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Composites of novel biodegradable copolyamides based on adipic acid, 1,6-hexane diamine and L-proline with short E-glass fibres: 1. Preparation and properties

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The current demand for environmentally degradable composites has initiated the use of novel biodegradable copolyamides reinforced with E-glass fibres by using the hand lay-up technique. Differential thermal analysis, wide-angle X-ray diffraction patterns and density measurements were employed for the characterization of polymeric composites. The thermal properties of composites, namely T_g and T_m, were determined using differential thermal analysis and dynamic mechanical thermal analyser measurements. The stress–strain curves and compression strength measurements were recorded and correlated with the glass fibre, void and amino acid content of the copolymers.

(Keywords: glass fibre composites; copolyamides; environmental degradability)

INTRODUCTION

The development of novel polymeric materials that degrade slowly is considered a very important research area, especially in view of their various current and potential applications as environmentally degradable materials[1–7]. Although D,L- or L-lactide and ε-caprolactone seem to be the most popular monomers, especially in the field of polymeric composite materials[8–12] mainly related to medical applications, polyamides are another promising class of polymers that appeal to a wider range of applications[13]. However, the lack of biodegradability of synthetic condensation copolyamides has been repeatedly confirmed and attributed to the amount and distribution of hydrogen bonds[14]. Therefore, it was suggested, and previously proved experimentally, that the statistical incorporation of α-amino acids in the polymeric chain of polyamides imparts to the polymers the desired susceptibility to biodegradation[15–18]. The present study investigates the effect of introducing short E-glass fibres in a series of copolyamides based on adipic acid/1,6-hexane diamine/L-proline (AA/1,6-HD/L-proline). Previous publications in the same field reported on the preparation and properties of glass/carbon fibre thermoplastic homopolyamide composites[19–23]. The main incentive for carrying out this investigation lies in the current increase in demand for thermoplastic matrices and, in particular, for novel environmentally degradable materials. It is anticipated that these novel materials will gain in importance even more in the future because of their inherent advantages over the majority of thermoset materials[24], namely, control of their percentage crystallinity (physicochemical properties)[25], ease of processing[19] and 'friendliness' to the environment.

EXPERIMENTAL

Materials

The copolyamides based on AA/1,6-HD/L-proline were reported in previous publications[15,25]. The short E-glass fibres were supplied by Ciba-Geigy S.A.

Preparation of the copolyamide composites – hand lay-up method

Both the moulding box and the method for preparation of composites have been previously reported in detail[23,25]. When the moulding box was taken out of the furnace, it was cooled down by using three different approaches[26]: (a) quenched in ice-water, (b) cooled in the air at room temperature and (c) cooled gradually in the oven.

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Characterization of the neat copolyamides and of the copolyamide composites

Density measurements. Densities were determined pycnometrically[27,28] at 23°C using a density gradient column (Davenport, UK). The polymer samples were previously degassed at 0.1 mmHg for 2 h. The density column was constructed by using toluene and carbon tetrachloride with a density range of 0.99–1.40 g cm^{-3}.

Differential thermal analysis (d.t.a.) measurements. The glass transitions (T_g) and melting points (T_m) were determined using a DuPont differential Thermal Analyzer (DTA, 900) connected to an IBM computer PC/2 and a Hewlett-Packard Colour Pro plotter. The heating rate was 5°C min^{-1} and the temperature range was from -50°C to $T_m + 20$°C. The calibration of temperature and heat enthalpy (J g^{-1}) of the DTA were made with indium. Five measurements were recorded per sample. Glass transitions were defined as the midpoints of step changes in heat capacities (ΔC_p); melting points and crystallization temperatures were defined as the peaks of endothermic and exothermic curves, respectively.

Dynamic mechanical thermal analysis (d.m.t.a.) measurements. D.m.t.a. measurements were carried out using a PL-DMTA (MarkII, UK) connected to an Olivetti PC286 and a Hewlett-Packard Colour Pro plotter. The heating rate was 5°C min^{-1}, frequency 1 Hz, and dimensions of the bars 40 mm long, 7 mm wide and 3.2 mm thick. Tan δ (E''/E') and E'' (loss modulus) were defined as the peaks of the curves, whereas E' (storage modulus) was defined by the intersection of the extrapolations of the two linear parts.

Wide-angle X-ray diffraction patterns (WAXDP). WAXDP ($2\theta = 5$–$35°$) were recorded using a Philips PW1050 diffractometer. Measurements were taken at intervals of 0.05° with a counting time of 4 s. Five measurements were recorded per sample to ensure the reproducibility of the results.

Mechanical properties. The tensile tests were conducted on a 5 ton Instron universal testing machine (TM-SM 1102, UK). The extension rate was maintained at 1 mm s^{-1}. The load elongation curves were plotted and tensile modulus, tensile strength, tensile stress and percentage strain were calculated from the curves. Compression tests were also carried out and the force was recorded for the evaluation of the compressive strength. The tensile specimens were of the following geometry: 6 mm width, 30 mm length and 5 mm thickness, whereas the dimensions of the compressive specimens were 8 mm diameter and 32 mm height. A minimum of five measurements was recorded per sample.

RESULTS AND DISCUSSION

Determination of the crystallinity of copolyamide matrix from WAXDP

The generally accepted procedure to construct the diffraction pattern of a composite material is as follows[29]: (a) record the diffraction pattern of the totally (100%) amorphous polymer (after having quenched it in liquid nitrogen); (b) record the totally (100%) crystalline polymer; (c) take the pattern of the reinforced phase and, after the required scaling up, (d) add the above three patterns together so that the composite pattern is formed. Bearing this 'additive' construction of the WAXDP in mind, the integrated total intensity Q of the X-rays scattered by the semicrystalline composite material could be further analysed to its three components:

$$Q = Q_{\mathrm{amor}} + Q_{\mathrm{cryst}} + Q_{\mathrm{fibre}} \qquad (1)$$

where Q_{amor} is the integrated intensity of the amorphous phase, Q_{cryst} the integrated intensity of the crystalline phase and Q_{fibre} the integrated intensity of the E-glass fibre.

