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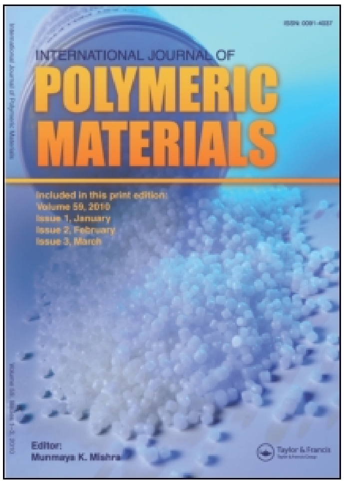

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EFFECTS OF CURING TEMPERATURE ON POLY(ETHYLENE TEREPHTHALATE)

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The effect on poly(ethylene terephthalate) (PET) of thermal curing in a particular temperature range ($T_{max} = 280° - 350° C$) in air have been studied. The changes in the structure were monitored using various characterization techniques such as differential scanning calorimetry, thermogravimetric analysis, optical microscopy equiped with hot-stage, and scanning electron microscopy.

It was observed that when (PET) is cured at very high temperature above its original melting point, cross-linking of the (PET) samples occurs. The cross-linking takes place in the melt in this case. With increasing the curing temperature, the area of the higher melting peak temperature decreases due to the increase in cross-linking of (PET). In terms of spherulitic texture, it was found that with increasing the curing temperature more inter-lamellar intra-spherulitic inclusions are observed in the material.

Keywords: poly(ethylene terephthalate), thermal treatment, crystallization, cross-linking

INTRODUCTION

The multiple melting behaviour of poly(ethylene terephthalate) (PET) has been extensively examined in the past three decades [1–7]. The presence of multiple melting peaks in the differential scanning calorimetry (DSC) scan is not an unusual phenomenon for many semicrystalline polymers. Nevertheless, the origin of such melting behaviour varies from polymer to another. For example, different crystal structure have been found to cause the multiple melting endotherms for *trans*-1,4-polyisoprene [8]. Different lamellar thickness in the spherulitic structure of poly(ether ether ketone) (PEEK), has been suggested. In isotactic polystyrene [10] and poly(ethylene terephthalate) [11] the melting of the polymers crystallized from the melt yields three endotherms. The lower endotherm peak was attributed to fusion of crystals grown during a secondary crystallization process. The middle peak due to the fusion of crystals grown by normal primary crystallization

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and the higher temperature peak has been proposed to melting of the recrystallized crystals during the DSC heating process.

Poly(ethylene terephthalate) is a semicrystalline thermoplastic polymer provided with excellent mechanical properties, thermal resistance, and heat stability. PET is a well known polymer with important industrial applications, and it can be easily obtained either amorphous by quenching from the melt or semicrystalline in a wide range of crystallinity as a result of thermal treatments above the glass transition region.

Thermally induced crystallization in PET develops a spherulitic structure, with diameters typically varying from 5 to 30 μm, depending on the thermal treatment above the glass transition. In PET two different amorphous phases may coexist when crystallization occurs [11, 12]. These two phases exhibit different molecular mobility and can be distinguished as amorphous phase between spherulites and amorphous inclusions between the lamellar structure inside spherulites.

The aim of the present paper is focused on the multiple melting behaviour of PET, and the influence of the melt temperature on the triple melting behavior of PET and its spherulitic structure. The changes in the structure of PET were monitored through various analytical techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (POM) and Scanning Electron Microscopy (SEM). The results are discussed in terms of the changes in the crystallization behaviour at different temperatures and morphology of the spherulitic structure.

EXPERIMENTAL

Material

Amorphous PET sheets (1 mm thick) were kindly supplied by Mr. R. H. Olley (Reading University, Physics Department). The molecular mass of this PET is not known exactly, but the mass average is known to be about 3.9×10^4.

