Structural analysis of polyamide-6,6 reinforced with glass fibre by the use of Fourier transform infra-red spectroscopy with photoacoustic detection and differential scanning calorimetry

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The effect of fibre reinforcement, industrial processing and subsequent annealing on the structure of polyamide-6,6 was analysed in this paper from the correlation between photoacoustic Fourier transform infra-red (PA *FT*i.r.) spectroscopic and differential scanning calorimetry (d.s.c.) thermal measurements. Using the band situated at 1650 cm^{-1} as an internal reference band, no spectral change was detected in the bands at 936 and 1146 cm^{-1}. Furthermore, the bands centred at 1335 and 1224 cm^{-1}, which are related to chain-folding, appear in the unannealed composite, whereas in the matrix these were only detected at the highest annealing temperatures. It seems that the manufacturing process used for the composite determines its microstructure and the subsequent annealing does not produce further conformational changes. On the other hand, the composite satisfies a two-phase conformational model, different from that of the matrix, which can be related to the strong interactions between the polymer and the glass fibres with surface treatment. In the thermal analysis, in contrast to the spectroscopic results, substantial changes in the endothermic melting peaks and in the degree of crystallinity can be noted. Up to an annealing temperature of ~120–150°C, the composite crystallinity is constant and lower than the matrix crystallinity, but above this temperature the value rises and tends towards the values of the matrix. Furthermore, there was a more homogeneous crystalline distribution detected in the unannealed matrix, along with a greater size and perfection of the crystals than that seen in those of the unannealed composite. We suggest that the d.s.c. variation in the crystallinity can be attributed to an improvement in the fibre–matrix interface, in which the crystals of the interfacial phase change to more perfect ones as a result of the annealing treatment.

(Keywords: polyamide-6,6; glass fibre; composite)

INTRODUCTION

Polyamides are probably one of the most versatile classes of reinforced polymers. All types of polyamides have been reinforced, although polyamide-6 and -6,6 are the most commonly used because of the low cost of industrial production. The advantages of polyamide-based reinforced composites include very high tensile, flexural and impact properties. The disadvantages include relatively high moisture absorption and a propensity to warp.

The increased use of thermoplastics has brought about a need for better understanding of the processing techniques used to manufacture these materials. In the case of semicrystalline polymers, both the manufacturing process of the composites and the presence of fibres gives rise to ultimate morphological changes in the matrix[1]. Some fibres provide nucleating sites on their surfaces. Isolated spherulites may then be seen to be attached to the fibres. However, where the nucleation density is sufficiently high along the fibre surface, the growth takes the form of a sheath surrounding tthe fibre and this feature is then known as transcrystallinity[2].

Although it has been proved[3] that the presence of glass fibres in polyamide-6,6 modifies the process of crystallization as regards the isolated matrix, this polymer crystallizes in the presence of glass fibres without the transcrystalline phase being observed. The study of non-isothermal crystallization of polyamide-6,6 by the use of the Ozawa theory[3] gives rise to Avrami exponent values which are difficult to understand. When the distance between the fibres decreases, i.e. the reinforcement content increases, the superficial effects become predominant over the bulk effects. Therefore, the crystalline entities cannot grow freely anymore and the assumptions of the Ozawa theory are not verified[3–5].

Sizing or various other types of surface treatment have been applied to glass fibres as they are drawn and before they are gathered into strands. The surface fibre is usually treated by applying a coating which can have many functions, e.g. to protect the fibre during handling, eliminate static electricity, facilitate strand impregnation

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by the matrix constituents, increase the fibre–matrix adherence and increase the interfacial zone resistance to shearing, particularly in the presence of humidity. Therefore, the interactions between the matrix and the fibre in the composite material have to be borne in mind in order to understand the composite microstructure. The nucleation of polyamide-6 and polyamide-6,6 on to graphite surfaces[6] has indicated that there are strong interactions between the polar groups of the polymer and the substrate. Furthermore, Bessel and Shortall[7] and Cinquin *et al.*[8] have proved that the surface treatment of reinforcing fibres appears to have a significant effect on both carbon-fibre reinforced polyamide-6 and glass-fibre reinforced polyamide-6,6.

