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The melting behaviour and superstructure of nylon-6 tyre yarn [a]

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Abstract

The melting behaviour and measured X-ray data were compared for two nylon-6 yarns produced by the two-step and high speed spin-drawing methods which lead to clear differences in their superstructure. A decrease in the melting point and a jump in the full width at half-maximum intensity of the (200) reflection of the yarn were found in the respective plots against shrinkage. These are associated with the destruction of a domain/network structure. The domain/network structure of the spin-drawn yarn is more perfect than that of the two-step one.

INTRODUCTION

It is well known that the mechanical properties of nylon-6 tyre yarn produced with the high speed spin-drawing method are generally superior to that made by means of the conventional two-step process [1]. The improvement is believed to be the result of some kind of modification of the superstructure of the yarn. The exact difference in superstructure between the two yarns has, however, been an unresolved problem for a long time. Undoubtedly, the investigation of the problem has great theoretical and industrial significance. In this work we attempt to elucidate the structural differences between the two kinds of nylon-6 yarns by carrying out melting behaviour investigations and X-ray measurements.

EXPERIMENTAL

Two series of experimental data were collected, one for the samples under tension and the other under relaxation. In the former case, the sample was

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pre-wound tightly under various tensions, i.e. strains, around a copper plate, whose size is such that it can be placed exactly into the DSC sample pan. In the latter case, the sample was first wound around the copper plate under a negligible load with a wire/wires inserted, as shown in Fig. 1. The wire was then pulled out before heating. During heating, the yarn shrinks. However, the shrinking must stop at a certain temperature below the melting point because of the limitation of the dimensions of the copper plate. This process is called controlled relaxation. By varying the number and size (radius) of the wire, a series of samples of varying shrinkages can be obtained. The shrinkage for all the samples investigated ranged from 0 to about 40%, and the load on winding for a single filament ranged from 0 to 20 g, corresponding to a strain of from 0 to about 10%. Both the two-step and spin-drawn yarns investigated were of total 1260 deniers and 210 filaments.

In order to ensure comparability between the DSC and X-ray results, the samples for X-ray measurement were first prepared in the same manner as those for DSC, and were then subjected to the same heating conditions in the DSC pan, followed by quenching just before the melting point. Quenching retains the high temperature superstructure in the sample at room temperature, which is then suitable for X-ray measurement.

The thermal behaviour was measured using a Perkin–Elmer DSC-2 calorimeter. The heating rate for all samples was 10 K min^{-1}, and the peak resolution of the DSC measurement was enhanced by using only 0.4–0.5 mg samples, about one-tenth of the amount normally used for solid materials. The X-ray diffraction measurement, from which the crystallite size [2] and the orientation distribution [3] are to be determined, was carried out using a rotating anode X-ray generator (RU200, Rigaku). The melting point, crystallite size and orientation distribution etc. were measured as functions of the shrinkage and the strain respectively.

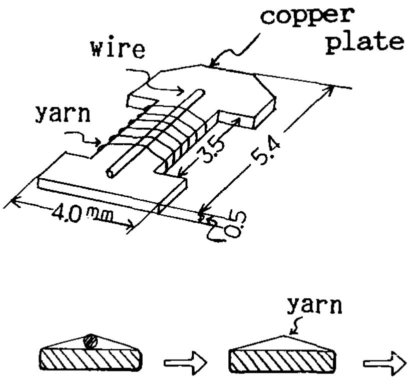

Fig. 1. A drawing of the sampling unit for controlled relaxation experiment.

RESULTS AND DISCUSSION

Figure 2 shows two DSC curves recorded with a small amount, approximately 0.2 mg, of (a) two-step and (b) spin-drawn nylon-6 yarns under free conditions (free ends). Both curves contain more than one peak, a sharp one at low temperatures and a broad one at higher temperatures, although the respective ratios of their areas are very different. The broad peak was considered at first to be due to the melting of the larger crystallites, or to the effect of the reorganization of the molecular chains [4] or to crystalline polymorphism. However, detailed examination of this behaviour casts doubt on the above attributions; the broad peak can be completely or partially eliminated by several cycles of heating and quenching between room temperature and the onset temperature of the first peak. This observation indicates that there could be other mechanisms in which the multiple melting peak [5] appears and at the same time shows that studying the melting behaviour should provide us with useful information for characterizing the superstructure of the two yarns.

