ^{1}H	NHCOCH_2 ^{13}C	OCOCH_2 ^{1}H	OCOCH_2 ^{13}C
Nylon 6,10	178.5	–	–	–	3.36	41.12	2.45	36.27	–	–
PEA610(0.9)	178.5	–	4.20	66.30	3.36	41.14	2.45	36.23	2.45	35.02, 34.48
PEA610(0.8)	178.5	178.3	4.20	66.29	3.36	41.14	2.46	36.19	2.46	35.00, 34.47
PEA610(0.65)	178.6	178.3	4.20	66.29	3.37	41.18	2.46	36.20	2.46	35.06, 34.48
PEA610(0.5)	178.6	178.4	4.20	66.29	3.37	41.20	2.46	36.15	2.46	35.04
Polyester 6,10	–	173.8	4.19	64.11	–	–	–	–	2.43	34.27
Nylon 12,10	180.2	–	–	–	3.59	43.96	2.76	34.39	–	–
PEA1210(0.5)	179.9	179.7	4.24	67.30	3.55	43.15	2.70	34.96	2.49	34.41, 34.12
Polyester 12,10	–	173.9	4.05	64.38	–	–	–	–	2.28	34.34

[a] Absorption bands in cm^{-1}.
[b] Chemical shifts in ppm and referred to TMS.

Table 3. Solubility of the synthesized polymers.

Solvent[a, b]	Nylon 6,10	PEA610 (0.9)	PEA610 (0.8)	PEA610 (0.65)	PEA610 (0.5)	PE 6,10	Nylon 12,10	PEA1210 (0.5)	PE 12,10
Water	1	1	1	1	1	1	1	1	1
Acetone	1	1	1	1	1	1	1	1	1
Ethanol	1	1	1	1	1	1	1	1	1
Diethyl ether	1	1	1	1	1	1	1	1	1
Ethyl acetate	1	1	1	1	1	1	1	1	1
Formic acid	5	5	5	5	5	1	5	5	1
DCA	5	5	5	5	5	5	5	5	5
TFA	5	3	3	3	3	5	5	4	5
Chloroform	1	2	2	2	2	5	1	2	5
CH$_2$Cl$_2$	1	2	2	2	2	5	1	2	5
CCl$_4$	1	2	2	2	2	5	1	2	4
DMSO	4	4	4	4	4	4	4	4	4
DMF	1	2	2	2	2	4	4	2	4
NMAA	4	4	4	4	4	4	4	2	4
Glycerin	1	1	1	1	1	4	4	2	4
1,4-Butanediol	4	4	4	4	4	4	4	4	4
MPD	4	4	4	4	4	4	4	4	4

[a] Abbreviations: DCA = dichloroacetic acid, TFA = trifluoroacetic acid, DMSO = dimethyl sulfoxide, DMF = N,N-dimethylform-amide, NMAA = N-methylacetamide, MPD = 2-Methyl-2,4-pentanediol.
[b] Number code: (1) Insoluble, (2) swelling, (3) partially soluble, (4) soluble when hot, (5) soluble.

ings)) logically diminish as the amide molar ratio x tends to 1.

