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Poly(ester amide)s derived from 1,4-butanediol, adipic acid and 6-aminohexanoic acid. Part II: composition changes and fillers

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Abstract

BAK poly(ester amide)s differing in the amide/ester ratio have been synthesized and characterized, considering spectroscopic data and both thermal and mechanical properties. Degradability under different media (water at 70 °C, acid or enzymatic catalysis at 37 °C) has also been studied by evaluating the changes in intrinsic viscosity, in the NMR spectra and in the surface texture of samples. The use of chain extenders, such as hexamethylene diisocyanate and 1,3-butadiene diepoxide, has been investigated and the optimal reaction conditions are reported here. Changes on mechanical properties due to the incorporation of biodegradable reinforces have also been evaluated. Finally, the synthesis and determination of thermal properties of related poly(ester amide)s constituted by glutaric or succinic acid instead of adipic acid have been investigated.

Keywords: Degradability; Poly(ester amide)s; Chain extenders

1. Introduction

Some polyesters and poly(ester amide)s have recently been developed as degradable materials with applications as commodities. BIONOLLE®, an aliphatic polyester mainly constituted by 1,4-butanediol and succinic acid [1–3], and EASTAR BIO®, a copolyester based on 1,4-butanediol, adipic acid and terephthalic acid are examples of the first group. The incorporation of the succinate and the aromatic units provides acceptable melting temperatures for this kind of polyesters. In the same way, strong intermolecular hydrogen bond interactions can improve thermal and mechanical properties and enhance the interest towards poly(ester amide)s.

In this way, BAK 1095® is an example of a poly(ester amide) that has recently been patented [4,5] and commercialised. This is a statistical polymer with an amide/ester ratio of 6/4 that is prepared by thermal polycondensation from 1,4-butanediol, adipic acid and caprolactame. Other aliphatic poly(ester amide)s constituted by some of these units have also been studied by different groups [6,7]. Basic characterization of BAK 1095® taking into account structural data, thermal and mechanical properties, and degradability in different aqueous and enzymatic media has been reported [8]. In the same way, the preparation of biocomposites based on a BAK 1095 matrix and lignocellulosic natural fibers [9] has been considered.

The influence of the monomer distribution (regular or random) on the polymer degradability has also been evaluated [8], indicating the results that polymers with regular sequences have a worse degradation rate. In this work, we study the effect of the amide/ester ratio on degradability and properties. Thus, we prepared two new derivatives with a higher (70/30) and lower (50/50) amide/ester ratio than the commercial sample. The theoretical amide/ester ratio will be used to name these new polymers (i.e. BAK 70/30).

Properties can also be improved with an increase of molecular weight, and consequently we have studied the applicability of different chain extenders. Changes on the polymer composition by adding natural reinforces or using different dicarboxylic derivatives are also evaluated. The possibility to introduce succinic or glutaric units in the polymer chain appears interesting due to the fact that they can be easily metabolised by microorganisms. The synthesis of glutaric (BGK) and succinic (BSK) derivatives related to BAK 1095 was also essayed. For the sake of completeness,

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we synthesized polymers described by the sequence:

$$-[NH(CH_2)_5CO-O(CH_2)_4O-CO(CH_2)_5 NH-CO(CH_2)_nCO]- \quad (n = 2, 3)$$

which are named as PAHBAHn taking into account the abbreviation previously used for related compounds [8] that describe sequence and composition: P, polymer; AH, aminohexanoic unit; B, 1,4-butanediol unit and 2 or 3, number of methylene carbons of the dicarboxylic unit.

2. Experimental section

2.1. Synthesis of BAK polymers

BAK 70/30 and 50/50 were synthesized following literature data for BAK 1095 [4].

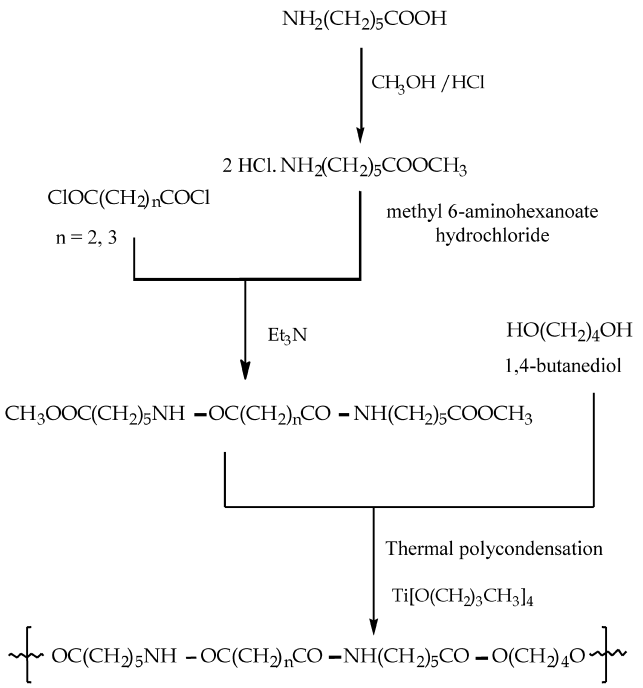
A two-neck, round bottom flask equipped with a magnetic stirrer and a condenser was charged with adipic acid (0.02 mol), 6-aminohexanoic acid (0.04 or 0.093 mol for BAK 50/50 or 70/30, respectively) and an excess of 1,4-butanediol (0.04 mol). Titanium butoxyde (0.3 mol%) was also added as a catalyst for the condensation reaction. The flask was heated in an oil bath at 190 °C in order to melt the mixture and begin the esterification reaction. Meanwhile, a slow stream of nitrogen was passed to help eliminate water and the excess of diol. After two hours, the second neck was connected to a vacuum pump (0.3 mm Hg) while the temperature of the bath was raised to 220 °C. In order to improve the removal of the diol, the reaction was periodically stopped (every hour) by cooling it at room temperature, and then the diol that had condensed in the flask wall was removed. The reaction was prolonged until no more diol was distilled off (4–5 h). After cooling down, the polymer was dissolved in formic acid, precipitated by a dropwise addition of ether, filtered and repeatedly washed with acetone, water and ethyl ether.

2.2. Synthesis of BSK and BGK

Polymers were synthesized following the same procedure explained for BAK polymers, varying only the monomer composition and ratio. Thus, 0.02 mol of glutaric acid or succinic acid, 0.06 mol of 6-aminohexanoic acid and an excess of 1,4-butanediol (0.04 mol) were employed.

2.3. Synthesis of succinic and glutaric derivatives with a sequential distribution

PAHBAH3 and PAHBAH2 were synthesized according to the thermal polyesterification method previously established for PAHBAH4 [8] and some glycine derivatives [10], as outlined in Scheme 1.



Scheme 1. Synthesis of PAHBAHn polymers.

2.3.1. N,N′-Bis(methoxycarbonylpentamethylene) glutaramide and N,N′-bis(methoxy-carbonylpentamethylene)succinamide

A round bottom flask equipped with a dropping funnel and a magnetic stirrer was purged with N_2 and charged with methyl 6-aminohexanoate hydrochloride (0.04 mol), triethylamine (0.08 mol) and 50 ml of chloroform. Then, 0.02 mol of glutaroyl or succinoyl chloride dissolved in 20 ml of chloroform were slowly added for 90 min, while the reaction was kept at 0 °C by means of an ice water bath. The reaction was prolonged for an additional period of 3 h at room temperature. The chloroform solution was extracted with 3 × 15 ml of water, dried with anhydrous sodium sulphate, filtered and evaporated under reduced pressure. The resulting solid was washed with ethyl ether and recrystallized from ethanol/water (1/2, v/v).

N,N′-Bis(methoxycarbonylpentamethylene)glutaramide. Yield: 44%. Mp: 93 °C. ^{1}H NMR ($CDCl_3$, TMS, int. ref.): δ 7.89 (m, 2H, NH), 3.75 (s, 6H, CH_3), 3.38 (m, 4H, CH_2NH), 2.61 (t, 4H, NHCOCH_2), 2.42 (t, 4H, OCOCH_2), 2.02 (m, 2H, CH_2CH_2CONH),1.62 (m, 8H, CH_2CH_2NH + OCOCH_2CH_2), 1.35 (m, 4H, OCOCH_2CH_2CH_2).

N,N′-Bis(methoxycarbonylpentamethylene)succinamide. Yield: 47%. Mp: 105 °C. ^{1}H NMR ($CDCl_3$, TMS, int. ref.): δ 8.09 (m, 2H, NH), 3.77 (s, 6H, CH_3), 3.39 (m, 4H, CH_2NH), 2.84 (t, 4H, NHCOCH_2), 2.43 (t, 4H, OCOCH_2), 1.61 (m, 8H, CH_2CH_2NH + OCOCH_2CH_2), 1.37 (m, 4H, OCOCH_2CH_2CH_2).