In several previous papers[9–11], pure poly(ethylene terephthalate) (PET) and glass-fibre-reinforced PET, obtained industrially and subsequently annealed, were analysed in detail by using vibrational spectroscopy and thermal analysis. In these studies, it was demonstrated that the PET in both the matrix and the composite satisfies the same two-phase conformational model. The annealing treatment produced a change in the isomer contents of the *trans* and *gauche* conformations in the matrix, but no evolution was observed in the composite. It was concluded from these studies, that the manufacturing process for glass-fibre-reinforced PET seems to determine its microstructure and subsequent annealing does not produce any further conformational changes. Nevertheless, an improvement of the fibre–matrix interface was detected.

The main purpose of this present work is to determine the effect of fibre reinforcement, industrial processing and subsequent annealing treatment on the structure of polyamide-6,6. In order to achieve comprehensive characterization of the polyamide composite, in particular the fibre–matrix interface, photoacoustic Fourier transform infra-red (PA *FT*i.r.) spectroscopic measurements and their further correlation with differential scanning calorimetry (d.s.c.) results have been carried out in this present study.

EXPERIMENTAL

Materials

The sample used in this work was supplied by SNPE (France) as a 2 mm thick plate obtained by a compression moulding process.

The material chosen as the matrix was commercial Polyamide-6,6 (trade name PA6,6 Technyl A218; formic acid viscosity ~140; $M_w \sim 33000$; $M_n \sim 16500$). The glass-fibre reinforcements used were Vetrotex R.o.99 2400 sizing 5175 (E-glass).

The impregnation and manufacturing processes that were employed to obtain the composite material have been previously described[10]. The density of the composite (ρ_c) is 1.94 g cm^{-3} and the glass weight fraction (w_f) is 80%.

Samples (3 × 2 × 2 mm^3) were cut from the plates and introduced into a stabilized oven at different annealing temperatures (T_{ann}) ranging from 45 to 250°C, kept there for 1 h and then cooled to room temperature.

Photoacoustic Fourier transform infra-red (PA FT*i.r.) measurements*

PA *FT*i.r. spectra of reinforced polyamide-6,6 samples were obtained at room temperature on a Mattson Cygnus 100 *FT*i.r. spectrometer equipped with a MTEC 200 PA cell.

A set of spectra were obtained at 8 cm^{-1} resolution and averaged over 312 scans. The best signal-to-noise ratio was obtained at a mirror speed of 0.12 cm s^{-1}.

Powdered carbon was used as a photoacoustically saturated (black) reference material.

Thermogravimetric (t.g.) measurements

For measurements of the crystallinity by using d.s.c., we need to know exactly the fibre quantity in the sample, since important changes in the apparent degree of crystallinity can stem from small local variations in the average glass-fibre content.

The glass-fibre content was obtained with a Perkin–Elmer Thermogravimetric Analyser (TGA 7). The experimental conditions included a heating programme from 25 to 700°C, at a temperature rate of 10°C min^{-1}, in which this latter temperature was maintained for 5 min. From these measurements, the width of the glass fibre distribution around the value given by the manufacturer (80%) was found to be ca. ±10%.

Differential scanning calorimetry (d.s.c.) measurements

The thermal analysis was carried out in an air atmosphere using specimens with weights ranging from 12 to 14 mg; the calibration of both temperature and melting enthalpy was made with a standard sample of indium. The d.s.c. experiments were performed on Mettler TA4000 (DSC 30) equipment at a heating rate of 10°C min^{-1}; each thermogram was recorded from 20 to 320°C.

To calculate the apparent degree of crystallinity, we used the weight of glass fibre obtained from the thermogravimetric measurements to obtain the mass of the matrix in the composite samples. A value of 46 cal g^{-1} was adopted for the heat of fusion of an ideal polyamide-6,6 crystal[12].

