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Application of discontinuous fibre-reinforced composite theory to polybutene-1 films containing needle crystals

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Studies of the structure-property relationship of polybutene-1 films containing needle crystals (shishes) without any epitaxial overgrowth have been carried out with the help of transmission electron microscopy, differential scanning calorimetry and density and mechanical measurements. The lengths of the needle crystals have been varied by changing the preparation conditions. The mechanical responses of these materials are found to be dependent mainly on the needle length (length to diameter ratios), and can be explained with reference to the fibre-reinforced composite theories for discontinuous fibres. The studies indicate that the properties of the material can be described in terms of a composite of hard needle crystals contained in a soft amorphous matrix in which the polymer molecules build up an interconnecting molecular network structure.

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1. Introduction

In the past few years, there has been an increasing interest in understanding the mechanical responses manifested by ultra high modulus polymeric materials [1–11] which are believed to be mainly of needle-type crystals. Various attempts have been made to describe semicrystalline polymers as composites and there are different model calculations in order to predict their mechanical behaviour [8–19]. However, in the bulk samples, it is difficult to investigate directly the morphology using transmission electron microscopy (TEM) and, as such, it is difficult to find out details, such as the shapes, sizes and dispersions of the phases. Hence, comparisons of the composite theories with the experimental results of bulk samples, so far obtained, are still a matter of debate.

Recently, a new experimental method for preparing oriented thin films (≈ 100 nm) of polybutene-1 (PB-1) containing needle crystals has been developed [20–22]. The major advantage of the method is that the morphology of the films can be directly investigated by TEM. For mechanical measurements, bulk samples can be prepared by a continuous wrapping of these films onto a glass plate. Within the films, the length of needle crystals can be varied by changing preparation conditions. The variation of needle dimensions obtained by changing the preparation conditions can be used to verify fibre-reinforced composite theories (FRCT). The purpose of the present communication is to demonstrate the applicability of fibre-reinforced composite theory for discontinuous fibres to inherently reinforced polymer composites.

2. Experimental details

PB-1 ($\bar{M}w = 3 \times 10^6$) used in the present work was supplied by Chemische Werke Hüls, Marl.

The bulk samples consisting of about 1000 single layers were pressed at 100° C and kept for 30 min at this temperature. The mechanical measurements were carried out on the bulk samples using a standard Instron machine at room temperature and at $-196°$ C using a straining rate of $0.4\,\text{min}^{-1}$. The sample size used for such measurements was 5 cm x 0.5 cm. The density of these bulk samples was measured by applying the floatation technique employing the solvent system, dimethyl-formamide–heptanol. The thermal

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behaviour of the samples with fixed and loose ends was studied using a Heraeus DSC 500 differential scanning calorimeter (DSC). The electron microscope used for the present investigations was a JEOL JEM 200 CX, operated at 100 kV.

The details concerning the method for preparing the highly oriented films of thermoplastics has been described previously [20, 21].

3. Results

The PB-1 films prepared by our method at temperatures ranging from 105 to 180° C contain well defined needle crystals without any lamellar overgrowth. Fig. 1 shows a phase contrast electron micrograph of needle crystals grown at 180° C. The average length of the needle crystals was measured from several phase contrast electron micrographs and the maximum length of the needle crystals measured from dark-field electron micrographs at different preparation temperatures are given in Table I. As pointed out previously [12], the length of the needle crystals obtained using dark-field electron microscopy can be considered to be the lower estimate of the needle length. The average needle diameter measured from the phase contrast and dark-field electron micrographs was about 10 nm and was found to be the same for the crystals prepared at all preparation temperatures. Heat treatments do not induce shish-kebab like structures within the films.

Fig. 2 shows stress–strain curves of the PB-1 films taken at room temperature and at − 196° C. The variation of the Young's modulus of the films as a function of needle lengths at room temperature and at − 196° C is given in Fig. 3 (see also Table I). Each value of the Young's modulus is an average of ten individual measurements. The uncertainty in the measurements is indicated in Fig. 3.

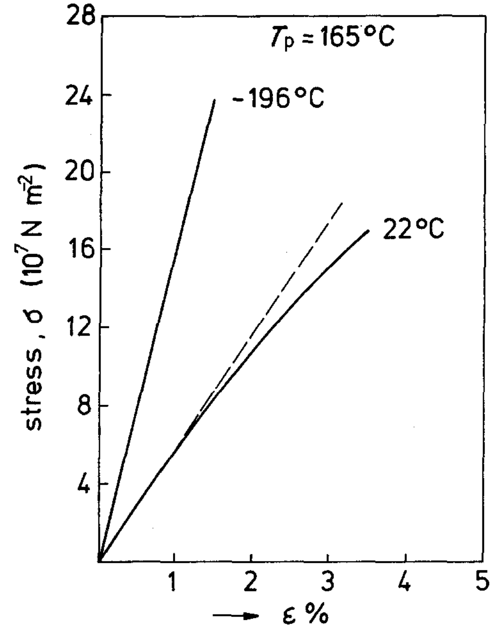

Figure 2 Stress–strain curves of samples prepared at 165° C.