2.3.4. Thermal polyesterification

A two-neck, round bottom flask equipped with a magnetic stirrer and a condenser was charged with 1,4-butanediol

(0.025 mol) and N,N′-bis(methoxycar-bonylpentamethylene)glutaramide (0.01 mol) or *N*,*N*′-bis(methoxycar-bonylpentamethylene)succinamide (0.01 mol). Titanium butoxyde was also added as a catalyst for condensation reaction. The polycondensation was carried out as indicated for BAK compounds, using a temperature of 150 °C for the step under the N_2 stream (2 h) and 180 °C for the step under vacuum (6 h). After cooling down, the polymer was dissolved in a mixture of formic acid/TFA (9/1, v/v), precipitated by a dropwise addition of ether, filtered and repeatedly washed with acetone and ethyl ether.

2.3.5. Chain-extended BAK polymers

An homogeneous mixture of the BAK poly(ester amide) (500 mg) and the appropriate chain extender was prepared by dissolution in chloroform (4 ml). Solutions were stirred at 50 °C during 30 min, and then the solvent was evaporated under vacuum. Chain extender reaction was carried out under vacuum at 180 °C, varying both reaction time and the mass percentage of chain extender.

2.4. Characterization

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 prepared by evaporation of formic acid solutions. NMR spectra of polymers were registered from deuterated chloroform/trifluoroacetic acid solutions. Chemical displacements 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 Perkin–Elmer DSC-PYRIS 1, using indium metal for calibration. Heating and cooling runs were performed under a flow of dry nitrogen at 20 °C/min and 10 °C/min, respectively.

Dynamic-mechanical behavior was analyzed using a rheometrics, PL-DMT MK3 instrument. After a rapid cooling, the dynamic spectrum was detected on heating the sample at 2 °C/min in the temperature range − 150 to 120 °C. Complex modulus and tan δ were obtained as a function of temperature.

Samples for mechanical and degradation studies were cut off from regular films of 200 μm of thickness prepared by melt pressing 200 mg of the appropriate polymer at a temperature of 10 °C below fusion. Plate samples with a length of 30 mm and a width of 3 mm were used for the evaluation of mechanical properties, whereas plates of 15 mm × 15 mm were usually employed in the degradation experiments. Samples of 25 mm × 10 mm and a thickness of 450 μm were similarly prepared by melt pressing and used in the dynamic-mechanical studies.

Mechanical properties were determined with a Zwick Z2.5/TN1S testing machine in stress–strain experiments, which were carried out at a deformation rate of 10 mm/min. Mechanical parameters were averaged from a minimum of ten measurements for each polymer sample.

Hydrolytic degradation assays were carried out under accelerated conditions provided by distilled water at 70 °C or a pH 2.3 sodium citrate buffer at 37 °C. Each plate was kept in a bottle 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. The remaining samples were dried to constant weight under vacuum, and stored over $CaCl_2$ before analysis. Enzymatic degradation studies were conducted at 37 °C by using a lipase from *Pseudomonas cepacia* (LPC), and proteinase K as a proteolytic enzyme. The enzymatic media, 10 ml, consisted of a pH 7.4 sodium phosphate buffer containing sodium azide (0.03 wt%) and 1 mg of the appropriate enzyme. All enzymatic solutions were renewed every 72 h because of enzymatic activity loss. After the immersion time, the retrieved samples were immersed in a HCl solution, rinsed with water, and dried as indicated for hydrolytic experiments.

Mass loss, intrinsic viscosity, changes in NMR spectra and mechanical properties were evaluated in these hydrolytic and enzymatic degradation studies.

Scanning electron microscopy was employed to examine the changes in the texture of samples after degradation. Gold coating was accomplished by using a Balzers SCD-004 Sputter Coater. The SEM micrographs were carried out with a JEOL JSM-6400 instrument.

3. Results and discussion

3.1. Synthesis and characterization

The molecular weight of BAK polymers were highly sensitive to the polymerization conditions; for example: addition of catalyst, the least possible polymerization time under the nitrogen stream in order to get non-volatile compounds, optimal time and temperature under vacuum to extend the polycondensation reaction and also to avoid the thermal decomposition. Thus, a slight brown coloration and a moderate intrinsic viscosity were attained after long reaction times and high temperatures. Although batches with different molecular weight were obtained, the higher intrinsic viscosities were 0.73 and 0.94 dl/g for BAK 50/50 and 70/30, respectively. The latter very close to the value of 1.04 dl/g for commercial BAK 1095.

New polymers were soluble, as usual, in strong acids such as formic, trifluoroacetic or dichloroacetic. A good solubility was also found in dimethylsulfoxide dimethylformamide and chloroform. However, the most remarkable feature was the ability of ethanol to dissolve BAK 50/50 at room temperature, and the 60/40 and 70/30 compositions at

higher temperatures. The infrared spectra were similar for all polymers with the characteristic amide, ester and methylene bands (Fig. 1). However, it is interesting to point out the small band at 3379 cm^{-1} clearly visible for the 50/50 composition, and detected as a small shoulder in BAK 70/30. This absorption, is attributed to the NH stretching mode in amide–ester hydrogen bond interactions, which seems to be established in addition to the characteristic amide–amide interactions.

^{1}H NMR spectra of the new polymers are similar to the reported one for BAK 60/40 [8], being determined the amide/ester content from the area ratio of the signals observed at 3.52 (CH_2NH) and 4.24 ppm (CH_2O). Experimental values agree with the expected composition of BAK 70/30, but a slight decreasing on aminohexanoic residues was found for BAK 50/50 giving an experimental ratio of 45/55. Although this value was used for all calculations, the polymer denomination based on the feed ratio was kept.

Multiple peaks are observed for the most significant carbons in the ^{13}C NMR spectra, as shown in Fig. 2 for the CO (182–180 ppm), CH_2O (69–67 ppm), CH_2NH (45–43 ppm) and CH_2CO (36–35 ppm) carbons. This feature is consequence of the sensibility to the different neighbours and clearly indicate a non-block distribution. In the previous paper [8], a sequence assignment was performed for the indicated methylenic carbons. However, the interpretation of the carbonylic carbon region was not possible due to its great complexity. Note that carbonyls of adipic and aminohexanoic units are different and furthermore their signals are split due to the neighbouring effect. Comparative data between the three BAK compositions, and data for polyester 4 6 (180.63 ppm), nylon 6 (181.25 ppm) and PAHBAH4 (180.79 and 180.47 ppm) allow us to give the assignment reported in Table 1. Deconvolution was performed for each group of signals, and the relative area percentages were compared with those calculated from the monomer composition and the assumption of both a statistical distribution and the logical chemical bond restrictions. Experimental and theoretical values, summarized also in Table 1, show a good agreement for the three BAK compositions.

All attempts to synthesize BSK and BGK samples were unsuccessful due to a secondary cyclization reaction that produces succinimide or glutarimide rings (Scheme 2(a)) and stops polymerization. This side reaction is clearly favoured in the temperature range required for polycondensation [11]. Furthermore, it is easily produced by the nucleophilic attack on the CO acid or ester carbon by the neighbouring amidic nitrogen. This feature is characteristic of the first stages of polymerization, and consequently the reaction medium did not become viscous during the step carried out under vacuum. A fact that is in clear disagreement with the behavior observed in the BAK syntheses. The ^{1}H NMR spectra (Fig. 3(a)) of samples recovered after precipitation of formic acid solutions with ethyl ether show signals at 2.68 ($NCOCH_2$) and 2.05 ($NCOCH_2CH_2$) ppm, and 2.95 ($NCOCH_2$) ppm that are attributed to the glutarimide and succinimide rings, respectively. Furthermore, hydroxyl and carboxyl terminal groups are clearly detected. Imide ring formation and polymerization seem to compete and oligomers are recovered from the reaction medium.