RESULTS AND DISCUSSION

Vibrational analysis

In a similar way to the study carried out on the pure polyamide-6,6[13], the quantitative analysis used to monitor the spectral changes promoted by the thermal treatment was focused on the bands situated at 936 cm^{-1} (C–CO stretching, *trans* conformation) and 1146 cm^{-1} (CO twisting, *gauche* conformation) (*Figure 1*).

The integrated intensity of the band situated at 1650 cm^{-1} (amide I) does not seem to be affected by the annealing, in coincidence with the behaviour displayed by the matrix. We were therefore able to use this band as an internal reference band in order to follow the intensity evolution of the bands at 936 and 1146 cm^{-1} with annealing treatment. In order to carry out the quantitative analysis, peak heights were measured with respect to baselines drawn between the valleys on either side. The dependence of the intensity ratios I_{936}/I_{1650} and I_{1146}/I_{1650} on the annealing temperature, both in the isolated matrix and the composite, has been plotted in *Figure 2*. A strikingly different behaviour can be noted. In the matrix[13], the intensity of the band situated at 936 cm^{-1} increases and that of the band situated at 1146 cm^{-1} decreases when the annealing temperature is greater than 180°C. However, in the composite no

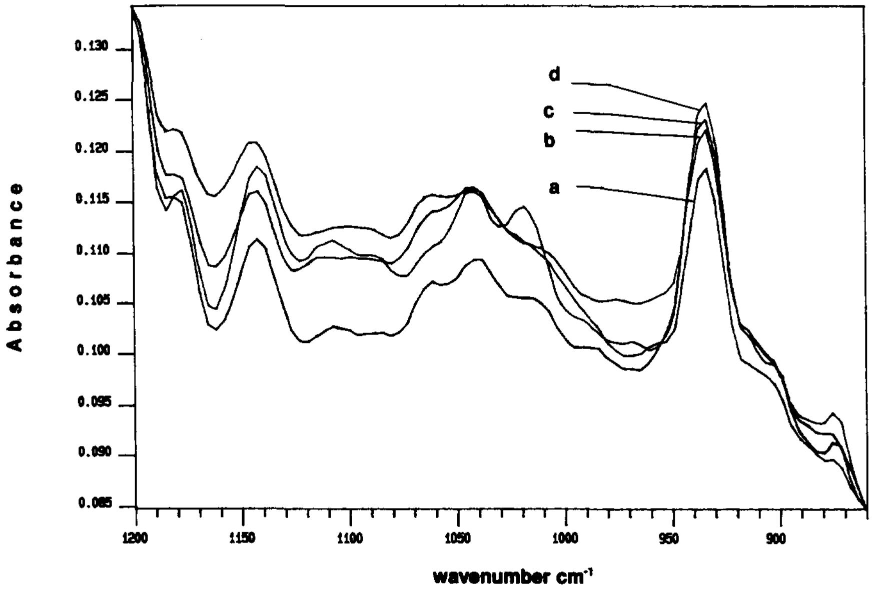

Figure 1 PA *FT*i.r. spectra of (a) unannealed glass-fibre-reinforced polyamide-6,6 and samples annealed at (b) 90, (c) 180 and (d) 230°C in the spectral range 860–1200 cm^{-1}

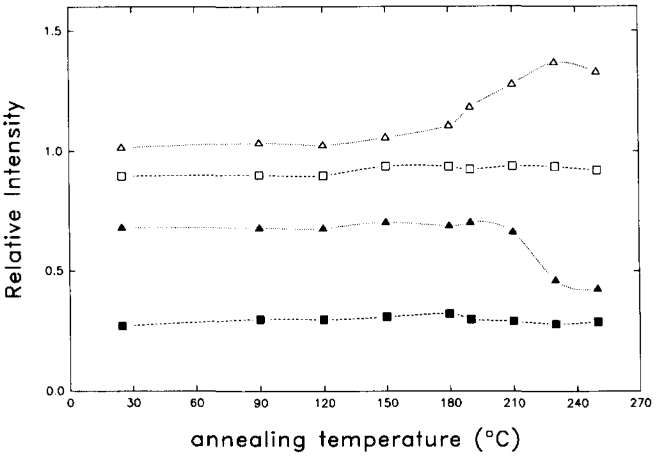

Figure 2 Relative intensities of the bands at 1146 (filled symbols) and 936 cm^{-1} (open symbols) *versus* annealing temperature: (▲, △) matrix (from ref. 13); (■, □) composite