PET Curing

The curing in air was carried out using a Mettler DSC FP85/ or a Mettler hot-stage FP84 mounted on a Nikon optical microscope (type Optiphot-Pol) under cross-polarizer conditions. The FP84 has differential thermal analysis DTA/DSC sensor. The sample in the FP84 hot stage is placed in a transparent crucible and together with an inert reference crucible is subjected to a temperature program. In this case the sample can be observed visually, photographed or filmed by video camera.

The sample, whose weight was approximately 5 mg, was heated in the DSC above its melting point to the curing temperature ($T_{\max}$). Five temperatures, namely 280°, 300°, 320°, 340° and 350°C, were chosen for the curing experiments. The sample was held at $T_{\max}$ for 2 min and then cooled quickly to the isothermal crystallization temperature T_c, and kept there for a predetermined crystallization time t_c. The effect of the curing temperature was monitored through changing in the melting and crystallization parameters, such as melting point (T_m), heat of fusion, (ΔH_f), temperature of crystallization. The value for theoretical 100% crystalline heat of fusion, used to determine the percentage crystallinity, was 136 J/g, based on calculations by Starkweather *et al.* [13], this value is similar to those measured in the other studies [14, 15].

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed on a Du Pont Thermal Analyzer 2000 system at a heating rate of 10°C/min in air.

Electron Microscopy

Morphological observation of the melt was performed, in a Mettler hot-stage FP84 mounted on an optical microscope stage, in a transparent crucible where the sample can be observed visually. According to that, the crystallization process can be interrupted at any instant during the isothermal crystallization by quenching the sample in cold water. This was followed by coating with gold in automatic sputter coater (Polaron SC500). The samples were transferred to SEM, and their surface structure was studied by applying an accelerating voltage of 20 kv.

RESULTS AND DISCUSSION

Figure 1 illustrates DSC scans for PET crystallized isothermally from the melt at 215°C, for samples heated to $T_{\max}$, 280°, 300°, 320°, 340° and 350°. All samples cured at $T_{\max}$ in air for 2 min. It is observed that PET exhibits three melting peaks, and as $T_{\max}$ is increased the area under the higher melting peak temperature was found to decrease and the peak shifts to a lower temperature. This behaviour continues as $T_{\max}$ increases until the upper melting peak completely vanishes at $T_{\max} = 340°\text{C}$, suggesting that this trend may be due to recrystallization or reorganization process, which is completely suppressed at high $T_{\max}$. The middle peak shifts to a lower temperature quickly as $T_{\max}$ increases to 300°C, and, above $T_{\max} > 300°\text{C}$ its shift to a lower temperature is slow, but its intensity obviously decreases. On the other hand, the melting temperature of the lower peak decreases slowly as the curing temperature increases from 280°C to 350°C. According to previous study [11], the lower melting peak temperature represents the melting of the less perfect crystals. These contain, more likely, short molecules and as the curing temperature increases their chance to become cross-linked is limited. However, the middle peak represents the melting of

