Third phase in poly(ethylene terephthalate)

V. B. Gupta and Satish Kumar
Textile Technology Department, Indian Institute of Technology, Delhi, New Delhi 110029, India
(Received 30 January 1978)

The concept of the oriented amorphous phase, which is also known as the intermediate or third phase, is discussed and a method is outlined for measuring it. It is suggested that the two phase models of polymer structure, which ascribe partial orientation to the amorphous regions, are in fact close to the three phase models, because the amorphous orientation factor and the third phase are representative of the same parameter, i.e. orientation in the amorphous phase.

INTRODUCTION

Various authors have discussed two types of disorder in polymers like poly(ethylene terephthalate) (PET) and nylon-6; one random and the other oriented. Lindner[1] suggested a method for phase index determination for PET which is based on the assumption that the intensity at a particular value of 2θ is proportional to the amount of crystalline, oriented amorphous or intermediate or third and random amorphous phases. The final values of the three phases are, however, determined with the help of azimuthal scans using the (010) reflection and taking the integrated area between +50° to –50° in the azimuth as being proportional to the three phases. This method appears to be arbitrary for phase index determination for the following two reasons. Firstly, it has been shown[2] by the present authors that in determining the crystallinity of PET, methods which take into account the integrated intensity over the whole reflection sphere are superior to the methods which depend on the ratio of intensities at a particular angle. Secondly, only one crystalline reflection is considered and the integration of azimuthal intensity is carried out between +50° to –50°. This is inadequate for the random amorphous phase which extends from +90° to –90°.

Ideally, integration of intensity must be carried out over the complete sphere of reflection to obtain accurate values of the three phases. In the case of fibres, which are transversely isotropic, however, it would be in order if integration were to be performed over one quadrant of the X-ray pattern on a flat plate. This has been attempted to a limited extent in the present investigation and the results are presented in this paper.

One of the requirements of these methods for determining the intermediate or third phase is that it should be possible to prepare an oriented amorphous standard. This is very difficult with some polymers and almost impossible with others. Thus, it becomes extremely difficult to compute the third phase in such materials. It is postulated in the present paper that the Hermans amorphous orientation factor obtained by the method first suggested by Stein and Norris[3], provides a reasonably good index of the oriented amorphous phase. This is not surprising since even in a two phase model, the amorphous phase may not be considered to be isotropic but may have partial orientation, and the amorphous orientation factor should thus be expected to be an index of the oriented amorphous phase, as is indeed the case. This postulate emphasises that two phase models, which allow the amorphous orientation factor to be calculated, are in fact close to the three phase model as envisaged by Lindner[1], the three phases being the crystalline phase, the oriented amorphous phase and the unoriented amorphous phase. This also makes it possible to obtain an idea of the third phase in any fibre through the amorphous orientation factor since the latter can be computed if the degree of crystallinity, crystallite orientation and birefringence can be measured and the intrinsic birefringence of the crystalline and amorphous phases are known. These quantities can either be measured or are known for a number of polymers.

EXPERIMENTAL

The starting material was commercial 76/36/0 PET multifilament yarn supplied by Shree Synthetics Ltd, Ujjain, India. The sample was heat-set in a silicone oil bath maintained at 100°, 160° and 220°C, respectively, for 1 min while free to relax. The heat-set samples were washed with carbon tetrachloride, dried and stored in a temperature- and humidity-controlled laboratory.

As-spun multifilament PET yarn supplied by Modipon Ltd, Modinager, India, was used to prepare the oriented amorphous standard by drawing the as-spun yarn on an Instron Tensile Tester at 100%/min to its natural draw ratio. No crystalline peak was observed in the X-ray diffraction pattern of this sample though the amorphous scattering was concentrated at the equator.

X-ray diffraction patterns of the various samples were recorded on flat plates by carefully taking a well-parallelized bundle of filaments and exposing it to the X-ray beam for 4 h.

The intensity measurements were made with a Joyce–Loebel microdensitometer.

The birefringence of the various samples was determined with a Leitz polarizing microscope, incorporating a compensator.