The first series of data concerns the relationship between the melting point (m.p.) and the tension (load) under which the sample was prepared. In general, only a single peak appears in the DSC curve of nylon-6 yarn under constraint conditons, i.e. with ends fixed [4]. The melting point is normally obtained from the peak temperature. Figure 3(a) shows a plot of the m.p. of the two-step yarn versus the load, and Fig. 3(b) shows a similar plot for the spin-drawn yarn. For both yarns, the m.p. increases steadily under low load and becomes constant when the load exceeds a certain value (about 8 g in Fig. 3). The two curves are almost the same except for the height of the plateaux; the m.p. value of the spin-drawn yarn is about 1°C higher than that of the two-step yarn.

Figure 4 gives the corresponding plots of the crystallite size and the orientation distribution versus load. The crystallite size is estimated from the peak width of the (200) equatorial reflection of the yarn in the equatorial direction [2] and the crystallite orientation distribution is characterized by the full width at half-maximum (fwhm) intensity of the same reflection in the azimuthal direction (see Fig. 5) [3]. As an indication of superheating (Fig. 3) [4,6], the fwhm decreases gradually at low load, but is constant at

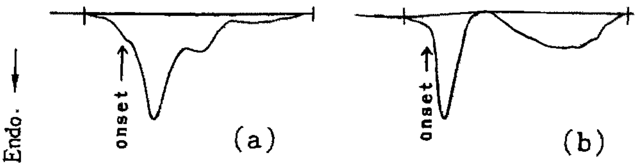

Fig. 2. DSC curves of nylon-6 yarns with free ends produced with (a) two-step and (b) spin-drawing methods.

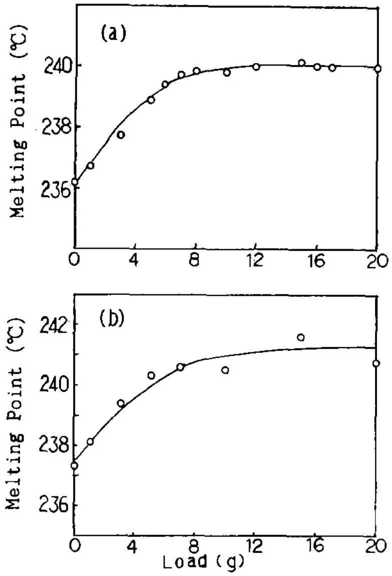

Fig. 3. Plots of the melting point vs. load for (a) two-step and (b) spin-drawn yarns.

high load. The constancy of the crystallite size for both yarns shows that in the present case the crystallite size is not the controlling factor in the melting behaviour of the yarns.

From the results presented above, it can be observed that in the tension region, the DSC and X-ray results are very similar for the two yarns in

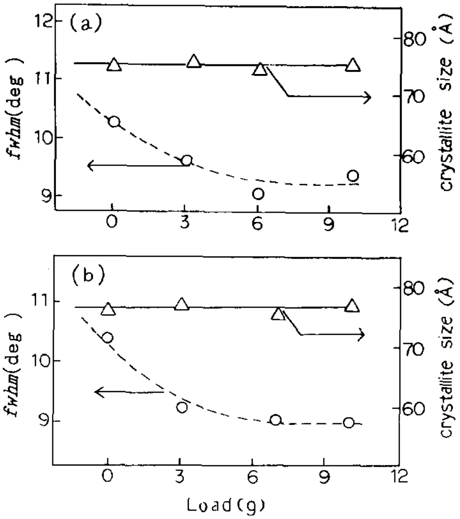

Fig. 4. Plots of the fwhm (o, in degrees Celsius) and the crystallite size (Δ, ångströms) vs. load for (a) two-step and (b) spin-drawn yarns.

