

Structure and thermal properties of blends of nylon 6 and a liquid crystal copolyester†

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(Accepted 18 February 1998)

Blends of nylon 6 with the liquid crystal copolyester Vectra have been prepared from the melt with different compositions, and their thermal behaviour has been analysed by differential scanning calorimetry (d.s.c.) and X-ray diffraction (WAXS) using synchrotron radiation, as a function of temperature and thermal treatment. The structural properties of these blends have been found to be very sensitive to the thermal history, and particular attention has been paid to the effect of the liquid crystal content in the polymorphic transformations of nylon 6. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: nylon 6; Vectra; blends)

INTRODUCTION

A considerable attention has been paid in the last few years to the blending of liquid crystal polymers (LCPs) with thermoplastic matrices^{1–3}. This is a convenient method to exploit some of the exceptional properties of LCPs with a reduced cost. On the other hand, LCPs are expected to act as reinforcement agents and processing aids when they are blended with conventional polymers, due to their tendency to form fibrillar structures and low melt viscosity.

Blends containing polyamides and liquid crystal polymers constitute a good example of these systems. Polyamides have been found to have interesting applications for the manufacture of automobile parts and textile fibres due to their good processability and outstanding mechanical behaviour. However, polyamides are very sensitive to humid environment, which can limit their use in structural parts. For this reason, polyamides have been usually blended with lower modulus polymers, such as polyolefins, to improve their moisture stability and processability conditions; previous studies have been carried out by our group on polypropylene/nylon 6 blends compatibilized with maleic anhydride-modified polypropylene^{4,5}.

Our interest is now focused on blends of nylon 6 with the liquid crystal copolyester Vectra, based on *p*-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid. It is known that LCPs are characterized by their low water absorption, and blending technology can offer the possibility of tailoring the sensitivity to humidity of these systems. It has been reported that the addition of small amounts of a LCP sample to a polyamide matrix leads to mechanical properties very similar to those of the glass fibre-reinforced nylons, but with a remarkable improvement of processability⁶. On the other hand, a strong interaction at the interface of the two immiscible phases is convenient in order to develop 'an in situ composite' such as morphology with good mechanical properties. Reactive compatibilizations have been described by blending nylon with polyesters and polymers containing acid functional groups, generating in situ graft copolymers

located in the interface, and thus enhancing compatibility¹.

In spite of the evident technological interest in these systems, only a few studies of nylon 6/LCP polymer blends have been published^{6–14}. Most were concerned with rheological and mechanical properties, and there is scarce information in the literature on the correlation between structure and technological behaviour; although impact resistance and many other properties are strongly dependent on the crystalline structure. On the other hand, the effect of blending in the thermal properties of these materials must be carefully considered in order to optimize the processability conditions. For this reason, we have investigated in this work the thermal and structural behaviour of blends based on nylon 6 and Vectra, with special emphasis on the effect of the thermal history and blend composition. Nylon 6 exhibits different polymorphous phases depending on thermal history. The addition of an anisotropic component can strongly affect the formation of the different structures. Real time experiments using synchrotron radiation have been performed in order to investigate the influence of the liquid crystal polymer in the structural transformation of nylon 6.

EXPERIMENTAL

The thermotropic liquid crystal copolyester used in this study is the commercial product Vectra A 950 from Hoechst Iberica S.A., a wholly aromatic copolyester consisting of 27 mol% of 2,6-hydroxynaphthoic acid (HNA) and 73 mol% of *p*-hydroxybenzoic acid (HBA). Nylon 6 Akulon K123 was supplied by La Seda S.A.

Both polymer pellets were dried in an oven at 120°C during 24 h. Blending was carried out in a Haake Rheocord System 60 rheometer equipped with a 60 g mixing head. The temperature was set at 290°C and the rotor speed at 50 rpm. Mixing was done for 5 min until the torque became stabilized, and samples were slowly cooled down to room temperature. Eleven compositions of nylon 6/Vectra blends were prepared in ratios of 100/0, 99/1, 98/2, 95/5, 90/10, 85/15, 70/30, 50/50, 30/70, 15/85 and 0/100 by weight.

The blends obtained directly from the Haake Rheocord System 60 were prepared as powder samples by grinding,

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†Dedicated to the memory of Prof. J.G. Fatou.

