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On the influence of molecular weight and crystallisation condition on the development of defect in highly drawn polyethylene

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Abstract

Longitudinal morphology of highly drawn high density polyethylenes has been investigated. Three grades of HDPEs with different molecular weights were used. Two different initial morphologies were obtained by quenching and slow cooling from the melt. The samples were drawn at 75 °C close to their breaking points and their longitudinal morphologies examined under SEM after etching. Two types of defects were observed. These are the structure containing a large number of parallel longitudinal etched pockets laid in the regions between almost parallel continuous transverse bands or 'Pisa' structure recently reported and transverse cracks. The appearance of these defects was found to correlate with molecular weight and thermal history of the samples. For all quenched samples, both Pisa structure and transverse cracks were observed. The number of transverse cracks was found to increase with increasing molecular weight. Apparently, the transverse cracks, which thought to limit the drawing to high draw ratios, can be retarded by drawing at higher temperature (100 °C). This suggests that the formation of transverse cracks relates to chain mobility and drawability of the materials. The Pisa structure was found to disappear from slowly cooled low molecular weight samples. For slowly cooled high molecular weight sample, the Pisa structure became less salient. It is suggested that the formation of Pisa structure is determined by molecular entanglement. Analysis of the band separation of the Pisa structure shows that there seems to be a characteristic value which depends on drawing temperature.

Keywords: Polyethylene; Deformation; Defect formation

1. Introduction

Mechanical behaviour of materials is determined by their internal structures. Drawing of polymers, especially those with semi-crystalline nature, is known to change their internal structures significantly. Mechanical properties are also improved significantly as a result of drawing. The characterisation of the internal structure of the fibre is therefore important in the understanding of their mechanical behaviour. This is particularly so for the dependence of strength on flaws [1]. For highly oriented fibres flaws of various types have been reported [2–9]. These include disc shape defects of about 10 nm in diameter, cracks with their major axis perpendicular to drawing direction with size of several microns or even longitudinal splitting. Due to their pseudo-brittle characteristic, the existence of flaws in highly drawn polyethylenes has been shown to result in the size (or diameter) effect on their strengths [10–12]. Therefore, in the specific case of fibre strength, the dependence on internal flaws and their origins is particularly important.

Recently, a very distinct longitudinal morphology was observed in highly drawn polyethylenes [13,14]. This morphology is remarkably regular consisting of an alternating entire bands and row of etched pockets, which has been termed 'Pisa' structure. Similar morphology was also observed in highly drawn polypropylene and polyoxymethylene [9,15,16] but less distinct. The knowledge with regard to its formation is rather limited. In the previous work, this Pisa structure is formed only in a particular type of polyethylene [13]. The draw ratio at which this Pisa structure was observed also varies depending on the starting materials. It was suggested that this type of defect would be formed near the breaking point. It is this type of defect which we are concentrating in this paper. Further investigation into factor controlling the formation of this Pisa structure will be presented.

2. Experimental

The materials used were commercially available HDPEs grade Thai-Zex 1600J, 2208J, and 6200B obtained from a local manufacture, Bangkok Polyethylene, Thailand. The

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Table 1
The average molecular weights of HDPEs

Material	$\bar{M}_w$	$\bar{M}_n$
1600J	150,000	36,000
2208J	190,000	50,000
6200B	250,000	38,000

Table 2
Crystallinity of starting materials

Material	Crystallinity (%)	
	Quenched	Slowly cooled
1600J	54	66
2208J	58	69
6200B	62	68

melt flow indices of these materials are 12, 4 and 0.3 g/10 min, respectively. The molecular weight characteristic, as obtained from GPC, is shown in Table 1. Sheets were prepared by compression moulding from polymer melt at a temperature of 160 °C and then crystallised by either quenching in cold water or slow cooling at a rate of approximately 1 °C/min. Dumbbell specimens (gaugelength = 20 mm and width = 5 mm) cut from the sheets were drawn at 75 ± 1 °C and 100 mm/min using an Instron tensile testing machine; the draw ratio was calculated from the separation of ink marks printed on the original surface.

A Perkin Elmer DSC-7 was used for thermal analysis at a scanning rate of 10 °C/min. The instrument was calibrated using high purity Indium. Crystallinity of the samples was calculated by using heat of fusion of perfect crystalline PE as 293 J/g [17].