In order to avoid the imide ring formation, we have synthesized the sequential PAHBAH2 and PAHBAH3 samples. In this case, a monomer is previously prepared with the succinic and glutaric units linked through amide bonds to two methyl 6-hexanoate units. Although polycondensation progress and the reaction medium becomes

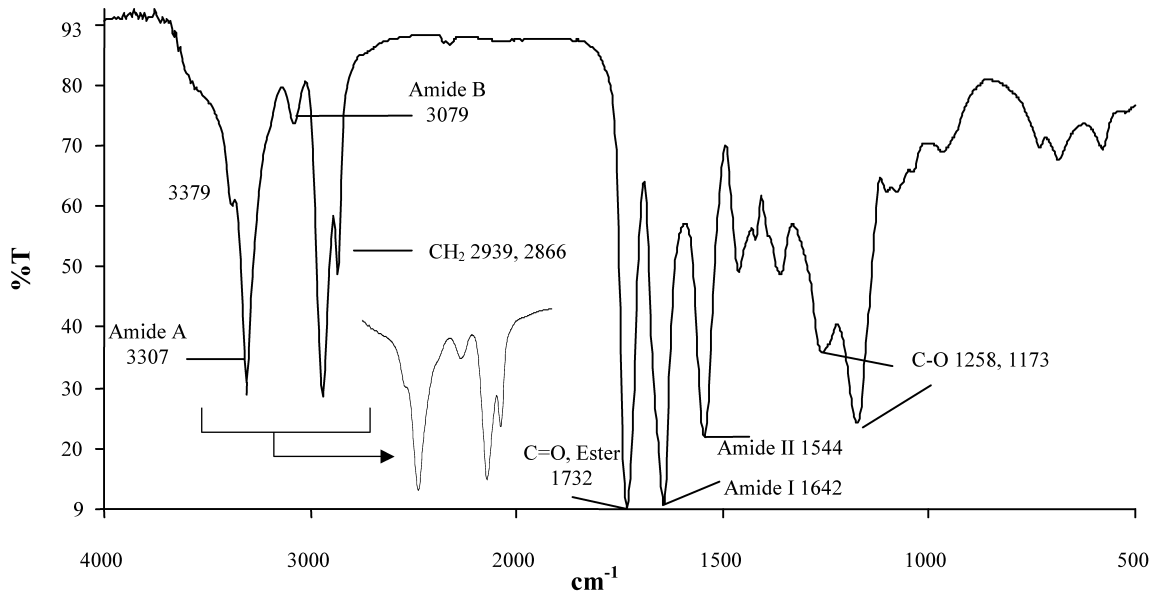


Fig. 1. Infrared spectrum of BAK 50/50 with labelling of most significant signals. Amide A absorption band of BAK 70/30 is also shown in the inset to manifest the lower intensity of the peak at 3379 cm^{-1}.

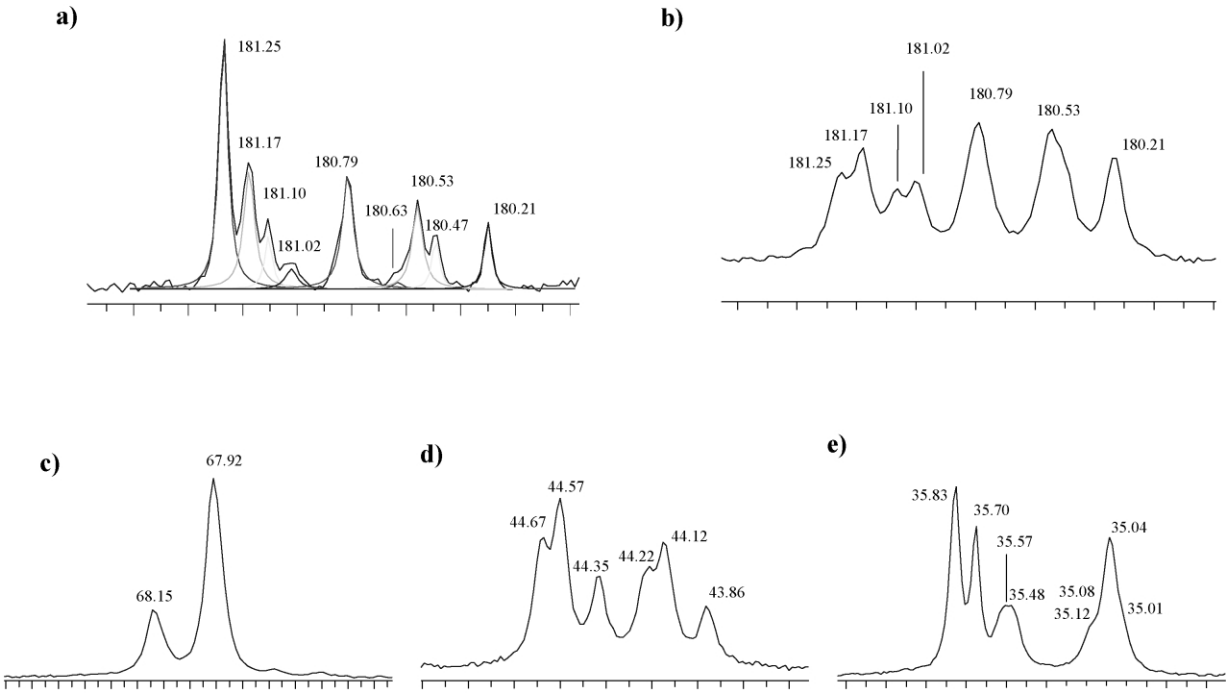
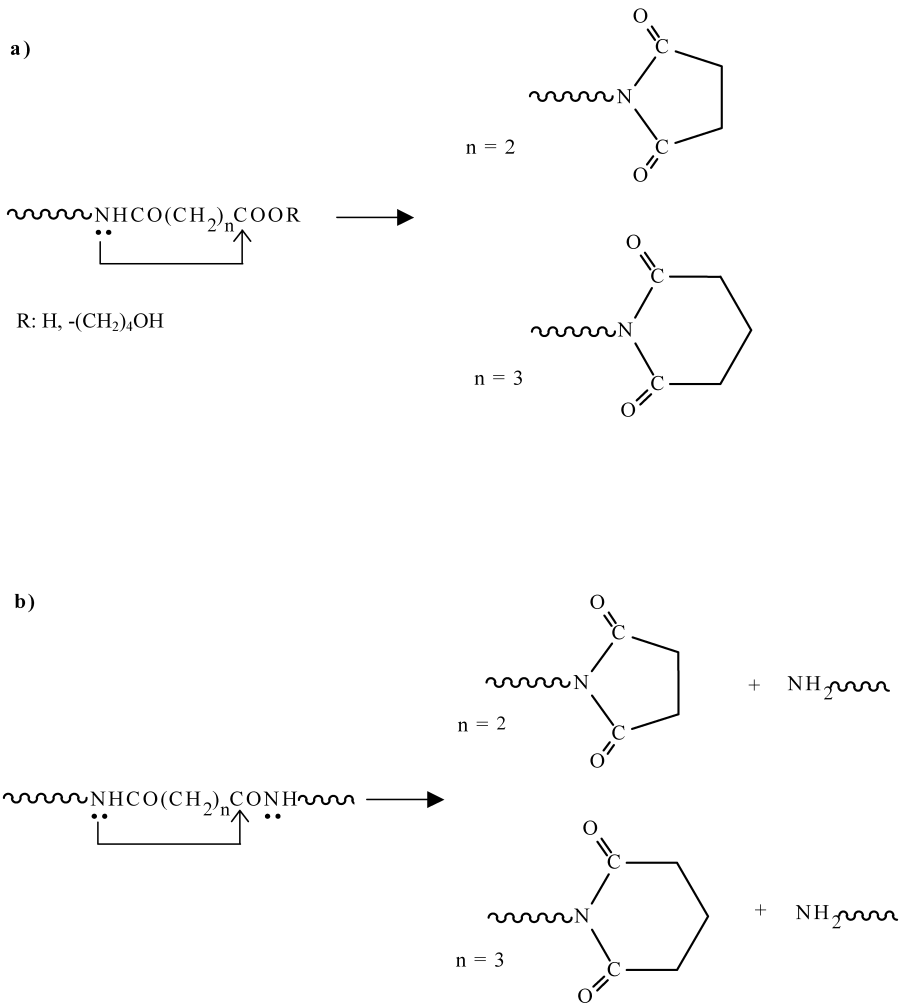


Fig. 2. ^{13}C NMR spectra of BAK 70/30 (a) and 50/50 (b)–(e) showing zones associated to the CO (a),(b), $-CH_2O$ (c), $-CH_2NH$ (d) and $-CH_2CO$ (e) carbons. Deconvolution of signals is indicated only for (a).

Table 1
Chemical shifts, assignments and ratio areas of the ^{13}C NMR spectra of BAK polymers with different amide/ester (A/E) ratios