^{1}H NMR spectra allowed us to determine the composition of the synthesized poly(ester amide)s. Thus, we used the area (I_1) of the peak corresponding to the —OCH_2— protons and the area (I_2) of the —NHCH_2— signal to obtain the amide molar ratio ($x = I_2/(I_1+I_2)$). The values calculated and reported in Table 1 are in close agreement with the feed ratio, although they are usually slightly higher than expected. This fact is more evident for the
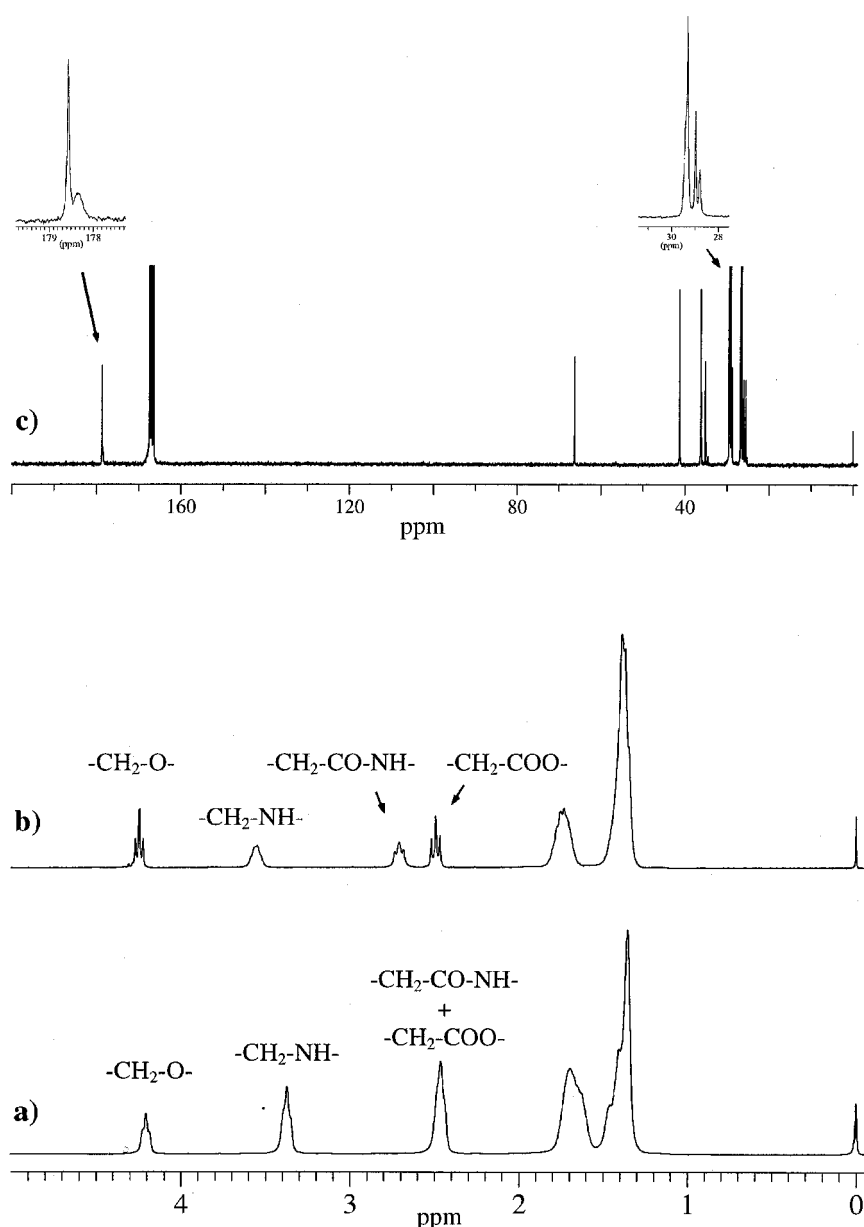
Figure 2. ¹H NMR spectra of PEA610(0.5) (a) and PEA1210(0.5) samples (b), and ¹³C NMR spectrum of PEA610(0.5) sample (c).

PEA610 series and may be due to some evaporation of the diol at the beginning of the condensation process.

Analysis of the type of sequences (random or block) could not be done from inspection of ¹³C NMR spectra due to the long units involved. Hence, only a splitting of the OCOCH$_2$— signal was significant. This is mainly observed in the spectrum of polymers with a high amide molar ratio and corresponds to the two possible linkages (ester or amide) for the second carboxylic group of the sebacic unit. In this sense, note that the oligoesters obtained after the first synthesis step should have a low degree of polymerization, as explained above.

Table 3 summarizes the behavior of the synthesized polymers in various solvents. Note that poly(ester amide)s show an intermediate behavior between the related polyamides and polyesters. It is significant that PEA610 samples swell in chlorinated solvents, such as chloroform, whereas polyester 6,10 and nylon 6,10 are soluble and insoluble, respectively. This fact clearly indicates that polyester chains are not present in the PEA610 samples.

Thermal Behavior

The calorimetric analysis of each polymer consisted of four DSC scans as shown in Figure 3 for PEA1210(0.5). In the first run, the samples coming directly from polymerization, were heated through fusion and left in the

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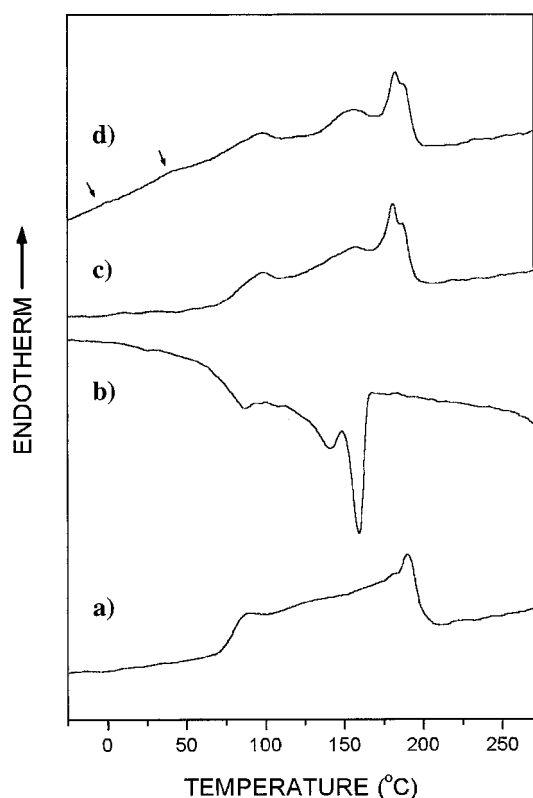
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Figure 3. Sequence of four DSC runs carried out with PEA1210(0.5) sample: a) heating run; b) cooling run after keeping the sample in the melt state for two minutes; c) reheating run; d) heating run after quenching the sample from the melt state. Arrows indicate glass transition temperatures.