To prepare the specimen for scanning electron microscope (SEM), the isotropic and drawn samples were embedded in Kraton® block copolymer (Shell). The longitudinal surface was removed with a glass knife with a microtome. The exposed surface was etched with a permanganic reagent [18] for 2 h at room temperature, with 1% solution of potassium permanganate in a 10:4:1 (by volume) mixture, respectively, of concentrated sulfuric acid, 85% orthophosphoric acid and water [19]. Etched specimens were coated with palladium and examined under a Hitachi-S2500 SEM operating at 15 kV with no specimen tilt. The image was analysed with UTHSCSA ImageTool program [20].

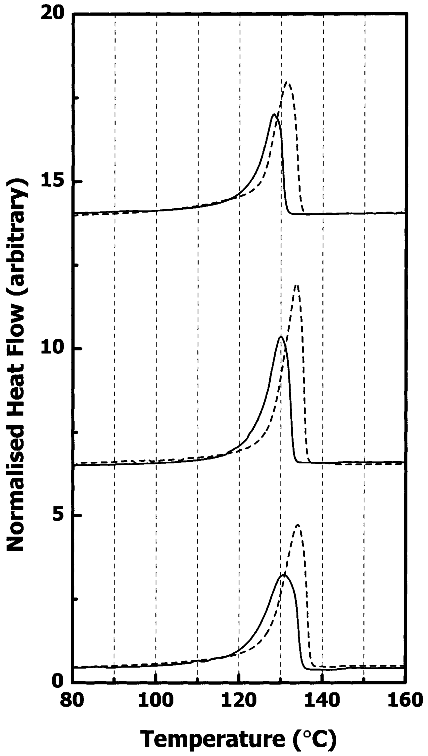


Fig. 1. Thermograms of isotropic starting materials obtained from two extreme thermal treatments, i.e. quenched (○) and slowly cooled (+); 1600J (top), 2208J (middle) and 6200B (bottom).

3. Results

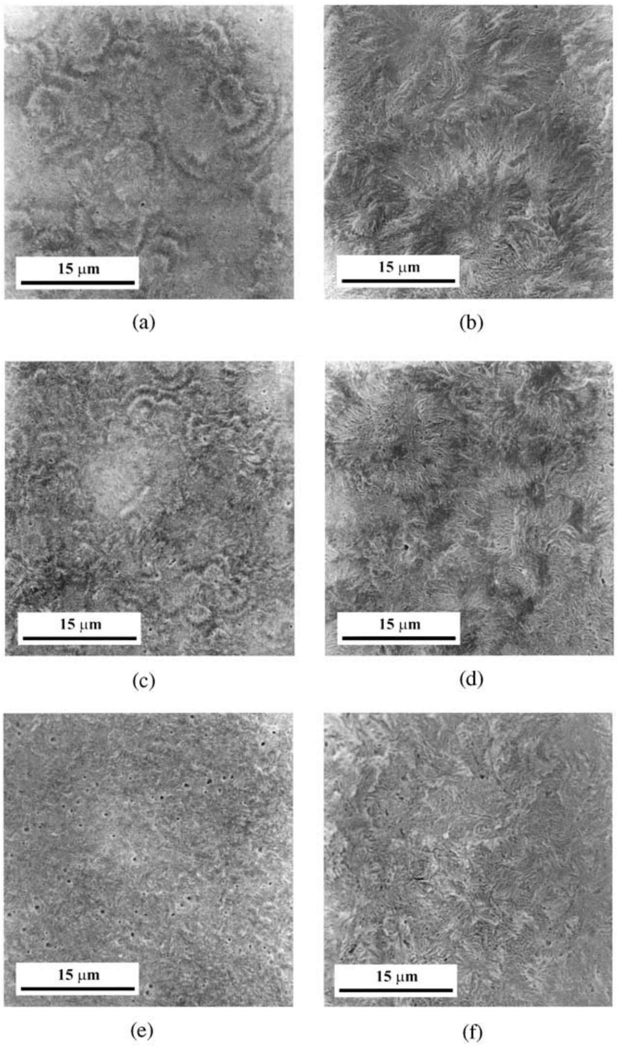
3.1. Isotropic starting materials

Thermal treatment was used as a tool to impart differences in initial morphology of the starting materials. Fig. 1 shows DSC thermograms of undrawn quenched and slowly cooled samples. It can be seen that the two extreme thermal treatments affect the crystalline melting characteristic of the samples to different extents depending on the molecular weight of the samples. The peak melting temperature increases with the molecular weight of materials. In addition, the peaks shift to higher temperature in slowly cooled condition. Crystallinity of the samples is shown in Table 2. Slow cooling can be seen to increase the crystallinity from that of quenched samples by about 10% in low molecular weight samples. The difference in crystallinity becomes smaller when the molecular weight increases. This indicates that by slow cooling of the high molecular weight samples, little can be changed.