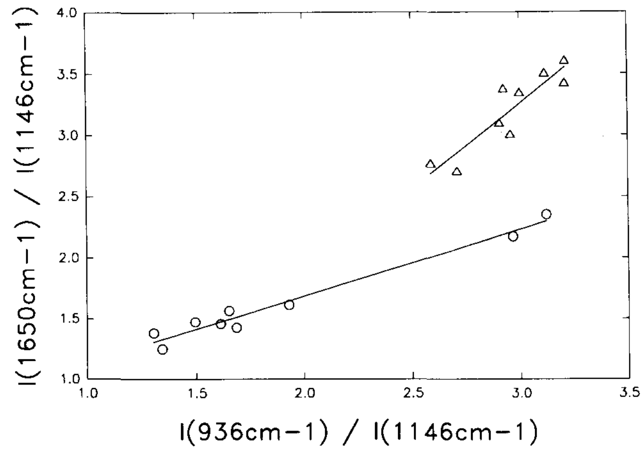

Figure 3 Intensity ratios I_{1650}/I_{1146} *versus* I_{936}/I_{1146}. Verification of the two-phase conformational model in pure polyamide-6,6 (○) (from ref. 13) and in glass-fibre-reinforced polyamide-6,6 (△)

intensity evolution with annealing temperature can be detected. Furthermore, in the matrix the bandwidth of the band centred at 936 cm^{-1} decreases from 23 cm^{-1} for the unannealed sample or for that annealed below 180°C to 20 cm^{-1} for the samples annealed above 180°C. In the composite, the bandwidth remains as a constant at a value of ~20 cm^{-1}.

In addition to the above peaks, the two bands situated at 1329 and 1224 cm^{-1} can be related to chain-folding conformations in the polyamide-6,6 crystals[14]. In the matrix[13], two shoulders situated at 1335 and 1224 cm^{-1} were detected in the spectra, but these only appeared at the highest annealing temperatures. This phenomenon arises from the fact that these annealing treatments are supposed to remove crystal imperfections and to improve chain packing at the amorphous–crystalline interphase. In the glass-fibre-reinforced polyamide-6,6, these two bands already appear in the unannealed sample.

In a previous paper[13], we proved that pure polyamide-6,6 satisfies a two-phase conformational model which can be described by the following equation:

$$1 = p_1\frac{I_{936}}{I_{1650}} + p_2\frac{I_{1146}}{I_{1650}} \tag{1}$$

where p_1 and p_2 are the band weights which are related to the radiation–matter interaction. Thus:

$$\frac{I_{1650}}{I_{1146}} = p_1\frac{I_{936}}{I_{1146}} + p_2 \tag{2}$$

Therefore, if glass-fibre-reinforced polyamide-6,6 verifies this model, a linear relationship between the (I_{1650}/I_{1146}) and (I_{936}/I_{1146}) intensity ratios has to be achieved. *Figure 3* shows the fitting from this expression of the experimental PA *FT*i.r. values for the matrix and the composite. Both the matrix and the composite follow the linear intensity ratio of equation (2) but, in contrast to PET and glass-fibre-reinforced PET, which both satisfy the same conformational model[9,10], the p_1 and p_2 parameters are different in the matrix and composite of the polyamide-6,6 system. Thus, the matrix and composite intensity ratios shown in *Figure 2* are not directly comparable because the relative significance of the bands has been changed with the reinforced process.