to evaluate the crystallinity of polymers (solution- and melt-crystallized samples) taking into account the heats of fusion for 100% crystalline materials. These values were estimated from the reported[21] group contributions of ester (−2.5 kJ/mol), amide (2.0 kJ/mol), and methylene (4.0 kJ/mol). Temperatures indicative of the beginning of the decomposition process ($T_{d,0}$) and the 50% weight loss ($T_{d,1/2}$) were determined by thermogravimetry. Table 4 summarizes the main calorimetric parameters of the studied polymers. The following considerations can be remarked on:

1. Poly(ester amide)s PEA610 show only the fusion peaks of nylon 6,10. No trace of a peak near 66 °C (melting temperature of polyester 6,10) was detected, although the ester molar ratio could reach the value of 0.35 within the series. Thus, polymer chains seem to be constituted by blocks of polyamide and small segments containing ester groups. The former give rise to crystalline domains, whereas the latter are incorporated within amorphous regions. On the contrary, PE1210(0.5) shows a small fusion peak at 81 °C, which corresponds to the melting temperature of polyester 12,10. In this case, the segments with ester groups seem to be large enough to render crystalline domains. Note also, that the fusion of PE1210(0.5) corresponds to a very broad interval extending up to the melting temperatures of nylon 12,10 (Figure 4). Thus, in addition to polyester and polyamide domains, a population of crystals with an intermediate character must be present.

2. Poly(ester amide)s are crystalline over the whole range of studied compositions. Crystallinity decreases in the PEA610 series as the amide molar ratio does so too (from 1 to 0.65) for both solution- and melt-crystallized samples.

3. The melt processing of poly(ester amide)s is not hindered, since they are stable through fusion. Comparison of decomposition temperatures indicates a major stability for polymers with a higher amide molar ratio.

melt state for two minutes. Subsequent cooling was performed to observe crystallization from the melt. A second heating was carried out to check the reproducibility of the transitions and to obtain data for melt crystallized samples. In order to determine the glass transition temperatures, a third heating run was performed with samples quenched from the melt state. Heats of fusion were used

Table 4. Calorimetric data of polymers synthesized in this work.

Polymer	1st run			2nd run			3rd run			4th run	$T_{d,0}$	$T_{d,1/2}$
	T_f [a]	ΔH_f	χ[b]	T_c [a]	ΔH_c	T_f [a]	ΔH_f	χ[b]		T_g	°C	°C
	°C	kJ/mol	%	°C	kJ/mol	°C	kJ/mol	%		°C		
Nylon 6,10	*175*, 218	29.0	48	192	22.6	*171*, 217	24.0	40		86	370	485
PEA610(0.9)	*192*, 218	25.3	43	*129*, 188	21.8	*174*, 216	22.8	39		–	375	470
PEA610(0.8)	*183*, 217	21.2	36	187	19.1	*171*, 217	21.8	37		–	375	469
PEA610(0.65)	*181*, 213	20.0	35	*130*, 180	17.2	*173*, 212	18.6	32		−15	377	470
PEA610(0.5)	*191*, 218	15.4	27	182	14.4	*172*, 215	15.3	27		−12, 90	375	461
Polyester 6,10	66	30.7	60	47	20.7	70	22.6	44		−55	360	435
Nylon 12,10	192	27.5	33	176	23.5	184, *194*	24.5	29		52	400	485
PEA1210(0.5)	*81*, 190	29.7	37	*85*, *138*, 160	24.0	*97*, *155*, 181, *189*	24.0	30		−6, 48	381	459
Polyester 12,10	84	38.9	52	63	38.6	85	40.3	54		−50	366	452