Fig. 2 shows the morphologies of starting material seen under SEM after permanganic etching. For quenched low molecular weight 1600J and 2208J, a familiar spherulitic morphology is seen. Much finer morphology is observed for high molecular weight 6200B indicating dense nucleation. All slowly cooled samples display much coarser morphology than the quenched counterparts.

3.2. Drawn samples

In general, the longitudinal morphology of drawn polyethylene is rather featureless. It is only at very high draw ratios, depending on starting materials, that a special morphology might develop. Therefore only longitudinal



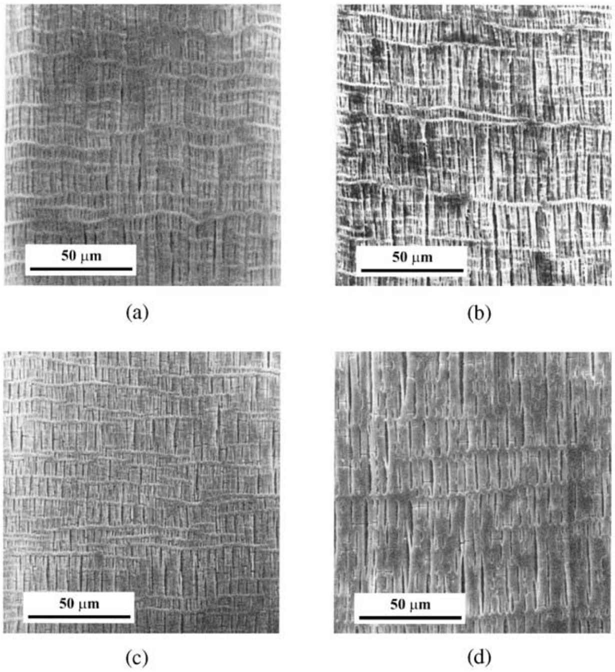
(a) (b) (c) (d) (e) (f)

Fig. 2. SEM of starting materials: (a,b) 1600J, (c,d) 2208J and (e,f) 6200B; quenched (a,c,e) and slowly cooled (b,d,f).

morphology of samples which had been drawn close to their breaking points are investigated.

3.3. Quenched samples

Longitudinal morphology of drawn quenched samples is shown in Fig. 3. The positions at which this morphology was observed were 23×, 22× and 15× for quenched 1600J, 2208J and 6200B, respectively. All samples display a characteristic of alternating structure of entire bands and rows of etched pockets or the Pisa structure. There are differences in the detailed structure of each sample, such as the distance between entire bands and this would be discussed in more detail later. In addition to the Pisa structure described earlier, cracks with their major axis perpendicular to the drawing direction or transverse cracks are also observed. The number of these transverse cracks appears to increase with increasing molecular weight of the sample.



(a) (b) (c) (d)

Fig. 3. SEM of longitudinal morphologies of drawn quenched HDPEs at a temperature of 75 °C: (a) 1600J, 23×; (b) 2208J, 20×; (c) 6200B, 15× and (d) 6200B, 19× drawn at 100 °C.

High molecular weight sample, 6200B, was also drawn at a temperature of 100 °C to increase the molecular mobility. Fig. 3(d) shows that the longitudinal morphology of the sample still contains similar feature as that drawn at 75 °C. However, the number of transverse cracks becomes smaller and the band separation farther.

The band separation of Pisa structure was analysed using an image analysis software and the results are shown in Fig. 4. For samples drawn at 75 °C, Fig. 4(a)–(c), it can be seen that the distribution of band separation among the samples are very similar. It is remarkable that the separation centres at about 4–6 μm for all samples, despite the differences in draw ratio. There is, however, a slight difference in the tail of the distribution curve at large separation. It can be noted that high molecular weight samples display greater number of bands with larger separation (10–25 μm). When the drawing was conducted at higher temperature, only for highest molecular weight sample, draw ratio slightly increased from 15× to 19×. The distribution pattern now shifts to higher value of band separation. It now centres at about 18 μm, with a relatively large fraction having even farther band separation.