Sequence	δ (ppm)	Experimental ratio area (%)			Ratio area (%) for a random distribution		
		A/E: 70/30	A/E: 60/40	A/E: 50/50	A/E: 70/30	A/E: 60/40	A/E: 50/50
…CO–NH(CH_2)$_5$*C*O–NH(CH_2)$_5$CO–NH…	181.25	30	22	9	34.3	21.6	9.1
…CO–NH(CH_2)$_5$*C*O–NH(CH_2)$_5$CO–O…	181.17	17	} 21	14	14.7	14.4	11.1
…O–CO(CH_2)$_4$*C*O–NH(CH_2)$_5$CO–NH…	181.10	6		6	4.4	5.8	6.1
…O–CO(CH_2)$_4$*C*O–NH(CH_2)$_5$CO–O…	181.02	3	3	7	1.9	3.8	7.5
…CO–NH(CH_2)$_5$*C*O–O…	180.79	18	23	24	21	24	24.7
…O–CO(CH_2)$_4$*C*O–O…	180.63	4	8	} 27	2.7	6.4	16.6
…NH–CO(CH_2)$_4$*C*O–NH(CH_2)$_5$CO–NH…	180.53	10	8		10.3	8.6	5.0
…NH–CO(CH_2)$_4$*C*O–NH(CH_2)$_5$CO–O…	180.47	5	5		4.4	5.8	6.1
…NH–CO(CH_2)$_5$*C*O–O…	180.21	7	10	12	6.3	9.6	13.6
…*C*H_2O–CO(CH_2)$_4$CO–NH…	68.15	24	24	23	21	24	24.7
…*C*H_2O–CO(CH_2)$_4$CO–O…	67.92	} 76	} 76	} 77	9	16	30.2
…*C*H_2O–CO(CH_2)$_5$NH–CO…	67.92				70	60	45
…O–CO(CH_2)$_4$*C*H_2NH–CO(CH_2)$_4$CO–O…	44.67	3	9	16	2.7	6.4	16.6
…O–CO(CH_2)$_4$*C*H_2NH–CO(CH_2)$_5$NH–CO…	44.57	24	25	28	21	24	24.7
…O–CO(CH_2)$_4$*C*H_2NH–CO(CH_2)$_4$CO–NH…	44.35	8	12	12	6.3	9.6	13.6
…NH–CO(CH_2)$_4$*C*H_2NH–CO(CH_2)$_4$CO–O…	44.22	8	10	13	6.3	9.6	13.6
…NH–CO(CH_2)$_4$*C*H_2NH–CO(CH_2)$_5$NH–CO…	44.12	44	30	22	49	36	20.2
…NH–CO(CH_2)$_4$*C*H_2NH–CO(CH_2)$_4$CO–NH…	43.86	14	14	8	14.7	14.4	11.1
…CO–NH(CH_2)$_4$*C*H_2CO–O…	35.83	24	25	28	21	24	24.7
…O–CO(CH_2)$_3$*C*H_2CO–O…	35.70	4	8	15	2.7	6.4	16.6
…CO–NH(CH_2)$_4$*C*H_2CO–NH(CH_2)$_5$CO–NH…	35.57	30	19	8	34.3	21.6	9.1
…CO–NH(CH_2)$_4$*C*H_2CO–NH(CH_2)$_5$CO–O…	35.48	12	15	13	14.7	14.4	11.1
…NH–CO(CH_2)$_3$*C*H_2CO–O…	35.12	8	7	11	6.3	9.6	13.6
…O–CO(CH_2)$_3$*C*H_2CO–NH…	35.08	5	} 18	} 20	6.3	9.6	13.6
…NH–CO(CH_2)$_3$*C*H_2CO–NH(CH_2)$_5$CO–NH…	35.04	15			10.3	8.6	5.0
…NH–CO(CH_2)$_3$*C*H_2CO–NH(CH_2)$_5$CO–O…	35.01	2	8	5	4.4	5.8	6.1



Scheme 2. (a) Succinimide and glutarimide ring formation during preparation of BSK and BGK samples. (b) Imide ring formation in PAHBAHn polymers that give rise to chain breakages and limited molecular weights during thermal polycondensation.

clearly viscous during the vacuum step, the molecular weights attained are moderate due to a chain breakage (Scheme 2(b)) caused for imide formation. This reaction corresponds, in this case, to a nucleophilic attack on a CO amide carbon and is less favoured than the aforementioned for BSK and BGK samples. However, ^{1}H NMR spectra (Fig. 3(b)) of the recovered polymers still show very small signals indicative of imide rings and also amine terminal groups (NH_2, CH_2NH_2), in agreement with the moderate intrinsic viscosities of 0.39 dl/g and 0.41 dl/g measured for the succinic and glutaric derivatives, respectively. Note also that CH_2OH terminal groups are practically not observed in the PAHBAH3 sample, in spite of its moderate molecular weight, reinforcing the mechanism postulated in Scheme 2(b).

3.2. Thermal behaviour

DSC heating runs of BAK precipitated samples from formic acid solutions showed multiple endothermic peaks with a low enthalpy of fusion that indicates a very low crystallinity and suggests the existence of different crystalline domains. DSC traces were highly sensitive to thermal treatment varying the predominant melting peaks and also the heats of fusion. Thus, as previously demonstrated [8] for BAK 60/40 annealing at temperatures some degrees lower than fusion during long times increases considerably crystallinity of precipitated samples. Thermal characterization of the new polymers was performed following a well established protocol that involves four scans (Fig. 4). First, a heating run of a sample that was previously annealed for 15 min at a temperature 20 degrees lower than fusion; second, a cooling run of a sample that was kept 2 min in the melt state; third, a new heating run to obtain data for the melt crystallized sample; fourth and finally a heating run from a sample quenched in liquid nitrogen from the melt state. Main calorimetric parameters are summarized in Table 2, including an estimation of crystallinity from the heat of fusion of a 100% crystalline material that was evaluated from the group contribution theory [12] (amide, 2 kJ/mol; methylene, 4 kJ/mol; ester, −2.5 kJ/mol). Some general remarks are the following:

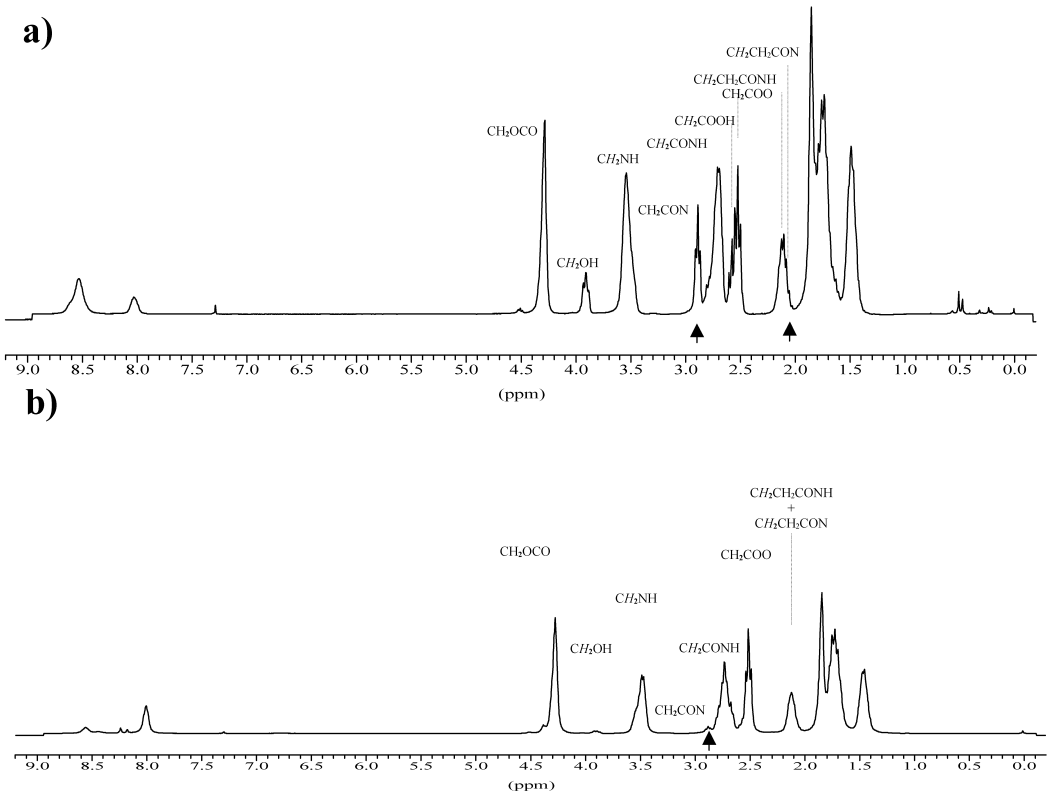


Fig. 3. [1]H NMR spectra of BGK (a) and PAHGAH3 (b) showing assignment of main signals and indicating by arrows the glutarimide peaks.

(a) BAK polymers have a very low crystallinity (12–14% range) for both cold- and hot-crystallized samples. A great variability could be observed in the first heating run, depending on the initial treatment of the sample, e.g. solution crystallization, precipitation or annealing. The low crystallinities observed are in agreement with a random distribution of units.

(b) Melting temperatures are higher than 100 °C and lower than 170 °C, which constitute an adequate range for both processing and applicability. Furthermore, these temperatures are far away from the decomposition temperatures (352 °C for BAK 60/40 [6]).

(c) Double melting peaks can be observed in some cases, a common fact of polyamides that is usually attributed to different thicknesses of crystalline domains. However, a variability in the composition of these domains is not absolutely discarded due to the statistical nature of the BAK polymers. Melting temperatures decrease, as expected, with the ester content.

(d) A hot-crystallization in the 97–125 °C range is observed when samples are cooled at 10 °C/min from the melt. This temperature and the corresponding undercooling (41, 35 and 23 °C for BAK 70/30, 60/40 and 50/50, respectively) decrease with the ester content.

(e) Melt quenched samples show a cold-crystallization in the 21–35 °C range, decreasing the temperature with the ester content.

(f) Glass transition temperatures increase from −20 to 1 °C with the amide content due to the increase of hydrogen bond interactions that reduce chain mobility.