[a] When multiple peaks are observed, the temperature of the peak with lower heat of fusion or crystallization is indicated by italics.
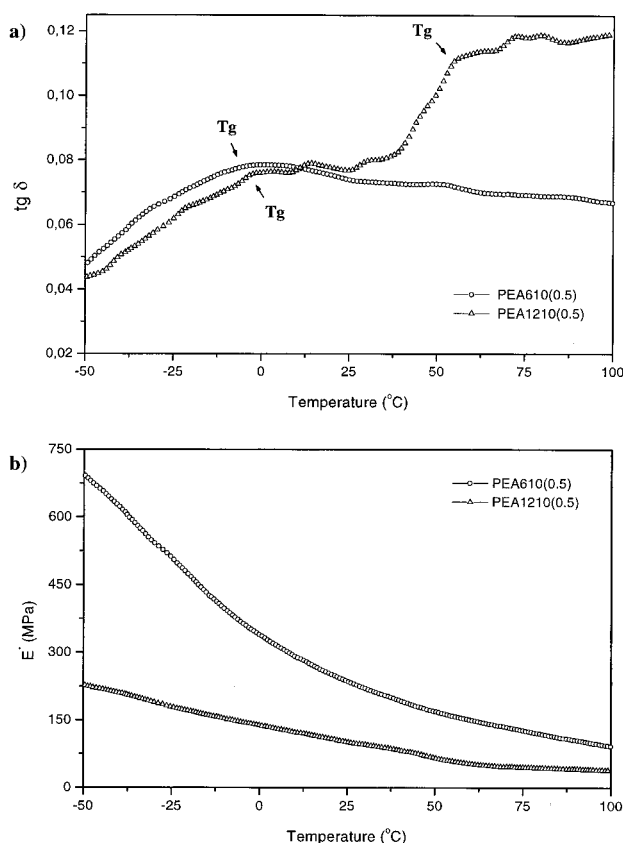[b] Crystallinity.

a)

b)

Figure 4. a) Loss term tan δ as a function of temperature for the poly(ester amide)s: PEA610(0.5) and PEA1210(0.5). Apparent glass transition temperatures are indicated by arrows. b) Complex modulus E^* reported as a function of temperature for the poly(ester amide)s: PEA610(0.5) and PEA1210(0.5).

4. Glass transition temperatures of poly(ester amide)s are hardly observed. In general, DSC baselines show two discontinuities that correspond to the glass transition temperature of the related polyamide and a value close to $-10\,^{\circ}$C. This is higher than the transition temperature of the related polyester and close to the expected value for a poly(ester amide).

Dynamic-mechanical behavior was also studied to determine glass transition temperatures. Data for PEA610(0.5) and PEA1210(0.5) are reported in Figure 4. Both polymers show a wide dissipation band in the tan δ function and a continuous decrease of the complex modulus E^*. This feature is an indication of a glass transition widely expanded in the temperature scale and suggests an intermediate situation between monophasic and biphasic amorphous regions. The lower temperature of the glass transition range is about $-12\,^{\circ}$C and $-4\,^{\circ}$C for PEA610(0.5) and PEA1210(0.5) samples, respectively, whereas the higher temperature is about $54\,^{\circ}$C for PEA1210(0.5). These observations are in good agreement with the DSC calorimetric results.

Table 5. Stress-strain parameters of synthesized poly(ester amide)s.

Polymer	Young's modulus	Tensile strength	Elongation at break
	MPa	MPa	%
PEA1210(0.5)	296	29	22
PEA610(0.5)	473	37	17
PEA610(0.65)	501	39	14
PEA610(0.8)	721	48	12
PEA610(0.9)	805	57	10
Nylon 6,10	910	59	10

Mechanical Properties

Stress-strain data (Table 5) show that the new poly(ester amide)s have elastic and plastic deformation regions, and that some differences can be detected depending on the amide molar ratio and the nature of the monomers. Thus, Young's modulus and the tensile strength decrease in the PEA610 series as the amide content does so too. In the same way, the elongation at break increases. These observations are the consequence of the different intermolecular interactions involving the ester and amide groups and reflect the drop in tensile properties between a polyester and its related polyamide. Note also that the increase in the methylene content (PEA1210(0.5) versus PEA610(0.5)) reduces both the modulus and the strength, since polymer composition resembles polyethylene only where weak van der Waals intermolecular interactions exist. Moreover, the measured values for Young's modulus are characteristic of partially crystalline materials essayed at temperatures above their glass transition temperature. Thus, the ester moieties act as a plasticizer that reduces the temperature at which chain mobility is apparent (from the $50-90\,^{\circ}$C range characteristic of nylons to a value close to $-10\,^{\circ}$C).

