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The dependence of tear behaviour on the microstructure of biaxially drawn polyester film

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The structure-property relationship between a biaxially oriented film from poly(ethylene terephthalate) and its fracture behaviour measured using the Trouser Tear method, has been explored. X-ray diffraction (XRD) was used to characterise the orientation distribution of crystalline and non-crystalline material in the plane of the film and compared with the fracture energy, G_c measured in four directions during tearing. The fracture energy averaged over the four directions ranged between 12 and 25 kJ m^{-2}, and was found to correlate closely to the draw ratio during manufacture and therefore the degree of molecular orientation. However the individual values of G_c displayed a further level of complexity.

The expected anisotropic character of the fracture energy was found to change systematically as a function of position across the original width of manufactured film. This feature compared well with the underlying, crystalline orientation distribution and provided strong evidence that under the mode III deformation of the tear test, the fracture mechanism involves the amorphous-crystallite surface boundary.

Further support for this mechanism was provided by a simple model which, based on this assumption was shown to predict reliably, the anisotropic character of the film.

1. Introduction

One of the simplest methods to determine the toughness of a self supporting polymeric film, is the out-of-plane or "trouser" tear test [1]. The test is widely practised because in addition to the convenience of its measurement, its test geometry is intuitively appropriate to many practical applications. Several studies have been published which explore the technique [2–6] however, considering the popularity of the method both in academia and industry, there are relatively few reports which relate measurements to the fundamental structure of the specimen [7–9].

This is true for film prepared from polyester and in particular poly(ethylene terephthalate), (PET). The fracture energy, G_c of isotropic amorphous PET has been shown in this test to be directly proportional to specimen thickness [7] and the dependence explained in terms of the ductile zone surrounding the cracktip [4].

Molecular orientation is also confirmed by experiment to affect profoundly the tear energy of film from polyester which has been stretched one way [10]. However film from PET is normally produced using a biaxial stretching process and possesses a microstructure which reflects this history. A more complicated interaction between its structure and its macroscopic tear properties is likely therefore to exist for polyester film which is used in most common applications and to date, no published account can be found which has examined and defined this interaction.

One report did recognise that the tear resistance of film from PET was anisotropic as a result of its biaxial process history and related this phenomenon to its

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principal optical axis [11]. However no elaboration was made about the underlying semicrystalline structure of the material, which can vary widely for any one direction of the optical axis.

More recently the essential work of fracture method, EWF has become a popular tool to characterise the toughness of a polymer film [12]. This method too has an associated fracture theory, and extensive studies have identified the essential work of fracture, w_e and non-essential work of fracture, w_c with distinct stages of the fracture test. These in turn have been related to the underlying sample morphology which is present initially or which may develop later in the test as a result of deformation. However the absolute values of w_e derived from the essential work of fracture and G_c from the tear test, are often in poor agreement.

This is because the sample deformation is different to that of the tear test and when applied to a specimen which possesses an anisotropic microstructure, an alternative fracture mechanism and corresponding energy can arise [13]. Thus the trouser tear test still appears to offer an unique and relevant assessment of polymer film.

In this present work, an attempt is made to establish more clearly the dependence of the fracture energy of a biaxial polyester film on its underlying morphology. Advantage is taken of an established method in X-ray diffraction, XRD to define the orientation of the two crystalline populations within the plane of the film, and of the availability of a set of film samples whose process history and subsequent microstructure have been closely controlled and systematically varied. Since the trouser test and the essential work method subject the test specimen to different modes of deformation [4, 13], both techniques have been employed to quantify the toughness of the material but interest has focussed on the structure-property relationship of the trouser test. For example only the fracture surfaces generated by this tearing method have been examined using electron microscopy for supportive evidence about the fracture behaviour of the biaxial film.

The tear behaviour of the biaxial polyester film is clearly anisotropic, and a simple model is used to demonstrate that the principal correlation is to the orientation distribution of the crystalline phase. This and several other observations allow the mechanism of the tear fracture to be discussed.

2. Experimental

Film from PET, 23 μm thick was obtained from a commercial scale biaxial film process [14]. During a trial production, process conditions were varied systematically to generate a series of experimental samples each with an unique underlying semicrystalline structure. The process history is summarised in Table I and by collecting film across the full width of the production process, specimens could be selected from both the centre and extreme edge of the web.

The overall level of order in each film was indicated from its density, measured using a density gradient column and further detail about its crystalline component, was provided through X-ray diffraction. By performing a Chi scan at a 2θ angle fixed to correspond to the 010 reflection, the distribution of orientations of the crystals in the plane of the film were plotted [14, 15]. The non-crystalline fraction of the film also possesses an orientation distribution and this was interrogated in an analogous way, by measuring diffracted X-ray intensity over an interval of 2θ. After fitting and subtraction of the overlapping intensity from crystalline diffraction the remaining amorphous scatter intensity was recorded and plotted against Chi. Initially two different ranges of 2θ were chosen for measurement, namely $2\theta = 11\text{–}14^\circ$ and $2\theta = 10\text{–}30^\circ$. However, since both methods were found to yield similar results, only those from the narrower interval are reported. This treatment is equivalent to that reported previously [16, 17] where the measured scatter is stated to arise from interchain periodicity.

TABLE I Process history of film

Film	Machine (forward) draw ratio	Transverse (sideways) draw ratio	Heat set temperature (°C)	Density (kg m^{-3})	
				Centre CE	Feed edge FE
1	3.5	3.8	215	1396.5	1394.9
2	3.2	3.8	215	1396.2	1394.9
3	3.2	3.8	228	1400.2	1399.5
4	3.5	3.8	228	1399.9	1399.0

Both fracture tests were performed at room temperature and in a manner similar to that reported for other work on polyester film [1, 13]. The essential work of fracture, EWF was measured in tensile mode using an extensometer, Instron model 4464 set at a deflection speed of 2 mm/min. Sample dimensions were 35 mm wide by 70 mm long and were deeply double edge notched (DDEN) such that ligament lengths ranged from 5 to 15 mm. The trouser tear test was carried out under the conditions specified in the test method, ASTM D 1938-67. The high tensile modulus of the polyester film meant that under the load applied in the test, no significant deformation occurred of the "legs" of the test specimen. Care was taken in all cases to include results only when the line of the fracture produced, was within a few degrees of the direction of interest in the film specimen and at least 5 repeats were made of each measurement using both methods. As Fig. 1. illustrates, the tests were applied to fracture the polyester film in

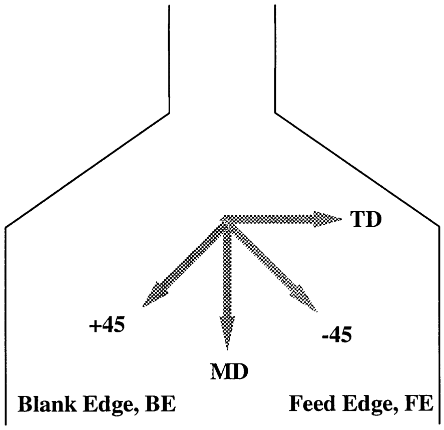


Figure 1 Plan view of film in stenter oven.

four principal directions namely in the machine or process direction, MD, in the transverse direction, TD and at two intermediate angles. In order for the intermediate angles to define their direction unambiguously each sample was viewed, mounted and tested with the same surface facing "upwards".