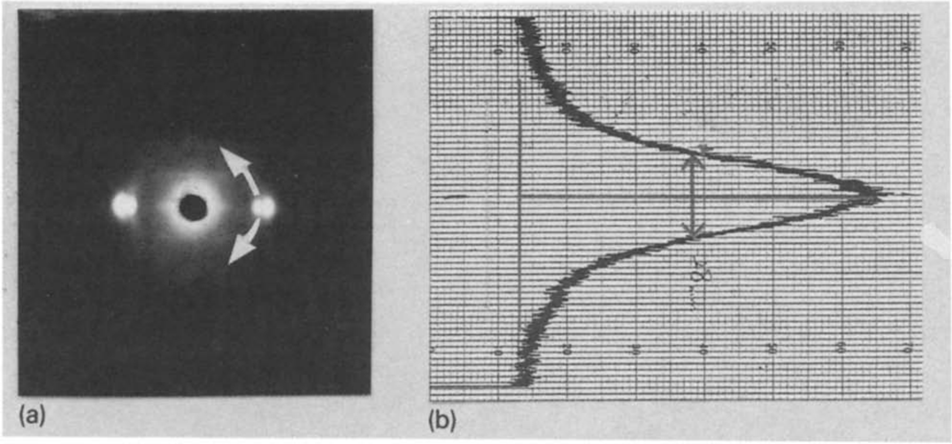

Fig. 5. (a) An X-ray photograph of the nylon-6 yarn. (b) A profile of the (200) equatorial reflection along the azimuthal direction.

question, that is to say, a distinction between the superstructures of the two yarns is, unfortunately, impossible on the basis of the results from this region.

The controlled relaxation method described in the experimental section yielded some interesting results concerning the melting point and the crystallite orientation distribution. The plots of the melting point and the orientation distribution versus the shrinkage β, defined as

$$\beta = (l_0 - l)/l_0 \tag{1}$$

where l_0 is the length of the sample segment before heating and l is that just before melting and is determined in advance on sampling, are presented in Figs 6 and 7 respectively.

As is obvious from Fig. 6, at first the melting point decreases linearly with the shrinkage β; it then shows a discontinuous change, i.e. the melting point falls at $\beta = 25$–30%; it subsequently varies linearly with β once again but with a slope different from the starting one. This behaviour is similar for both the two-step and the spin-drawn yarns except for the depth and position of the fall; it is more dramatic for the two-step yarn than for the spin-drawn one and appears at smaller β values for the former, about 24%, than for the latter, about 29% (cf. Figs. 6(a) and 6(b)).

As in the case of the melting point behaviour, the crystallite orientation distribution also shows a sharp jump at moderate shrinkage, about 18% (Fig. 7). Surveying Fig. 7 and comparing it with Fig. 6, one may notice that the shrinkage β^* at which crystallite orientation randomization becomes appreciable is clearly consistent with the fall in the melting point. The above observations show that the two behaviours must be related.

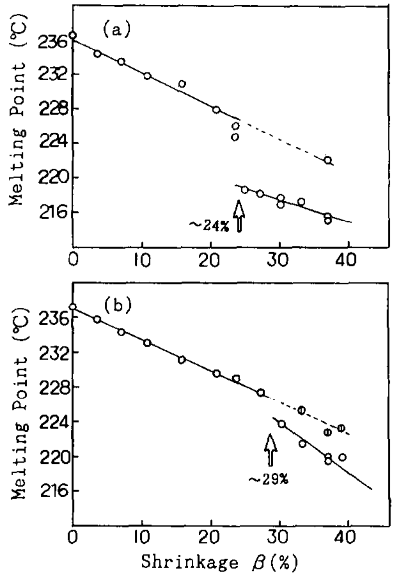

Fig. 6. Dependence of the melting point on the shrinkage after controlled relaxation for (a) two-step and (b) spin-drawn yarns.

