

Structural Analysis of Poly(ethylene terephthalate) Reinforced with Glass Fiber: Thermal Behavior and Correlation Between PA-FTIR and DSC Measurements

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SYNOPSIS

In this article, the correlation between PA-FTIR and DSC techniques was carried out to obtain a more comprehensive interpretation for the fiber–matrix interface of glass fiber-reinforced PET and the dependence on annealing temperature. In contrast to the thermal behavior of an unannealed matrix or an annealed one at low temperatures (below 110°C), glass transition is barely perceptible and no crystallization peak can be found in the composite. Therefore, the lack of these thermal characteristics indicates the absence of the primary isomerization in the matrix. Similarly to the isolated matrix, low-melting and high-melting peaks appear in the thermograms of the annealed composite beyond 135°C, but the size and perfection of crystallites seems to be less in the composite. Conversely to the spectroscopic results, the crystallinity values of the composite tend only to coincide with those of the annealed isolated matrix at temperatures beyond 150°C, and below this temperature, they are always lower, until the primary isomerization of the matrix. A comparison between the results obtained with both techniques seems to indicate an improvement on the fiber–matrix interface in which an interfacial structure with low degree of perfection changes to more perfect crystals due to the annealing treatment. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of continuous fiber-reinforced thermoplastics is a well-established way of producing composite components having high modulus, specific strength, high fracture toughness, unlimited shelf life, and rapid low-cost production.

In the case of semicrystalline polymers, the crystalline nature of the matrix and how that is affected by processing conditions will have a direct effect on the properties of the composite. Furthermore, aside from the influence of orientation and fiber length on these properties, the nature of fiber–matrix interface plays a important role.^{1–5}

Glass fibers are probably the most common of all reinforcing fibers for polymer matrix composites;

their principal advantages are their low cost and high strength. It is well known that this kind of fiber acts as a nucleating agent modifying the process of crystallization.^{2–4} Moreover, the fiber content must be taken into account. In a 60% weight-filled composite such as our sample, the matrix spacing between the fibers is usually small, resulting in an enormous increase of the region around the fiber and, therefore, a decrease of the influence of the matrix bulk effects.

Poly(ethylene terephthalate) (PET) is a well-known semicrystalline polymer. This material is widely used as films or fibers and, recently, as a reinforced compound to produce composite materials.

Thermal treatments give rise to important conformational changes in PET. Below the glass transition temperature (75–80°C), there is little change in the isomer distributions with temperature. Above this temperature, drastic changes (with sigmoidal

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evolution) in the relative amounts of the *gauche* and *trans* isomers of the ethylene glycol moiety are detected (primary isomerization); on a molecular level, this isomerization can be described as a process of "local" chain rearrangements which need no obvious diffusion or reorganization of chain segments. At high annealing temperature (above 140°C), there is a second change in the slope of the *gauche* and crystalline *trans* isomers as a function of the temperature (secondary isomerization : linear evolution). These isomeric transformations occur in a cooperative fashion and the mobility of the segments is high enough to proceed with segmental rearrangements which distinguish this isomerization from the primary transformation.^{6,7}

This article is focused on the structural characterization of annealed glass fiber-reinforced PET. In a previous work,⁸ PA-FTIR measurements were carried out to characterize the dependence of conformer distributions in PET composite on annealing treatment. Some important spectroscopic conclusions were achieved: First, from the analysis of the spectroscopic features, no conformational change over the range of thermal treatment was detected. Moreover, for all the annealing temperatures, the conformational distributions were similar to that of the annealed isolated matrix at the highest temperatures. Thus, the manufacturing process determines the composite microstructure and the subsequent annealing does not produce further conformational changes. Second, the disordered *trans* isomer content in the composite was found to be negligible in the untreated and annealed samples. Therefore, the *trans* isomer content in the composite corresponds to the crystalline one. Although spectroscopic and thermal techniques are measuring, in general, different things, in this particular case, they should give the same information.

To give a deeper interpretation for the interface region of the composite, thermal analysis and further correlation with PA-FTIR measurements have been performed in this work.

EXPERIMENTAL

Materials

The sample used in this work was furnished by SNPE (France) as 2 mm-thick plate obtained by a compression-molding process. The material chosen as the matrix was commercial PET (trademark: PET 92T) and the glass fiber reinforcements were Vetrotex R.o.99 2400 sizing 5175 (E-glass).

The impregnation process to manufacture an unidirectional prepreg of continuous fiber-reinforced thermoplastics involves the passage of one or more bundles of reinforcement, electrostatically charged by friction on plastic rollers, through an aerosol of the polymer. The aerosol is made of very fine divided polymer powder (particles of 60–100 μm) suspended in nitrogen gas. The powder is also electrostatically charged, attached to the reinforcement, and then fixed by passing through an infrared oven.