Despite some approximations and assumptions[29–31] required by this model (i.e. simulation of 100% crystalline copolyamide and totally randomly oriented glass fibre-reinforced copolyamides could be mentioned as the most important ones), its determination of percentage crystallinity is usually considered reliable and found to be reproducible[24,29] on several occasions. Furthermore, a complete analysis of both advantages and disadvantages of this method has been previously reported[29]. *Figure 1* shows curves of neat copolyamide AA/1,6-HD/L-proline (45/45/10) (expressed in mol%), traces of amorphous copolymers (quenched in water), E-glass fibre and their composites (glass fibre with the above-mentioned copolymers). Both the neat copolyamide patterns and their E-glass fibre composites were fit as previously[24] by simulating the main peaks within the range 5–35°. *Figure 1* depicts schematically the method followed

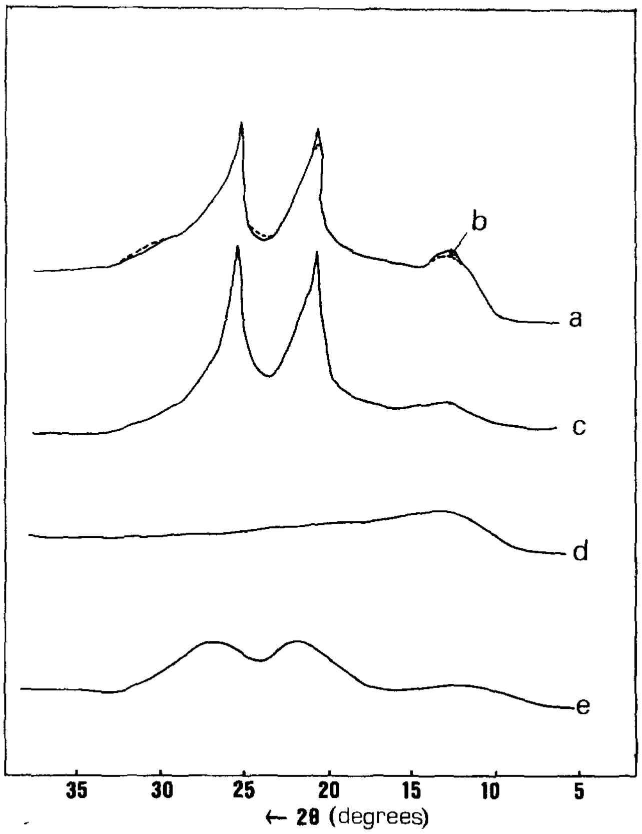

Figure 1 Comparison of experimental and calculated WAXDP for E-glass fibre-reinforced AA/1,6-HD/L-proline, 45/45/10 (mol%) copolyamides: (a) experimental; (b) calculated; (c) simulated 100% crystalline; (d) glass fibre; (e) 100% amorphous

toward the attainment of the 'calculated' copolyamide composite. *Table 1* gives the percentage crystallinity results for the glass fibre-reinforced AA/1,6-HD/L-proline copolyamides.

Differential thermal analysis (d.t.a.)

The application of d.t.a. to composite polymeric materials is more difficult than to neat polymers because in the former the crystallization process can also occasionally be initiated at the surface of the filler or fibre. The occurrence of such nucleation fronts on the glass fibre, in addition to the statistical nucleation from the melt, is termed 'transcrystallinity'. The appearance of several (two or three) melting peaks (d.t.a.) could be attributed as previously suggested[24,32] to different spherulite morphologies resulting from constrained growth in thermoplastic composites, that is, high and low nucleating density, respectively. At this point, it should be mentioned that the addition of fibres increases considerably the complexity of the system because of the occurrence of two antagonizing tendencies toward the crystallization: enhancement of crystallization by providing nuclei but also constrained growth by an impingement mechanism. Recently an attempt was made to separate these two effects by computer simulation[33]. Some representative d.t.a. traces are given in *Figure 2*, where several endothermic peaks can be observed. *Table 2* gives the glass transitions (T_g), melting points (T_{m1}, T_{m2}, T_{m3}) and heats of fusion (ΔH_m) of the composites for E-glass fibre-reinforced AA/1,6-HD/L-proline copolyamides.

The presence of several endotherms has been previously identified in several homo- and copolyamide composites[24,34] and was attributed to primary (initial) and secondary nucleation occurring at a later stage where the initially laid lamellae are used as cores for further nucleation. Previous investigation of thermal properties (d.t.a.) of nylon 6,6 reinforced with E-glass fibres also showed a bimodal endotherm peak attributed to thermodynamically and kinetically favoured crystal formation, in agreement with our experiments[34]. The heats of fusion (*Table 2*) show that the extent of transcrystallinity increases as the fibre nucleation density increases for a fixed bulk nucleation density. The increase in fibre nucleation density at high fibre contents

Table 1 Percentage crystallinity (X_c) found using WAXDP of AA/1,6-HD/L-proline copolyamides reinforced with glass fibre

AA/1,6-HD/L-proline (mol/mol/mol)	Glass fibre content (%)	X_c (%)
47.5/47.5/5.0	0	23.0
	15	24.9
	30	27.2
	45	29.5
45.0/45.0/10.0	0	14.8
	15	16.3
	30	17.9
	45	18.8
42.5/42.5/15.0	0	10.0
	15	11.4
	30	13.0
	45	14.2
40.0/40.0/20.0	0	4.2
	15	4.9
	30	5.3
	45	5.6
37.5/37.5/25.0	0	–
	15	–
	30	–
	45	–

Table 2 Thermal properties (glass transitions [T_g], melting points [T_m], heats of fusion [ΔH_m]) for glass fibre-reinforced AA/1,6-HD/L-proline copolyamides