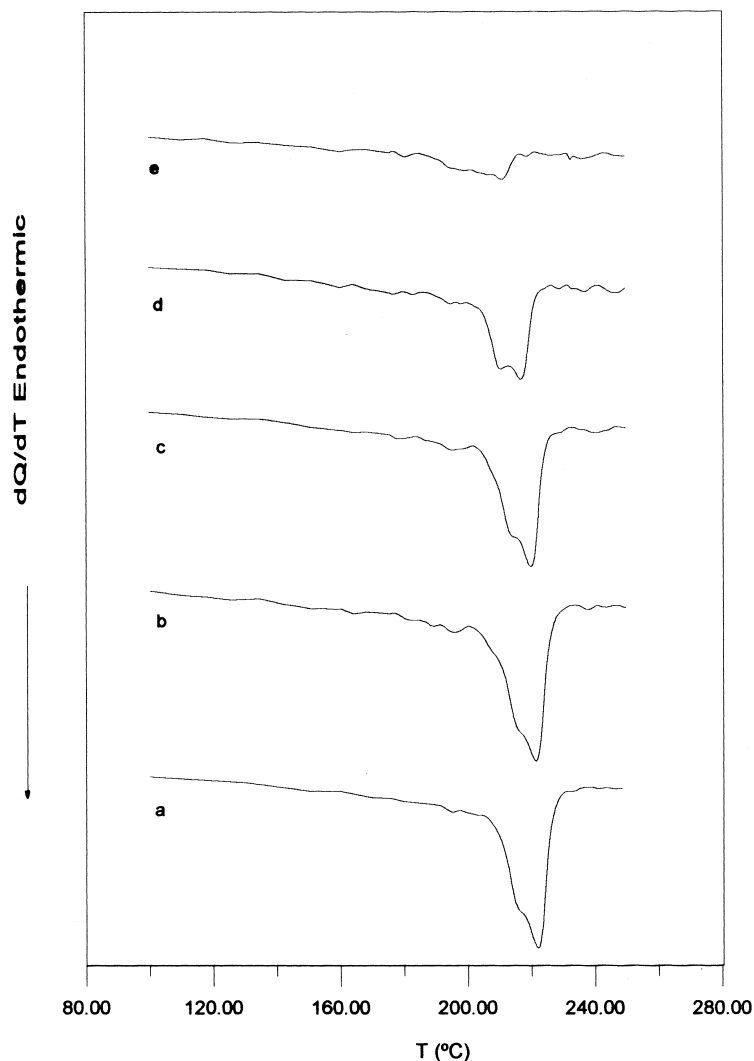


Figure 1 D.s.c. curves corresponding to the second heating cycle in nylon 6/Vectra A original samples at the following compositions: (a) 100/0, (b) 85/15, (c) 50/50, (d) 30/70, (e) 15/85

and as films by compression moulding at 290°C and 130 bar and quenching down to room temperature with circulating water. These samples were named original and quenched samples, respectively.

The thermal properties of the blends were analysed under dynamic conditions in a nitrogen atmosphere using a heating rate of 10°C min⁻¹. The experiments were carried out in a Mettler TA 4000 differential scanning calorimeter equipped with a DSC-30 oven with automatic temperature control. Several heating and cooling cycles were performed in the temperature range between 30 and 300°C. The sample weight was around 10 mg and the peak maxima were taken as the transition temperatures. Crystallinity levels of the nylon 6 phase, (1 - λ), were determined by using the following relation:

$$1 - \lambda = \frac{\Delta H_{N6}}{\Delta H_{N6100\%} \cdot w_{N6}}$$

where ΔH_{N6} is the apparent enthalpy of melting of nylon 6, w_{N6} is the weight fraction of nylon 6 in the blends and $\Delta H_{N6100\%}$ is the extrapolated value of the enthalpy corresponding to the melting of 100% crystalline sample.

Nylon 6 can exhibit different polymorphic forms and several values are proposed in the literature for the $\Delta H_{100\%}$ values.¹⁵⁻¹⁸ Illers¹⁶ reported 241 J g⁻¹ as the most probable

value for the heat of fusion of the completely crystalline α form. These data are considerably higher than those obtained by using calorimetric approximations (134–188 J g⁻¹). A compromise value of 230 J g⁻¹ has been suggested by Wunderlich¹⁷ with an error interval of ± 30 J g⁻¹. Different results have been also described for the extrapolated heat of melting of 100% γ polymorph: 175 J g⁻¹ using a density value of 1.163 g cm⁻³ or 239 J g⁻¹ by Illers¹⁶ when using a crystal density of 1.190 g cm⁻³. On the other hand, the γ^* modification leads to an enthalpy of melting of about 60 J g⁻¹ at its 100% crystalline specific volume of 0.871 cm³ g⁻¹.

As described below, a mixture of α and γ^* crystalline forms is observed in most of the samples analysed in this paper and, for this reason, an intermediate value of 190 J g⁻¹ has been chosen¹⁸. This value was reported by Ioune using several nylon 6 samples with different molecular weights and crystallinities and plotting the heat of fusion obtained by calorimetric techniques from the area under the peak against the crystallinity determined by density measurements.

X-ray diffraction patterns of the original and thermally treated samples at room temperature were obtained using a Rigaku Geigerflex-D/max X ray diffractometer fitted with a Rigaku RU-200 rotating anode generator. The diffraction patterns were recorded at 1° min⁻¹ in a 2θ range between 5 and 35° using Ni-filtered Cu K α radiation.