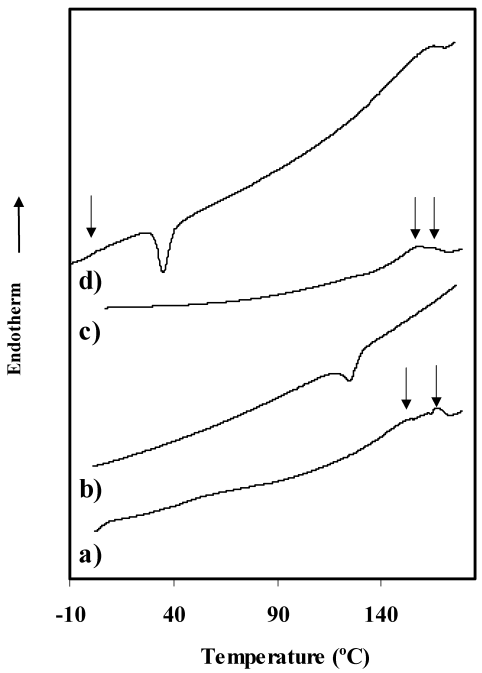


Fig. 4. Sequence of four DSC scans performed with BAK 70/30. (a) First heating run, (b) cooling run, (c) second heating run and (d) third heating run. Arrows indicate melting peaks and glass transition temperature.

Table 2 also includes calorimetric data for the sequential

Table 2
Calorimetric data of BAK samples

Polymer	First heating run			Cooling run		Second heating run			Third heating run				
	T_m [a] (°C)	ΔH_f (kJ/mol)	X [b] (%)	T_c [a] (°C)	ΔH_c (kJ/mol)	T_m [a] °C)	ΔH_m (kJ/mol)	X [b] (%)	T_g [a] (°C)	T_c [a] (°C)	T_m [a] (°C)	ΔH_m (kJ/mol)	X [b] (%)
BAK 70/30	**153**, 166	2.7	14	125	2.7	**156**, 166	2.7	14	1	35	160	2.7	14
BAK 60/40[c]	**126**, 137	5.7	30	101	2.9	136	2.6	14	−10	28	138	2.2	12
BAK 50/50	104, **119**	0.6	3.4	97	2.0	109, **120**	2.0	12	−20	21	120	2.0	12
PAHBAH2	149	16.0	25	136	12	**150**, 155	19	30	−19	85	144, 152	16.1	25
PAHBAH3	92, **100**	19.0	28	12	7	97[d]	8	12	−25	51	98	8.2	12
PAHBAH4[c]	159	30.1	42	147	19.2	157	22.7	32	−15	99	153	17.0	24

[a] When multiple peaks are observed the most intense is indicated with bold characters.
[b] Crystallinity estimated assuming 19.4, 19.1, 17.3, 63, 67 and 71 kJ/mol as the heat of fusion (ΔH_m^{100}) for 100% crystalline samples of BAK 70/30, BAK 60/40, BAK 50/50, PAHBAH2, PAHBAH3 and PAHBAH4, respectively. $X = (\Delta H_m/\Delta H_m^{100})100$.
[c] Values for the cooling run and the first and second heating runs were previously reported.
[d] A cold-crystallization peak is observed at 47 °C.

PAHBAH2 and PAHBAH3 samples, which are compared with the reported results for PAHBAH4. It can be seen that the glutaric derivative has a lower melting point than the adipic one, in spite of the decrease on the number of methylene groups in the repeat unit. Structural changes due to the odd or even number of carbon atoms may cause a signification variation in the melting temperatures, as it is well established for aliphatic polyamides [13] where the odd members melt at lower temperatures than even nylons with an additional methylene group. Calorimetric data show also that the glutaric derivative hardly crystallizes in the cooling rate from the melt, and a cold-crystallization develops during the second and third heating runs. Both succinic and glutaric derivatives appear more amorphous than PAHBAH4, probably due to the imide rings that hinders crystallization. Furthermore, melting temperatures are decreased by the low molecular weight fractions.

3.3. Degradation of BAK samples

Fig. 5 shows the remaining weight percentages (a) and the changes in intrinsic viscosity (b) of BAK samples after immersion in distilled water at 70 °C, whereas the equivalent data after immersion in a pH 2.3 medium are shown in Fig. 6. The results clearly demonstrated that polymers degrade under the accelerated conditions provided by the high temperature or the acid catalysis medium. However, the increase in temperature (from 37 to 70 °C) is the main factor due to the higher solubility of the degradation fragments, as can be seen from the weight loss of the exposed samples. Furthermore, it is demonstrated that the increase on the ester content enhances the hydrolytic degradability. Thus, after 30 days of immersion in water at 70 °C the remaining weights are 62, 45 and 35% for polymer compositions with 30, 40 and 50% of ester groups, respectively. A similar trend, is observed for degradation under the acidic conditions, being 95, 92 and 91% the remaining weight of the indicated samples after the same period of exposition. In all cases, the samples show a high decrease on the intrinsic viscosity in the beginning of degradation, and then a stabilization to a constant value close to 0.3 dl/g. It seems that cleavage of some labile bonds, a fact that it is possible within the studied 30–50% ester content, has a great repercussion on the intrinsic viscosity due to the high molecular weight of the initial samples. However, viscosity is less sensitive to degradation when samples have a very low molecular weight.

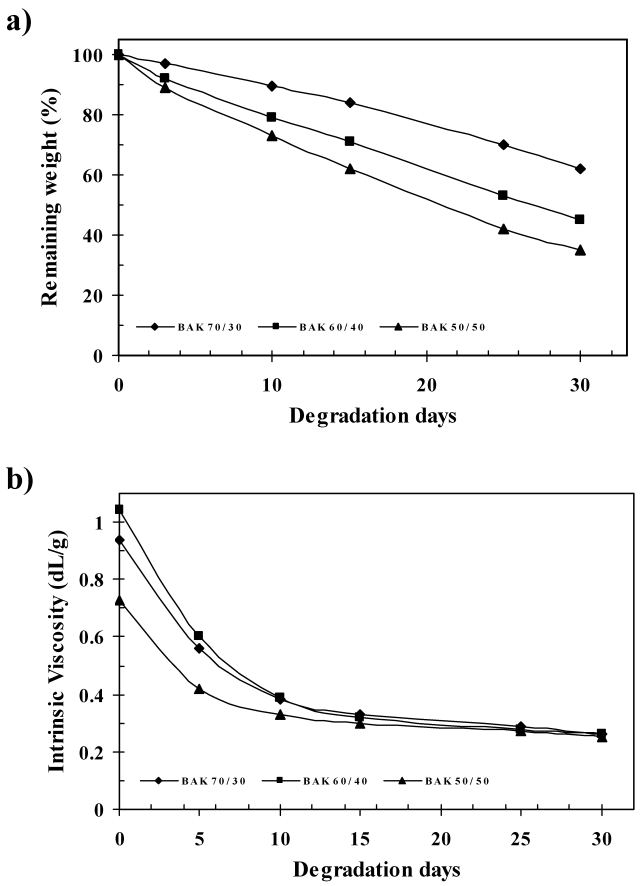


Fig. 5. Remaining weight percentages (a) and intrinsic viscosity (b) of BAK samples versus the days of exposure in distilled water at 70 °C.

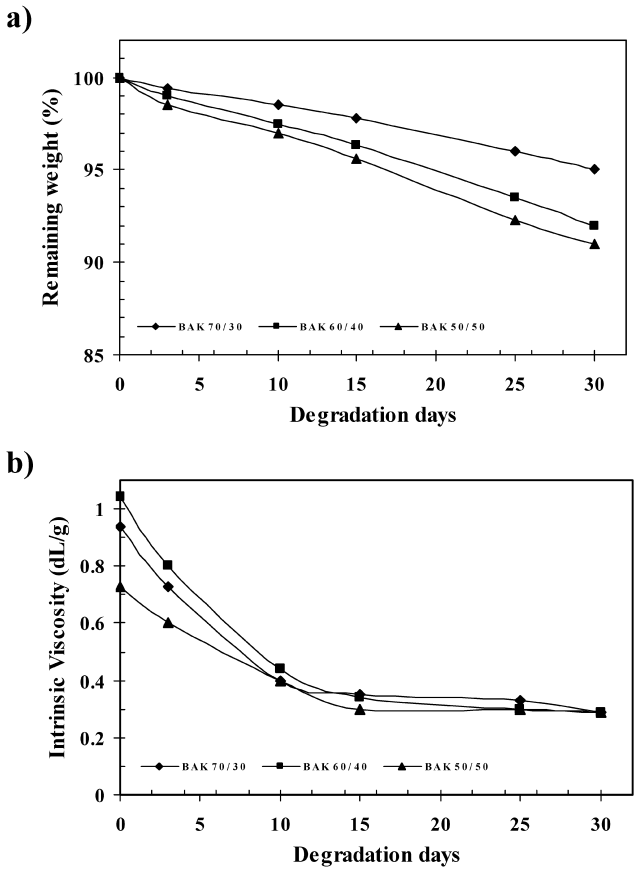


Fig. 6. Remaining weight percentage (a) and intrinsic viscosity (b) of BAK samples versus the days of exposure in a pH 2.3 sodium citrate buffer at 37 °C.