AA/1,6-HD/L-proline (mol/mol/mol)	Glass fibre content (%)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°)	ΔH_m (J g^{-1})
47.5/47.5/5.0	0	56.0 ± 2.0	247.8 ± 2.3	231.4 ± 2.5	–	63.3 ± 2.4
	15	57.2 ± 1.5	249.2 ± 3.6	232.3 ± 1.9	213.4 ± 2.3	68.2 ± 3.4
	30	58.6 ± 3.2	251.1 ± 2.8	234.0 ± 2.8	215.2 ± 3.0	72.4 ± 2.5
	45	59.1 ± 2.4	252.4 ± 3.3	235.2 ± 3.0	216.4 ± 1.7	75.6 ± 3.0
45.0/45.0/10.0	0	54.9 ± 1.9	235.6 ± 2.1	218.8 ± 3.1	–	58.1 ± 1.9
	15	56.1 ± 2.5	237.1 ± 3.9	219.9 ± 2.0	201.8 ± 1.8	61.7 ± 2.5
	30	57.0 ± 2.2	238.3 ± 2.8	220.8 ± 1.8	203.0 ± 2.4	64.5 ± 2.7
	45	57.8 ± 3.1	239.2 ± 2.8	222.5 ± 2.2	204.3 ± 2.2	68.4 ± 3.1
42.5/42.5/15.0	0	53.4 ± 2.3	221.7 ± 1.8	203.8 ± 3.1	–	56.9 ± 2.2
	15	54.2 ± 3.1	223.1 ± 3.5	205.0 ± 2.3	186.2 ± 3.4	59.3 ± 2.0
	30	55.1 ± 2.7	224.5 ± 2.0	206.2 ± 2.6	187.4 ± 1.8	61.9 ± 3.2
	45	55.8 ± 2.5	226.2 ± 2.7	207.5 ± 1.8	189.1 ± 2.3	64.2 ± 1.8
40.0/40.0/20.0	0	52.6 ± 1.7	212.0 ± 1.9	–	–	52.5 ± 2.1
	15	53.2 ± 2.3	213.2 ± 2.4	196.7 ± 2.7	–	55.9 ± 3.0
	30	54.0 ± 2.8	214.5 ± 1.8	198.2 ± 3.0	–	59.5 ± 2.5
	45	54.7 ± 3.0	216.1 ± 2.0	200.1 ± 2.4	–	61.7 ± 2.3
37.5/37.5/25.0	0	49.2 ± 1.5	199.7 ± 2.0	–	–	47.3 ± 1.9
	15	50.2 ± 2.8	201.2 ± 2.4	183.9 ± 1.5	–	50.1 ± 2.4
	30	51.0 ± 2.4	202.5 ± 1.8	184.8 ± 2.1	–	53.2 ± 2.1
	45	51.6 ± 2.5	203.7 ± 2.2	186.1 ± 1.7	–	55.7 ± 3.0

Results are given as mean ± standard deviation for five measurements

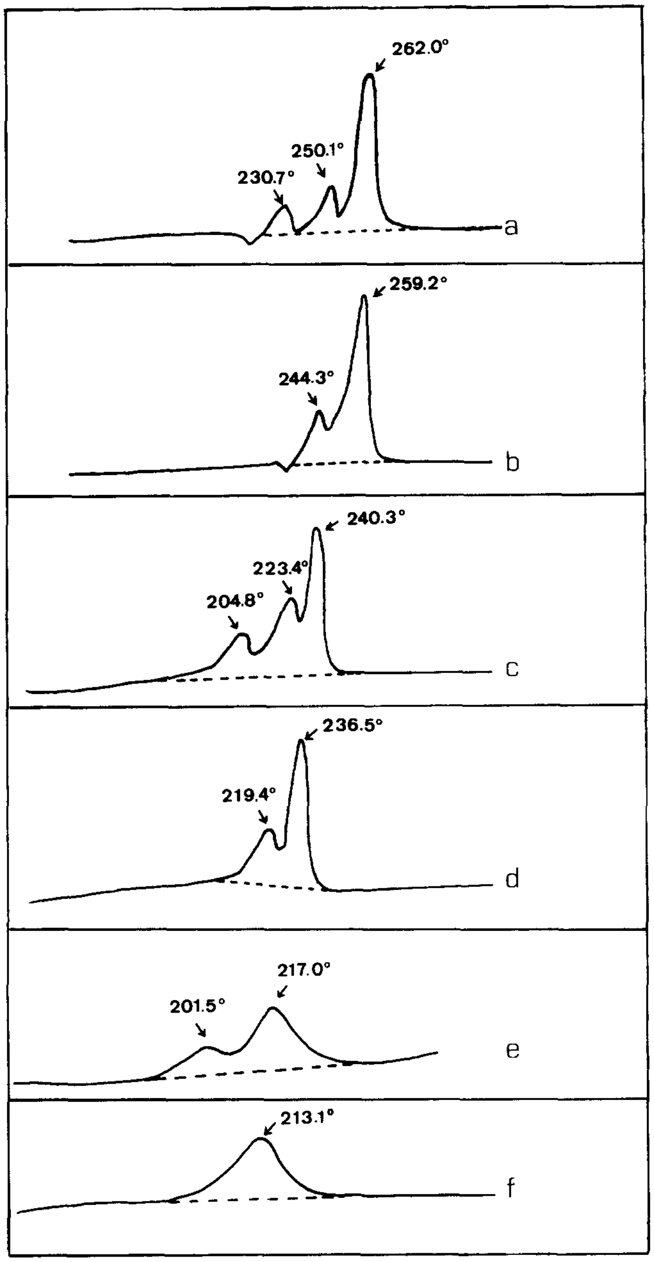

Figure 2 D.t.a. traces for the following neat polymers and their glass fibre composites (for $V_f = 45\%$): (a) (nylon 6,6) AA/1,6-HD composite; (b) neat (nylon 6,6) AA/1,6-HD; (c) AA/1,6-HD/L-proline (45/45/10 (mol%)) composite; (d) neat AA/1,6-HD/L-proline (45/45/10 (mol%)); (e) AA/1,6-HD/L-proline (40/40/20 (mol%)) composite; (f) neat AA/1,6-HD/L-proline (40/40/20 (mol%))

(>20–30%) was found to result in decrease of the average spherulite size because of the presence of many more nucleation sites (transcrystallinity effect)[33]. Therefore, although the fibre-reinforced systems can, in theory, crystallize more slowly or more quickly than a corresponding unreinforced system depending on the interplay between the enhancing and depressing effects of fibres upon the crystallization rates, in this particular case the effect of transcrystallinity proved to be the preponderant one by significantly increasing the crystallization rates.