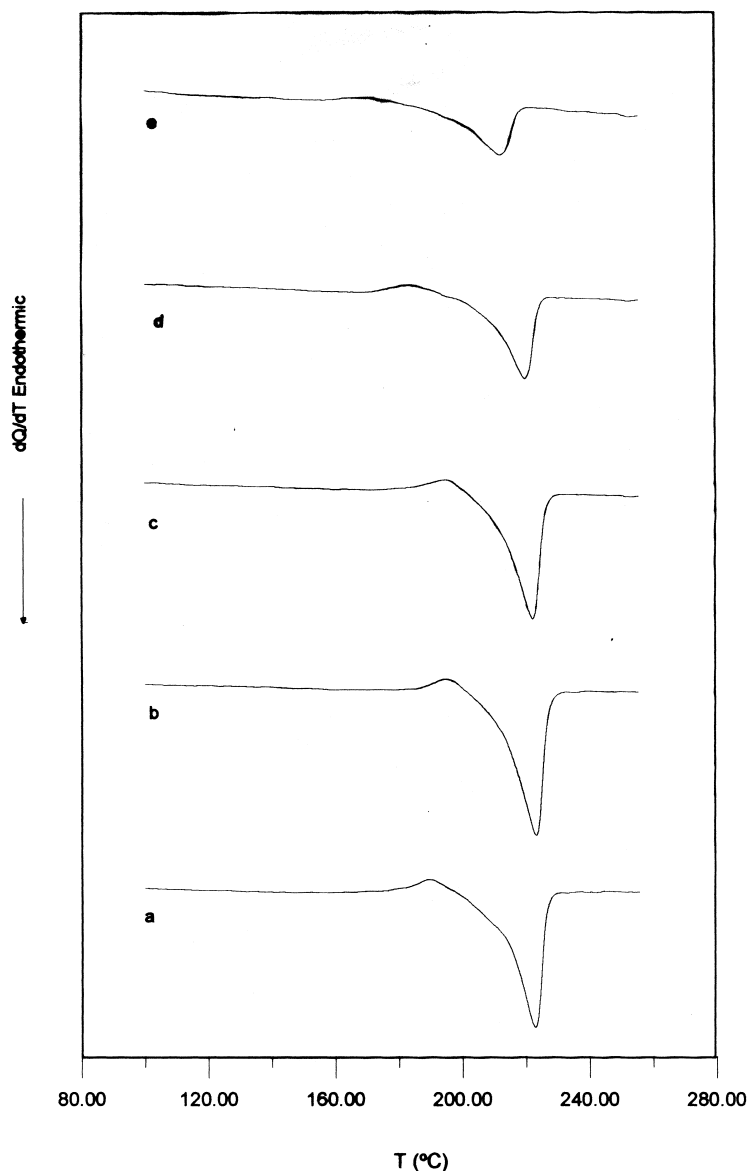


Figure 2 D.s.c. curves corresponding to the first heating cycle in nylon 6/Vectra A blends quenched samples at the following compositions: (a) 100/0, (b) 85/15, (c) 50/50, (d) 30/70, (e) 15/85

Wide-angle X-ray diffraction patterns were also recorded as a function of the temperature using synchrotron radiation at the polymer beam line at Hasylab (DESY, Hamburg). The design of the experiments were similar to those described above for the calorimetric experiments. The beam was monochromatized (1.5 Å) by Bragg reflection through a germanium single crystal in order to focus the beam in a horizontal direction. For focusing in the vertical direction a mirror was used. The scattering was detected by means of a linear Gabriel detector. Further details concerning the instrument are given elsewhere¹⁹.

DISCUSSION

A calorimetric and X-ray diffraction analysis of the nylon 6/Vectra A blends were performed as a function of the composition and thermal treatment because, to the best of our knowledge, only few data have been published about this subject for these types of blends⁷⁻⁹.

A thermogravimetric study of these systems²⁰ has been previously done in order to discard degradation effects due

to the applied thermal treatments. The original and quenched nylon 6/Vectra A blends were analysed by differential scanning calorimetry under dynamic conditions using different heating and cooling cycles. The corresponding d.s.c. curves are shown in *Figures 1 and 2* for different blend compositions.

Vectra A displays a very weak broad endothermic transition at about 280°C upon heating, which is related to the transition from crystalline to nematic mesophase order. On cooling, an exothermic transition was observed at 241°C, with an associated enthalpy value of 1.2 J g⁻¹. For this reason, the thermal transitions corresponding to Vectra A could not be easily evaluated in the blends.

The thermal and structural analysis of HBA/HNA copolymers have been reported before²¹⁻²⁵. Annealing leads to an improvement of crystallinity and crystal perfection and also can affect the chain packing depending on copolymer composition and molecular weight. The packing is hexagonal if low crystallization temperatures are considered, but an orthorhombic form can be obtained at higher temperatures. It has been described in the literature

Table 1 Thermodynamic parameters and crystallinity values obtained for original samples of nylon 6/Vectra A blends

Nylon 6 (%)	T_m (°C) ^a	T_c (°C) ^b	$1 - \lambda^a$
15	215.1	173.3	34.0
30	219.0	186.2	31.6
50	220.2	190.3	32.0
70	221.5	189.8	31.9
85	222.5	189.4	28.3
90	222.5	189.8	27.8
95	222.5	189.8	29.3
98	223.3	189.7	31.2
99	223.4	189.4	30.1
100	223.5	188.7	31.0

^aFirst heating cycle^bCooling cycle

that the orthorhombic form shows an endothermic transition at higher temperature (320°C). This transition has not been observed in our experiments.

The structure of polyamide has been widely investigated due to its commercial interest^{26–37}. It has been reported that nylon 6 can show two polymorphous forms: α and γ . We have prepared the two pure crystalline forms of nylon 6 in order to analyse their thermal behaviour by d.s.c. The melting temperature associated to the α form ($T_m = 223^\circ\text{C}$) is slightly higher than that of the γ form ($T_m = 219^\circ\text{C}$) and a crystallinity value close to 40% was estimated in both cases.

The thermal parameters of the original samples of nylon 6/Vectra A blends are presented in *Figure 1* and *Table 1*. Nylon 6 pure component shows a melting endotherm at 223°C with an enthalpy of 59 J g⁻¹ in the first heating cycle, while a crystallization peak was observed at 189°C in the corresponding cooling cycle. When the sample is subsequently heated, a multiple endotherm is observed corresponding to the melting transition with a main peak at 222°C and an associated shoulder in the low temperature range (217°C), as is seen in *Figure 1*. This behaviour is also observed in the blends and can be attributed to a higher percentage of the γ^* form in the samples cooled from the melt. A crystallinity value close to 30% was estimated in all the cases from the calorimetric data using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline samples^{15,18}.

The calorimetric analysis also showed that an increasing amount of Vectra A causes an important decrease of the melting and crystallization temperatures associated to nylon 6 in blends with more than 50% of liquid crystal copolyester, although the crystallinity values seem to be affected to a lesser extent by blend composition.

The depression of the observed melting temperatures can be considered as evidence of compatibility in blends^{38–40}. Blends of poly(ethylene terephthalate) (PET) with Vectra A have been reported⁴⁰, and a depression of the melting temperature of PET with an increasing amount of liquid crystal copolyester has been related to compatible mixing between both components.