3.4. Slowly cooled samples

Slowly cooled samples were found to exhibit rather low drawability especially low molecular weight 1600J and 2208J. The longitudinal morphology of drawn slowly cooled polyethylene is shown in Fig. 5. Only transverse cracks are observed in slowly cooled 1600J and 2208J. The Pisa structure now totally disappears from low

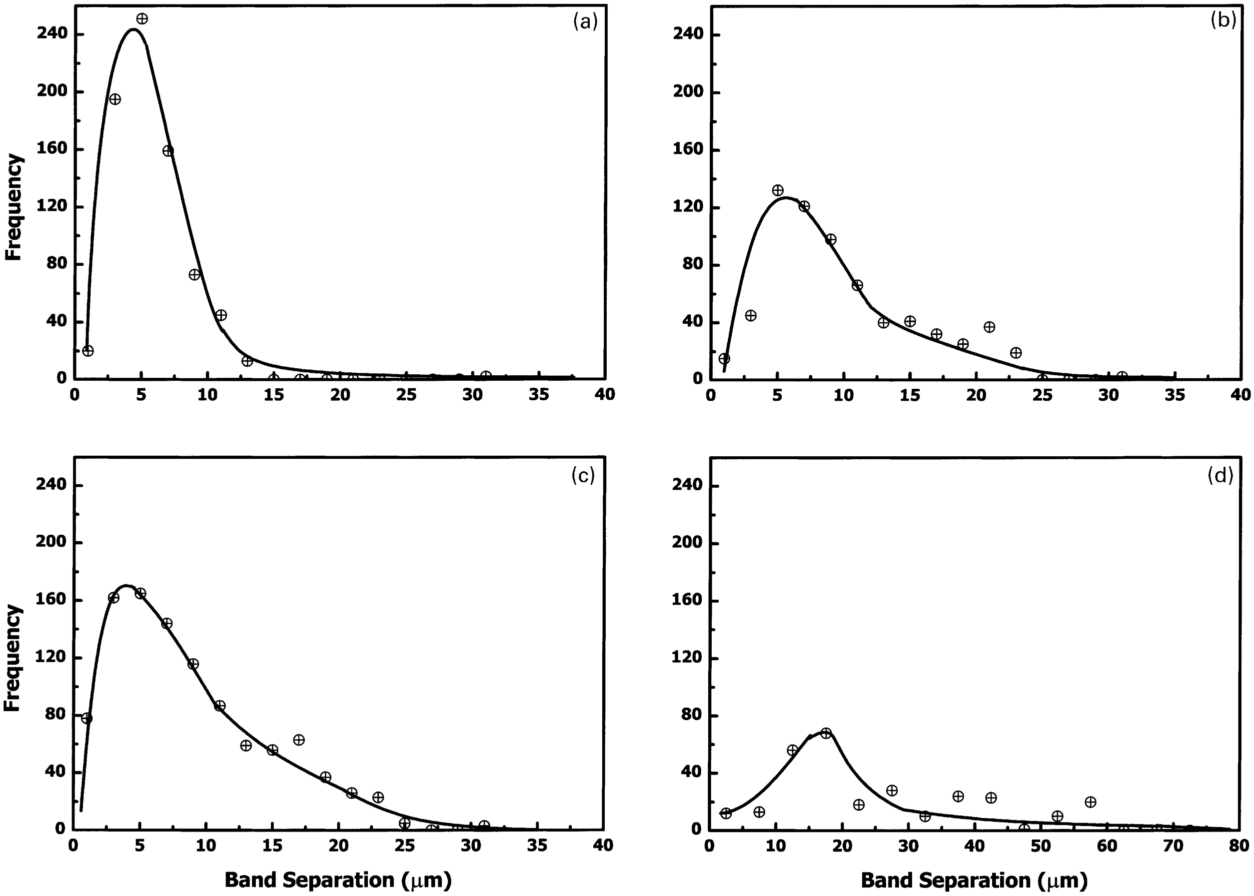


Fig. 4. Band separation in drawn quenched samples: (a) 1600J, 23 ×; (b) 2208J, 20 ×; and (c) 6200B, 15 × drawn at 75 °C and (d) 6200B, 19 × drawn at 100 °C.

molecular weight 1600J and 2208J. It is only high molecular weight 6200B that still displays the Pisa structure but not as salient as in the case of quenched materials. The distribution curve of band separation for slowly cooled 6200B is shown in Fig. 6. The curve has very similar appearance to that of the quenched materials and also peaks at around the band separation of 1–5 μm.