X-Ray Diffraction

X-ray powder patterns of poly(ester amide)s PEA610 (Figure 5a) show strong well-defined rings that demonstrate the crystalline character of these materials. The patterns are similar to the reported ones for the sheet structures (α- or β-forms) of nylon 6,10.[22] Spacings (i.e., 4.42 Å and 3.72 Å for 100 and 010 reflections, respectively) and relative intensities did not appreciably change with variations on the amide molar ratio within the 1–0.65 range. Oriented fibers could also be obtained from the melt after annealing under steam. Their X-ray diffraction patterns also show the above mentioned reflections with an equatorial orientation and the appearance of layer lines with streaks indicative of α/β mixtures (Figure 5c). However, the α-form is clearly predominant as shown by the well defined 002 off-meridional reflection. Powder patterns also show a very weak ring close to 4.10 Å that
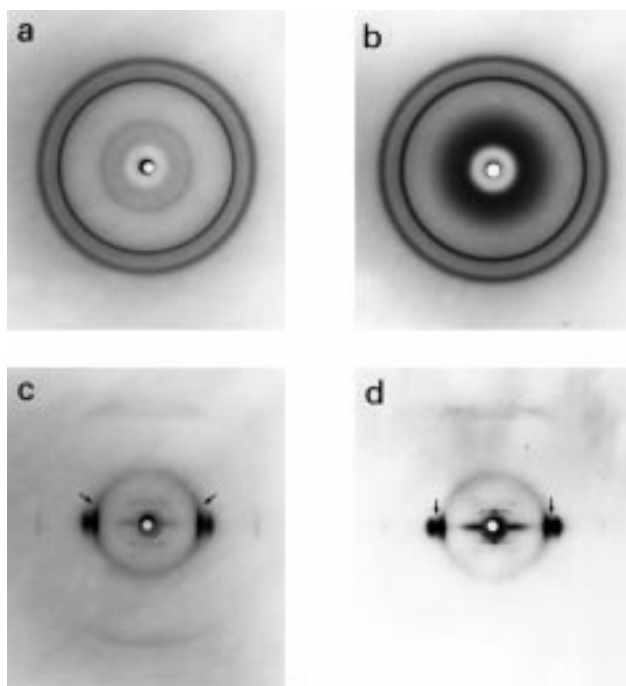
Figure 5. Powder (a, b) and fiber (c, d) X-ray diffraction patterns of PEA610(0.5) (a, c) and PEA1210(0.5) (b, d) samples. Arrows in the fiber patterns indicate the reflection close to 4.10 Å. Specimen to film distances: 5 cm.

could be assigned to an $hk2$ reflection, considering its non equatorial orientation in the fiber patterns. Thus, no trace of a polyester structure was found in the X-ray diffraction patterns. A fact that is consistent with the absence of a polyester 6,10 fusion peak (close to 66 °C). As discussed above, poly(ester amide)s PEA610 seem to be composed of blocks of polyamide (responsible for the observed melting peaks and diffraction reflections) and small segments with ester groups.

The crystalline character and the ability to give oriented fibers of the poly(ester amide) PEA1210(0.5) are

also worth noting (Figure 5 b and d). The main reflections (11.3 Å, 4.44 Å, and 3.75 Å, indexed as 100, 010, and 002, respectively) correspond to the α-structure of nylon 12,10.[20] However, in this case it is interesting to mention the appearance of an equatorial reflection at ≈ 4.12 Å and a meridional reflection in the second layer line (14.45 Å) that may be related to either an orthorhombic polyester structure or the monoclinic structure (γ-form) found in some nylons.[23] The former possibility appears to be more feasible, since the γ-form is not characteristic of even-even nylons. In particular, it could not be detected in previous structural studies on nylon 12,10.[20] Furthermore, the 002 spacing indicates a practically all-trans conformation which is not in agreement with the γ-form. Thus, PEA1210(0.5) has microcrystals with both a polyamide and a polyester structure. Some ester moieties are likely to be long enough to form these crystalline domains. Note in this sense that a melting peak associated to polyester 12,10 (81 °C) was found in the DSC scans.