Finally, fracture surfaces generated at ambient temperatures using the deformation of the trouser tear, were characterised using electron microscopy.

3. Results

The average density of the polyester film is listed in Table I, opposite its process history. The density correlates as expected with the heat set or crystallisation temperature of the process. A further trend between samples collected from the centre and the extreme edge of each film also implies that slightly lower temperatures were experienced in the process at the edge of a film web than at its centre.

Fig. 2 summarises the results of the trouser tear measurements of all specimens cut from films 1–4. A value, represented by a vertical bar is plotted for each of the four directions in the plane of the film and the associated error bar represents 2 standard deviations, calculated from the repeat measurements made in each case. In Fig. 2a, a correlation between process history and film property is again noted, where the lower forward draw ratio is associated with a higher average fracture energy, but there is little convincing evidence of any dependence of the fracture on the direction of measurement for this set of film. In contrast the fracture energy of samples collected from the extreme edge of the manufactured web, is anisotropic and upon inspection, Fig. 2b reveals a systematic variation in fracture energy does exist. In all cases, the energy of fracture recorded when tearing in the +45 direction is higher than that for the direction −45. When the anisotropy is removed by averaging the four fracture energies of each film, the overall tear performance is seen in Table II to be similar for identical draw histories, irrespective of location across the film. However the samples from the edge position of the film web do offer an opportunity to gain further insight to the structure-property relationship by considering their anisotropic behaviour and associated morphology.

Additional information about the fracture of the film was provided using the EWF method. The essential work of fracture of films 3 and 4, also listed in Table II confirms that samples selected from the edge of the experimental film do exhibit anisotropic behaviour. In fact the relative values of the essential component, w_e measured in the four principal directions of film sampled from both the edge and the centre of the manufactured