The effect of several cooling modes on percentage crystallinity was investigated and the results are given in *Table 3*. It was found that slow cooling rates promote higher crystallinities because they lead to the formation of more perfect crystals, whereas the faster the cooling rate (i.e. quenching) the lower the developed crystallinity. Similar results have been obtained for the copolyamides (nylon 6/nylon 12) reinforced with E-glass fibres[24].

Density measurements – detection of void content

The main purpose of carrying out the density measurements was to determine the void volume fraction. Among the various factors that have been considered responsible for promoting the occurrence of voids in polymer composites the most important ones are the following: possible entrapment of air within compounded pelletized material, residual moisture and shrinkage of volume of the core region[24,35,36]. The void volume fraction (v) was calculated from the measured (p) and calculated (p_{calc}) composite densities as follows:

$$v = 1 - \frac{p}{p_{\mathrm{calc}}} \tag{2}$$

The solid, void-free density of the composite (p_{compos}) was calculated from the density of the pure copolyamide (p_{p}) and that of the glass fibre (p_{f}) as shown in equation (3):

$$p_{\mathrm{compos}} = \frac{p_{\mathrm{f}} p_{\mathrm{p}}}{(1 - w_{\mathrm{f}})p_{\mathrm{f}} + w_{\mathrm{f}} p_{\mathrm{p}}} \tag{3}$$

where w_{f} is the glass fibre weight fraction (determined by burning off the copolyamide).

Table 3 summarizes the results of the density values for neat and glass fibre-reinforced composites and the void fraction and percentage crystallinity (from WAXDP) developed at three different cooling rates.

The observed increase in void volume fraction with glass fibre content (*Table 3*) has been reported in previous publications[24,26,36] and attributed to insufficient adhesion of the polymer matrix to the E-glass fibres (untreated in this case), deformation of crystals, transcrystallinity[36] and, most importantly, bubble formation[37,38]. Investigation of the effect of different cooling modes on the density and void content showed that higher void contents are related to very fast cooling. Therefore the void content order is as follows: quenched in ice-water > air cooled > oven cooled. The drastic cooling conditions imposed upon the composite material when quenched in ice-water could result in external partial surface solidification whereas the interior cannot be freely contracted, thus resulting in undesirable high internal void contents as previously reported[24,26].

Mechanical properties

Tensile strength. The stress–strain curves of the reinforced copolyamides showed that an increase in the glass fibre content was always related to an increase in the tensile strength of the copolyamide composites. The curves of the composites were essentially linear and showed only a slight curvature near the breaking point, whereas the neat copolyamides showed definite yield points before their fracture. All the results derived from the stress–strain curves and the compressive strength–time (distance) plots both for neat and E-glass fibre-reinforced copolyamides are given in *Table 4*.

The three equations (the assumptions for which were reported in our previous publication[24]) applied for

Table 3 Effect of cooling conditions on density (p), void fraction (v) and percentage crystallinity (%X_c) of glass fibre-reinforced AA/1.6-HD/L-proline copolyamides

AA/1,6-HD/L-proline (mol/mol/mol)	Glass fibre content (%)	Measured density (g cm^{-3})	Calculated[a] density (g cm^{-3})	Void[b] fraction (v)	%X_c[c]
Ice-water					
47.5/47.5/5.0	0	1.1539	–	–	13.7
	15	1.2025	1.2565	0.043	18.0
	30	1.2964	1.3791	0.060	21.4
	45	1.3326	1.5282	0.128	25.2
45.0/45.0/10.0	0	1.1785	–	–	9.8
	15	1.2325	1.2812	0.038	12.5
	30	1.3264	1.4036	0.055	16.3
	45	1.3640	1.5518	0.121	19.2
42.5/42.5/15.0	0	1.1890	–	–	3.9
	15	1.2466	1.2918	0.035	6.7
	30	1.3447	1.4140	0.049	10.5
	45	1.3946	1.5617	0.107	13.9
37.5/37.5/25.0	0	1.2053	–	–	–
	15	1.2689	1.3081	0.030	–
	30	1.3686	1.4301	0.043	–
	45	1.4700	1.5772	0.068	–
Oven-cooled					
47.5/47.5/5.0	0	1.1875	–	–	30.0
	15	1.2529	1.2903	0.029	34.6
	30	1.3504	1.4125	0.044	38.9
	45	1.4043	1.5603	0.100	43.2
45.0/45.0/10.0	0	1.2124	–	–	23.1
	15	1.2876	1.3152	0.021	27.6
	30	1.3882	1.4371	0.034	33.4
	45	1.4492	1.5838	0.085	36.3
42.5/42.5/15.0	0	1.2285	–	–	15.0
	15	1.3113	1.3313	0.015	18.3
	30	1.4137	1.4529	0.027	22.1
	45	1.4886	1.5989	0.069	26.6
37.5/37.5/25.0	0	1.2433	–	–	–
	15	1.3299	1.3461	0.012	–
	30	1.4365	1.4673	0.021	–
	45	1.5239	1.6126	0.055	–
Air-cooled					
47.5/47.5/5.0	0	1.1690	–	–	23.4
	15	1.2234	1.2717	0.038	27.9
	30	1.3244	1.3941	0.050	31.0
	45	1.3730	1.5427	0.110	34.8
45.0/45.0/10.0	0	1.1988	–	–	15.7
	15	1.2626	1.3016	0.030	18.6
	30	1.3640	1.4238	0.042	22.0
	45	1.4123	1.5710	0.101	26.4
42.5/42.5/15.0	0	1.2085	–	–	9.8
	15	1.2798	1.3113	0.024	13.9
	30	1.3830	1.4332	0.035	18.5
	45	1.4411	1.5802	0.088	21.4
37.5/37.5/25.0	0	1.2264	–	–	–
	15	1.3013	1.3292	0.021	–
	30	1.4073	1.4508	0.030	–
	45	1.4995	1.5969	0.061	–