Moreover, it has been described that blending polyamides with polymers containing acid functional groups can lead to in situ reactive compatibilizations^{1,2}. In these cases, the amino end groups of nylon can react with hydroxyl and carboxyl end groups in polyesters to form a block or graft copolymer that acts as compatibilizer for the blend. This behaviour was also reported between nylon 6 and polypropylene modified with maleic anhydride used as a compatibilizer in nylon 6/iPP blends^{4,5}. On the other hand, it is known that the polyamides are capable of forming

Table 2 Thermodynamic parameters and crystallinity values obtained for quenched samples of nylon 6/Vectra A blends

Nylon 6 (%)	T_m (°C)	T_c^a (°C)	$1 - \lambda$
15	212.0	169.8	40.3
30	219.7	183.0	34.0
50	222.1	195.0	37.4
70	223.0	195.0	37.5
85	223.0	194.8	36.7
90	223.6	191.7	35.73
95	223.6	190.4	35.95
98	223.6	192.6	35.98
99	222.9	191.1	35.08
100	222.6	189.4	35.63

^aTemperature corresponding to the crystallization exotherm prior to the melting

hydrogen bonds in polymer blends, improving the miscibility and the interfacial adhesion between phases⁴¹. Pillon *et al.*⁴² have analysed poly(amide-6,6)/PET blends finding that hydrogen bonding was an important contribution to the solution blending of the two polymers.

The enhancement of the compatibility and interfacial adhesion between nylon 6 and Vectra A blends for the compositions richer in the liquid crystal copolymer can also explain the degradation behaviour of these systems which has been described in a previous paper²⁰.

A similar depression of the thermal transition temperatures is observed in the d.s.c. analysis of the quenched samples, although the crystallinity values are slightly higher than those obtained with the original samples, as is seen in *Table 2*. However, a crystallization exotherm is observed previous to the melting transition, as is shown in *Figure 2*. This crystallization peak is centred around 190°C with an associated enthalpy of 6.1 J g⁻¹ and also shifts to lower temperatures as the amount of Vectra increases.

In order to clarify these data, quenched samples of nylon 6/Vectra A blends were annealed at 190°C and analysed by X-ray diffraction. The results were compared with the diffraction patterns obtained for the original samples and the quenched samples before the annealing treatment.

As has been pointed out previously, nylon 6 can show different polymorphic forms that have been investigated over many years^{26–37}. The α form exhibits a monoclinic unit cell with a zig-zag planar conformation, and the hydrogen bonds of neighbouring chains present a sheet-like structure where the adjacent chains in the sheet are antiparallel^{28,32,33}. The γ form is characterized by a parallel arrangement of the chains with hydrogen bonds in which the amide groups are twisted out of the zig-zag plane of the methylene groups, leading to a shorter repeat distance than the α form^{28,34}. Finally, a third polymorph form called γ^* has been described as pseudohexagonal. This form has structural characteristics similar to the γ form, but it is more disordered and can easily be transformed in the α form upon annealing^{27,28}.

Two different forms can be observed in our experiments, which have been assigned as α and γ^* forms, as is seen in *Figures 3–5*. The α form exhibits two reflections at $2\theta = 20$ and 23° , while only one reflection at $2\theta = 21^\circ$ is observed for the γ^* form. It has been reported that the α form seems to be more stable in nylon 6 because of the short distance between amide groups that enhances the planarity of the chains²⁸.

The X-ray diffraction patterns of Vectra A show one main reflection at 19.8° and a broad one centered at 27° , related to hexagonal packing, as is shown in *Figure 3e* and *Figure 4e*. It has been previously described^{22,25} that