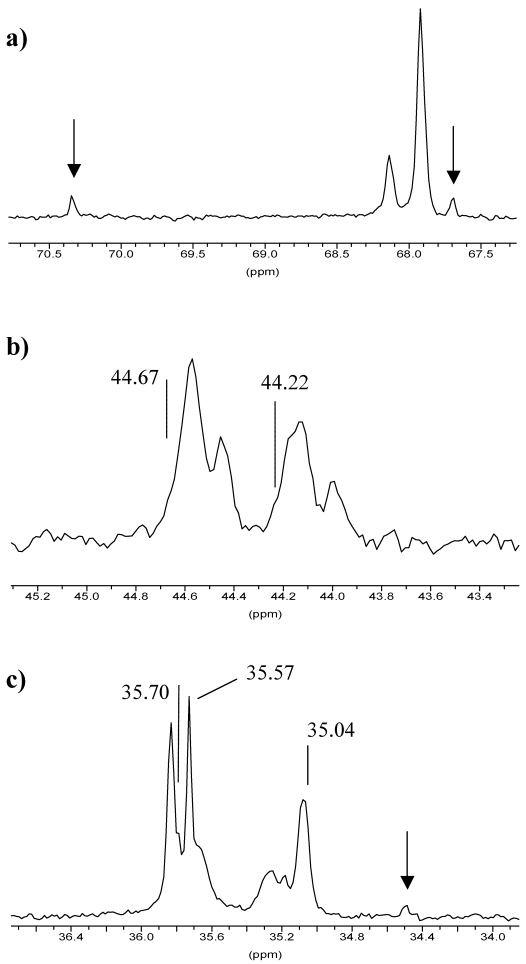


Fig. 7. ^{13}C NMR spectra of BAK 50/50 exposed to distilled water at 70 °C for 10 days. Only the $-CH_2O$ (a), $-CH_2NH$ (b), and $-CH_2CO$ (c) carbons are shown. Arrows indicate terminal groups. Full lines indicate peaks, which relative intensity changed during degradation.

Degradation data at 70 °C suggest also that insoluble fragments have a minimum molecular weight, which is responsible of the measured intrinsic viscosity. Data of samples exposed to the pH 2.3 medium are more difficult to interpret, since fragments of low molecular weight still remain in the sample due to their higher insolubility and consequently have a great influence on the measured intrinsic viscosity.

It was demonstrated from ^{1}H NMR spectra that degradation of BAK 1095 took mainly place through the cleavage of ester linkages. In the same way, the analyses of the ^{13}C NMR spectra of samples exposed to degradation show (Fig. 7) the appearance of two new signals into the 70.5–67.5 ppm region attributed to $-CH_2OH$ and $-CH_2OCOCF_3$ terminal groups that are indicative of ester bond cleavages. A small signal at 34.48 ppm associated to $-CH_2COOH$ end groups can also be detected, whereas no evidences of $-CH_2NH_2$ terminal groups are found. On the other hand, the spectra clearly show that the relative intensity of sequences constituted by amide linkages are increased, whereas those with ester bonds diminish (see Fig. 2 and Table 1 for comparison).

Scanning electron micrographs of samples exposed to degradation in distilled water at 70 °C indicate an autocatalyzed process. Fig. 8(a) shows that the film surface of the exposed samples are practically smooth and only some deep holes appear as a consequence of the degradation, which develops from the inner part. In fact the fracture surfaces of the films reveal that the samples are porous inside, justifying the weight losses detected during degradation. It is clear, that the ester bond cleavages produce acid groups that enhance degradation and obviously the inner part of the samples reach a lower pH than the external surfaces due to the local concentration of acid groups. When a pH 2.3 medium is employed the sample surfaces show evidences of erosion (Fig. 8(b)) that clearly contrast with the non-surface degradation observed in the neutral medium.

Degradation of BAK was also studied in different media containing enzymes with an estearase (lipase from *Pseudomonas cepacia*) or a protease (proteinase K) activity. Degradation was only evaluated through the weight loss and the inspection of the scanning electron micrographs, since it is a surface process due to the large molecular size of enzymes. Fig. 9 demonstrates that proteinase K degrades

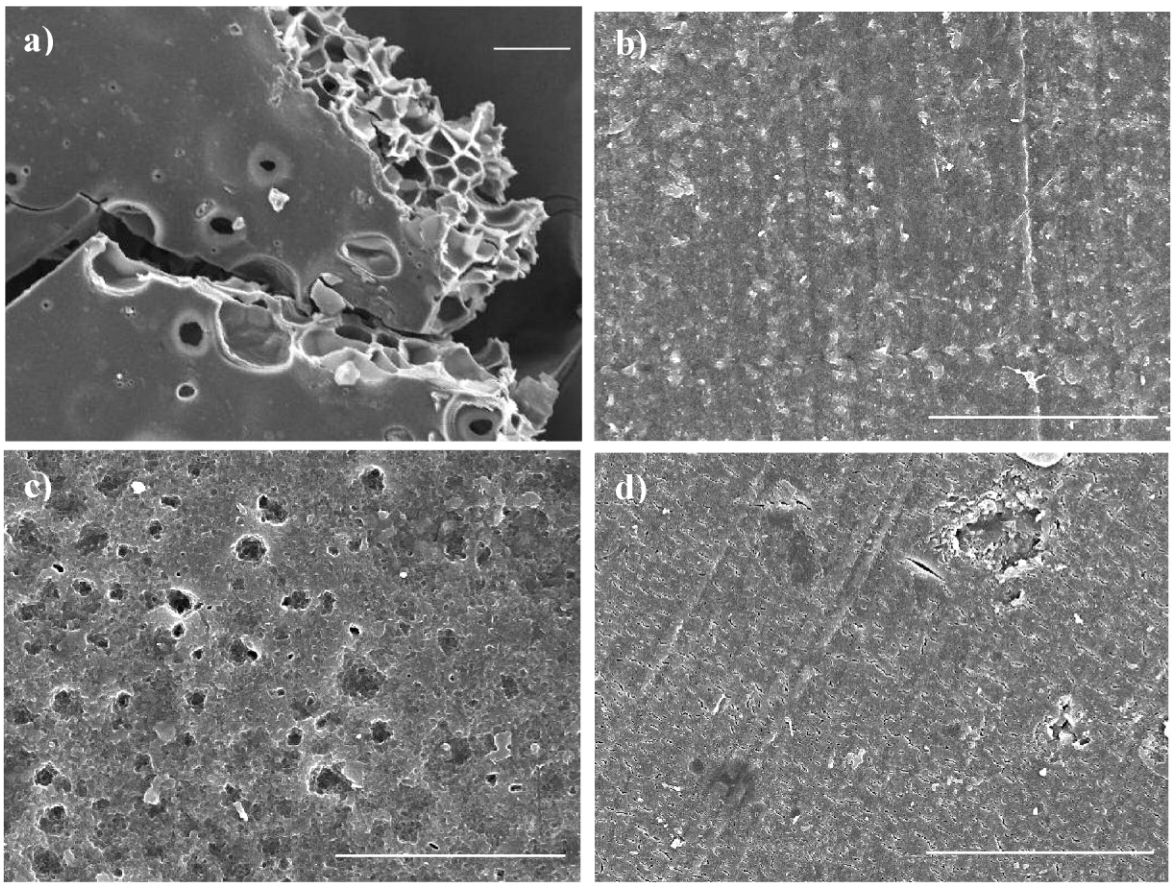


Fig. 8. Scanning electron micrographs of BAK 50/50 exposed to distilled water for 30 days (a), pH sodium citrate buffer for 30 days (b), proteinase K enzymatic medium for 15 days (c), and lipase enzymatic medium for 15 days (d). Scale bars: (a) 150 μm, (b)–(d) 100 μm.

BAK polymers faster than lipase, independently of the ester/amide ratio. Thus, BAK 50/50 has weight losses of 42 and 12% after 21 days of exposure in proteinase K and lipase media, respectively. Degradation in both cases is also enhanced with the decrease on the amide/ester ratio of samples and consequently BAK 50/50 is the most degradable polymer. Fig. 9 shows also that there is a critical composition were degradation is more effective. For example, a 50/50 amide/ester ratio is necessary to produce a significant degradation on the lipase medium. In the same sense, the degradation on proteinase progress shows a very slow rate when the ester content decrease to 30%. Scanning electron micrographs (Fig. 8(c) and (d)) also demonstrate the different surface attack of the assayed degradation media. Thus, numerous holes of different size are clearly visible on the surface of a BAK 50/50 sample exposed 21 days in the proteinase K media, whereas a lower erosion is detected in the lipase media for an equivalent exposition time. In this case, crevasses develop on the surface and only a few number of holes can be observed.