Results are given as the mean of five measurements

[a] Calculated according to equation (3)

[b] Calculated according to equation (2)

[c] Determined from WAXDP

Table 4 Theoretical and experimental ultimate tensile strength values for AA/1,6-HD/L-proline copolyamide composites of various glass fibre contents

		Tensile strength (MPa)							
AA/1,6-HD/L-proline (mol/mol/mol)	Glass fibre content (%)	Experimental[a]	Calculated according to eq. (4)	Calculated according to eq. (5)	Calculated according to modified eq. (5)	Corrected multiplication coefficient instead of 0.7	Calculated according to eq. (6)	Calculated according to modified eq. (6)	Corrected multiplication coefficient instead of 0.7
47.5/47.5/5.0	0	68 ± 8	–		–	–	–		
	15	158 ± 12	242	367	151	0.41	349	145	0.29
	30	310 ± 16	415	735	301	0.41	723	300	0.29
	45	417 ± 15	589	1102	452	0.41	1126	462	0.29
45.0/45.0/10.0	0	57 ± 7	–		–		–		
	15	143 ± 11	232	367	140	0.38	349	135	0.27
	30	282 ± 17	407	735	279	0.38	723	279	0.27
	45	415 ± 20	583	1102	419	0.38	1126	430	0.27
42.5/42.5/15.0	0	44 ± 5	–		–		–		
	15	123 ± 9	221	367	125	0.34	349	120	0.24
	30	240 ± 15	398	735	250	0.34	723	248	0.24
	45	375 ± 23	575	1102	375	0.34	1126	383	0.24
40.0/40.0/20.0	0	35 ± 5	–		–		–		
	15	104 ± 8	214	367	110	0.30	349	105	0.21
	30	219 ± 14	392	735	221	0.30	723	217	0.21
	45	348 ± 20	571	1102	331	0.30	1126	335	0.21
37.5/37.5/25.0	0	27 ± 3	–		–		–	–	–
	15	90 ± 6	207	367	89	0.24	349	85	0.17
	30	172 ± 13	386	735	176	0.24	723	176	0.17
	45	261 ± 10	566	1102	264	0.24	1126	271	0.17

[a] Experimental results are given as the mean ± standard deviation of five measurements

Table 5 Theoretical and experimental tensile moduli values and compressive strength of AA/1,6-HD/L-proline copolyamides reinforced with various glass fibre contents

		Tensile modulus (GPa)			Compressive strength (MPa)				
AA/1,6-HD/L-proline (mol/mol/mol)	Glass fibre content (%)	Experimental	Theoretical lower limit according to eq. (8)	Theoretical upper limit according to eq. (7)	Experimental	Calculated according to eq. (9)	Calculated according to eqs. (10) and (11)	Calculated according to modified eqs. (10) and (11)	Correction coefficient instead of 0.63
47.5/47.5/5.0	0	2.06 ± 0.19	-	-	67.2 ± 4.3	-	-	-	-
	15	2.93 ± 0.22	2.40	7.60	95.1 ± 5.8	652	523	117	0.141
	30	6.12 ± 0.15	2.88	13.14	137.5 ± 6.0	2033	635	142	0.141
	45	7.47 ± 0.17	3.59	18.68	220.0 ± 4.5	4214	808	181	0.141
45.0/45.0/10.0	0	1.95 ± 0.24	-	-	55.9 ± 4.6	-	-	-	-
	15	2.88 ± 0.20	2.27	7.51	88.5 ± 5.9	634	495	105	0.134
	30	5.95 ± 0.32	2.73	13.06	119.0 ± 6.5	1978	601	128	0.134
	45	7.14 ± 0.16	3.41	18.62	198.5 ± 7.2	4100	765	163	0.134
42.5/42.5/15.0	0	1.76 ± 0.18	-	-	44.3 ± 3.5	-	-	-	-
	15	2.43 ± 0.15	2.05	7.34	70.0 ± 4.8	603	447	90	0.127
	30	5.52 ± 0.26	2.47	12.93	106.5 ± 5.6	1879	542	109	0.127
	45	6.87 ± 0.18	3.09	18.51	171.2 ± 4.9	3895	690	139	0.127
40.0/40.0/20.0	0	1.57 ± 0.10	-	-	31.5 ± 2.6	-	-	-	-
	15	2.17 ± 0.21	1.83	7.18	57.6 ± 4.3	569	398	78	0.123
	30	5.24 ± 0.14	2.20	12.80	92.5 ± 5.0	1774	484	94	0.123
	45	6.95 ± 0.09	2.76	18.41	153.4 ± 3.8	3679	616	120	0.123
37.5/37.5/25.0	0	1.26 ± 0.11	-	-	22.6 ± 2.8	-	-	-	-
	15	2.03 ± 0.14	1.47	6.92	49.8 ± 2.6	510	320	68	0.133
	30	4.78 ± 0.20	1.78	12.58	81.0 ± 4.2	1590	388	82	0.133
	45	6.33 ± 0.16	2.23	18.24	133.5 ± 3.7	3296	494	104	0.133

Experimental results are given as the mean ± standard deviation of five measurements calculating theoretically the tensile strength of the glass fibre-reinforced copolyamides were as follows:

(i) rule of mixtures:

$$\sigma_u = n\sigma_f V_f + \sigma_m(1 - V_f) \tag{4}$$

where σ_u is the tensile strength of the composite, σ_f the tensile strength of the glass fibre, σ_m the tensile strength of the matrix (in our case copolyamide), V_f the fibre volume fraction and n the Krenchel's efficiency factor ($n = 0.5$ for cross-ply fibre composites)[23,24].