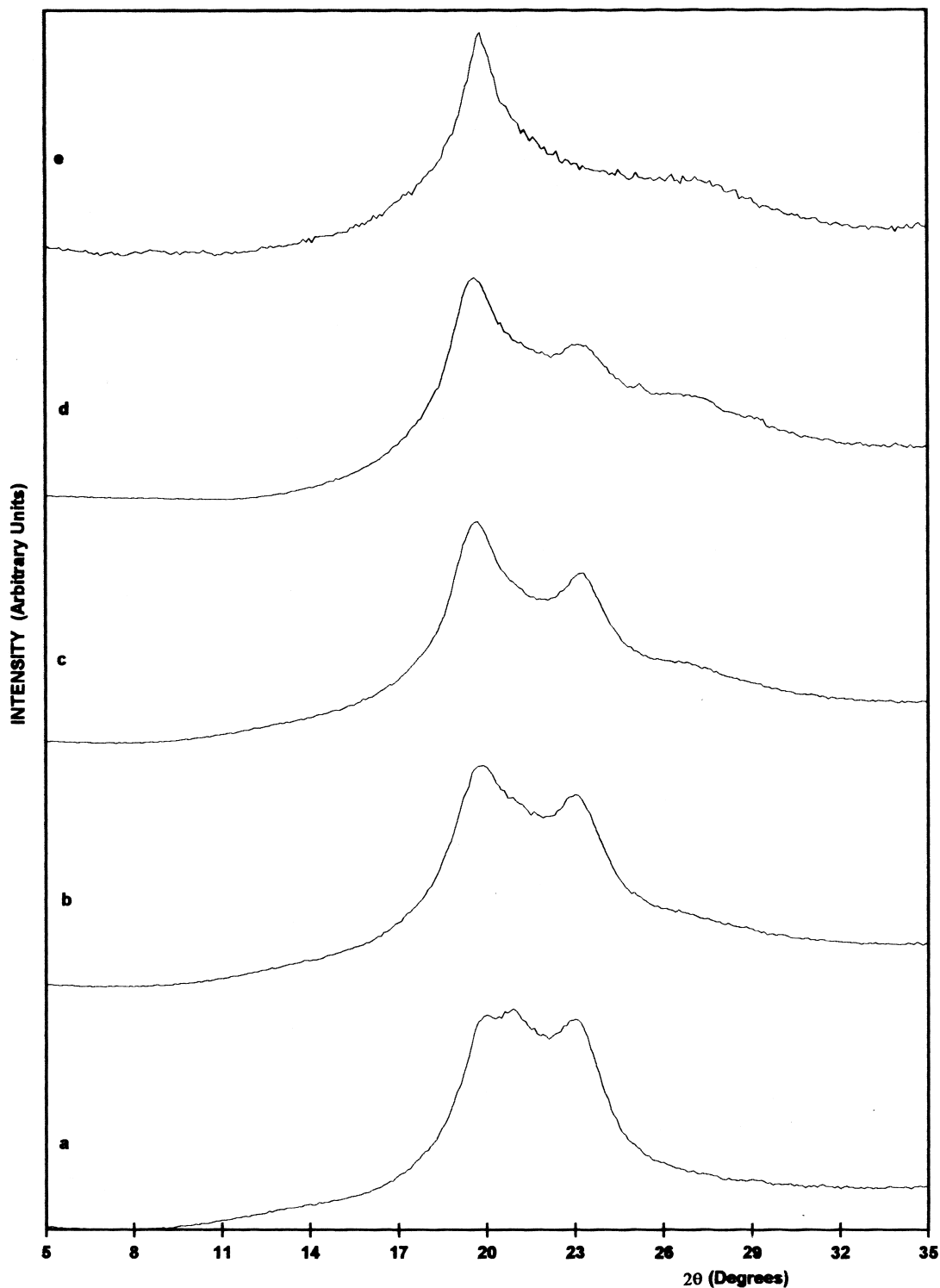


Figure 3 X-ray diffraction patterns obtained at room temperature for the nylon 6/Vectra A original samples at the following compositions: (a) 100/0, (b) 70/30, (c) 50/50, (d) 30/70, (e) 0/100

annealing at temperatures higher than 230°C can induce a transition from pseudohexagonal to orthorhombic packing. This structural change is characterized by the emergence of two new reflections at $2\theta = 22.5$ and 16° , but these reflections have not been detected in our experiments. The transformation from pseudohexagonal to orthorhombic packing has been reported to occur at temperatures as low as 120°C for the HBA/HNA 75/25 copolymer²⁴.

The X-ray diffraction patterns obtained for the nylon 6/Vectra A blends at room temperature are presented in Figures 3–5 for different compositions. WAXS analysis

of original samples (Figure 3) shows that both polymorphs α and γ^* coexist for pure nylon 6, but the reflections at $2\theta = 21^\circ$ associated to the γ^* form almost disappear gradually in the blends as the concentration of liquid crystal polymer increases.

When the samples are prepared as films at 290°C and quenched to room temperature (Figure 4), the γ^* form is mainly observed in the diffraction patterns corresponding to pure polyamide, although very weak shoulders associated to the α form could also be detected (Figure 4a). The corresponding reflections of the α form gradually increase