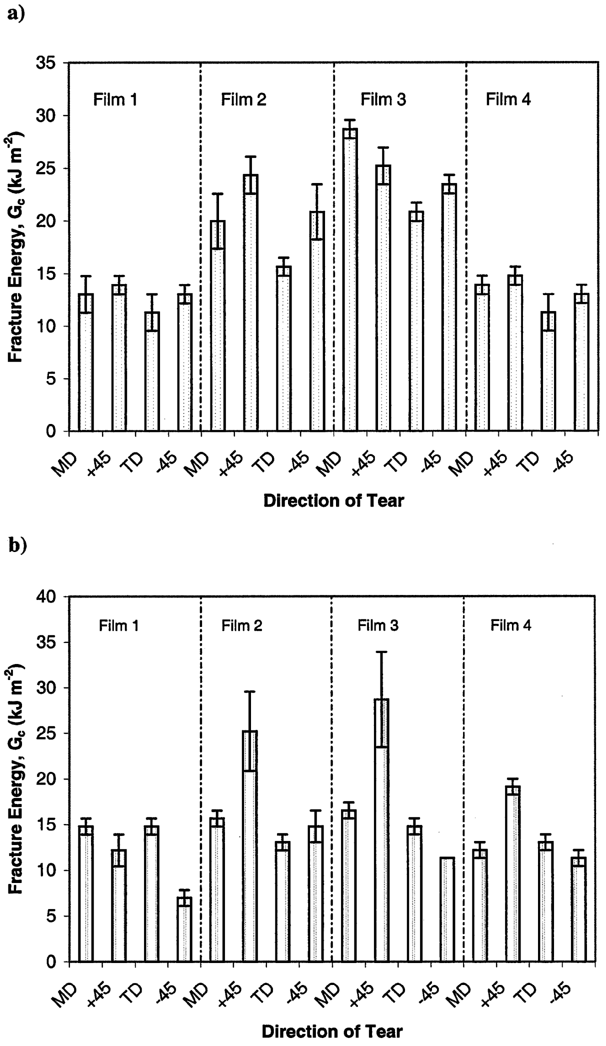


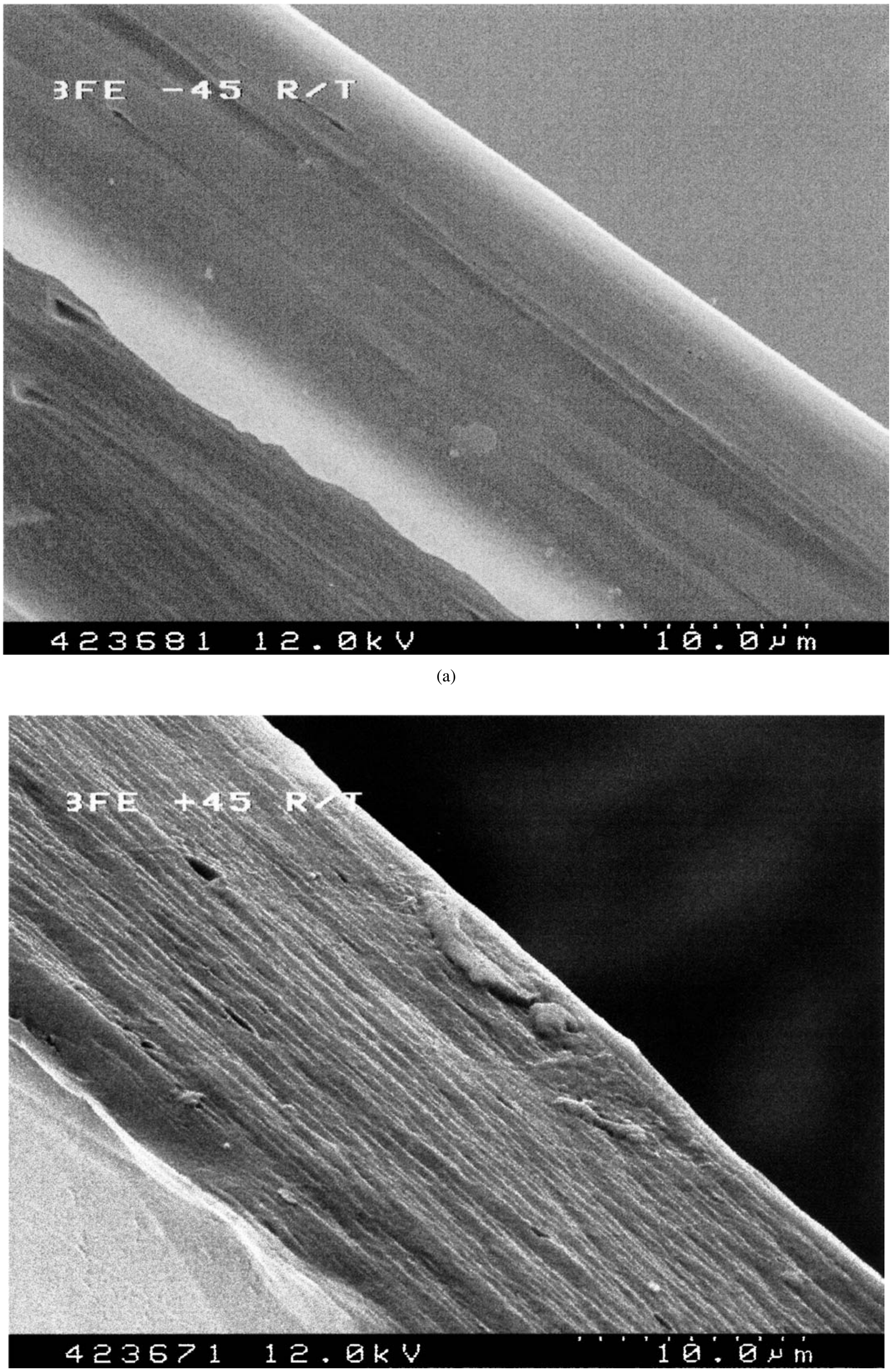
Figure 2 Fracture energy by tear test: (a) Centre of film web and (b) Edge of film web.

TABLE II Energy of fracture of film

Film	Direction	Trouser test, G_c (kJ m^{-2})	Average, G_c (kJ m^{-2})	Essential work, w_e (kJ m^{-2})
1	MD	13.0	12.8	
Centre	+45	13.9		
	TD	11.3		
	−45	13.0		
1	MD	14.8	12.2	
Edge	+45	12.2		
	TD	14.8		
	−45	7.0		
2	MD	20.0	20.2	
Centre	+45	24.4		
	TD	15.6		
	−45	20.9		
2	MD	15.6	17.5	
Edge	+45	25.2		
	TD	13.0		
	−45	14.8		
3	MD	28.7	24.6	70.6
Centre	+45	25.2		63.2
	TD	20.9		28.2
	−45	23.5		46.6
3	MD	16.5	18	55.4
Edge	+45	28.7		64.8
	TD	14.8		41.5
	−45	11.3		20.8
4	MD	13.9	13.4	44.6
Centre	+45	14.8		64.9
	TD	11.3		21.2
	−45	13.0		28.8
4	MD	12.2	13.8	66.8
Edge	+45	19.1		71.1
	TD	13.0		48.7
	−45	11.3		52.6

web, reflect very closely the variation in the value recorded for G_c, for the same sample. With the exception of only one entry in Table II the highest, lowest and intermediate fracture energies are assigned to identical directions in the film, using both test methods.

The energies of fracture, G_c provided by the trouser test and w_e from the EWF method do not agree in absolute terms however this has been recognised in previous work with thick polyester film which contained high amounts of inorganic filler [13]. Given that the non-essential work of the EWF test is performed in advance of the final necking and fracture, the essential work of fracture actually relates to a region of film which has lost its original structure and will be close



(a)

(b)

Figure 3 Fracture surface at edge of film web by tearing: (a) Tear in −45 direction and (b) Tear in +45 direction.

to uniaxially oriented. In contrast, micrographic evidence reveals very little distortion of the original polymer structure after tearing. The plastic zone appears to be smaller and more constrained than that present in the EWF test, consistent with the smaller value for G_c found by tearing [18] and infers that G_c relates more closely to the original morphology measured using XRD.

The micrographs in Fig. 3 explore further the observation that for film located at the edge of the web, the tear energy in the +45 direction is always greater than that in the −45 direction. Both micrographs shown are of film sample 3 at the edge of the web, however the characteristics of the fracture surfaces are representative of those found for all four film samples in this study.

The micrograph in Fig. 3a reveals a simple fracture by tearing, approximately normal to the plane of the film and in the direction −45. The fracture surface is relatively smooth and in contrast to reports elsewhere there is little evidence of extensive delamination. In other reports of multiple delamination [19], the direction of fracture relative to the microstructure of the film is not specified and it is possible that by tearing sample 3 of the present work in a direction of low fracture energy, the extent has been suppressed of the accompanying delamination mechanism. However the principal feature in Fig. 3a is the relatively featureless nature of the fracture surface. The smooth appearance is a characteristic legacy of a fast propagating crack and low fracture energy [20, 21], in contrast to the evidence for ductile character on fracture surfaces of PET film elsewhere [19, 22], but consistent with the lowest fracture energy values from the trouser tear measurements in this study.

Fig. 3b shows fracture surfaces, which are also representative of those produced in several samples when torn in the direction +45 and reveals a different surface topography. While there is no evidence of ductile deformation, the surface in Fig. 3b does show more varied relief which in turn implies the crack must follow a more tortuous route during fracture at +45. The new surface is consistent with fracture in tougher material requiring greater work to propagate the crack and resulting in a larger surface area. Again this observation is consistent with the highest fracture energy values recorded during tearing in this direction.