Degradation Studies

Hydrolytic degradation under simulated physiological conditions was studied for all the synthesized polymers. The results obtained indicated that no significant weight losses were detected in the different plate samples after 210 d of exposure. However, intrinsic viscosities clearly decreased (Figure 6), indicating that degradation took place. Moreover, the evolution of intrinsic viscosity was slightly distinct for the different studied samples. Thus, polyesters showed a higher degradation rate than nylons, whereas the highest rate was found for poly(ester amide)s, probably as a consequence of their lower crystallinity. PEA1210(0.5) was degraded more slowly than the related PE610(0.5), as expected from its lower hydrophilicity. Note also that the ratio between polar (amide and ester) and methylene groups decreased.
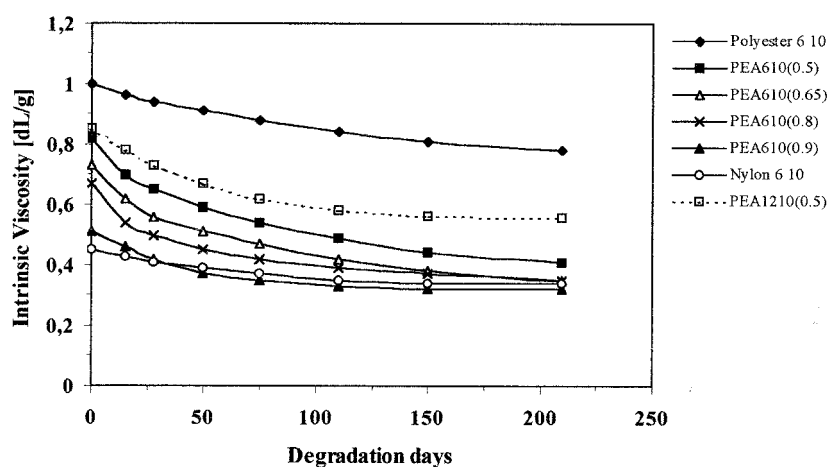

Figure 6. Plot of intrinsic viscosity versus degradation time in a pH 7.4 sodium phosphate buffer at 37 °C for PEA1210(0.5) (- - -) and the series of poly(ester amide)s PEA610 (—). Data for nylon 6,10 and polyester 6,10 are also included as reference.
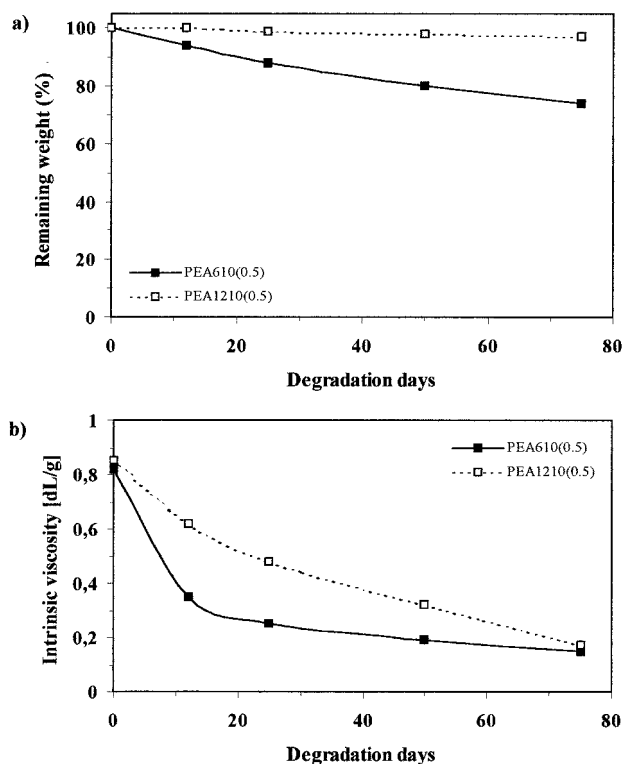
Figure 7. Plot of remaining weight (a) and intrinsic viscosity (b) versus degradation time under accelerated conditions (distilled water at $70\,^{\circ}$C) for PEA610(0.5) and PEA1210(0.5) samples.

Figure 7 compares the degradation of PEA610(0.5) and PEA1210(0.5) plate samples under the accelerated hydrolytic conditions provided by raising the temperature up to $70\,^{\circ}$C. In this case, weight loss was significant for PEA610(0.5). A value close to 26% was determined after 75 d of exposure, whereas only 3% of the PE1210(0.5) sample was solubilized after the same degradation time. However, intrinsic viscosity measures (Figure 7b) show that both samples are similarly degraded after the indicated period, and consequently the weight loss differences might be mainly attributed to a minor solubility of the PEA1210(0.5) degradation products.

Intrinsic viscosity profiles (Figure 7b) show also a different behavior for the two samples. Thus, it is worth noting that PE610(0.5) degrades very fast at the beginning of exposure and then (after 18 d) viscosity smoothly decreases. The change in the intrinsic viscosity of PEA1210(0.5) is more gradual, since its degradation is delayed by its low hydrophilicity.