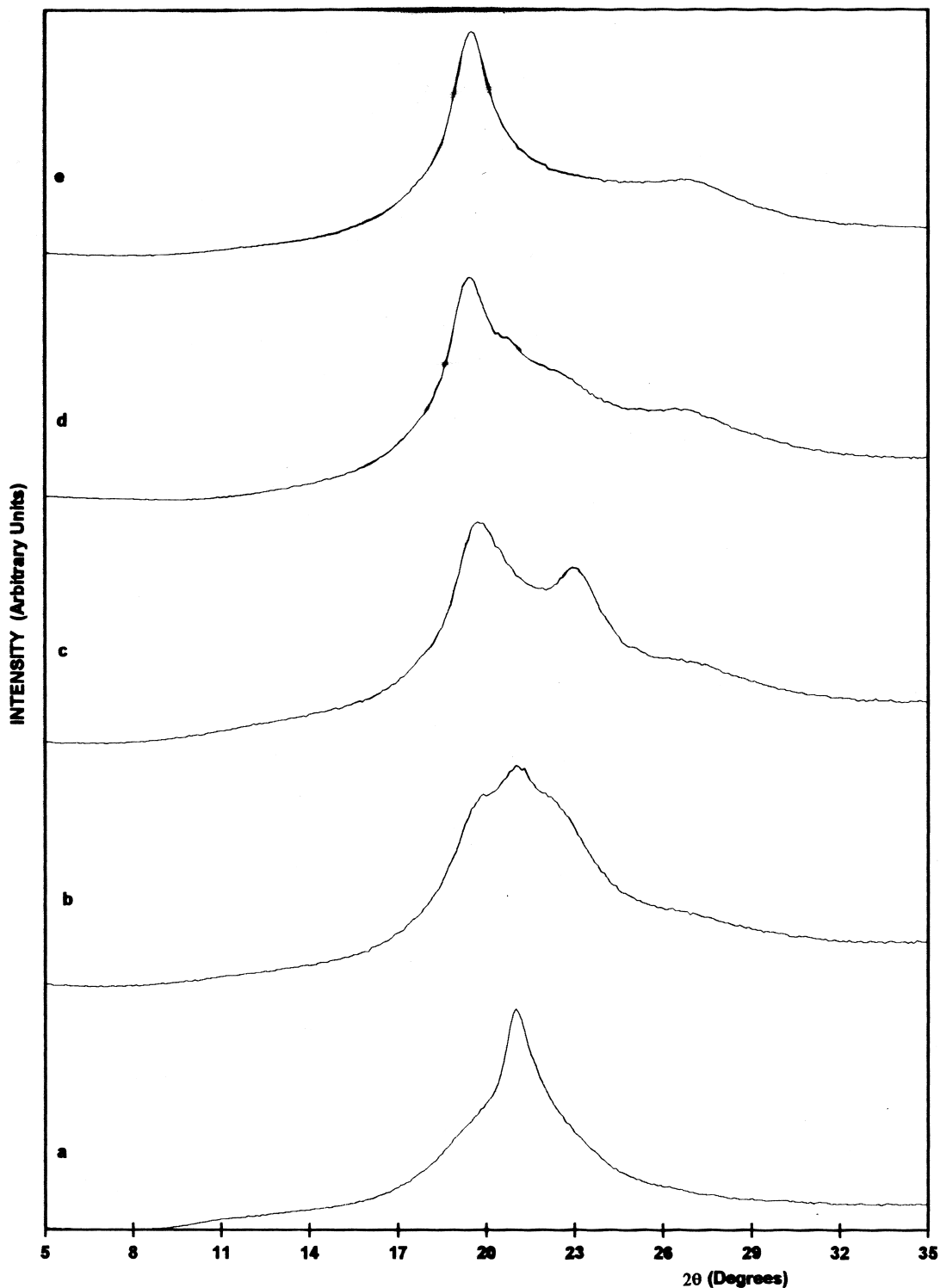


Figure 4 X-ray diffraction patterns obtained at room temperature for the nylon 6/Vectra A quenched samples at the following compositions: (a) 100/0, (b) 70/30, (c) 50/50, (d) 30/70, (e) 0/100

for the blends of up to 50% of liquid crystal (*Figure 4b*). For higher percents of Vectra A, the reflections associated to the α form are predominant.

Finally, the annealing of the quenched samples at 190°C (*Figure 5*) enhances the development of the α form for N6 pure component and low Vectra content blends, although the other crystalline form is observed. This effect is more pronounced as the Vectra content increases. This behaviour agrees with the d.s.c. results described above, as the crystallization exotherm observed at 190°C in the d.s.c.

curves of the quenched samples can be related to the formation of the α form before the melting process.

In order to confirm these results, the change of the scattering during melting of the quenched samples was followed in real time using synchrotron radiation. The corresponding X-ray diffraction patterns, recorded as a function of the temperature for the quenched 85/15 nylon 6/Vectra A blends, are presented in *Figure 6*. A mixture of the α and γ^* crystalline forms appears at room temperature, although the percentage of γ^* form increases slightly at

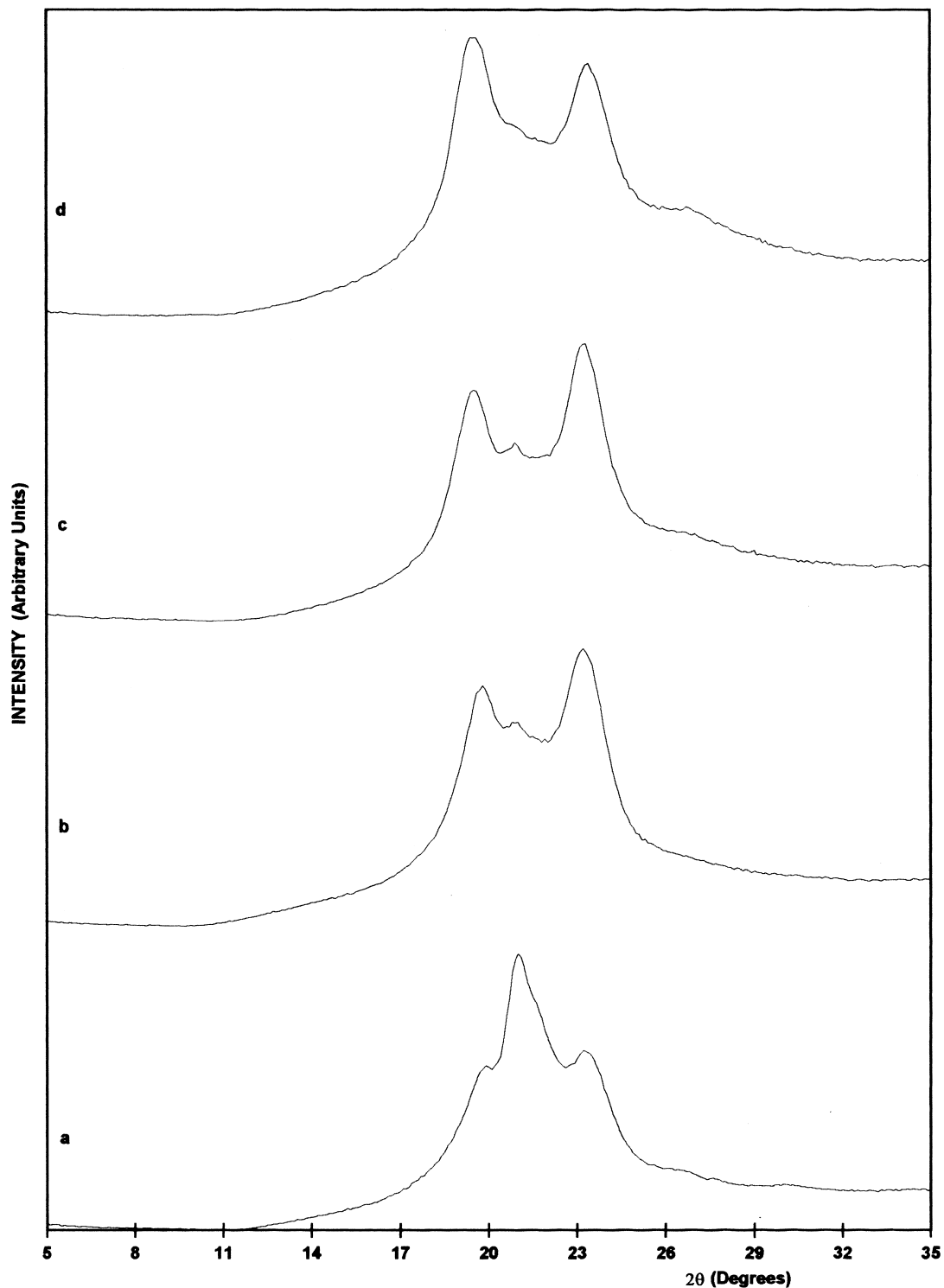


Figure 5 X-ray diffraction patterns obtained at room temperature for the nylon 6/Vectra A quenched samples annealed at 190°C, at the following compositions: (a) 100/0, (b) 90/10, (c) 70/30, (d) 50/50