In Fig. 4 the so-called Chi scan is plotted for each film at both the centre and edge of the web. The Chi scan

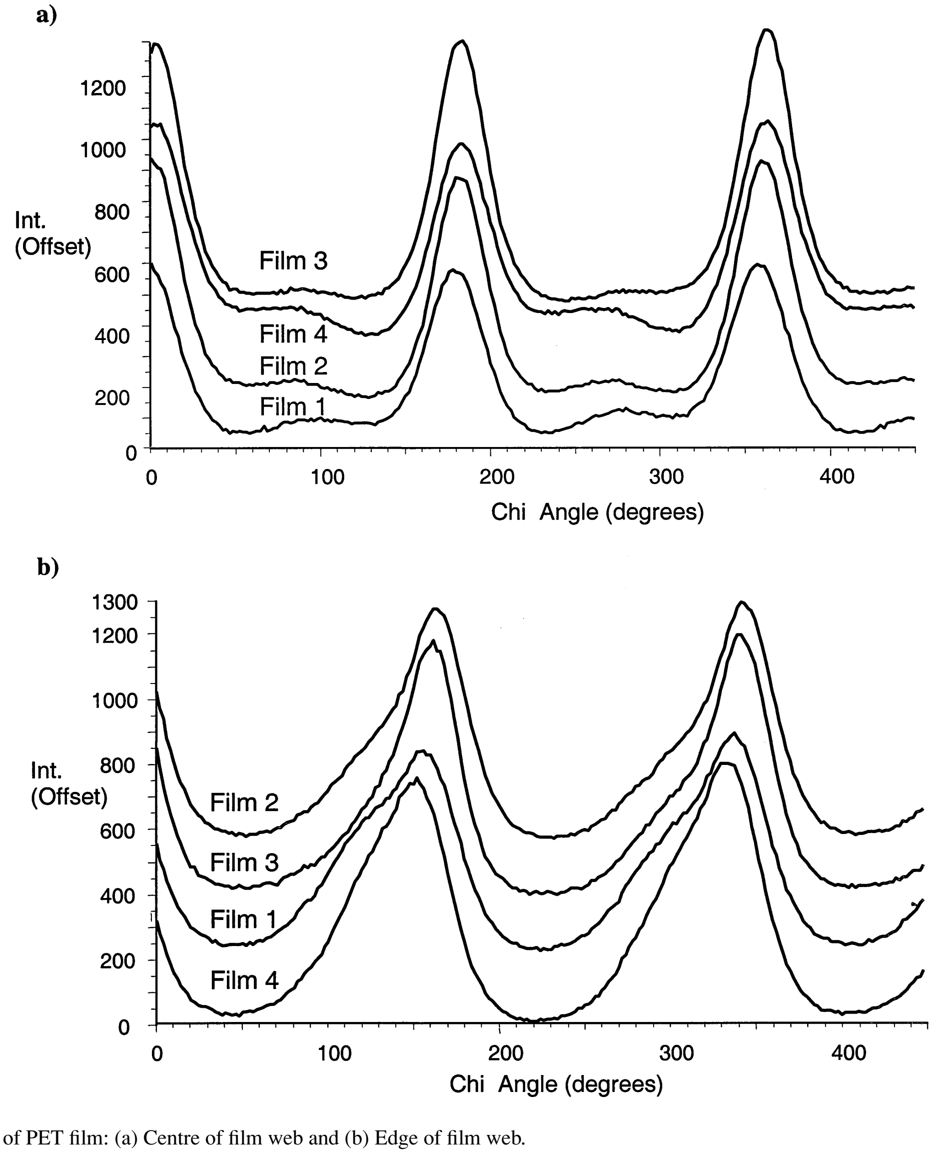


Figure 4 Chi scan of PET film: (a) Centre of film web and (b) Edge of film web.

TABLE III Parameters of XRD Chi scan

Film	MD FWHM (°)	TD FWHM (°)	Chi ratio[a] $I_{TD}/(I_{TD}+I_{MD})$	TD position (°)	Position MD-TD (°)
1 centre	50	80	0.75	−1	86
2 centre	41	85	0.80	2	95
3 centre	40	84	0.84	3	90
4 centre	47	90	0.72	3	99
1 feed edge	51	73	0.66	−22	47
2 feed edge	46	82	0.77	−16	50
3 feed edge	43	78	0.78	−19	49
4 feed edge	53	81	0.73	−28	45

[a] Chi ratio calculated from the integrated intensity of fitted curves.

plots the intensity of X-ray diffracted by the 010 plane of the crystalline phase, versus the angle through which the sample is rotated in the beam. This provides direct evidence of the orientation distribution of the crystallites and therefore the molecular chain in the crystalline phase, within the plane of the film [15]. It is well established that two discrete populations of crystallites exist, associated with the first and second draw directions of the manufacturing process [14], and the scale and width of the two distributions reflect the order and extent of the draw stages. This can be seen in Table III for films 1–4 where, after subtraction of a baseline and suitable curve-fitting, the size and shape of each intensity distribution correlates closely to the relevant draw ratio in the process history.

The Chi scan is replotted for one film in Fig. 5 to map out the orientation distribution of molecular chains in the crystalline phase, with respect to the reference axes of the macroscopic film. Illustrated as a polar plot, Fig. 5a highlights the close adherence of the centre of alignment of each population to the forward draw or machine directions and the second draw or transverse directions. However Fig. 5b shows the effect on this distribution of the in-plane shear to which the stenter subjects the very edge of the film web during its manufacture [16, 23]. Here, relative to the macroscopic reference axes of the film, the underlying semicrystalline microstructure is clearly anisotropic and asymmetric.

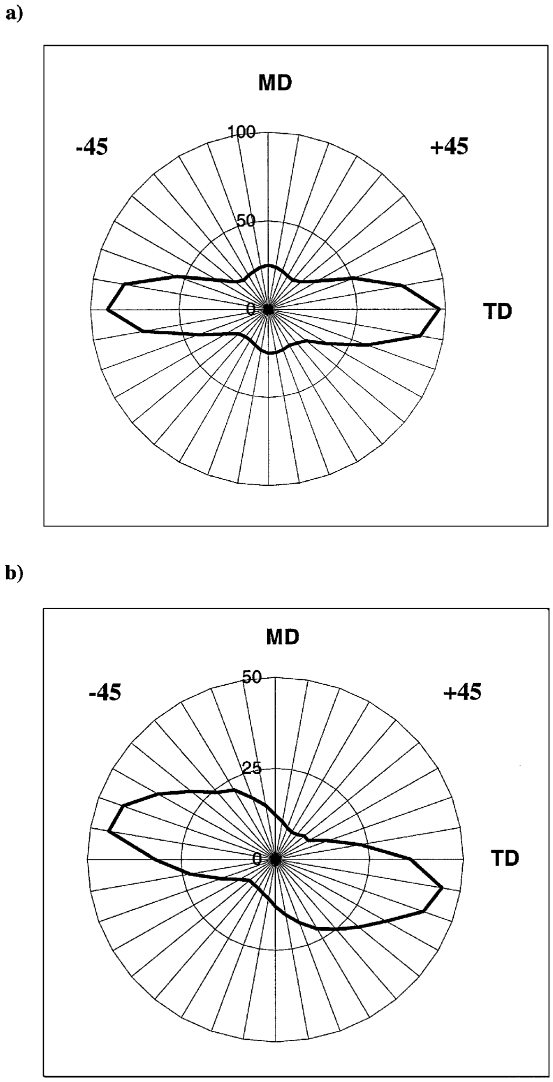


Figure 5 Crystallite orientation distribution of film 2 replotted from Fig. 4: (a) Centre of film web and (b) Edge of film web.