4. Discussion

It has been established by Capaccio and Ward [21,22] that thermal treatment affects drawability of polyethylene to varying degrees depending on molecular weight of the sample. The difference in deformation behaviour was due to molecular network, which has been identified as a key factor in the drawing process. Although the DSC traces could not provide information regarding the state of molecular entanglement in the sample, the difference in the morphology of starting materials can still be seen from the traces. Therefore the followings may still be assumed for the present study. For low molecular weight sample, the number of molecular entanglement is low. If the molten polymer is quenched, these molecular entanglements will be trapped in the solid samples. By slow cooling, the molecules are able to disentangle and crystallise in a more regular fashion with low entanglement density. When the molecular weight increases, the chains would be highly entangled. Disentanglement would become more difficult or even unlikely, hence trapped entanglements in high molecular weight samples would still be high. This should be reflected in a difference in DSC traces and SEM micrographs of quenched and slowly cooled samples. The difference in low molecular weight sample would be greater than that in high molecular weight and this was already shown earlier.

The two initial morphologies indeed result in different longitudinal morphology upon drawing. For quenched materials, all display both Pisa structure and transverse cracks. Jarecki and Meier [5,6] have reported that these transverse cracks are formed in highly drawn polyethylene. By increasing drawing temperature, the formation of this type of crack would be retarded. Our finding described earlier is in good agreement with this. It is, therefore, concluded that the formation of transverse cracks relates to molecular mobility of polymer chains. Drawing temperature has slight effect on the appearance of the Pisa structure, and details of which will be discussed later.

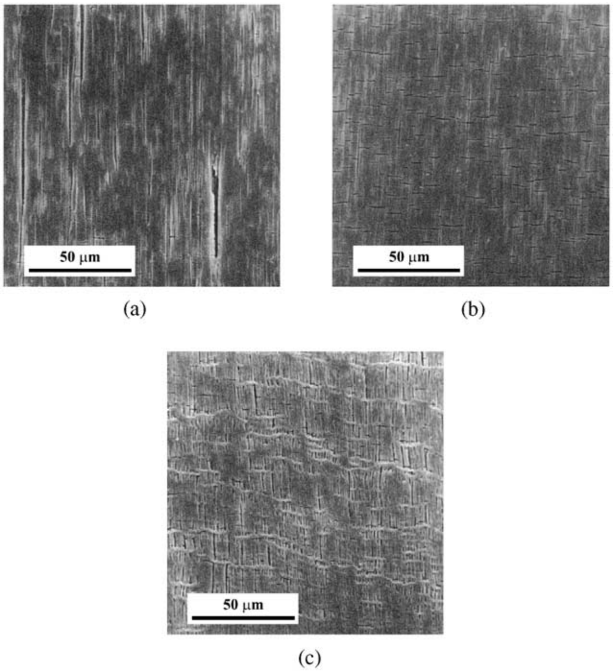


Fig. 5. SEM of longitudinal morphologies of slowly cooled samples drawn at 75 °C: (a) 1600J, 10 ×; (b) 2208J, 20 ×; and (c) 6200B, 20 ×.

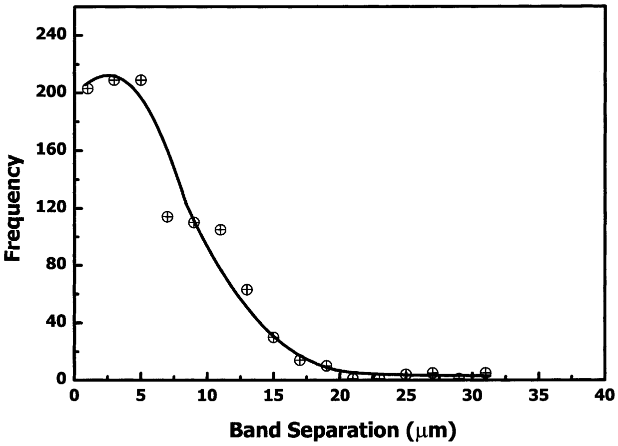


Fig. 6. Band separation in drawn slowly cooled 6200B, 20 × drawn at 75 °C.

It is remarkable that the size of band separation found for all quenched samples and slowly cooled 6200B drawn at 75 °C is centred at about 4–6 μm, despite the differences in draw ratio. This is also comparable to those previously reported [13] for different polyethylenes. It is still not certain why it is so. It is likely that this might relate to either the initial structure of the samples or the drawing mechanism. This would be considered in turn.