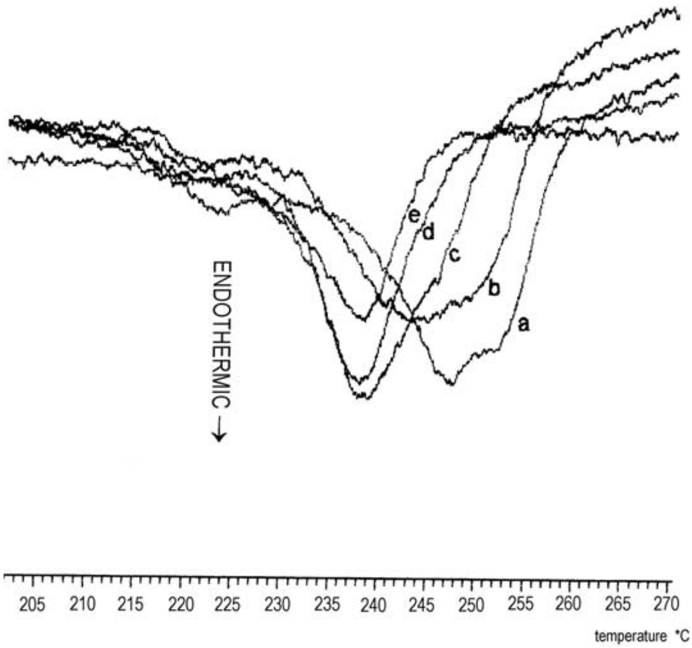

FIGURE 1 DSC heating scans for PET crystallized isothermally from the melt at 215°C for samples cured at different temperatures: (a) 280°C (b) 300°C (c) 320°C (d) 340°C (e) 350°C.

more perfect crystals which are more likely to contain long molecules and as the curing temperature increases their chance to become cross-linked is more likely, so that their ability to recrystallize is suppressed. The cross-linking process reduces the area of the middle peak, and decreases the ability of the long molecules to recrystallize due to their inability to correctly pack in the crystal latice as a consequence of their branching. As the curing temperature increases, the reorganization of the cross-linked molecules decreases gradually and finally it ceases when the curing temperature reaches 340°C. At $T_{\mathrm{max}} = 340$°C, the upper melting peak vanishes since the molecules, after curing and becoming highly branched at that temperature, do not have the ability to reorganize.

As the curing temperature increases its effect on the decreasing of the position and intensity of the lower melting peak is not highly noticeable. The thermal parameters for cured samples are summarized in Table 1, and it can be noticed that the heat of fusion (ΔH_f) was found to decrease with increasing the curing temperature, indicating a progressively lower degree of crystallinity. The reduced crystallinity of PET as a result of curing temperature increasing

TABLE 1 Melting data of melt crystallized PET at 215°C

Curing temp. (°*C*)	*Lower peak* (°*C*)	*Middle peak* (°*C*)	*Higher peak* (°*C*)	ΔH_f (*J*/*g*)	*Crystallinity* χ_c (%)
280	217.1	235.6	243.3	54	39.7
300	216.4	228.9	237.6	53.1	39
320	215.9	228.7	235.6	47.9	35.2
340	215.6	227.6	–	32	23.5
350	214.5	225.7	–	23	17.5

may be attributed to increased branching due to the crosslinking which reduces the reorganization ability of the molecules.

TGA scan for PET samples cured in air is shown in Figure 2. The (PET) sample exhibits a drop in weight at 380°C. This result indicate that, there is a change in the chemical structure of PET due to degradation. Therefore, the DSC traces shown in Figure 1, have nothing to do with chemical degradation, since the higher curing temperature attained was 350°C. Figure 3 shows a representative scanning electron micrograph of the spherulitic