(ii) Weibull's simplified equation:

$$\sigma_u = 0.7\sigma_f V_f \tag{5}$$

and (iii) Dow and Rosen's analysis (cited by Srivastava and Lal[23]) which resulted in the following formula:

$$\sigma_u = \sigma_r V_f \left[\frac{(1 - V_f)^{0.5}}{V_f^{0.5}}\right]^{-1/2\beta} \tag{6}$$

where σ_r is the reference stress level depending on the particular combination of fibre and matrix (copolyamide in our case) properties and β is a statistical parameter of the Weibull distribution related to the fibre strength, which is equal to 7.7 for commercial E-glass fibre[23].

Comparison of the experimental results with those obtained from equations (4)–(6) showed that a modified equation (5) gives the closest possible fit to the experimental results, as previously reported[23,24], whereas equations (4) and (6) fail to provide a good fit. Possible reasons for these discrepancies could be the high hygroscopicity of the copolyamide matrix (because of α-amino acid as the comonomer unit), the void content and eventual fibre misalignment due to usage of multifibre strands, which are locally organized but this local organization is generally anticipated to deviate from the overall mean direction of the entire fibre population[39–42]. It could be suggested that the fracture of the composites is initiated originally by matrix failure near fibre ends followed by a transversal crack propagation which results in fracture of the composite without necessitating the breaking of the glass fibres, as was observed on several occasions. This suggestion is supported by the results of computer simulation of the fracture mechanics of composite materials[42] and by scanning electron microscopic analysis of polyamides reinforced with short E-glass fibres[43].

Tensile modulus. Depending on the direction of the applied stress relative to the fibre orientation in the copolyamide composite, it was previously shown[24] that two estimates are available for tensile modulus ($E_{\text{composite}}$) of the glass fibre-reinforced copolyamides; equations (7) and (8) give the upper and lower limits, respectively.

$$E_{\text{composite}} = V_f E_f + (1 - V_f)E_m \tag{7}$$

$$E_{\text{composite}} = \frac{1}{\left\{\dfrac{V_f}{E_f} + \left(\dfrac{1 - V_f}{E_m}\right)\right\}} \tag{8}$$

Table 5 summarizes the results of the estimates and the experimentally found values for tensile moduli. The higher the contribution of the α-amino acid in the copolyamide, the weaker the matrix, thus resulting in an easier failure of the copolyamide reinforced with short glass fibres. The experimental values are shifted rather toward the lower estimate (equation (8)) which could be due to the inherent complexity of short fibre-reinforced thermoplastics (SFRTP) because they consist of misaligned arrays of variable length fibres, dispersed in a viscoelastic matrix[44,45]. The copolyamides with lowest glass fibre content showed the lowest extent of discrepancies between theoretical and experimental values.

By correlating the tensile strength with the void content developed at various cooling modes (see *Tables 3* and *4*) it becomes obvious that high fibre contents result in void contents which, in their turn, are related to high percentage crystallinities and high tensile strength.

Compression strength. The three equations which were applied for calculating the compression strength are as follows:

$$\sigma_{ce} = 2V_f\left[\frac{V_f E_m E_f}{3(1 - V_f)}\right]^{0.5} \tag{9}$$

$$\sigma_{cs} = \frac{G_m}{1 - V_f} \tag{10}$$

$$G_m = \frac{E_m}{2(1 + \nu)} \tag{11}$$

where σ_{ce} is the compressive strength in the extension mode, σ_{cs} the compression strength in the shear mode, E_m the modulus of the elasticity of the matrix (copolyamides), E_f the modulus of the elasticity of the fibre (glass fibre), G_m the shear modulus and ν is the Poisson ratio (dimensionless) which equals 0.44 for nylon 6,6[46].

It was found that the introduction of a correction factor in equation (10) is required so that this equation in its modified form can give a good fit for the experimental values. In previous publications it was explicitly shown that, depending on the kind of the matrix/fibre system, the correction coefficient may vary substantially, i.e. from 0.100 for copolyamide/glass fibre[24] up to 0.63 for epoxy/boron composites[47]. In our case the correction coefficient was in the range 0.20–0.24 which is in agreement with a previous investigation on nylon 6,6/glass fibre composites[23]. The results obtained from the compression test measurements and the calculated values are given in *Table 5*.

Hygrothermal ageing

Moisture penetration into composite materials is conducted mainly by diffusion, capillarity and transport by microcracks[48]. The rate of moisture absorption by a polymeric composite depends on the following factors: type of matrix and fibre, the fibre orientation with respect to the direction of diffusion, the conditioning temperature, the difference in water concentration between the composite and the environment and whether or not the absorbed water reacts chemically with the matrix[44]. The diffusivity or diffusion coefficient, D, can be calculated from the following simplified equation (initial linear portion of the absorption curve):

$$\frac{M_t}{M_m} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{h^2}\right)^{1/2} \tag{12}$$

where M_t and M_m are mass of water absorbed at time t and at saturation, respectively, and h is the thickness of infinitely large plates.

When the diffusion is Fickian or a function of temperature only, an Arrhenius relationship describes it:

$$D = D_0 \exp(-E_\alpha/RT) \qquad (13)$$

where D_0 is the pre-exponential coefficient, or permeability index, and R, E_α and T are the gas constant, activation energy and absolute temperature, respectively.

The moisture absorption was determined by the following equation:

$$M_t(\%) = \frac{(W - W_d)}{W_d} \times 100 \qquad (14)$$

where W_d and W denote the weight of dry material (i.e. the initial weight of the material prior to exposure to the environment) and weight of moist material, respectively. The percentage equilibrium moisture absorption, M_m, was calculated as an average value of several consecutive measurements that showed no appreciable additional absorption.