Donald and Kramer [23] observed a strong correlation between the fibril length in the crazes and the contour length between entanglement in glassy polymers provided that there is no slippage or breakage of entanglement network points or chains. Similar observation was also reported on crazing in ultra-high molecular weight polyethylene gel-fibres [24]. It is very striking that the Pisa structure and crazing are very similar in appearance. However, it must be emphasised that their size differed more than an order of magnitude. Theory would predict that, for melt crystallised polyethylene, contour length is in the nanometre range whereas the distance of the Pisa band is in the range of 4–6 μm. The other difference is that the Pisa structure is a result of etching of what was originally largely solid surface [14] whereas crazing contains a large amount of voids. Thus the size of band separation could not be related to structural parameter like contour length of the chains as in crazing.

It may be envisaged that extrapolation of the size of band separation to draw ratio 1 could result in the dimension of the related structural element. However, this is complicated by the fact that band separation appears to have a certain value and hardly change with draw ratio [13]. Further complication arises due to the fact that the Pisa structure is in fact an overlaid structure which develops at certain points and overwrite the true morphology [14]. Attempting to relate this band separation to the dimension of any structures in the isotropic state would be difficult to rationalise.

The fact that the Pisa structure appears to have characteristic band size distribution and remain unchanged with draw ratio [13] might suggest the involvement of local heterogeneous deformation [16] and also sliding mechanism at this very late state of drawing. Presumably, sliding of the structural elements [25] may occur near the breaking point. In other words, the point at which the Pisa structure is observed, the material draws out by sliding of the structural elements to accommodate the imparted strain. By this mechanism the band separation, once formed, would remain unchanged with draw ratio.

The sliding is expected to relate to lateral cohesion between structural elements. It was found that the lateral cohesion of drawn polyethylenes increase with increasing molecular weight [12]. This is due to an increased bond strength between the structural elements for the higher molecular weight [10] and could be due to the inter-microfibrillar tie molecules proposed by Prevorsek et al. [26]. Therefore, the sliding mechanism may be prevented in high molecular weight samples, which contain greater amount of entanglement density. This would result in more effective draw out of the entire band. The band would become further separated as draw ratio is increased. This is in agreement with the finding that greater fraction of band in 2208J and 6200B displays distribution tail as shown in Fig. 3(b) and (c). This may be further supported by an increase in band separation when 6200B is drawn at 100 °C. By increasing drawing temperature from 75 to 100 °C, the peak band separation shifts from 4–6 μm (at 15×) to 18 μm (at 19 ×). An increase in draw ratio would only contribute to an increase in band separation by approximately 30%. The large remaining is likely to arise from the higher molecular mobility at high temperature which would allow the material to draw rather than slide.

The disappearance of the Pisa structure from drawn slowly cooled 1600J and 2208J and the sustainability, but less salient, of the structure in 6200B would suggest that the formation of such structure relates to a degree of molecular entanglement. It is suggested that the formation of the Pisa structure requires a certain degree of molecular entanglement. It is noteworthy that in previous work [13] all samples were prepared by slow cooling from the melt and displayed the Pisa structure. In the light of the present study, this probably indicate the differences in molecular architecture of the polymers employed which affects the ability of the chains to disentangle during slow cooling. It is also interesting to note that it has been previously suggested that the entire bands are the residual locations of molecular entanglement which have become concentrated as extension proceeds [13]. Our finding would reinforce this suggestion. As stated earlier, the similarity between the Pisa and crazes formation that crazing can be suppressed by lowering the entanglement density of the polymer solution [24]. The question that remains to be answered is whether there is a link between the Pisa structure and the crazes.

5. Conclusions

Longitudinal morphology of highly drawn polyethylenes of different molecular weight was studied. Particular attention was paid to the formation of the Pisa structure recently reported. Crystallisation condition was found to affect the observed morphology. The following conclusions may be drawn from the present study.

1. Two types of defect may develop during drawing of high density polyethylene. These are transverse cracks and Pisa structure, which is dominant depends on the morphology of the starting materials.
2. The formation of transverse cracks relates to sample drawability and the ability of the chain to move. Higher temperature is required for higher MW or higher viscosity materials.
3. The formation of Pisa structure is suppressed when the material is slowly cooled from the melt. It is believed to relate to the number of molecular entanglement in the material.
4. The banding characteristic, i.e. the band separation, was found to be rather similar despite a large difference in molecular weight and draw ratio in case of drawing at 75 °C. At higher temperature the band is farther separated. This probably suggests that the formation of the Pisa structure may relate to some kind of drawing mechanism.

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