The least-squares curve fitting method was carried out in order to obtain the parameters in the matrix and the composite, which provide information about the material microstructure. Unfortunately, the values obtained for the composite do not allow us to calculate the percentage isomer content in a similar way to as they were evaluated in the matrix[13]. The two analysed bands involve the vibration of polar groups (CO) which are directly related to the structure of polyamide-6,6 through the hydrogen bond. The microstructure of the composite material may be modified, with regard to the matrix, as a result of strong interactions between these polar groups in the macromolecule and the sized glass fibres, as has been previously reported for other types of fibre[7].

We have shown in a previous study[13] that the experimental (spectroscopic) behaviour of pure PET and polyamide-6,6 are quite similar, and a two-phase conformational model was satisfied by both polymers. However, the conformational evolution in the isolated polyamide-6,6 is ultimately different to the pure PET. We have suggested that the spectral variations in the band situated at $936\,cm^{-1}$ are related to conformational changes, with contributions of the amorphous and crystalline *trans* conformations both being found[13]. It was shown in pure polyamide-6,6[13] that the conformational content of the amorphous *trans* isomer shows an approximately linear increase above 180°C. Therefore, in the glass-fibre-reinforced polyamide-6,6 the band situated at $936\,cm^{-1}$ involves contributions from both ordered and disordered *trans* conformations, even at the highest annealing temperatures, in contrast to the glass-fibre-reinforced PET where the disordered *trans* conformation vanishes at 110°C (primary isomerization)[10,11].

Thermal analysis

The d.s.c. thermograms of an unannealed sample and samples annealed at 150, 190 and 230°C are presented in *Figure 4*.

Attention must be paid to the changes that occur in the thermograms of the samples that have undergone an annealing process. For the unannealed sample and those annealed below 150°C, a broad endothermic peak appears at ~262°C, indicating the melting of the polyamide-6,6 composite. A slight shoulder at ~250°C is also detected, which proves the existence of another peak incorporated in the main melting peak. This endothermic shoulder appears clearly in the thermograms of samples which have been annealed above 150°C; it shifts toward higher temperatures and grows in size with increasing T_{ann} and, eventually, two endothermic peaks can be detected in the thermogram of the sample annealed at 230°C (at 253 and 261°C).

In fact, two endotherms were also found in the pure matrix[13]. In this material, the low melting peak (LM peak) appeared in the thermograms of samples annealed