The amorphous orientation factor was determined using the following expression:

$$\Delta n = \chi f_c \Delta n_{c_0} + (1 \quad \chi) f_{am} \Delta n_{am_0}$$

where Δn is the measured birefringence of the sample, χ is the degree of crystallinity, f_c is the Hermans orientation factor for the crystallites, Δn_{c_0} is the intrinsic birefringence of the crystalline phase, f_{am} is the Hermans orientation fac-

0032–3861/78/1908–0953$01.00

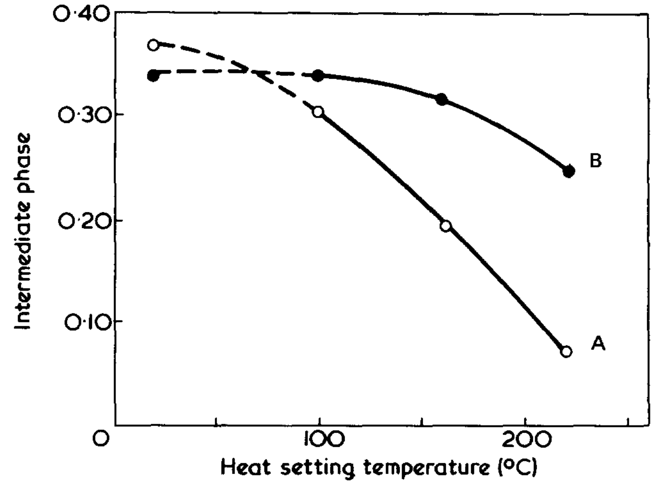

Figure 1 The intermediate phase as determined: A, by Lindner's method and B, by the integrated intensity method, as a function of heat-setting temperature

tor for the amorphous phase and Δn_{am_0} is the intrinsic birefringence of the amorphous phase. Δn_{c_0} and Δn_{am_0} were taken to be 0.212 and 0.275, respectively.

Measurement of the intermediate phase

The intermediate or oriented amorphous phase was first determined using the method suggested by Lindner[1].

The integrated intensity method should ideally be able to separate the total intensity in one quadrant of the flat plate X-ray pattern into three clear-cut parts, i.e. crystalline, intermediate and random amorphous. This can be done in theory by taking radial scans at short intervals along the azimuth for the unknown sample, the oriented amorphous standard sample and a random standard amorphous sample (in the case of the last sample, only one radial scan will suffice). Then the radial scans at any particular azimuthal angle can be superposed in such a way as to separate the three phases. This procedure can be followed at various azimuthal angles in one quadrant. Integration over the whole quadrant will thus allow the separation of the intensity into three desired components. In practice this approach is very difficult because it is difficult to draw the background accurately and compute the random amorphous phase, particularly at azimuthal angles considerably away from the equator. Hence the following method was adopted.

The radial scans of the X-ray patterns of the unknown samples and the oriented amorphous standard sample were taken at short intervals along the azimuth from $\alpha = 0°$ to 90°, where α is the angle which the radial direction makes with the equator. It was observed that in the case of the oriented amorphous sample, the intensity was concentrated between $\alpha = 0°$ and 30°. It was also observed that in the various samples examined the amorphous intensity was large at small azimuthal angles, but above $\alpha = 30°$ the amorphous area became small and almost constant, thus implying that the oriented amorphous phase was concentrated up to $\alpha = 30°$. It was therefore assumed that up to $\alpha = 30°$ the amorphous phase may be considered as oriented amorphous and the rest may be taken as random amorphous. The radial scans of the unknown samples and the oriented amorphous standard for the same azimuthal angle were then matched assuming that the intensity away from the main crystalline peaks was entirely due to the oriented amorphous phase up to $\alpha = 30°$. Above $\alpha = 30°$, the contribution from the crystalline phase alone was obtained. The areas below the intensity curves for the crystalline and oriented amorphous phase were then plotted as functions of the azimuthal angle and the total areas for the crystalline (A_c) and oriented amorphous or intermediate (A_i) phases were obtained. If the area for the random amorphous phase is A_{am} we may write:

$$\frac{A_c}{A_c + A_i + A_{am}} = \text{Degree of crystallinity}$$

The degree of crystallinity of the various samples was determined using the method of Farrow and Preston[4] and this allowed A_{am} to be computed. The three phases, crystalline, intermediate and random, were then taken to correspond to the respective areas.

The intermediate phase as obtained by Lindner's method and the integrated intensity method for PET samples heat-set at different temperatures and the parent sample are shown in *Figure 1*. It is immediately clear that both Lindner's method and the method suggested in this paper show a similar trend, i.e. that the intermediate phase decreases as the heat-setting temperature increases. This would be expected, because as the samples are allowed to shrink during annealing the intermediate phase will be reduced.

The Hermans amorphous orientation factor, obtained using the method described earlier, is shown for the same set of samples in *Figure 2*. The similarity between the decrease of the amorphous orientation factor and the intermediate phase with increasing heat-setting temperature may be noted.