To explain the above phenomena, we introduce a microdomain concept to describe the superstructure of the yarn. A microdomain may comprise a number of crystallites lying in the same microfibril or over several micro-

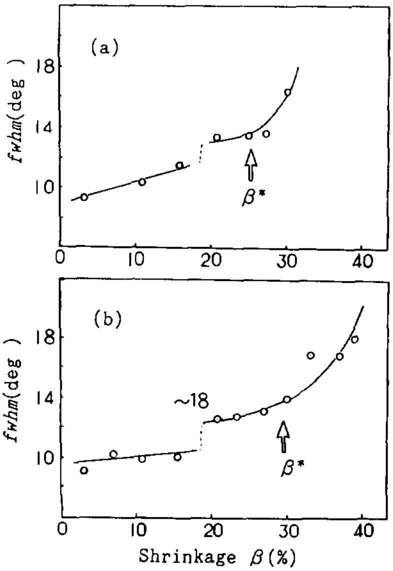

Fig. 7. Dependence of the fwhm on the shrinkage after controlled relaxation for (a) two-step and (b) spin-drawn yarns.

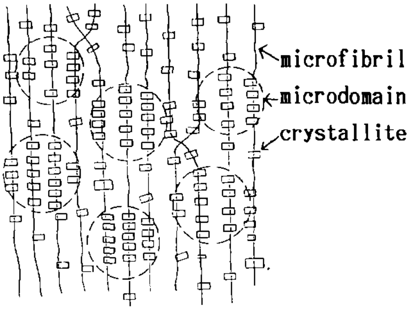

Fig. 8. A model of the microdomain structure.

fibrils which should, of course, be correlated with each other; a microfibril may penetrate several domains. Such a model is shown schematically in Fig. 8. With this model, it is not difficult to imagine that the crystallites inside and outside a domain undergo different constraints and that this may also be true for different domains.

With the aid of the concept of constrained domain structure, the above melting point and fwhm behaviour can be explained reasonably well. If there are a large number of such domains in the yarn, according to the domain concept, it should be true that the crystallites within a domain are subject to a constraint stronger and more difficult to release than those outside it. At low shrinkage the constraint is gradually released first from the outside crystallites with increasing disorder of orientation while leaving the domain morphology unchanged. According to Todoki and Kawaguchi [4], the extent of superheating is determined by the extent and effectiveness of the constraint at the moment of melting. Evidently as the shrinking progresses the average constraint decreases both in its magnitude and quality, so that the melting point decreases correspondingly. This is the case in the region up to the drop point (see Fig. 6). With increasing shrinkage, disordering of the material outside the domain proceeds (A → B in Fig. 9), i.e. the entropy becomes large, which exerts an increasingly disturbing thermodynamic effect on the domain that is still in a state of relatively low entropy, and finally collapses it (B → C). Owing to the domain's collapsing, the average constraint decreases steeply, causing the fall in the melting point. However, the collapse of the domain does not mean that all the crystallites are relieved simultaneously from the constraint. A certain ratio of crystallites may "survive", i.e. remain in a somewhat constrained state even after the domain has collapsed, state C in Fig. 9. The drop in melting point should be determined by the ratio of these crystallites. Therefore the larger drop for the two-step yarn indicates that its domain structure is loose compared with that in the spin-drawn one. This is obvious as in the former the constraint drops rapidly to a very low level after the collapse of the domains (Fig. 6(a)), whereas it is still retained to a certain extent in the latter (Fig. 6(b)).