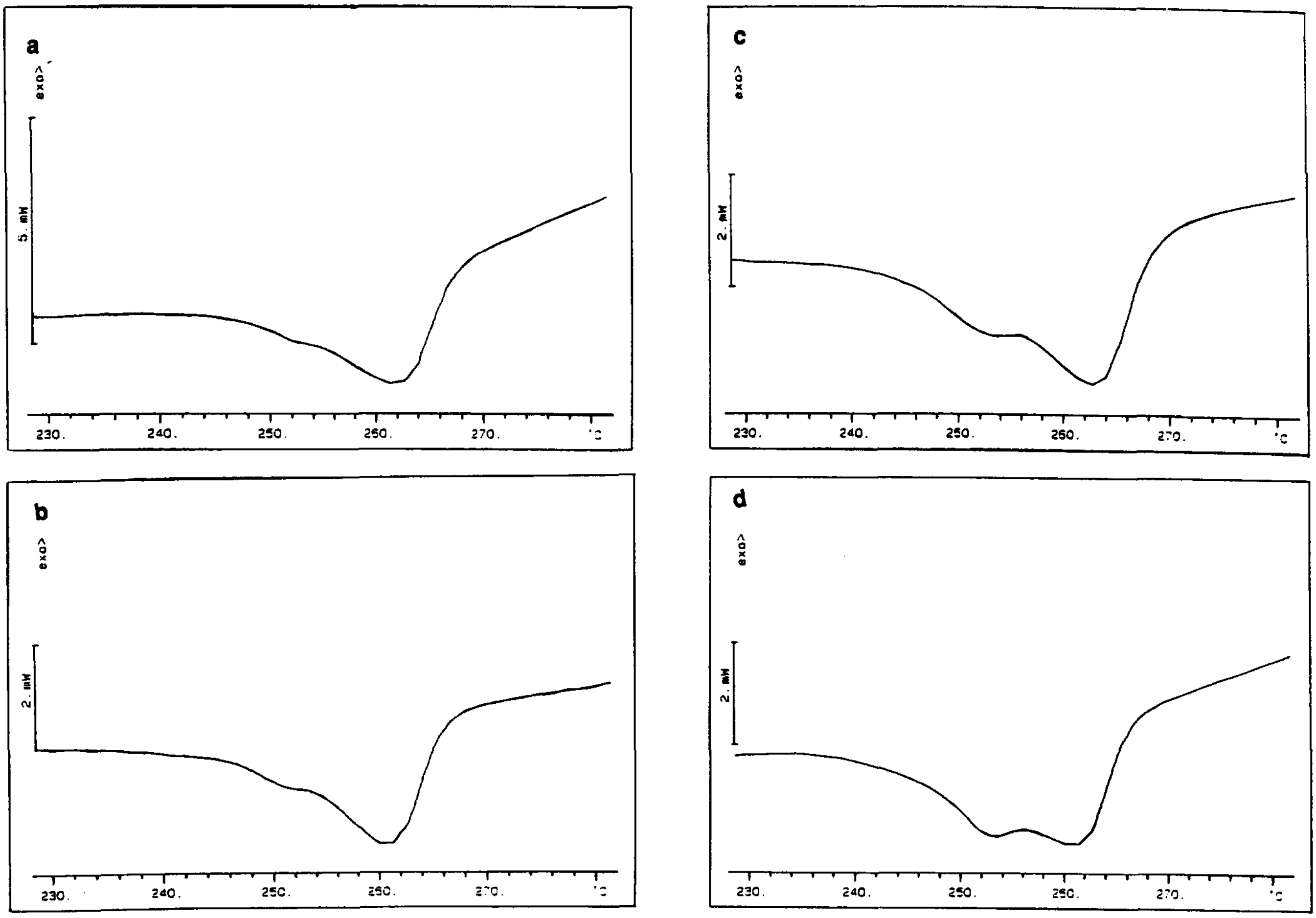

Figure 4 D.s.c. thermograms of (a) unannealed glass-fibre-reinforced polyamide-6,6 and samples annealed at (b) 150, (c) 190 and (d) 230°C

above 150°C, followed by another endothermic high melting peak (HM peak) at the melting range. The LM peak continually shifts towards higher temperatures and grows in size with increasing T_{ann}, according to the following equation:

$$T_m = 1.2T_{\text{ann}} - 8$$

Finally, only one endothermic peak was detected in the thermogram. From the similar thermal behaviour displayed by PET and polyamide-6,6, we have suggested[13] that the low endothermic peak can be attributed to melting or to some type of internal reorganization process which leads to a higher perfection of crystals, with the increasing perfection due to the annealing treatment, while the high endothermic peak represents melting of the crystalline structure that has been reorganized during the d.s.c. heating scan.

From the integrated area of the endothermic peak and the shoulder, the latent heat of fusion in the composite was calculated, and the apparent degree of crystallinity of the matrix and the composite are plotted in *Figure 5*. In the matrix, only a slight increase of crystallinity ($\sim 5\%$) can be detected above 180°C; this was related to various reorganizations which occur in the crystalline part of the matrix due to the annealing process, involving a higher perfection and regularity of the crystals[13]. However, in the composite, the increase is found to occur at $\sim$120–150°C and the crystallinity variation was more significant ($\sim 10\%$). Finally, at 250°C, the crystallinity decrease can be related to premelting or degradation, similar to the pure matrix[13]. No crystallinity variation can be detected below 120°C in either of the matrix or the composite.

The endothermic melting peak of the unannealed matrix (continuous line) and composite (dotted line) are plotted in *Figure 6*. Two important differences need to be pointed out. First, the bandwidth of the matrix peak is less than that of the composite, which involves a more homogeneous crystalline distribution in the matrix. Secondly, the melting peak temperature appears at 268°C in the matrix and at 262°C in the composite. This implies a higher size and perfection for the crystals of the matrix than for those of the composite. The difference in the intensities of the peaks is due to the different mass of polymer in the matrix and composite samples used in the d.s.c. scans.