In the process of a plate manufactured by compression molding, five prepreps are joined by applying a pressure of 150–180 kN at a temperature of 280°C. Plates are produced of 200 × 100 × 2 mm.

Some characteristics of the composite are density (ρ_c) = 1.94 g/cm³ and glass weight fraction (w_f) = 61.8%. Samples of 3 × 2 × 2 mm were cut from the plates and introduced into a stabilized oven at different annealing temperatures (T_{ann}) ranging from 65 to 230°C, kept there for 1 h, and then cooled to room temperature.

Thermogravimetric (TG) Measurements

It is known that the reinforcement of a matrix is a statistical process and only the average of fiber distribution with a statistical dispersion can be found. However, in crystallinity measurements by DSC, a crucial question is to know exactly the fiber quantity in the sample since important changes in the apparent degree of crystallinity can stem from small local variations in the glass fiber average content.

To measure the exact content of glass fiber in the samples analyzed in our experiments, a Perkin-Elmer thermogravimetric analyzer (TGA 7) was used. The experimental conditions included a heating program from 25 to 700°C with a temperature ramp of 10°C/min and the maintaining of this latter temperature for 5 min. The purge gas was an air flow of 200 mL/min. These conditions were enough to give rise to complete pyrolysis of the polymer material in the composite sample, as can be deduced from the constant weight finally obtained in the TG thermogram. Therefore, the remaining material is only glass fiber. From these measurements, the glass fiber content was found to vary in a range of ±10% around the value given by the manufacturer (61.8%).

Differential Scanning Calorimetric Measurements

The DSC experiments were performed on a Mettler DSC 30 at a heating rate of 10°C/min; each thermogram was recorded from 25 to 320°C. The mea-

measurements were carried out in an air atmosphere with specimens whose weight ranges from 12 to 14 mg; the calibration of both temperature and melting enthalpy was made with indium. As the same sample was used in the DSC and TG analysis and to calculate the apparent degree of crystallinity, we subtracted the weight of glass fiber obtained from the thermogravimetry, thus obtaining the mass of the matrix in the composite samples.

From the measured heat of fusion (ΔH_{exp}), an apparent degree of crystallinity ($\%C_{\text{DSC}}$) was determined according to the equation

$$\%C_{\text{DSC}} = \frac{\Delta H_{\text{exp}}}{\Delta H^0}$$

where ΔH^0 is the heat of fusion of an ideal PET crystal and the value of 117.6 J/g was adopted.⁹

RESULTS AND DISCUSSION

We reported a spectroscopic study of the composite by PA-FTIR in Ref. 8. Following the work done for the matrix in a previous article,¹⁰ the correlation between spectroscopic and DSC measurements was carried out.

Thermal Analysis

In Figure 1 DSC thermograms of composite samples are shown. Conversely to the thermal behavior of

an unannealed isolated matrix or annealed at low temperatures (below $T_{\text{ann}} \approx 110^\circ\text{C}$),¹⁰ the glass transition is barely perceptible and no crystallization peak can be found in any composite sample. Therefore, the lack of these thermal characteristics indicates the absence of primary isomerization,¹⁰ in good agreement with spectroscopic results where no experimental change related to the primary transformation was detected.⁸ Both measurements support the hypothesis that the microstructure of the composite is determined mainly by the fabrication process.⁸

In composite thermograms, annealing treatment beyond $T_{\text{ann}} \approx 135^\circ\text{C}$ results in an endothermic peak which shifts to higher temperatures and grows in size when the annealing temperature increases. A peak with a similar behavior can also be found in the isolated matrix (low melting [LM] peak) beyond $T_{\text{ann}} \approx 135^\circ\text{C}$. Annealing treatment of PET beyond the primary isomerization produces crystallites with a degree of perfection which depends on the annealing temperature. During the DSC scan, some of these crystals melt and recrystallize with a higher perfection. This explanation does not necessarily imply that the crystallites melt completely; there may exist some type of internal reorganization process which leads to a higher perfection.¹⁰⁻¹²

In the pure matrix,¹⁰ we obtained the relation

$$T_{m(\text{matrix})} = 13 + 1.02T_{\text{ann}}$$

where T_m is the LM temperature peak.