The non-crystalline fraction of oriented film is also known to exhibit a distribution of orientations in the plane of the film but not normally with the same degree of anisotropy as the crystalline component [16, 17]. Fig. 6 shows a plot corresponding to that in Fig. 4 where the intensity scattered from amorphous material over the interval $2\theta = 11–14^\circ$ is plotted against the rotation (Chi) of the sample in the X-ray beam. Some anisotropy exists in the intensity, which again is interpreted as directly related to the distribution of alignments of molecular chains in the non-crystalline fraction of the film. By assigning the amorphous scatter in this region of 2θ to interchain periodicity, the Chi scan is redrawn as a polar plot in Fig. 7, to indicate the preferred chain orientation relative to the macroscopic coordinates of the film sample. Some anisotropy is apparent in the specimen from the edge of the film web, which is seen broadly to mimic the preferred alignment of the crystalline fraction. In contrast, the amorphous component of film sampled from the centre of the web appears virtually isotropic. However the key observation is that by comparison with Fig. 5, the degree of molecular orientation is far lower in the non-crystalline than in the crystalline fraction of the film.

This result agrees well with the amorphous orientation distribution in biaxial PET film when measured using an alternative method [16]. It also stands up to reason. Amorphous chains must be "connected" to crystalline chains and hence must reflect at least broadly the distribution of alignment displayed by the crystallites.

4. Discussion

It is always useful to invoke a structural model for any material in order to rationalise its structure-property behaviour. Various studies have been made of the structure of biaxially drawn film from PET [24, 25] and evidence from small angle X-ray scatter, electron microscopy and solid state nmr provide particularly useful insight [26–28]. For this discussion a simple, 2-dimensional image of the biaxial structure of the film, as depicted in Fig. 8, is considered. Viewed normal to the plane of the film it has a semicrystalline morphology, in which the ordered regions comprise a mosaic

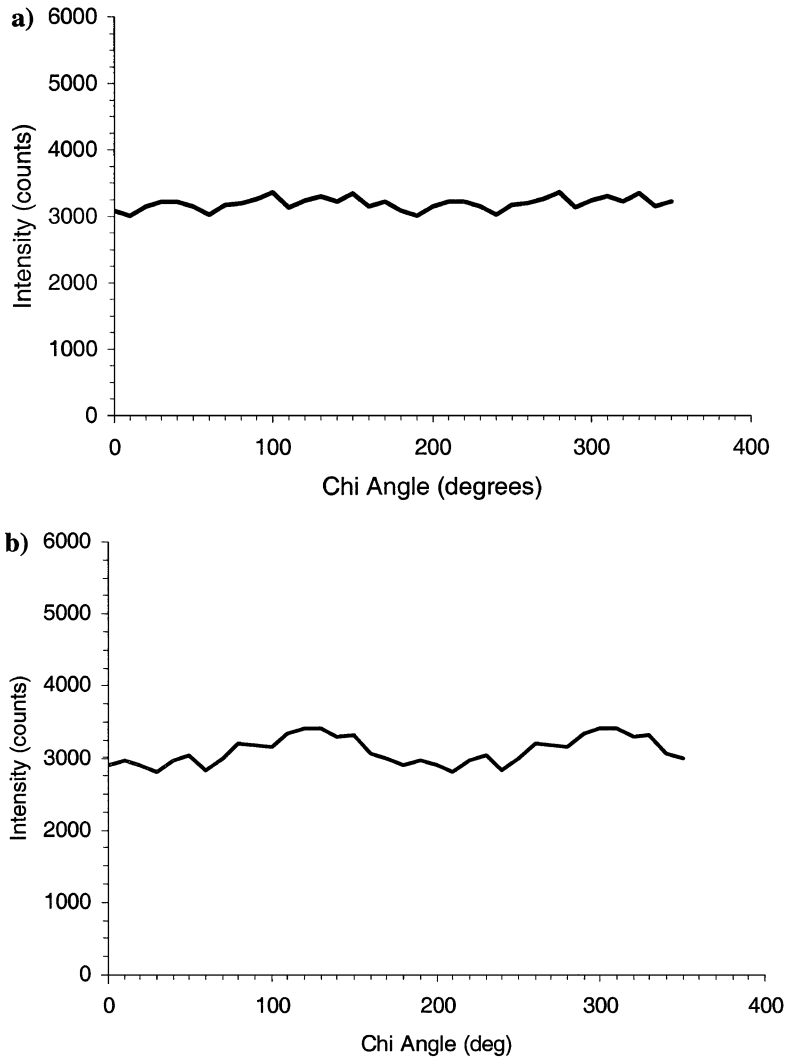


Figure 6 Chi scan of amorphous scatter from PET film 2: (a) Centre of film web and (b) Edge of film web.

of crystallites or aggregated crystallites accounting for nearly 50% of the material. Most of the crystallites lie in the plane of the film, that is the bc plane of the crystal is found to be coincidental with the macroscopic plane of the film, and tend to align along one of two preferred directions. However adjacent crystallites may not necessarily share similar orientations. Only the sum of the individual orientations is known, making up the overall measured directions recorded in the XRD study.

The disordered region also possesses some preferred orientation, as seen from measurements here and elsewhere. This is the consequence of its molecular connectivity to the ordered phase. Tie molecules will still exist and these will mimic the orientation distribution of the ordered fraction but loose loops and cilia also present in the non-crystalline phase will adopt a broader distribution of orientations. Thus overall, the anisotropy will be lower than that of the crystalline fraction [28].

It follows that this morphological model must include phase boundaries, between the crystalline and non-crystalline regions, and these are likely to have varying degrees of sharpness. For example the crystal ac and bc surface boundaries will appear relatively sharp whereas the ab crystal surface from which most tie molecules and cilia will emerge, will be less well defined. The former surfaces, which run parallel to the molecular chain axis will have sharper interfaces and when exposed to a developing crack would be expected to act as planes of weakness, encouraging fracture along their boundary.