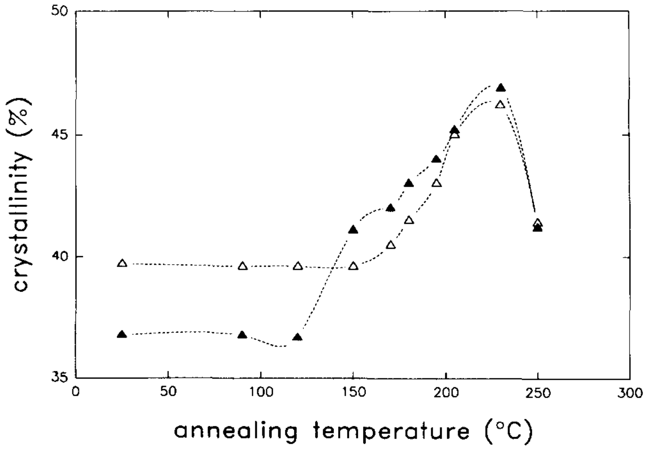

Figure 5 Evolution of the degree of crystallinity as a function of annealing temperature: (△) matrix[13]; (▲) composite

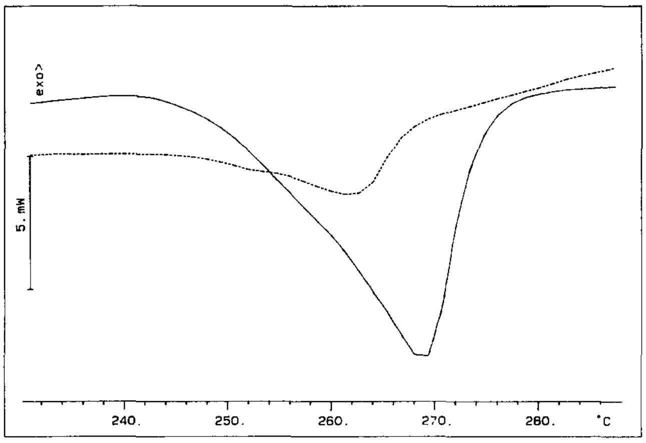

Figure 6 Melting peaks of unannealed samples of pure polyamide-6,6 (——) and glass-fibre-reinforced polyamide-6,6 (– – –)

Qualitative correlation between PA FT*i.r. and d.s.c. measurements*

From the spectroscopic results, no conformational changes can be detected over the range of thermal treatment examined. We suggest that the manufacturing process of the composite determines its microstructure and that subsequent annealing does not produce any further conformational changes, in contrast to the variations which appeared in the spectroscopic evolution of the annealed matrix[13].

However, in the d.s.c. curve (*Figure 5*) two different regions can be distinguished: up to annealing temperatures of $\sim$120–150°C, no crystallinity change can be detected in the composite, and lower values than those found in the matrix were obtained. Above this temperature, the degree of composite crystallinity rises and tends towards that of the matrix. Therefore, there seems to be an apparent inconsistency between the spectroscopic and thermal results, similar to that observed with the PET composite system[11].

Although the spectroscopic results show that the total *trans* isomer content does not seem to vary with the annealing treatment, it can be thought that a change from a disordered *trans* conformation to an ordered form might occur as a result of the thermal treatment, with the total *trans* content remaining constant. Furthermore, this process would involve the same conformational transformation rate from the ordered conformation to the disordered one. It has been proved[13,15] that the crystalline regions in pure polyamide-6,6 are quite rigid, due to the limited mobility of the amide group, and that most of the conformational changes occur in the amorphous phase where the hydrogen bonds have less organization than those of the crystalline regions. Therefore, it is difficult to accept that the above condition is satisfied and so there has to be another explanation for the d.s.c. crystallinity change.