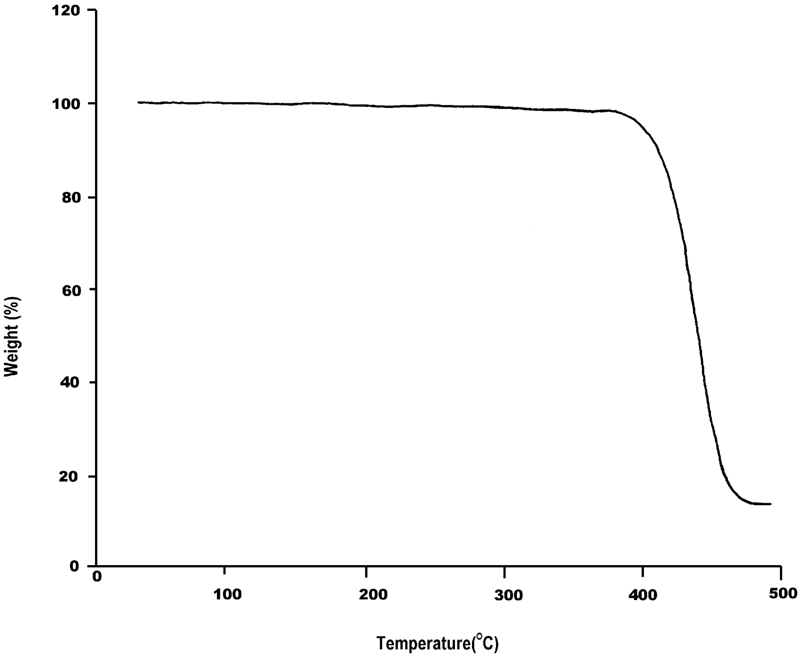

FIGURE 2 Thermogravimetric analysis curve for PET heated at a rate 10°C/min in air.

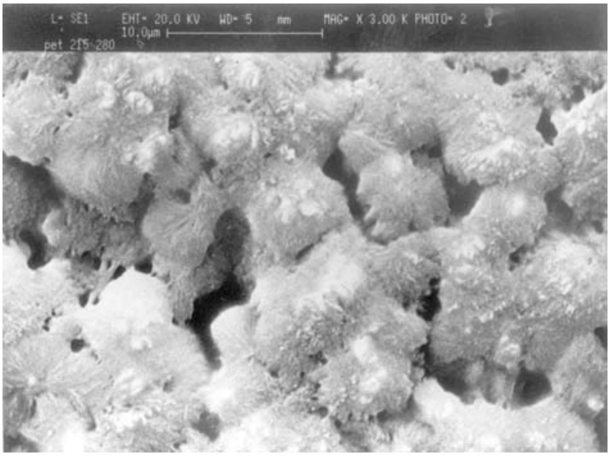

FIGURE 3 Scanning electron micrograph showing spherulitic structure of PET at crystallization temperature 215°C for sample cured at 280°C.

structure of PET obtained by crystallization from the melt ($T_{\max} = 280°C$) at 215°C. At higher magnification of the same sample (Fig. 4) the spherulite can be seen to consist of radial lamellae growing outwards. Figure 5 shows the spherulitic structure for cured sample at 340°C crystallized at 215°C and, in this figure, the inclusions between the lamellae are greater than that in Figure 4 due to the large content of the amorphous material which consists crosslinked molecules due to the curing at higher temperature.

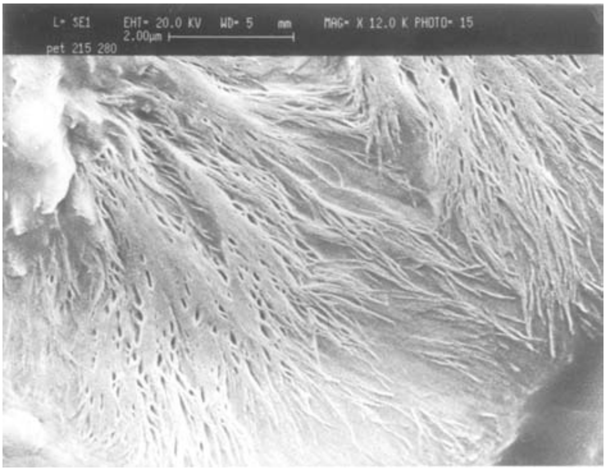

FIGURE 4 High magnification of spherulitic structure shown in Figure 3.

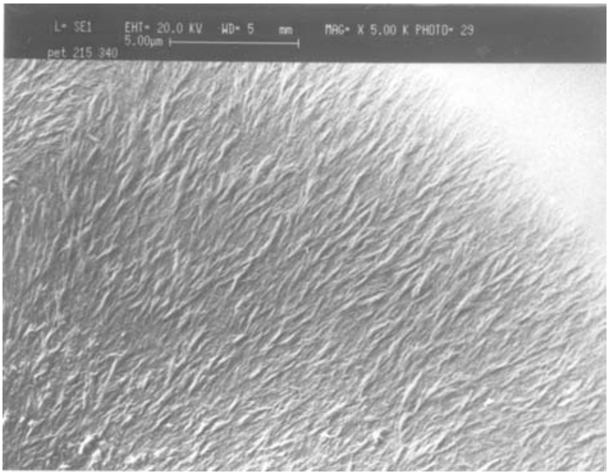

FIGURE 5 Morphology of PET sample at $T_c = 215°C$, cured at 340°C.