Although the d.t.a. curves of AA/1,6-HD/L-proline copolyamides and their glass fibre-reinforced composites before and after moisture absorption did not show any significant change within the first 24 h, neither in the shapes nor in the positions of the melting peaks, they gradually began to show lower T_m and ΔH_m values, as shown in *Figure 3*. The observed differences in the heats of fusion of the samples after having been subjected to

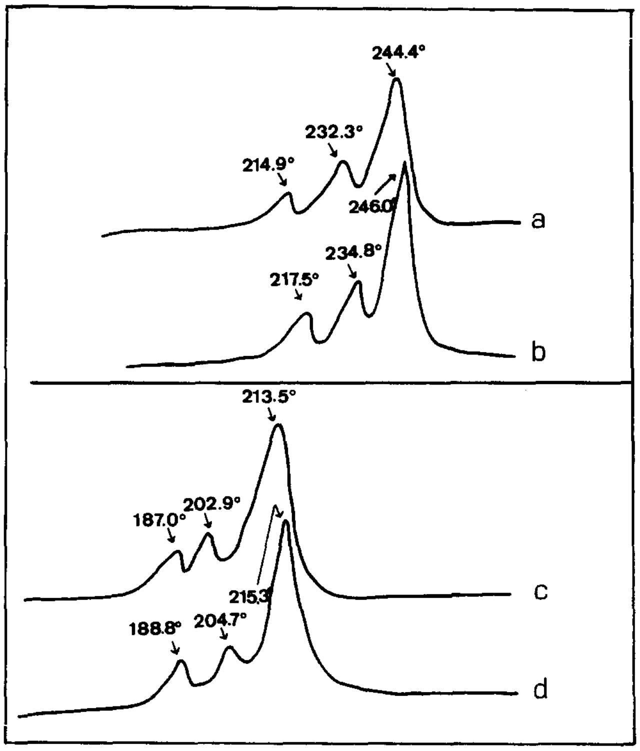

Figure 3 D.t.a. traces of copolyamides reinforced with glass fibres (V_f=45%) before and after their hygrothermal ageing (conditioning at 80°C for 7 days): (a) and (b) AA/1,6-HD/L-proline (47.5/47.5/5.0 (mol%)) copolyamide composites after and before conditioning, respectively; (c) and (d) AA/1,6-HD/L-proline (42.5/42.5/15.0 (mol%)) copolyamide composites after and before conditioning, respectively

Table 6 Effect of moisture conditioning upon the thermal properties (T_g, T_m, ΔH_m) of AA/1,6-HD/L-proline reinforced copolyamides: determination of water diffusion activation energies (E_α)

AA/1,6HD/L-proline (mol/mol/mol)	Glass fibre content (%)	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})	E_α (kJ mol^{-1})
50.0/50.0/0.0	0	56.0±2.3	256.1±2.5	106.5±2.4	52.0
	15	57.8±2.7	258.0±3.2	111.3±1.9	60.5
	30	58.7±3.1	259.4±2.8	117.7±2.2	68.8
	45	59.9±2.0	260.8±2.0	123.9±2.0	78.2
47.5/47.5/5.0	0	51.8±2.1	243.5±1.7	60.0±3.1	46.8
	15	53.3±1.8	246.0±2.4	62.5±2.3	53.3
	30	54.1±2.4	247.8±2.6	65.7±1.8	61.0
	45	56.0±2.6	249.1±1.9	68.3±2.5	69.3
45.0/45.0/10.0	0	50.0±2.1	229.5±1.8	54.6±1.8	41.6
	15	50.8±1.3	231.4±2.2	57.2±2.3	49.5
	30	52.1±2.3	235.2±1.3	59.4±1.9	56.7
	45	53.4±2.1	236.7±1.9	63.0±2.6	64.0
42.5/42.5/15.0	0	47.9±1.4	217.0±2.2	50.4±1.5	40.8
	15	49.0±1.7	218.6±2.4	52.6±2.1	45.7
	30	50.2±1.6	220.0±1.7	55.3±2.3	53.5
	45	51.4±1.8	221.8±2.0	59.0±1.7	61.4
40.0/40.0/20.0	0	45.8±1.5	207.2±1.5	44.7±2.3	41.6
	15	47.0±1.9	208.5±2.2	47.1±1.4	43.8
	30	48.2±2.2	210.1±1.8	52.7±2.5	51.9
	45	49.1±2.0	212.0±1.3	56.1±2.0	60.0
37.5/37.5/25.0	0	43.0±1.4	194.1±2.3	39.8±1.7	37.4
	15	44.5±1.8	195.7±1.7	42.4±2.4	43.0
	30	45.7±1.2	197.2±2.2	46.7±1.9	49.8
	45	47.0±1.9	199.5±2.0	50.0±1.8	58.2

Results are given as the mean±standard deviation of five measurements moisture absorption could be attributed to small-scale reorganization of the molecules which could eventually result in local disruptions of the ordered structure, as previously reported for nylon-6,6[44]. *Table 6* gives the melting points and heats of fusion of the neat AA/1,6-HD/L-proline copolyamides and their glass fibre-reinforced composites after moisture conditioning.

Figure 4 shows the plot of ln *D versus* the inverse of absolute temperature ($1/T$) for the neat and reinforced copolyamides with various L-proline contents. High L-proline contents promote lower activation energies because of the hydrophilicity imparted upon the polymeric chain by the incorporation of L-proline units. The diffusion activation energies (E_α) both for neat and glass fibre-reinforced copolyamides are given in *Table 6*. The determined E_α (kJ mol^{-1}) values agree satisfactorily with previously reported values (55–61 kJ mol^{-1})[44,49] although they seem to be somewhat lower for copolyamides rich in L-proline (37–52 kJ mol^{-1}) and rather higher (43–78 kJ mol^{-1}) for the copolyamides with high glass fibre content. Although the presence of fibres could, in theory, promote two minor mechanisms of moisture absorption, namely via capillarity or transport by microcracks, this expected moisture increase is likely to have been counterbalanced in our case by the effect of transcrystallinity. Furthermore, the fact that glass fibres do not absorb any moisture[41], at least for the duration of our experiments, implies that they may eventually cause discontinuities along the water diffusion path.