It is possible that the orientation and broader morphology is changed ahead of an advancing crack, as the material becomes included in the plastic zone and that the molecular orientation as characterised before fracture is no longer present [18]. However the low values of G_c, recorded in this work during tearing and the absence of ductile features on the fracture surface suggest a highly constrained plastic zone is present [29]. Thus for the biaxial film whose morphology remains relatively unchanged up to the point of fracture, the path of least resistance to a crack seems logically to coincide with the direction of principal orientation. Certainly, this is supported by the energy of fracture for all samples collected from the centre of the film web. In each case the maximum in the distribution of orientations coincides with the TD and Table II shows this direction also to record the lowest fracture energy, by tearing.

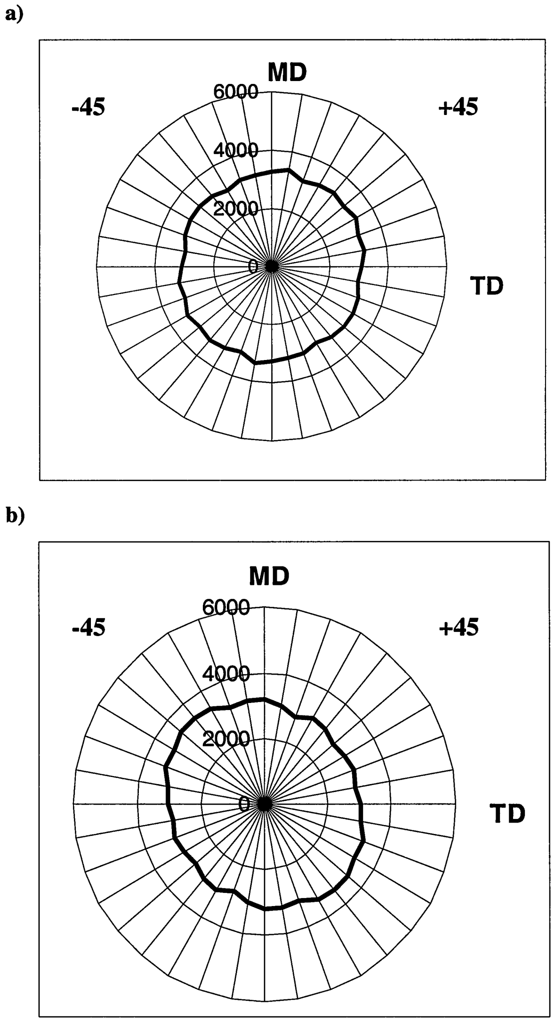


Figure 7 Amorphous orientation distribution of replotted from Fig. 6: (a) Centre of film web and (b) Edge of film web.

It is tempting to expect the direction of greatest G_c to be perpendicular to the main preferred orientation, namely the MD and this would be true if fracture was dictated by bond rupture. However bond scission is known in some cases not to play a significant role during fracture [30] and in practice we see the MD is not the direction of maximum G_c for three films. The biaxial morphology of the film means there are sufficient planes of weakness, provided by the MD population of crystallites to propagate fracture in this direction, at moderate energy cost, and to cause the direction of greatest G_c to appear at the intermediate angle, +45. In Fig. 8a, the possible path of a fracture propagating in the machine, transverse and +45 directions is drawn to demonstrate that the last case coincides only rarely with planes of weakness at the crystal-amorphous boundary. The tear behaviour at the edge of the film web can be explained in similar terms.

Fig. 5b illustrates how the maximum orientation of both the first and second populations of crystallites in the sample from the film edge are rotated significantly towards the direction, −45 with the combined effect of causing the lowest fracture energy to be measured at that angle. As before the fracture will proceed easily along the direction closest to that of the molecular alignment. However since the biaxial orientation now does not possess the symmetry of the samples from the centre of the film web, few weak planes or other morphological features exist which would precipitate a crack travelling perpendicular to the weakest direction. Fig. 8b therefore suggests that the mechanism to propagate a crack at +45 probably involves a greater amount of molecular deformation, pull-out and even bond rupture, and as a consequence, the direction of highest resistance to tear is invariably seen at +45, approximately perpendicular to the average principal molecular orientation.

Combining the observations about tear with a model of the biaxial morphology of the film suggests that the direction of tear, relative to the principal molecular alignment dominates the fracture energy. That is a fracture or tear propagates with least resistance when directed parallel to highly oriented polymer chains. From Table II, other considerations such as overall molecular extension also play a role where greater extension through high process draw ratios appears to sharpen and weaken the boundary between crystalline and non-crystalline material.

However, if the simple interpretation of the structure dependence of tear is correct, namely that to a first order the orientation of weak planes or crystal surfaces dictates G_c, it should be possible to predict the observed tear anisotropy from a knowledge of the crystal orientation distribution. Thus a very simplistic model was developed by firstly defining θ as the angle between the direction of a propagating crack and the local molecular orientation in its path. From the observations above, one can assign an arbitrary value for the resistance by the local molecular structure to a propagating crack of $|\sin\theta|$, which denotes the absolute magnitude of $\sin\theta$. This yields a maximum when the crack direction is perpendicular to the chain direction and zero when it is parallel. The contribution to the total energy to fracture of the material by all morphological elements with identical orientation is therefore the product of their abundance and $|\sin\theta|$. However since the whole material comprises a distribution of molecular orientation, the total energy to fracture of the film is the sum over all angles of this product. That is for a fracture propagating in a fixed direction, the fracture energy will be proportional to

$$\int_0^{2\pi} \chi(\theta)|\sin\theta|\, d\theta$$

where χ is the distribution function of molecular orientation measured experimentally. In practice an approximation for the fracture energy was calculated as a summation where the product, $\chi \sin\theta$ was calculated at intervals of 10° between 0° and 180° and the final sum normalised with respect to a measured G_c.