3.4. Chain extenders

Hexamethylene diisocyanate (HDI) and 1,3-butadiene diepoxide were selected as chain extenders due to their capability to react (Scheme 3) with both hydroxyl and carboxyl terminal groups [14–16] that may be present in the BAK polymers Note that the epoxy derivative give rise to secondary hydroxyl groups.

Chloroform and dimethylformamide are BAK solvents without functional groups that could react with the chain extender. However, the former was selected to produce an homogeneous mixture between the polymer and the coupling agent due to its higher volatility and also to the fact that similar results were attained in preliminary assay carried out with both solvents under the same experimental conditions.

Polymers with a low molecular weight (intrinsic viscosity close to 0.25 dl/g) were initially used to determine the optimum proportion between polymer and chain extender, since hydroxyl terminal groups were clearly visible in the ^{1}H NMR (Fig. 10). Molecular weights could consequently be estimated, assuming the approximation that only these kind of terminal exists. For example, a number average molecular weight of 4.600 g/mol was determined for the sample of BAK 70/30 used in this study. Fig. 11(a) shows the final intrinsic viscosity of this polymer after treatment for 20 min at 180 °C with the indicated percentages of the coupling agents. A maximum intrinsic viscosity was found for both chain extenders when a percentage close

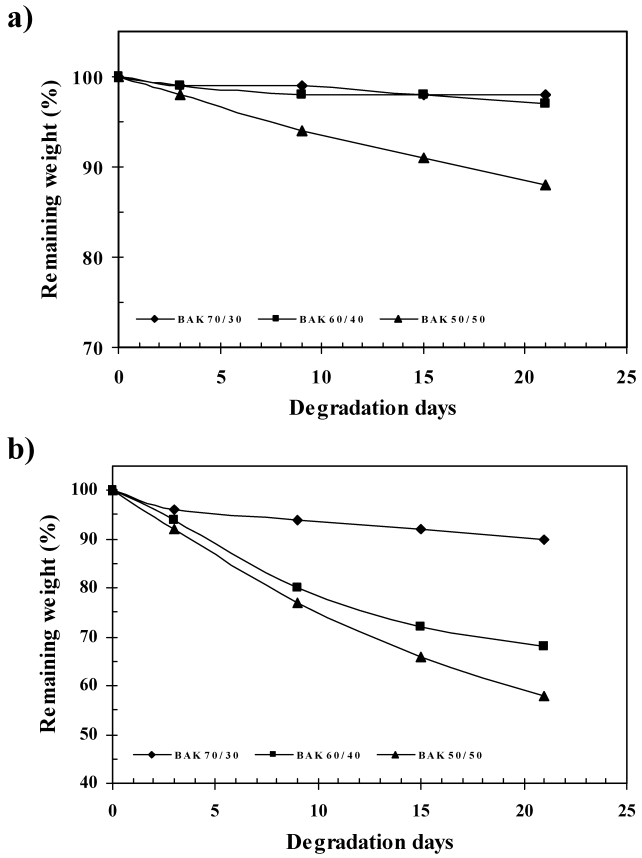


Fig. 9. Remaining weight percentages of BAK samples exposed to lipase from *Pseudomonas cepacia* (a) and proteinase K (b) enzymatic media.

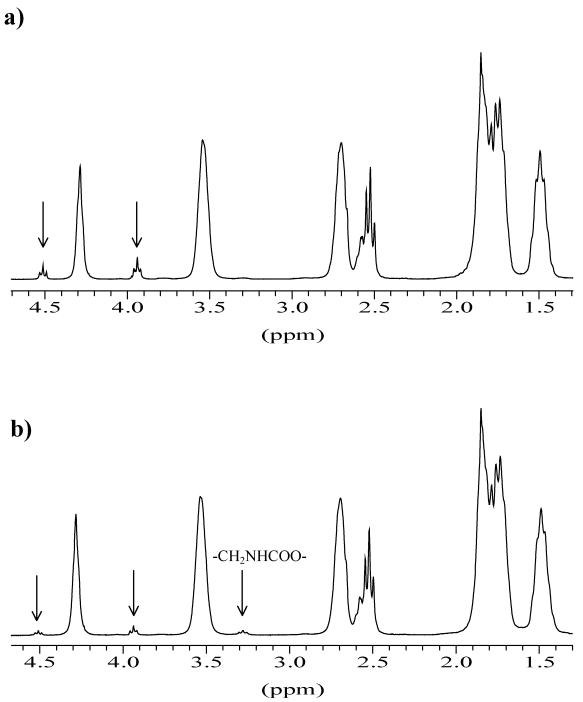
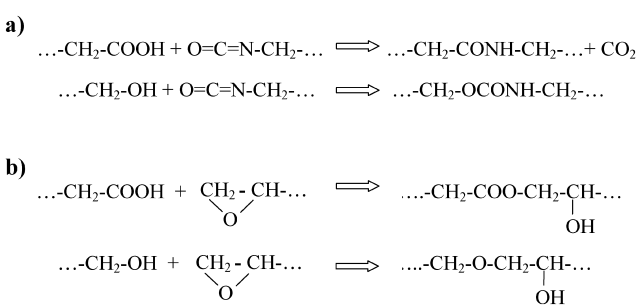


Fig. 10. (a) ^{1}H NMR spectra of a BAK 70/30 sample with an intrinsic viscosity of 0.26 g/dl, terminal $-CH_2OH$ and $-CH_2OCOCF_3$ peaks are indicated by arrows. (b) ^{1}H NMR spectra of a BAK 70/30 sample after treatment with the equimolar amount of HDI, note the decrease on the relative area of the indicated terminal group signals and the appearance of a new $-CH_2NHCOO$ peak indicative of the coupling reaction.

to an equimolar mixture of polymer and coupling agent was used. Saturation of terminal groups with the coupling agent hinders the chain extender reaction and consequently the final molecular weight decreases when a high concentration of the reagent is employed. Both coupling agents seem effective, giving rise to similar viscosities of 0.43 and 0.36 dl/g for the diepoxide and HDI, respectively. Unfortunately, molecular weights could not be estimated when diepoxide was used due to the generation of new hydroxyl groups. However, terminal groups clearly decrease in the ^{1}H NMR spectra of samples treated with HDI (Fig. 10(b)), and



Scheme 3. Reaction of isocyanate (a) and epoxide groups (b) with carboxyl and hydroxyl terminal groups. Coupling reactions were performed at 180 °C in chloroform solutions.

a molecular weight of 10.000 g/mol could be estimated for the optimum ratio.

The influence of the reaction time was also evaluated, as shown in Fig. 11(b) for different BAK 50/50 samples, using equimolar ratios between polymer and chain extender. The results indicate that the diepoxide reacts faster than HDI, being the optimum times close to 10 and 20 min, respectively. After these times a slight decrease on the viscosity is observed probably due to the occurrence of some thermal degradation during the long reaction time at 180 °C.

Samples with different initial intrinsic viscosities were also studied in order to test the effectively of the coupling agents. In all cases, the chain extent reaction was produced under the optimal conditions, in spite of the expected decrease on the chain mobility in the melt state for high molecular weight samples. Obviously, viscosity changes were more apparent when the initial molecular weight was higher. Thus, intrinsic viscosities of 0.36, 0.75 and 1.20 dl/g were attained using the HDI coupling agent and BAK 70/30 samples with 0.26, 0.41 and 0.94 dl/g initial intrinsic viscosities, respectively.

We also tested the effect of using an equimolar mixture of the two indicated chain extenders. The results showed a synergetic effect probably due to the fact that the diepoxide reacts faster producing secondary hydroxyl groups, which could then react with the isocyanate groups of HDI giving

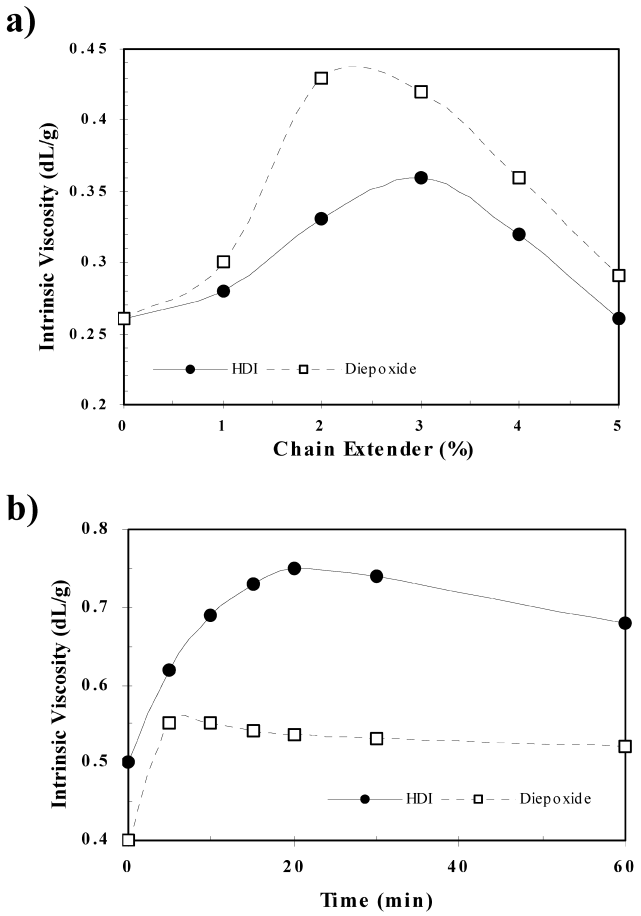


Fig. 11. Intrinsic viscosity changes for BAK 70/30 versus mass percentage of coupling agent (a), and for BAK 50/50 versus reaction time (b). An equimolar amount of the coupling agent was employed in the experiences performed in (b).

rise to a branched polymer. In this way, the intrinsic viscosity of BAK 50/50 can increase from 0.5 to 1.4 dl/g, whereas only 0.75 dl/g was reached by using only the HDI coupling agent.