Some preliminary results of mechanical properties (stress–strain curves) for both unreinforced and reinforced

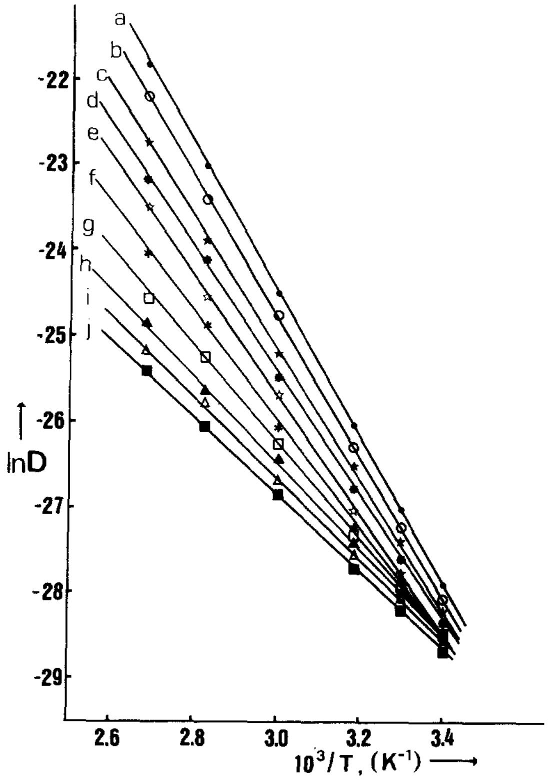

Figure 4 Arrhenius plot to determine the apparent activation energy for water diffusion for the following neat copolyamides and their glass fibre ($V_f = 45\%$) composites: (a) and (f) neat nylon 6,6 and its composite; (b) and (g) neat AA/1,6-HD/L-proline (47.5/47.5/5.0) and its composite; (c) and (h) neat AA/1,6-HD/L-proline (45.0/45.0/10.0) and its composite; (d) and (i) neat AA/1,6-HD/L-proline (40.0/40.0/20.0) and its composite; (e) and (j) neat AA/1,6-HD/L-proline (37.5/37.5/25.0) and its composite

Table 7 Effect of moisture conditioning (80°C, 7 days) on the tensile strength, tensile modulus and compressive strength of AA/1,6-HD/L-proline copolyamides reinforced with short E-glass fibres

AA/1,6-HD/L-proline (mol/mol/mol)	Glass fibre content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Compressive strength (MPa)
50.0/50.0/0.0	0	68 ± 4	1.13 ± 0.21	60.0 ± 5.4
	15	185 ± 16	2.51 ± 0.18	107.5 ± 7.2
	30	350 ± 18	5.70 ± 0.29	161.0 ± 8.9
	45	475 ± 23	7.14 ± 0.34	266.8 ± 5.5
47.5/47.5/5.0	0	50 ± 5	1.02 ± 0.12	53.9 ± 2.7
	15	129 ± 16	2.31 ± 0.21	82.6 ± 5.6
	30	280 ± 18	5.20 ± 0.28	109.8 ± 10.5
	45	362 ± 23	6.85 ± 0.33	191.7 ± 18.0
45.0/45.0/10.0	0	43 ± 3	0.92 ± 0.30	41.2 ± 3.1
	15	116 ± 10	2.17 ± 0.19	73.0 ± 4.6
	30	248 ± 15	4.75 ± 0.25	98.5 ± 6.8
	45	327 ± 13	6.43 ± 0.38	172.3 ± 11.4
42.5/42.5/15.0	0	32 ± 4	0.81 ± 0.11	33.5 ± 2.5
	15	97 ± 8	1.92 ± 0.20	61.0 ± 4.2
	30	217 ± 17	4.53 ± 0.34	87.8 ± 6.5
	45	298 ± 20	6.14 ± 0.29	153.2 ± 11.7
40.0/40.0/20.0	0	28 ± 4	0.80 ± 0.07	23.0 ± 3.6
	15	88 ± 7	1.73 ± 0.20	45.9 ± 2.8
	30	185 ± 11	4.15 ± 0.34	77.8 ± 6.0
	45	260 ± 14	5.62 ± 0.41	130.0 ± 12.3
37.5/37.5/25.0	0	20 ± 2	0.67 ± 0.05	14.9 ± 1.53
	15	74 ± 6	1.56 ± 0.18	37.2 ± 2.42
	30	153 ± 10	3.82 ± 0.19	58.9 ± 4.50
	45	227 ± 15	5.34 ± 0.24	110.2 ± 7.40

Results are given as the mean ± standard deviation of five measurements

AA/1,6-HD/L-proline copolyamides conditioned at 80°C for 7 days are reported synoptically in *Table 7*. Although the conditioning temperature of our reinforced copolyamides is rather low for achieving drastic changes in percentage crystallinity compared with the one used in recent publications[50,51] (150°C for nylon 6 reinforced with short E-glass fibres) measurements of tensile strength, tensile modulus and compressive strength gave lower values for conditioned samples than for the dry ones. This decrease could be attributed to the synergistic effect of plasticization of the matrix[51,52] (hydrophilic copolyamide in our case) and some limited degradation of the polymer–fibre interface (debonding). Similar results were reported for the short glass fibre-reinforced nylon 6,6 composites, further supported by fractographic studies[41].

Additional experimentation using scanning electron microscopy (s.e.m.) is required for examining the strength of the glass fibre–copolyamide interfacial bond and the prevailing fracture mechanism.

CONCLUSIONS

The thermal and mechanical properties of novel biodegradable copolyamides reinforced with short E-glass fibres were examined both before and after their moisture conditioning. Several theoretical models concerning the prediction of mechanical properties and moisture absorption were applied and modifications were suggested for better fit with the experimental results. The effect of transcrystallinity could be summarized as follows:

- thermal properties: appearance of multiple peaks
- mechanical properties: higher tensile and compressive strength
- diffusion of water: limited because of crystal formation.

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