splicing film in paper manufacture; (ii) heat sealed dosage sachets for objectionable powdery processing additives such as carbon black, intense dyes and hazardous chemicals which are to be introduced into aqueous or partially aqueous media e.g. duplicating inks, emulsion paints, pharmaceuticals etc. The possibility of using comminuted dry film for moulding purposes is being investigated currently.

The most significant feature of this investigation, however, is the use of starch. In the present formulation, it comprises half of the constituent polymers, is cheaply available from renewable (i.e. non-fossil) sources and opens up exciting new perspectives in materials technology.

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Effect of chain composition of PET on small-angle X-ray scattering

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Introduction

The results reported here are part of an investigation into the effect of chain composition on structure, unit cell dimensions and melting behaviour of poly(ethylene terephthalate) (PET). PET is a copolyester generally containing a variable amount (at least 1–5 mol %) diethylene glycol (DEG)[1], the quantity of which affects the structure and properties of the polymer. Here, the influence of DEG content on the small-angle X-ray scattering (SAXS) of PET is examined.

Experimental

Commercial PET (BASF, W. Germany) with different amounts (up to 15 mol %) of DEG was melted and spun in air. The bristles were drawn about 5 times and isothermally annealed (with fixed ends) in vacuum for 6 h at various temperatures between 80° and 250°C. SAXS measurements were carried out with a Kratky camera (slit collimation) using Ni-filtered CuKα radiation and a scintillation counter. Equal amounts of samples were used. The volume crystallinity, w_c, was calculated from density measurements[2].

Results and Discussion

Curves for bristles with different amounts of DEG are shown in *Figure 1*. During these measurements the fibre axis was oriented perpendicular to the slit direction of the X-ray camera. A strong increase of the overall intensity with increase of DEG content was observed. In addition, the position of the maximum was shifted to smaller values, indicating an increase in the long spacing L with increase of amount of DEG in the chain molecules (*Figure 2*).

This scattering behaviour is surprising since the volume fraction (*Table 1*) of the crystalline phase w_c falls by at least three times with increase of DEG content almost independently of the annealing temperature (*Table 1*). Moreover, the situation most often observed is that scattering power increases with crystalline fraction[3]. The unit cell parameters, however, do not depend on the comonomer (DEG) content in the PET molecules[4]. Hence, we concluded that the chains or chain segments containing a higher amount of

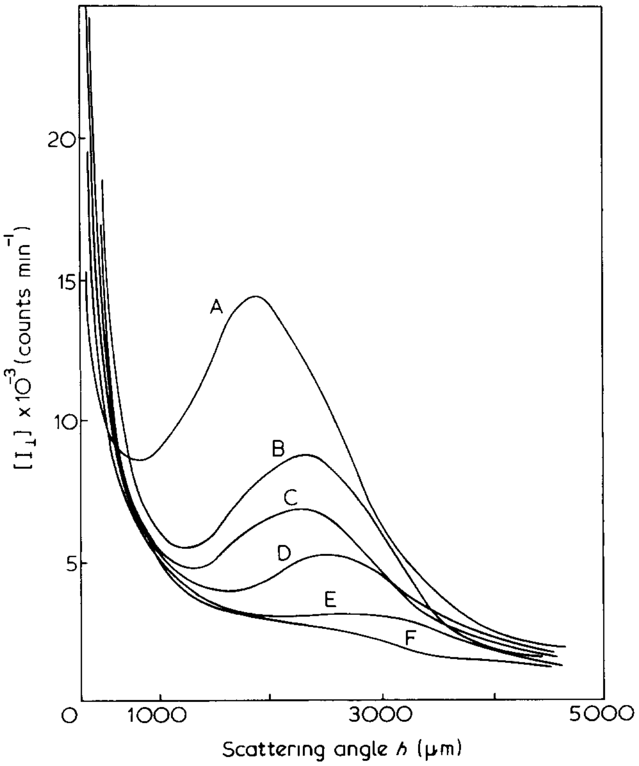

Figure 1 SAXS curves $I_\perp(\theta)$ of drawn PET with different DEG contents annealed at T_a = 240°C for 6 h. DEG content (mol %): A, 14.90; B, 5.80; C, 4.27; D, 1.83; E, 3.09; F, 3.60. $h = 2.2 \times 10^5 \tan 2\theta$

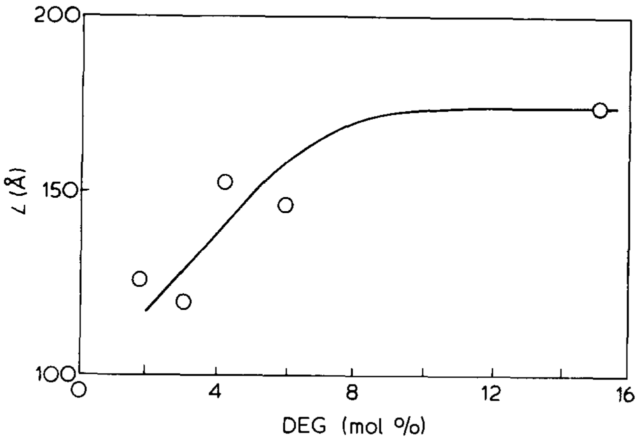

Figure 2 Dependence of long spacing L on amount of comonomer DEG in PET. The data are calculated on the basis of the scattering curves in *Figure 1*