about 100°C. An enhancement of the α form is observed starting at 175°C. The transformation is practically complete at temperatures above 200°C. It has been reported^{27,28} that the γ form of nylon 6 grows predominantly at lower crystallization temperatures (below 130°C), while the α form is predominant at higher temperatures (200°C). In addition, it is well known that polyamides can experience a transition of the α form in a pseudohexagonal unit cell between 80 and 170°C, named the Bill transition^{36,37}. Therefore, the synchrotron results completely agree with the d.s.c. and X-ray diffraction data described above, and

confirm that the exotherm detected in the calorimetric experiments of the quenched samples is related to the development of the α form.

It is known that the presence of water can affect the structural properties of polyamides. Gurato *et al.*³⁵ investigated the effect of water absorption in the ordered and amorphous regions of nylon 6. They observed that the quenched sample with 0.3% of the α form, 42.2% of the γ form, and 75.6% of amorphous phase, experiences a transition to the α and γ forms when it is treated with water. As the humid absorption of polyamide can be also be

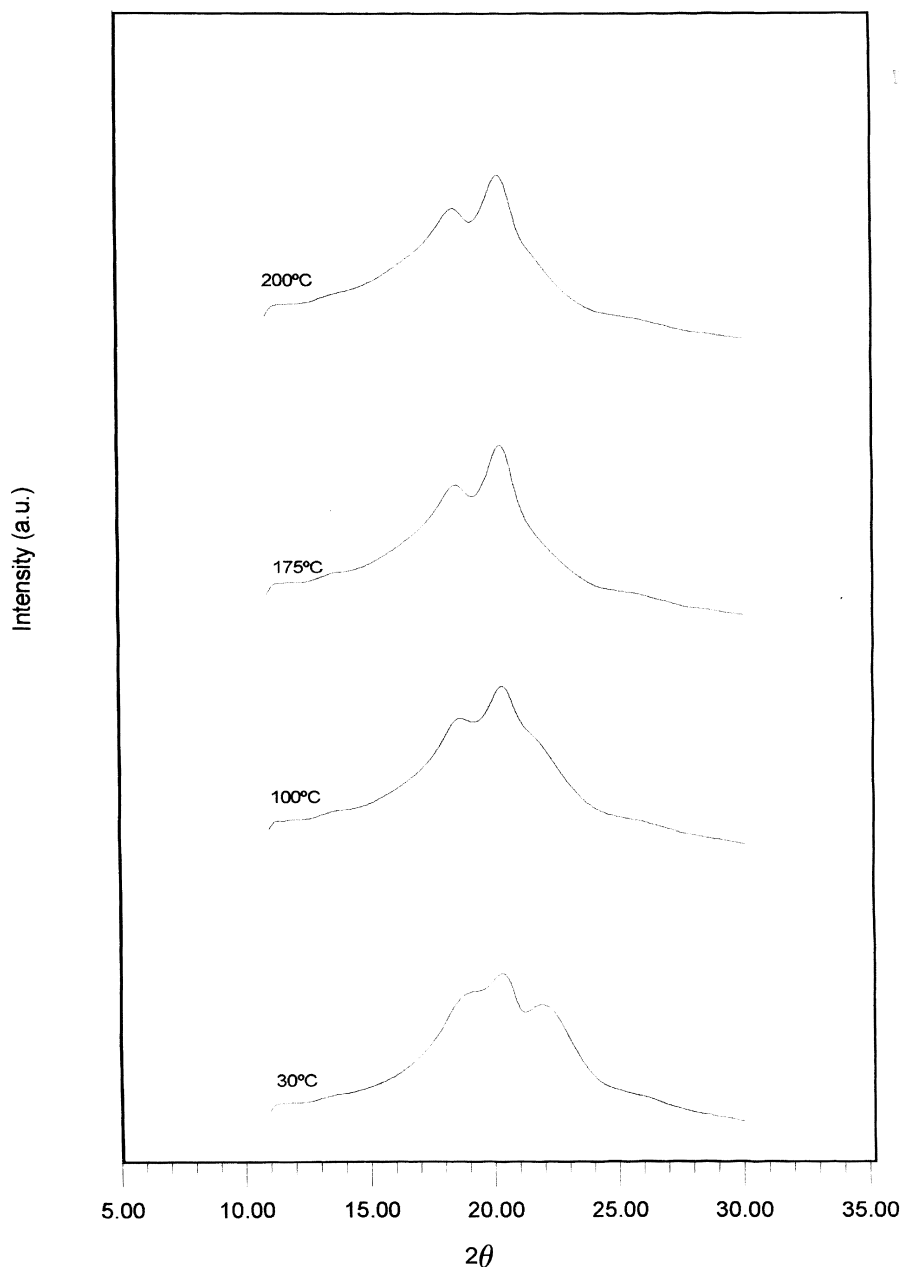


Figure 6 Real time WAXS patterns of the 85/15 nylon 6/Vectra A blend quenched sample as a function of temperature

affected by the presence of the liquid crystal component, the effect of water in the structure of these blends was also considered. An X-ray study was carried out using samples with different moisture contents. The results demonstrated that the water absorption increases the intensity of the reflections at $2\theta = 20$ and 23° and favours the formation of the α form of the polyamide component in the blends, as is shown in *Figures 7a* and *7b* for nylon 6 and the 50/50 blend, respectively. On the other hand, these data confirm that the increase in the percentage of the α form due to the liquid crystal content in these blends is also observed when these samples are exposed to moist conditions.