The Hermans orientation factor, f_{am}, would be expected to be related to that fraction of molecules in the amorphous phase which is oriented. Therefore, f_{am} should correlate with that fraction of the amorphous phase which is oriented, i.e. with $I_i/I_i + I_{am}$. The fractional intermediate phase is shown in *Figure 3* and this shows reasonably good correlation with the change in amorphous orientation factor shown in *Figure 2*.

It was originally suggested by Prevorsek *et al.*[5,6] that mechanical properties such as modulus, tensile strength, etc. should be related to the third phase and this was found to be the case for one set of PET samples of different draw

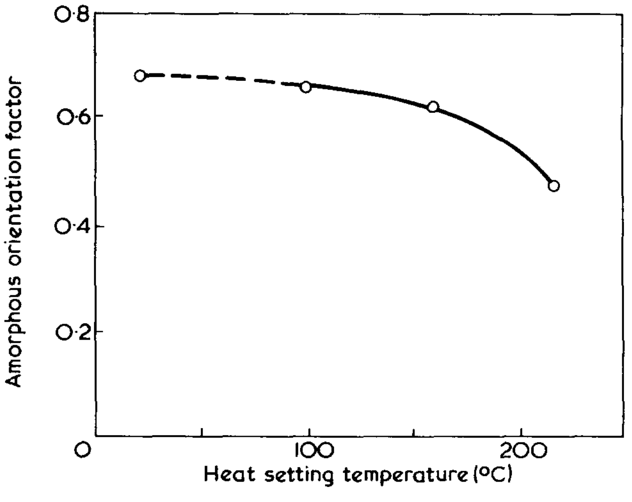

Figure 2 Amorphous orientation factor as function of heat-setting temperature

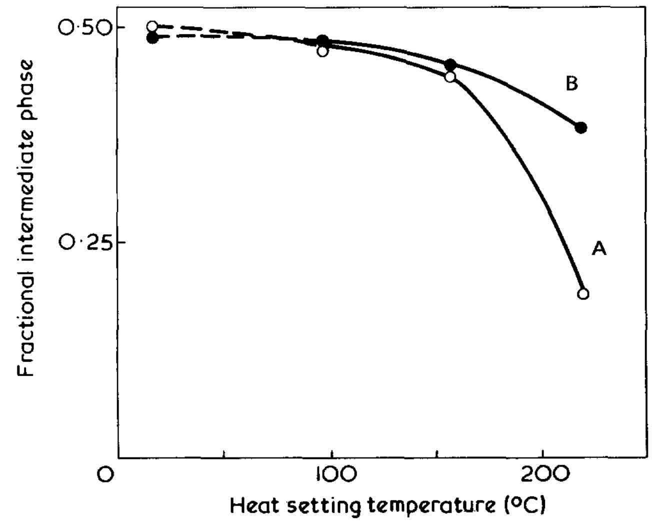

Figure 3 Fractional intermediate phase A, determined by Lindner's method and B, by the integrated intensity method, as function of heat-setting temperature

ratios[7]. These properties have been shown[8] to depend on amorphous orientation for some polymers and this clearly is a vindication of the present postulate that the amorphous orientation factor is an index of the third phase. The concept of the third phase is thus not peculiar to PET (which is the only case for which it has been reported) clearly because an oriented amorphous standard can be prepared. This concept, when considered in terms of the amorphous orientation factor, extends to a large range of polymers as reported in the literature. It may be added, however, that the concept will be strictly applicable to oriented polymers in which the amorphous part is composed of two distinct phases, a random unoriented amorphous phase and a highly oriented amorphous phase. In the case of oriented polymers in which the amorphous part is closer to a single phase having a complete distribution of orientations, as would be expected from affine deformation of a simple rubber network; the concept of an oriented amorphous phase is not very meaningful and the validity of the present approach should not be automatically extended to such systems.

REFERENCES

1 Lindner, W. L. *Polymer* 1973, **14**, 9
2 Gupta, V. B. and Kumar S. *Indian J. Text. Res.* 1976, **1**, 72
3 Stein, R. S. and Norris, F. H. *J. Polym. Sci.* 1956, **21**, 381
4 Farrow, G. and Preston, D. *Br. J. Appl. Phys.* 1960, **11**, 353
5 Prevorsek, D. C., Harget, P. J. and Sharma, R. K. *J. Macromol. Sci. (B)* 1973, **8**, 127
6 Prevorsek, D. C., Tirpak, G. A., Harget, P. J. and Reinaschuessel, A. C. *J. Macromol. Sci. (B)* 1974, **9**, 733
7 Deopura, B. L., Sinha, T. B. and Varma, D. S. *Text. Res. J.* 1977, **47**, 267
8 Samuels, R. J. 'Structured Polymer Properties' Wiley, New York, 1974