Spectroscopic analysis demonstrated that degradation mainly takes place through the hydrolysis of ester groups. Thus, IR data of PEA610 series show a decrease in carbonyl ester absorption intensity, whereas amide absorptions remain practically unchanged (Figure 8a). In the same way, changes in NMR spectra mainly correspond to the CH_2O— signal. Note the new small peaks near 4.20 ppm that may be attributed to different degradation products
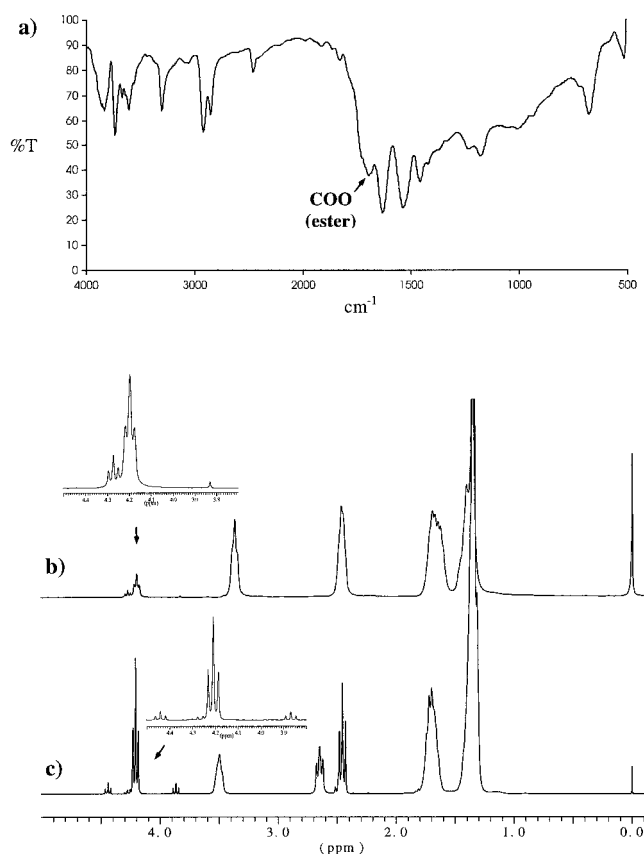

Figure 8. (a) Infrared spectra of PEA610(0.5) after 75 d of degradation under distilled water at $70\,^{\circ}$C. ^{1}H NMR spectra of PEA610(0.5) (b) and PEA1210(0.5) (c) samples after 75 d of degradation under accelerated hydrolytic conditions. Insets correspond to signals related to the —CH_2O— protons.

(Figure 8b and c). Furthermore, PEA610(0.5) shows a decrease in the intensity of signals attributed to CH_2O—, which is in agreement with the solubilization of degradation products. In this way, the amide molar ratio increases to 0.8 for the PEA610(0.5) sample. On the contrary, no significant solubilization was detected in the degradation of PEA1210(0.5). Consequently, the amide molar ratio remains practically constant when all signals attributed to the different CH_2O— groups are considered to evaluate the I_2 area.

The texture of PEA610 and PEA1210 samples after degradation is also quite different. Thus, the initially transparent PEA1210(0.5) plates become opaque, whereas PEA610(0.5) samples remain transparent. In the same way, PEA610(0.5) plates become very brittle during exposure. Scanning electron micrographs (Figure 9) also reveal a distinct surface degradation process for the two polymers. Thus, a great number of deep fissures appear on the surface of PEA610(0.5) samples, whereas the surface of PEA1210(0.5) plates becomes rough and appears to chip off.