DSC traces of the samples taken with loose ends, are assembled in Fig. 4a. The increase of the melting peak temperature with the needle lengths is apparent and lies in the range 124 to 132° C. The completion of melting occurs in the range of

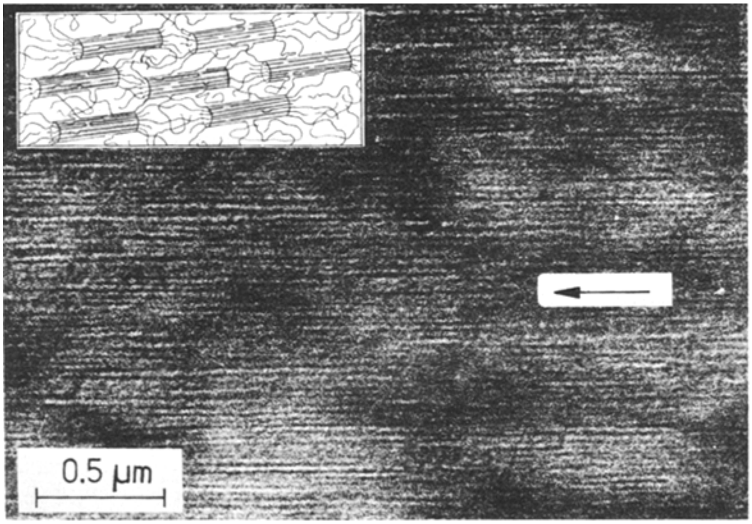

Figure 1 Phase contrast electron micrograph of needle crystals (dark lines) grown at 180° C. Inserted is a sketch of the morphology.

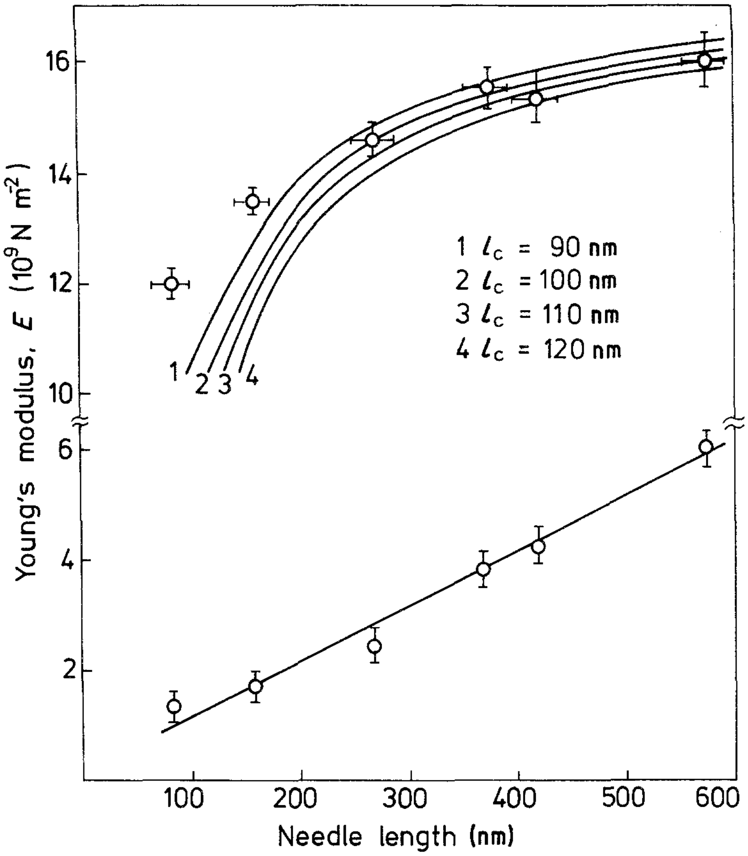

Figure 3 Young's modulus against needle length (⊢ϕ⊣ measuring temperature −196° C, ϕ measuring temperature 22° C). Curves 1 to 4 are theoretical calculations for different values of l_c.

135 to 140° C. Considerable increase in the melting temperature is observed when the DSC traces are scanned (Fig. 4b) with the ends of the sample held fixed. For the scanning rate used, the melting peaks lie in the temperature range of 170 to 175° C, while completion of the melting occurs at about 180° C. The multiple endothermic peaks in the scans of the samples prepared at 150 and 180° C result from a local loosening of the tightened samples. In order to minimize the behaviour, a higher scanning rate for the samples with fixed ends has been used.

4. Discussion

For some years, the reinforcement of polymeric materials by using high modulus fibres has remained a major means for the generation of high-strength materials and its study is of both academic and technological interest. Glass and carbon fibres are commonly utilized for the reinforcement of polymers. As soon as it was realized that polymer fibres or filaments prepared under special conditions also exhibit high modulus and high strength [3, 7, 9, 10], additional interest arose to utilize these films for the reinforcement of polymers.