3.5. Mechanical properties of BAK samples. Natural reinforces

Table 3 compares the mechanical parameters of BAK polymers with different amide/ester ratio. It can be observed a gradual increase on the Young's modulus with the amide ratio, as expected from the establishment of a great number of strong hydrogen bond interactions. In the same way the tensile strength increases, but the results on the elongation at break are less logical, since they are also greatly influenced by the molecular weight. In this sense, BAK 50/50 shows a very low elongation due to its lower molecular weight. However, this parameter was spectacularly increased when the molecular weight was raised by using a chain extender. Values of 24% and 780% were found for intrinsic viscosities of 0.73 and 1.04 dl/g, respectively, whereas the Young's modulus remained practically constant (128 and 149 MPa).

The effect of biodegradable reinforces, such as gluten and starch, was also evaluated for the commercial BAK 60/40 sample. Mixtures with 20, 40 and 60% mass percentages of the reinforce were prepared by mechanical mixing of filler and polymer at a temperature 30 °C above fusion, and controlling the stirring speed in order to avoid the formation of voids. Temperature was critical when gluten was used, since it decomposes at temperatures close to 180 °C. In all cases, the morphology of composites was tested by quenching the samples in liquid nitrogen and studying the fracture surface. As can be seen from scanning electron micrographs, i.e. Fig. 12(a) for the sample with 40% of starch, a regular distribution of the filler particles (with an oblate geometry of $20 \times 20 \times 10\ \mu m^3$) is produced inside the continuous BAK matrix phase. No voids are observed, and furthermore the starch granules appear fractured suggesting adhesion between polymer and filler.

Mechanical parameters are also compared in Table 3, showing best results with the use of starch granules. The behaviour is characteristic of the effect of rigid particulate fillers in a thermoplastic matrix [17]: an increase on the modulus and a decrease on the elongation at break.

Table 3
Stress–strain parameters of BAK samples

Polymer	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
BAK 70/30	285	29	432
BAK 60/40	250	27	570
BAK 50/50	128	11	24
BAK 50/50[a]	149	24	780
BAK 60/40 (20% of starch)	303	16	62
BAK 60/40 (40% of starch)	477	16	7
BAK 60/40 (60% of starch)	767	17	3
BAK 60/40 (20% of gluten)	300	16	21
BAK 60/40 (40% of gluten)	420	14	10
BAK 60/40 (60% of gluten)	567	10	3

Polymers with intrinsic viscosities of 0.73, 1.04, 0.94 dl/g were tested for the 50/50, 60/40 and 70/30 compositions, respectively.
[a] Sample with an intrinsic viscosity of 1.4 dl/g after treatment with the combination of hexamethylene diisocyanate and 1,3-butadiene diepoxide coupling agents.

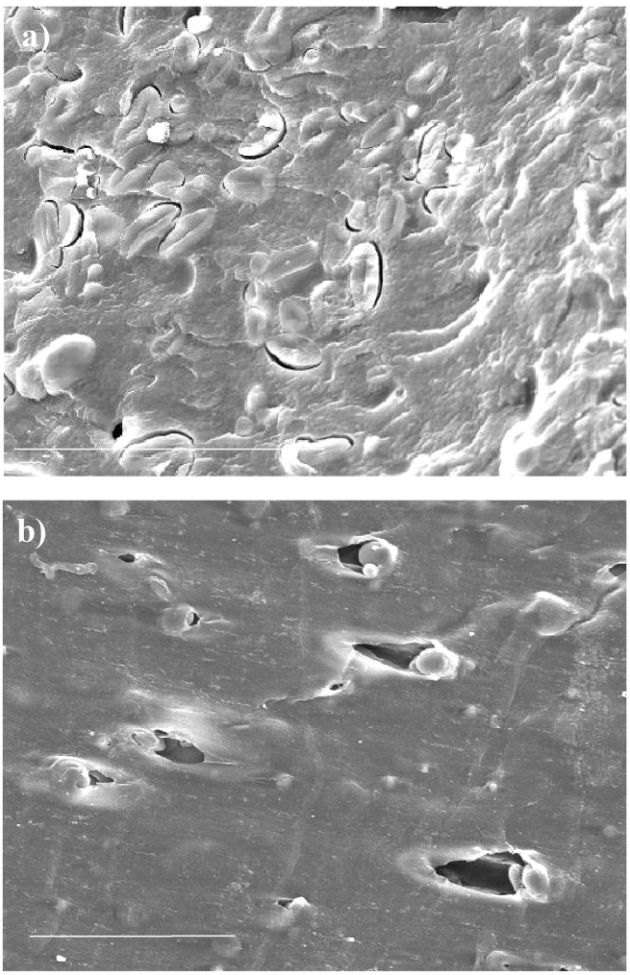


Fig. 12. Scanning electron micrographs corresponding to BAK 60/40 reinforced with 40% (a) and 20% (b) of starch. (a) Fracture surface of a quenched sample showing both a regular distribution of the starch particles and a good adherence. (b) Longitudinal section through the fracture surface of stress–strain tested samples. Voids originating from the interfaces between components are evident after deformation. Scale bars represent 100 μm.

Dynamic-mechanical behaviour shows a regular increase on the glass transition temperature with the percentage of the filler, demonstrating also the stiffness increase with the incorporation of the rigid particles. However, the change is moderate, increasing regularly the glass transition temperature of BAK 60/40 from −5 °C to a maximum value of 4 °C for the 60% starch percentage.

Fig. 12(b) reveals that voids are created and drawn along the tensile axis, as a result of the imposition of dynamic stress on a composite sample. In this way, particles interrupted the energy transfer within the matrix, creating voids, which ultimately led to the failure and yield observed in the composites.

4. Conclusions

The results of this investigation indicate:

(a) Thermal polycondensation of mixtures of 6-aminohexanoic acid, 1,4-butanediol and adipic acid are effective, yielding polymers with a high molecular weight. On the contrary, this synthesis is unfeasible when succinic or glutaric acid derivatives are employed due to the formation of imide rings, preferentially in the beginning of reaction.

(b) The succinimide and glutarimide rings are easily produced at high temperatures when one carboxylic group of the diacid is involved in an amide linkage, whereas the second one remains as an acid group or forms an ester bond. In this sense, poly(ester amide)s including glutaric and succinic residues can be synthesized when these units were previously reacted with amino acids, giving rise to diamide linkages.

(c) Spectroscopic analyses of BAK poly(ester amide)s with 50/50, 60/40 and 70/30 amide/ester ratio show a random distribution of monomers, which is in agreement with the low crystallinity of these samples.

(d) BAK polymers show a decreasing in the melting and glass transition temperatures when the ester/amide ratio is increased. In the same way, Young's modulus decreases.

(e) BAK polymers are degradable, in a process that mainly involve the cleavage of ester linkages. Results indicate that the amide/ester ratio must be lower than certain values in order to obtain samples with a high susceptibility to enzymatic catalysis.

(f) Hydrolytic degradation progresses faster at higher temperatures, and mainly develops in the inner part of disk samples, due to the local concentration of acidic groups during the cleavage of the ester bonds. Enzymes with a protease activity appear more effective than those with only an estearase activity.

(g) Coupling agents, such as hexamethylene diisocyanate and 1,3-butadiene diepoxide, can react with hydroxyl terminal of BAK polymers giving rise to a significant molecular weight increases. Optimum reaction times are within 10–20 min when the reaction was conducted at 180 °C. In the same way, the maximum effect was observed by using equimolar proportions of polymer and coupling agents.

(h) The chain extension reaction was effective for all the essayed polymers, independently of the initial molecular weight, i.e. coupling was possible for samples with an intrinsic viscosity of 1.04 dl/g, in spite of the expected decrease in the polymer chain mobility.

(i) Starch and gluten are effective as biodegradable reinforces, giving rise to both a significantly increase in the Young's modulus and a decrease in the elongation at break.

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