Table 1 Density of fully amorphous PET ρ_a and volume crystallinity w_c of PET with different bonded DEG contents, annealed at various temperatures T_a for 6 h[2]

DEG (mol %)	ρ_a (g cm^{-3})	w_c for T_a = 190°C	w_c for T_a = 220°C	w_c for T_a = 240°C
1.83	1.341	0.25	0.34	0.62
3.09	1.339	0.24	0.31	0.55
3.60	1.338	0.20	0.26	0.50
4.27	1.334	0.13	0.19	0.34
5.80	1.331	0.07	0.12	0.22
14.90	1.328	0.03	0.10	0.19

DEG leave the crystalline regions and build up the amorphous interlamellar phase. The amorphous phase thus grows strongly with increasing DEG content, leading to higher values of the long period (*Figure 2*), although the volume crystalline fraction and probably the lamellar thickness decrease (*Table 1*). To prove this assumption the thickness of crystalline lamellae was calculated using the w_c values given in *Table 1* and the long spacings plotted in *Figure 2*. The data obtained are demonstrated in *Figure 3*. A strong decrease (up to two-fold) of the average lamellar thickness can be observed when the DEG content reaches 5.80 mol %. Further increase in DEG content in the PET molecules does not affect the thickness of the crystalline lamellae – a constant value of about 40 Å is observed.

This result is supported by a simple calculation. If we suppose that the DEG comonomer units are regularly distributed in the PET macromolecules, the segment length of DEG units would depend only on the DEG concentration. For instance the distance between two DEG units is 590 Å at 1.83 mol % DEG, 350 Å at 3.09%, 185 Å at 5.80% and only 72 Å at 14.9% of DEG. This means that for the material with low (1–3%)* DEG content the average lamellar thickness must depend only on the crystallization conditions[3], but not on the concentration of DEG. In contrast higher DEG content in PET represents a limitation on the lamellar thickness (*Figure 3*).

The experimentally determined increase in the long spacing with increasing DEG content is due to the increase in the average thickness of amorphous regions. Using these special properties of the amorphous regions we can also explain the 'uncommon' scattering behaviour – the simultaneous three-fold increase of intensity (*Figure 1*), e.g. curves A and D) and three-fold decrease in the amount of crystalline fraction (*Table 1*).

One of the most important factors determining the usefulness of SAXS is the difference in density between the crystalline and amorphous regions and their ratio[5]. The conventional value for totally amorphous commercial PET[6] is ρ_a = 1.355 g cm^{-3} and for fully crystalline PET[7] ρ_c = 1.515 g cm^{-3}. Our data for fully amorphous PET show that this ρ_a value corresponds to a sample with a DEG content of about 4% (*Table 1*). The sample with reduced DEG content have a higher ρ_a and those with increased DEG content have a lower ρ_a (*Table 1*). Thus, for constant ρ_c, the higher the DEG content, the higher the density difference becomes, causing a stronger SAXS intensity and *vice versa*. The scattering intensity should be much stronger because the ρ_a value cited is not the density of amorphous regions. Their densities are lower than ρ_a and decrease when the amorphous phase becomes richer in DEG units. The significant increase in the number of interlamellar amorphous regions (*Table 1*) also contributes to the rise in the scattering power.

Summarizing the data we may conclude that the increase in SAXS intensity as well as in the long period with increasing DEG content in PET originates from the formation of larger interlamellar amorphous regions with lower density.

Besides their influence on scattering behaviour, other changes in the amorphous regions must be taken into account in the calculation of the volume crystalline fraction on the basis of density data. This, however, is beyond the scope of this communication and the results will be published later.

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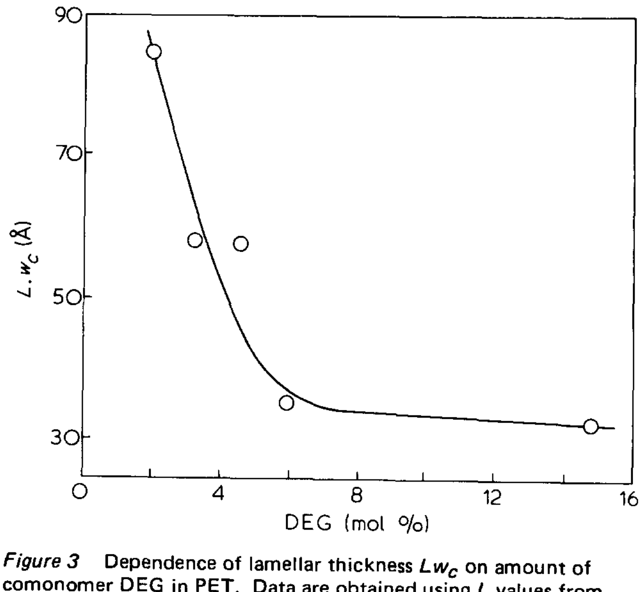

Figure 3 Dependence of lamellar thickness Lw_c on amount of comonomer DEG in PET. Data are obtained using L values from *Figure 2* and w_c values from *Table 1*

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* The experimental point corresponding to 3.09 mol % DEG (*Figure 3*) has a low value due to the following reasons: (i) the long spacing L is measured uncertainly because the scattering curve (*Figure 1*, curve E) has no well-defined maximum; (ii) the w_c value for this sample is lower than that of the sample with 1.83 mol % of DEG (*Table 1*)

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