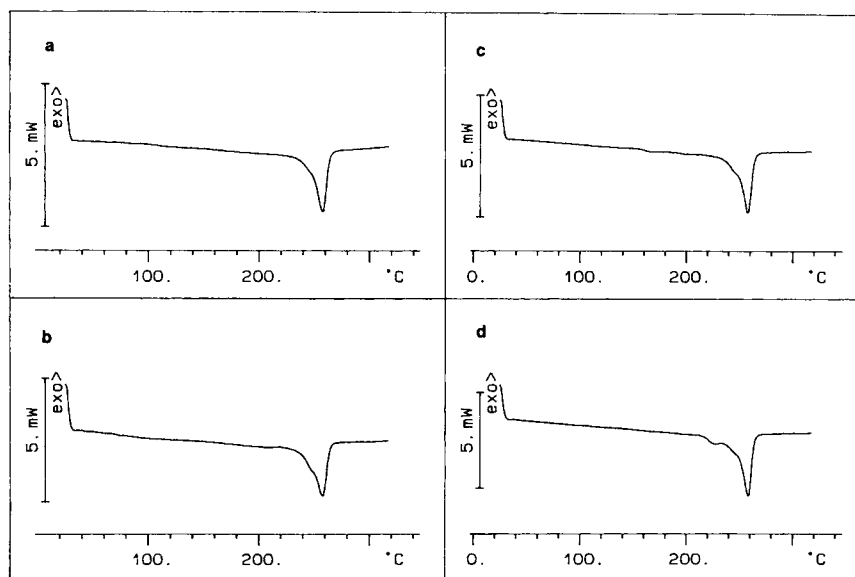


Figure 1 DSC thermograms of (a) unannealed glass fiber-reinforced PET; (b) annealed at 90°C; (c) annealed at 150°C; (d) annealed at 205°C.

Now, in the composite, the following linear relation was obtained:

$$T_{m(\text{composite})} = 5 + 1.05T_{\text{ann}}$$

Since the slopes of both straight lines are similar and the intercept on the ordinate axis is higher in the matrix than in the composite, it can be concluded that the LM temperature peak is always higher in the matrix for a given annealing temperature. Therefore, the size and perfection of crystallites seems to be higher in the matrix.

Aside from the low melting peak, another endothermic peak appears in the melting range of the composite (high melting [HM] peak) which is related to the melt of restructured crystallites after the LM peak.^{11,12} Similarly to the pure matrix,¹⁰ the HM peak does not depend on T_{ann} . The evolution of both peaks as a function of T_{ann} is plotted in Figure 2.

To obtain the latent heat of fusion of the composite, the area between the apparent DSC trace and the constructed base line from the beginning of the LM peak to the end of the HM peak was calculated. The evolution of the isolated matrix and composite crystallinity with annealing temperature is drawn in Figure 3. In the matrix, the primary isomerization (sigmoidal evolution) about 110°C and the linear increase beyond 135°C (secondary isomerization) can be observed. In the composite, primary isomerization cannot be detected; however, conversely to the spectroscopic results where every composite value tends to that of the annealed matrix at the highest temperatures, the crystallinity values of the composite tend only to coincide with those of the matrix at annealing temperatures beyond 150°C,

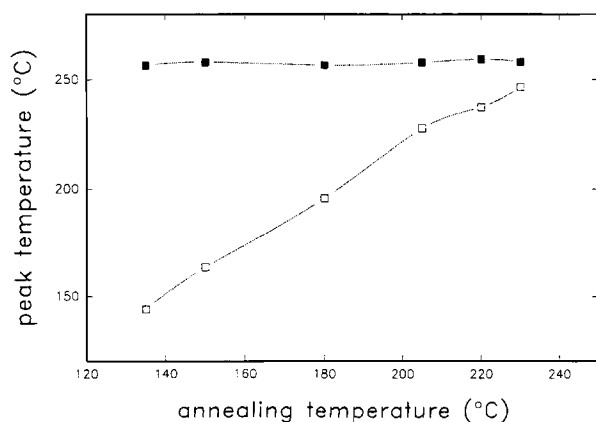


Figure 2 Dependence of the (□) LM and (■) HM temperature peaks on annealing temperature.

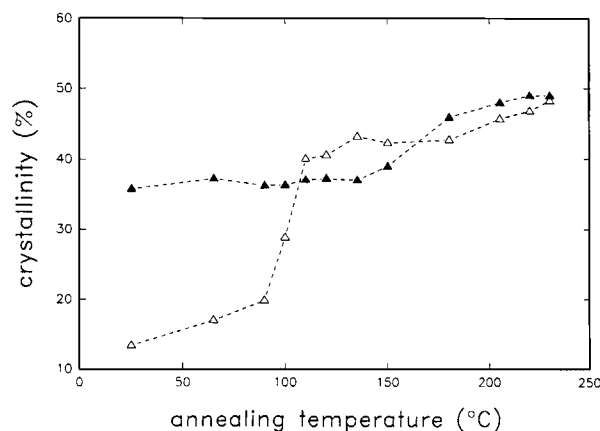


Figure 3 Evolution of (Δ) matrix (from Ref. 10) and (▲) composite crystallinity value as a function of annealing temperature.

and below this temperature, they are always lower, until the primary isomerization of the matrix.