Figure 6 shows the spherulitic structure of PET crystallized from the melt at 230°C and the *b*-axis which represent the growth direction of spherulitic structure in this figure is perpendicular to the page. The curing temperature of the sample shown in Figure 6a is 280°C while in Figure 6b is 340°C. However, by comparing Figures 6a and b, we can observe that in Figure 6a the lamellae are more branched, thicker and protruding out of their

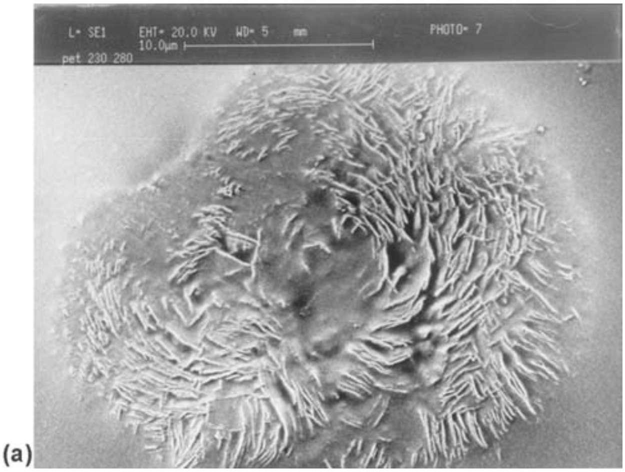

FIGURE 6 Morphology of PET crystallized from the melt at 230°C. (a) $T_{\max} = 280°C$, (b) $T_{\max} = 340°C$.

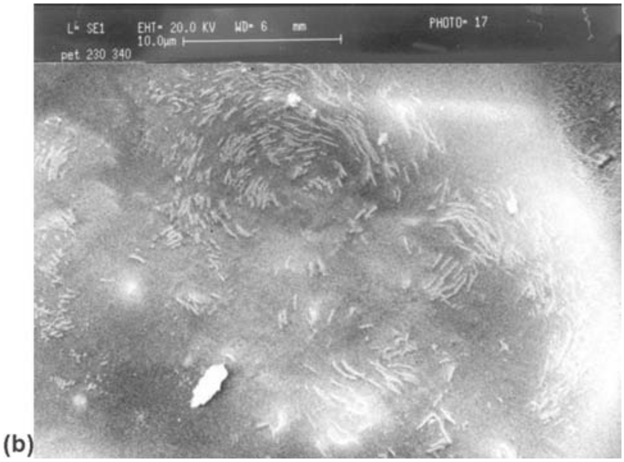

FIGURE 6 (Continued).

surrounding amorphous matrix. This discrepancy of the lamellar habit is probably due to the molecules which become branched when the sample is cured at higher temperature. In this case, there is probability for random branching, so that side groups will be unevenly distributed along a molecule creating the possibility that branch-free segments may be incorporated within the lamellae and portions of crowded branching of the same molecule be rejected out to the regions between neighboring lamellae. This certainly appears to be the case for branched polyethylene [16] where, in particular circumstances, only methyl side groups have been found to be included within the lamellar structure of spherulite while ethyl and longer branches are excluded.

CONCLUSIONS

PET shows triple-melting peaks when crystallized from the melt at 215°C. When it is cured in air at a temperature above its melting point, the size of the higher melting peak temperature is affected by the crosslinking that occurs during annealing at the curing temperature, so that curing at high temperatures, above the melting point, results in a decrease in the crystallinity.

The spherulitic morphology is affected, leading to coarse structures for samples cured at higher temperatures due to incremental increase of the inter-lamellar inclusions which contain the cross-linked parts of the molecules.

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