Degradation of poly(ester amide)s was also studied with different media containing enzymes with an estear-
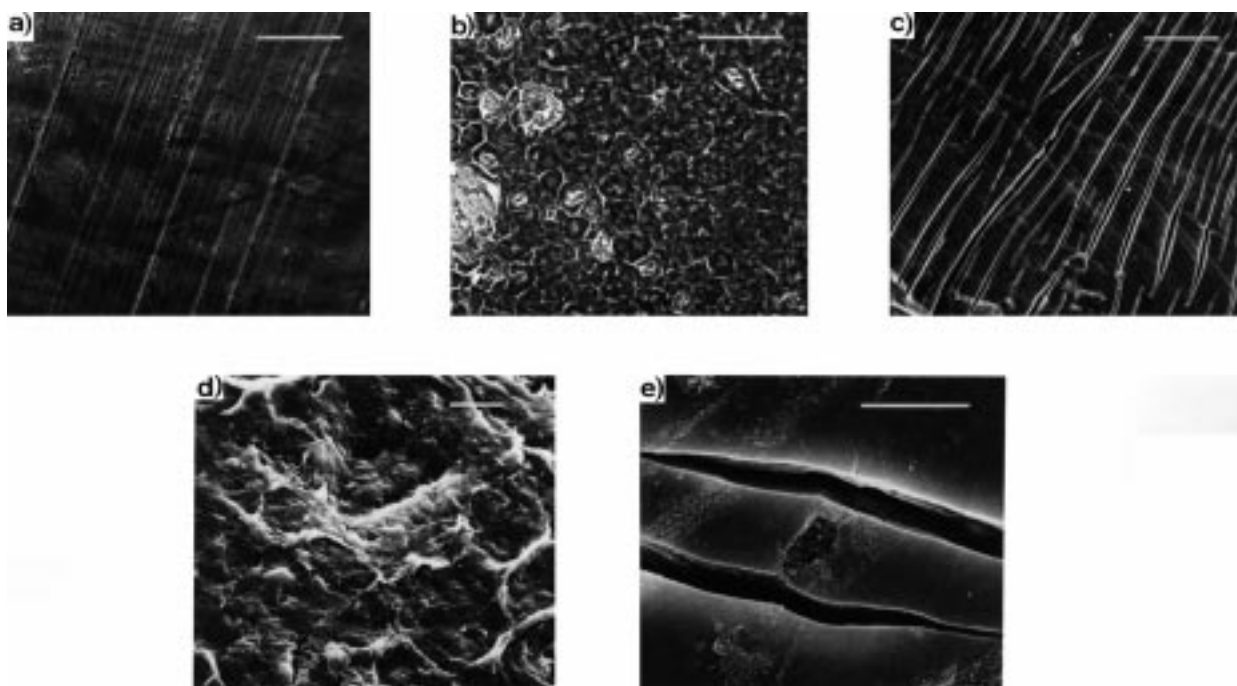
Figure 9. Scanning electron micrographs of: (a) Surface of a PEA1210(0.5) plate before hydrolysis; (b) and (d) PEA1210(0.5) plate after 75 d of incubation under distilled water at 70 °C; (c) and (e) PEA610(0.5) plate after 75 d of incubation under accelerated hydrolytic conditions. Scale bars: 100 µm (a, b, and c) and 10 µm (d and e).
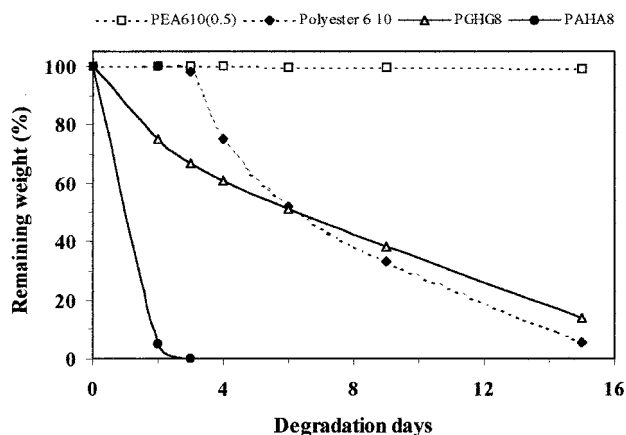

Figure 10. Plot of remaining weight (%) of PEA610(0.5), polyester 6,10 and poly(ester amide)s derived from glycine (PGHG8) and alanine (PAHA8) versus degradation time in different enzymatic media: lipase from *pseudomonas cepacia* (- - -) and papain (—). PGHG8 and PAHA8 data correspond to powder samples.[24]

ase (lipases from *Pseudomonas cepacea* or *Rizophus delemar*) or a protease (papain) activity. The weight of the samples remained practically constant for a 15 d exposure period, indicating that this kind of polymers is scarcely susceptible to the enzymatic attack. On the contrary, polyesters were easily degraded by lipases from *Pseudomonas cepacea* after a short induction time of three days (Figure 10). Thus, the increase of amide components (nylon 6,10 or 12,10) considerably reduces the degradation rate in the estearase enzymatic medium.

The stability of the studied poly(ester amide)s in protease enzymatic media contrasts with our previous results[24] obtained for sequential poly(ester amide)s derived from 1,6-hexanediol, sebacic acid and α-amino acids as glycine (PGHG8) or L-alanine (PAHA8), and characterized also by an amide molar ratio of 0.5. For comparison purposes, Figure 10 plots the results obtained with papain, which clearly demonstrated that α-amino acids are fundamental to enhance degradability in this kind of enzymes.

Conclusions

The results reported in this work can be summarized as follows:

1. Poly(ester amide)s related to nylons 6,10 or 12,10 and polyesters 6,10 or 12,10, respectively, could be obtained with high yields by interfacial polymerization. Polymers have adequate molecular weights to render film and fiber-forming properties.

2. New poly(ester amide)s show a complex melting behavior. However, fusion peaks characteristic of the related polyamides were always found. Consequently, these polymers may be used at higher temperatures than parent polyesters.

3. The hydrolytic degradation rate of the new poly(ester amide)s depends on the amide molar ratio and the nature of monomers. Thus, the decrease of the ratio and the increase in hydrophilicity enhance degradability.

4. New poly(ester amide)s do not seem susceptible to enzymatic degradation. The stability towards proteolytic enzymes contrasts with previous results obtained with related poly(ester amide)s derived from α-amino acids.

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