Quantitative Correlation Between PA-FTIR and DSC Measurements

The relationship between the composite *trans* isomer content obtained by PA-FTIR and the apparent degree of crystallinity obtained by DSC as a function of annealing temperature is plotted in Figure 4. In the DSC curve of the composite, two different regions can be distinguished: Below $T_{\text{ann}} \approx 150^\circ\text{C}$, no crystallinity change can be noted and these crystallinity values are always lower than are the *trans* isomer contents obtained by PA-FTIR; beyond this temperature, the degree of crystallinity rises and tends to the conformational value. Therefore, there seems to be an apparent inconsistency between the thermal and spectroscopic results, because in the latter, no conformational change with annealing temperature was found.

To explain this inconsistency, the analysis of the manufacturing process of the composite material should be taken into account. The thermal conductivity mismatch of fiber and matrix results in a temperature gradient across the fiber–matrix interface and, therefore, the molecular crystallization is less perfect. Moreover, this interface is the major part of the composite due to its enormous fiber content. It is suggested that the region near the fiber has less perfection in its crystalline phase than in the “bulk” crystalline state and, probably, its crystallinity is undervalued in DSC measurements.

Taking into account that the *gauche* and ordered *trans* isomer contents of a composite do not vary with thermal treatment, the variation

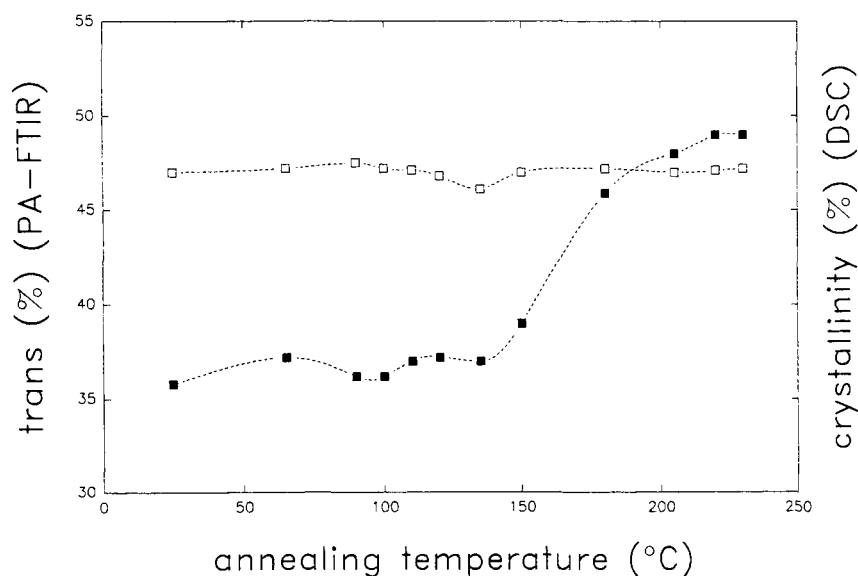


Figure 4 (□) Evolution of composite *trans* isomer content obtained by PA-FTIR (from Ref. 8) and (■) degree of composite crystallinity obtained by DSC with annealing temperature.

on the crystallinity obtained by DSC (Figs. 3 and 4) around 150°C could be attributed to an improvement on the fiber-matrix interface in which the crystals of the interfacial phase change to a more perfect ones, due to the annealing treatment.

In principle, Raman spectroscopy could provide valuable morphological information on the PET/glass fiber composite system. However, one of the problems of pure PET is the fluorescence level present in its Raman spectrum. In glass fiber-reinforced PET, this level is much higher and dispersive Raman cannot be used; however, the FT-Raman technique is a very promising method to obtain Raman spectra of composite materials suffering from a high fluorescence level.

CONCLUSIONS

To obtain a more comprehensive interpretation for the interface region of glass fiber-reinforced PET and the evolution with annealing temperature, the correlation between spectroscopic and thermal techniques was carried out. In the thermal behavior of the annealed composite, two different regions may be identified: At low annealing temperatures (below 110°C), neither base-line deflection due to the glass transition nor exothermic crystallization peak in-

duced by the DSC heating can be detected (both thermal characteristics are related to the primary isomerization). Beyond $T_{\text{ann}} \approx 135^\circ\text{C}$, the LM peak appears directly related to annealing, but the size and perfection of crystallites seems to be higher in the isolated matrix than in the composite. Conversely to the spectroscopic results, the crystallinity values of the composite tend only to coincide with those of the isolated matrix at annealing temperatures beyond 150°C, and below this temperature, they are always lower, until the primary isomerization of the matrix.

From the spectroscopic results, no conformational change induced by the annealing treatment seems to take place in a composite and the isomer contents tend to the values of the annealed isolated matrix at the highest temperatures; moreover, the disordered *trans* isomer content can be considered negligible in a composite.

From the correlation between spectroscopic and thermal measurements, we suggest that the DSC crystallinity change which appears at about 150°C for the composite could be related to an improvement on the fiber-matrix interface in which the interfacial structure changes to more perfect crystals.

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