CONCLUSIONS

The depression of the thermal transition temperatures of nylon 6 have been attributed to an improvement of the compatibilization between the polyamide and Vectra for the blends with higher liquid crystal content.

Moreover, different structural polymorphs can be observed in nylon 6 depending on the thermal history and humid conditions, and this behaviour is also found in its blends with Vectra A. In spite of the influence of the thermal history, it became clear from the thermal and structural analysis that the crystalline structure of nylon 6 in the blends is strongly determined by the presence of the liquid crystal. There is a change in the relative amounts of the two crystalline polymorphous forms of nylon 6 depending on the copolyester concentration. In this sense, Vectra seems to enhance the stability of the α crystalline form of the polyamide independently of the thermal treatment imposed on the samples.

ACKNOWLEDGEMENTS

Financial support from the research projects MAT 95-0189 and I-96-40EC from Desy Hasyllab is gratefully acknowledged. I. Campoy also thanks the Ministerio de

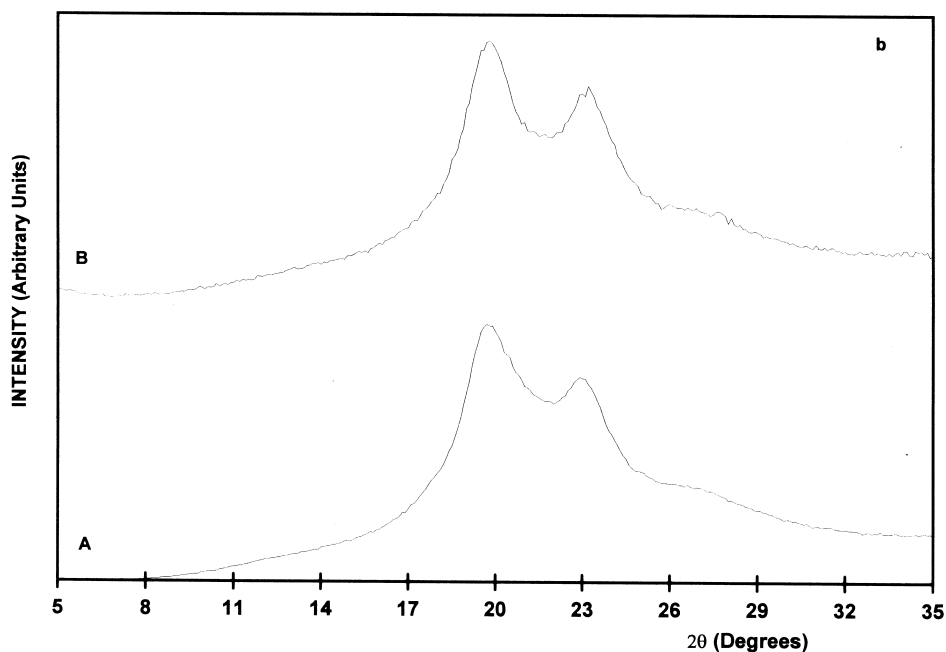
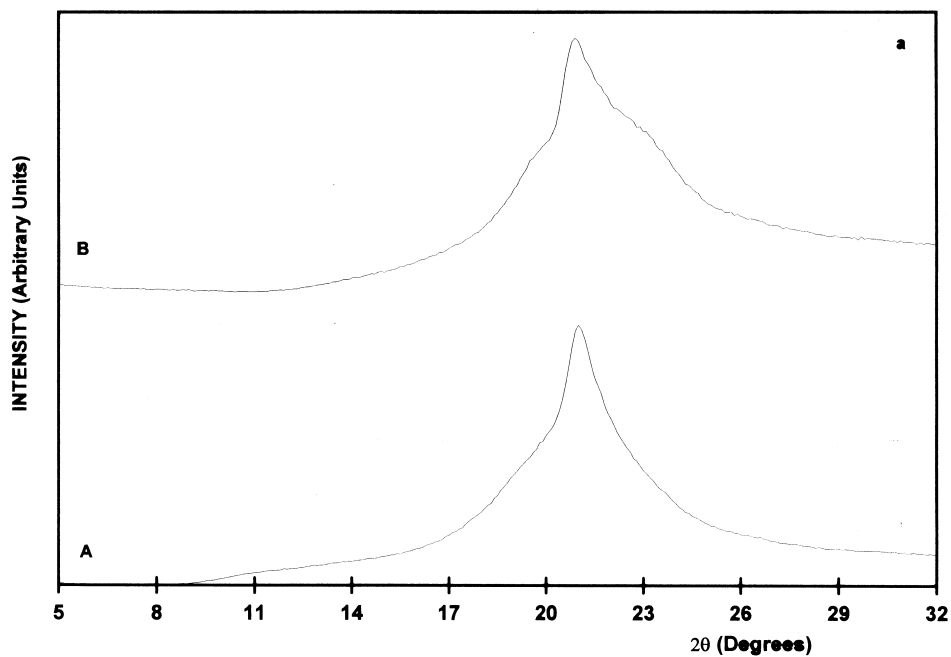


Figure 7 X-ray diffraction patterns obtained for quenched samples of (a) nylon 6 and (b) 50/50 nylon 6/Vectra A blend with different water content: (A) dried samples, (B) humid samples

Educación y Ciencia for providing a contract from the 'Programa Nacional de Formación del Personal Investigador. Acciones para la Incorporación a España de Doctores y Tecnólogos'. The authors also wish to thank Hoechst Iberica S.A. and La Seda S.A. for supplying the polymers used in this study.

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