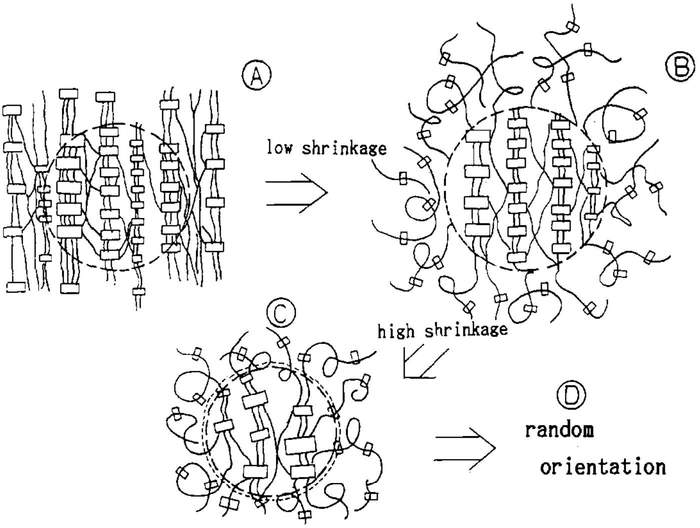

Fig. 9. A schematic representation showing the process of the destruction of the domain structure. State A → B corresponds to the region before the drop in melting point, B → C to the drop and C → D to the region after the drop (see Fig. 6).

Likewise, the behaviour of the fwhm may be explained using similar considerations. As can be seen from Fig. 7, before the jump in fwhm occurs, the fwhm apparently increases with shrinkage in the case of the two-step yarn, whereas it changes little for the spin-drawn one. To account for this behaviour, it is assumed that there is a network between the domains, as is depicted schematically in Fig. 10. The network is thought to be maintained by the microfibril segments lying outside the domains in the longitudinal direction and the interlinks between fibrils in the lateral direction. The interlinks may be an entanglement and/or hydrogen bonds. Such a network would somehow prevent the domain orientation from disordering with

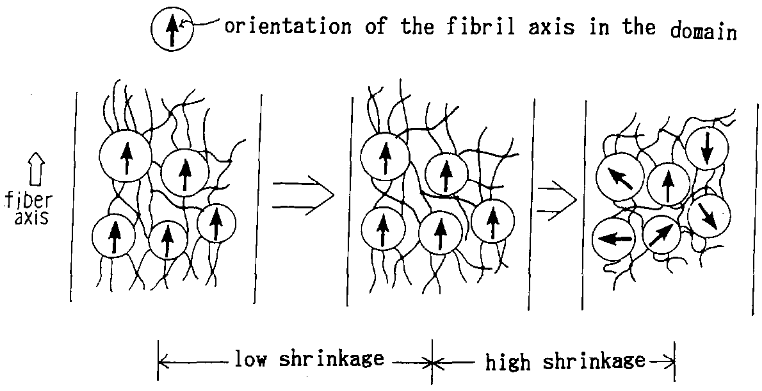

Fig. 10. A model of the network structure.

shrinking. Therefore, the smaller slope before the fwhm jump for the spin-drawn yarn (Fig. 7(b)) implies that its network is more effective than that of the two-step yarn (Fig. 7(a)).

The network, however, is destroyed or inactivated with increasing shrinkage. Because of the destruction of the network, disordering proceeds rapidly, resulting in the jump in fwhm (Fig. 7). With further shrinkage, the domain structure eventually collapses, after which the crystallites become free, so that fwhm increases remarkably. This explains the agreement between β^* (Fig. 7) and the β value at which the fall in melting point takes place (Fig. 6).

CONCLUSIONS

The multiple melting behaviour in the DSC curves of the nylon-6 yarns studied is attributed to the existence of microdomains with different constraint environments. This explains why the broad peak disappears after the appropriate heating cycles.

There is a network structure in the nylon yarns consisting of a large number of microdomains. The microdomain is crystalline and consists of a number of crystallites which are strongly correlated with each other. The domain/network structure is supported strongly in previous studies by Zheng and co-workers [7,8] on the small-angle X-ray scattering of the yarn, where a three-dimensional macrolattice, here called microdomains, was assumed and a quantitative analysis of the superstructure was carried out.

The perfectness of the domain/network structure is different in the yarns produced by the two-step and the spin-drawing processes.

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