In order to explain the above inconsistency, an analysis of the manufacturing process of the composite material should be taken into account. A temperature gradient results from the thermal conductivity mismatch of the fibre and the matrix, and the fibre surface (which has good thermal conductivity) can be cooler than the matrix. This lower surface temperature usually generates a rapid cooling near the interfacial regions, whereas in the 'bulk' the molecules can crystallize better. Moreover, owing to the very large fibre content of the composite, this interface forms the major part of the material. It can be suggested that the region near the fibre has less perfection in its crystalline phase than the 'bulk' crystalline state and therefore it is likely that its crystallinity is undervalued in the d.s.c. measurements.

Bearing in mind that (1) the fibre–matrix interface comprises the major part of the composite, (2) the *gauche* isomer content does not vary with the thermal treatment and (3) the stiffness of the crystalline structure, the variation of the crystallinity obtained by d.s.c. measurements at around 120–150°C may be attributed to an improvement in the fibre–matrix interface in which the crystals of the interfacial phase change to a more perfect form as a result of the annealing treatment. Furthermore, the crystallinity variation (about 10%), and the annealing temperature range in which the increase of composite crystallinity was detected, agree with those found for glass-fibre-reinforced PET[10,11].

CONCLUSIONS

In this work, the effect of fibre reinforcement, industrial processing and subsequent annealing treatment on the structure of glass-fibre-reinforced polyamide-6,6 was analysed. From the correlation between spectroscopic (PA *FT*i.r.) and thermal (d.s.c.) measurements, a study of the fibre–matrix interface was carried out.

In the spectroscopic analysis, using the band centred at $1650\,\mathrm{cm}^{-1}$ as an internal reference band, the bands situated at $936\,\mathrm{cm}^{-1}$ (C–CO stretching, *trans* conformation) and $1146\,\mathrm{cm}^{-1}$ (CO twisting, *gauche* conformation) were used to monitor the spectral changes promoted by the thermal treatment.

No change as a result of the annealing process has been observed in either the intensity or the bandwidth of the above bands, in contrast to the spectroscopic changes promoted by annealing of the isolated matrix. Furthermore, the bands centred at 1335 and $1224\,\mathrm{cm}^{-1}$, and related to chain-folding, appear in the unannealed composite, whereas in the matrix they were only detected at the highest annealing temperatures. On the other hand, the polyamide-6,6 composite also satisfies a two-phase conformational model (different to that of the matrix), which can be related to the strong interactions between the polar groups of the macromolecules and the treated surface of the glass fibres. As a result, it can be suggested that the manufacturing process employed for the composite determines its microstructure and subsequent annealing does not lead to any further conformational changes.

In the thermal analysis, an endothermic peak and a shoulder can be observed over the melting range, i.e. at 262 and 250°C, respectively. The shoulder shifts toward higher temperatures and grows in size with increasing T_{ann} and, eventually, two endothermic peaks (at 253 and 261°C) can be detected in the thermogram of the sample annealed at 230°C.

From comparison between the endotherm peaks of the unannealed matrix and the composite, two important conclusions were reached. First, a more homogeneous crystalline distribution is present in the matrix, and secondly, the size and perfection of the crystals is higher in the matrix than in the composite.

In contrast to the isolated matrix, where only a slight crystallinity increase ($\sim 5\%$) was observed at 180°C, an increase of 10%, at temperatures above 120–150°C, can be detected in the composite. Furthermore, the degree of composite crystallinity remains constant, with a value lower than that of the matrix, up to annealing temperatures around 120–150°C, but above these temperatures, the value rises and tends towards the matrix value.

Although some conformational changes from the disordered *trans* to the ordered *trans* might be possible while still retaining the total *trans* content as a constant, based on the stiffness of the crystalline structure of polyamide-6,6 we suggest that the d.s.c. variation in the crystallinity can be attributed to an improvement in the fibre–matrix interface in which the crystals of the interfacial phase change to a more perfect form as a result of the annealing treatment.

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