Fig. 9 shows the results where predictions are compared with measured values for G_c, in the samples collected from the edge of the original film web. In each figure the predicted values are normalised by an arbitrary value for convenient comparison on the scale of the measured fracture energy. It appears that the simple model can account for the anisotropic behaviour of G_c between the + and −45 directions, and in most

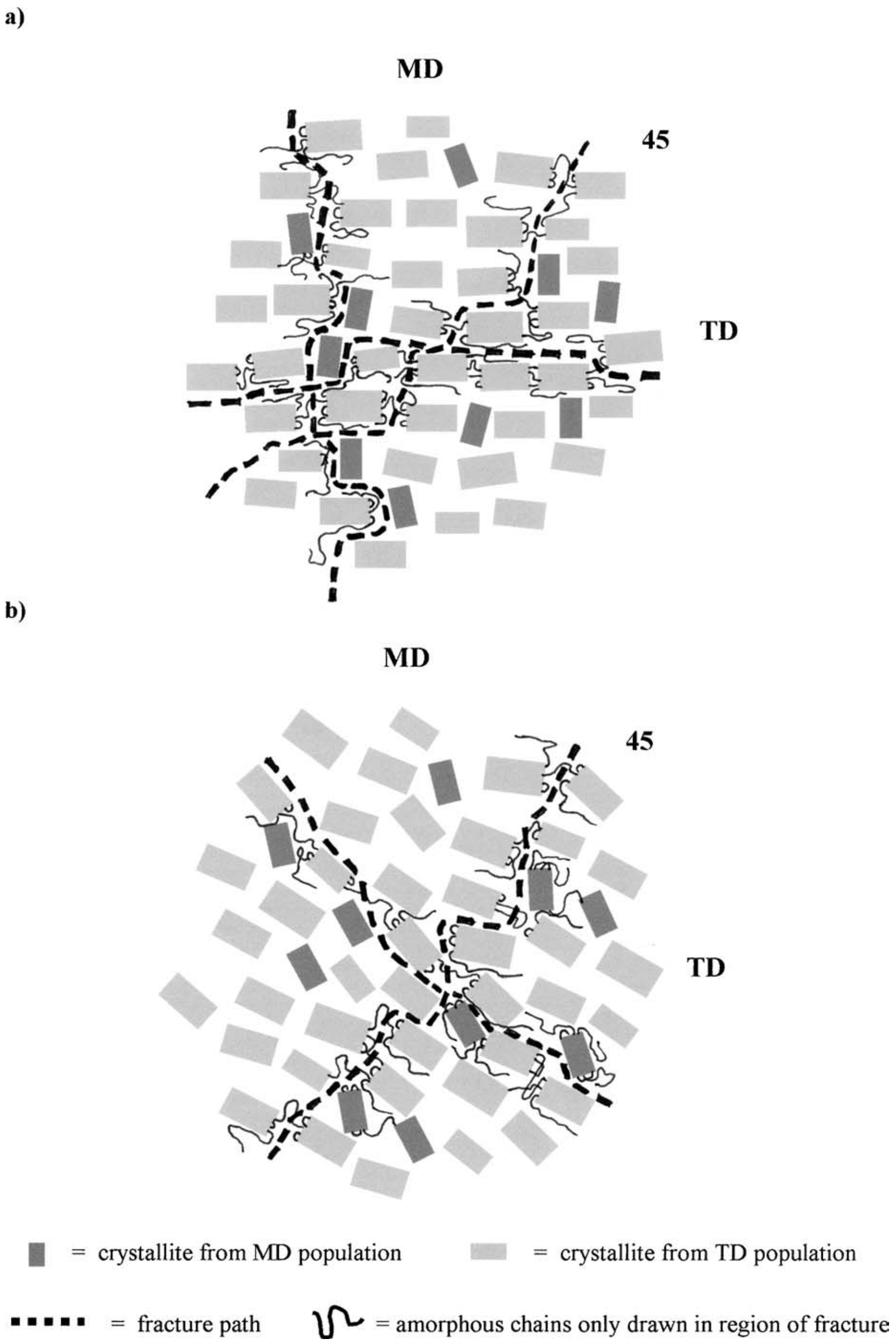


Figure 8 Semicrystalline structure of biaxially drawn film: (a) Centre of film web and (b) Edge of film web.

cases for the intermediate MD and TD. It cannot explain however the degree of the anisotropy, since the predicted G_c at +45 is, relative to the other directions, always significantly lower than that found in practice. Moreover the difference in the average fracture energy between films drawn to forward ratios ×3.5 and ×3.2 cannot be predicted by this simple approach.

Given the similarity between these films of their crystalline fraction, the range in average energy of fracture recorded in Table II must correlate more to differences in their non-crystalline component, where the extension of the molecular chain influences features such as the boundary region at the crystallite surface.

Reports, which demonstrate that the crystallite surface changes with draw ratio and as a consequence exerts a further effect on fracture during tear, could be cited from literature [31, 32]. However evidence obtained from the specimens in this study using for example X-ray scatter methods would be more relevant, and must form the object of future work.

In this report we have explored the structure-property relationship associated with the trouser tear test for a biaxially oriented polyester film. The observed anisotropic behaviour correlates closely with the orientation distribution of the crystallite populations in the film. In addition, features such as the amorphous-crystallite boundary, are believed important to the fracture mechanism and therefore fracture energy. Thus conditions in the process history, which influence the crystallite surface boundary will also determine the tear behaviour of the film. One clear example is the draw ratio, which probably dictates the amorphous-crystallite boundary through its influence on both the local amorphous and crystalline fractions.

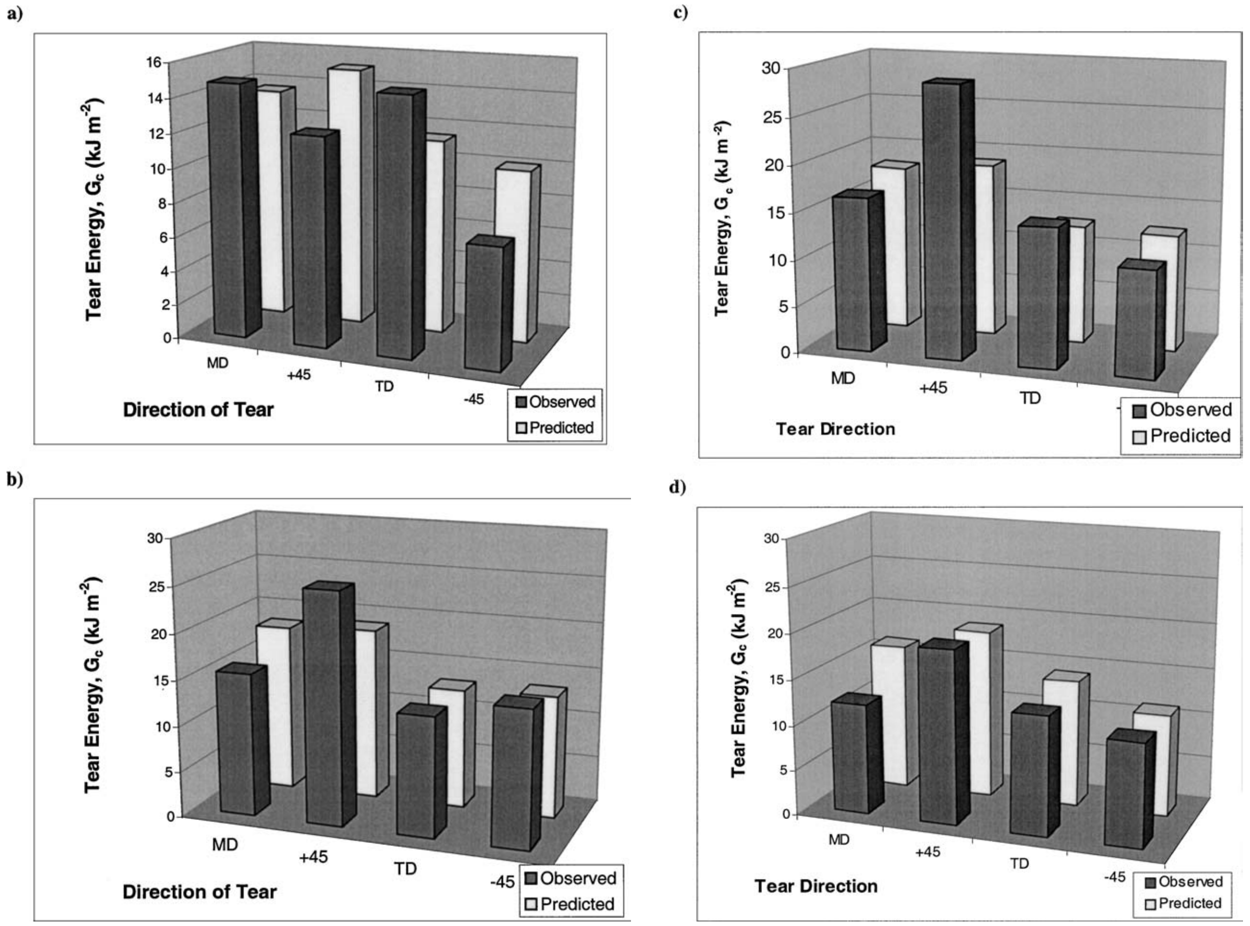


Figure 9 Anisotropy of the tear fracture energy: (a) Sample 1 edge of film, (b) Sample 2 edge of film, (c) Sample 3 edge of film and (d) Sample 4 edge of film.

Acknowledgments

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References

1. "ASTM D1938-67, Annual Book of ASTM Standards" (American Society for Testing and Materials, Philadelphia, 1986).
2. A. G. THOMAS, *J. Polym. Sci.* **18** (1955) 177.
3. H. W. GREENSMITH, L. MULLINS and A. G. THOMAS, *Trans. Soc. Rheol.* **4** (1960) 179.
4. J. A. HINKLEY and C. A. HOOGSTRATEN, *J. Mater. Sci.* **22** (1987) 4422.
5. R.-Y. WU, L. D. MCCARTHY and Z. H. STACHURSKI, *Int. J. Fract.* **68** (1994) 141.
6. G. DHONT, A. CHERGUI and F.-G. BUCHHOLZ, *Eng. Fract. Mech.* **68** (2001) 383.
7. P. I. VINCENT, in "Encyclopedia of Polymer Science and Technology," edited by N. M. Bikales (Wiley, New York, 1967) Vol. 7.
8. D.-S. CHUI, A. N. GENT and J. R. WHITE, *J. Mater. Sci.* **19** (1984) 2622.
9. A. N. GENT and J. JEONG, *ibid.* **21** (1986) 355.
10. M. KONO, T. OGATA and M. NOMURA, Patent JP49058172 (1974).
11. R. W. ZOLG, *Polym. Eng. Sci.* (1967) 194.
12. J. KARGER-KOCSIS, in "Handbook Thermoplastic Polyesters," edited by S. Fakirov (Wiley-VCH, Weinheim, 2002) Vol. 1.
13. J. KARGER-KOCSIS and T. CZIGANY, *Polymer* **37** (1996) 2433.
14. W. A. MACDONALD, D. H. MACKERRON and D. W. BROOKS, in "PET Packaging Technology," edited by D. W. Brooks and G. A. Giles (Sheffield Academic Press, Sheffield, 2002).
15. C. J. HEFFELFINGER and R. L. BURTON, *J. Polym. Sci.* **47** (1960) 289.
16. G. H. KIM, C.-K. KANG, C. G. CHANG and D. W. IHM, *Eur. Polym. J.* **33** (1997) 1633.
17. A. AJJI, K. C. COLE, M. M. DUMOULIN and J. BRISSON, *Polymer* **36** (1995) 4023.
18. A. C. CHANG, S. P. CHUM, A. HILTNER and E. BAER, *ibid.* **43** (2002) 6515.
19. D. BOLLEN, J. DENEIR, E. AERNOUDT and W. HUYLLE, *J. Mater. Sci.* **24** (1989) 2957.
20. Z.-S. FU, Z.-Q. FAN, Y.-Q. ZHANG and L.-X. FENG, *Eur. Polym. J.* **39** (2003) 795.
21. Y. X. GAN, H. AGLAN, P. FAUGHNAN and C. BRYAN, *J. Rein. Plast. Comp.* **20** (2001) 766.
22. C. ARCONA and T. A. DOW, *J. Mater. Sci.* **31** (1996) 1327.
23. K. TSUNASHIMA, K. TOYODA and T. YOSHII, in "Film Processing," edited by T. Kanai and G. A. Campbell (Hanser, Munich, 1999).
24. J. B. F. DE CHAMPCHESNEL, J. F. TASSIN, L. MONNERIE and P. SERGOT, *Polymer* **38** (1997) 4165.
25. J. B. F. DE CHAMPCHESNEL, J. F. TASSIN, D. I. BOWER, I. M. WARD and G. LORENTZ, *ibid.* **35** (1994) 4092.
26. H. CHANG, J. M. SCHULTZ and R. M. GOHIL, *J. Macromol. Sci.* B **32** (1993) 99.
27. R. PENDLEBURY, "The Morphology of Oriented Poly(ethylene terephthalate) Film," PhD Thesis, University of Teesside, 1996.
28. P. M. HENRICHS, *Macromolecules* **20** (1987) 2099.

29. J. S. S. WONG, D. FERRER-BALAS, R. K. Y. LI, Y-W. MAI, M. L. MASPOCH and H.-J. SUE, *Acta Materialia* **51** (2003) 4929.
30. J. JANCAR, *Adv. Polym. Sci.* **1** (1999) 139.
31. C. MARTIN, "X-ray Fibre Diffraction Studies of Crystallisation in Forward-Drawn Poly(ethylene terephthalate) Films," MPhil Thesis, University of Keele, 1994.
32. D. SALEM, *Polymer* **33** (1992) 3182.

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