TABLE I

Preparation temperature, T_p (° C)	Length of needle crystals		Young's modulus, E_c	
	Phase contrast average length, l (nm)	Dark-field maximum length, l (nm)	Room temperature (× 10^9 N m^{-2})	− 196° C (× 10^{10} N m^{-2})
105	85.0	90.0	1.3	1.20
115	160.0	165.0	1.7	1.35
135	270.0	280.0	2.4	1.46
150	370.0	375.0	3.8	1.55
165	570.0	580.0	6.0	1.60
180	420.0	400.0	4.20	1.54

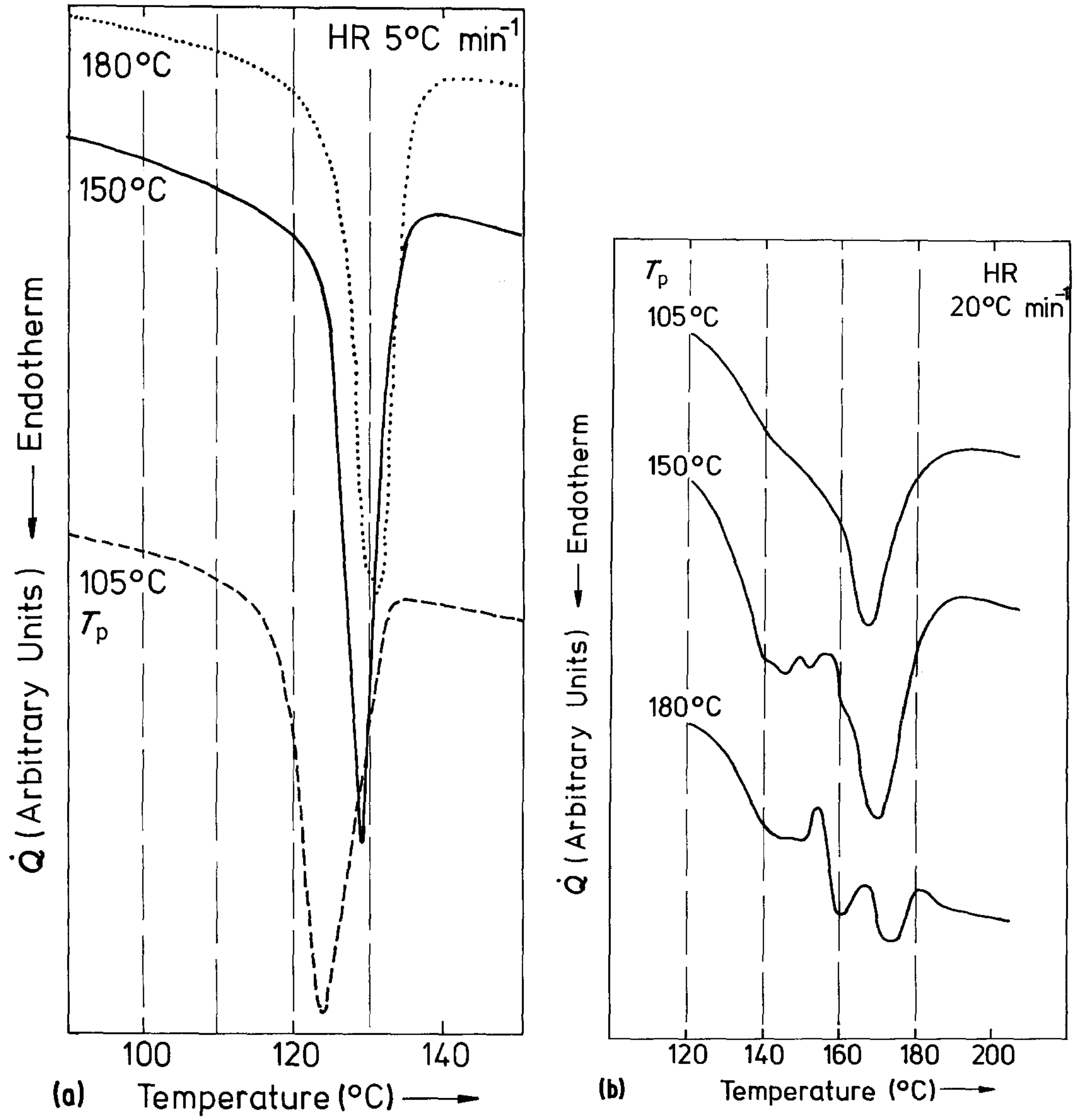

Figure 4 (a) DSC-scans of samples with loose ends, and (b) DSC-scans of samples with fixed ends.

Among others, a major advantage of these sorts of composites is that the polymer fibres or fibrillar crystals can be directly grown in the polymer matrix [12, 20]. On examining the structure of our polybutene-1 films (see Fig. 1) the fibrillar nature of the crystals (dark lines) is apparent [22], and on analysing the mechanical data it will be shown that the theory of discontinuous fibre-reinforced materials is applicable to this class of polymeric materials. The principle of composites [23, 24], is that the fibre (hard part of the composite, here needle crystals) serves to support the applied load, whilst the ductile matrix (here the amorphous phase of the PB-1) serves to bind the fibres. The strength of the fibre composite depends upon the successful transfer of the load from the ductile matrix to the strong fibres. To attain maximum strength, it is desirable to load the fibres to their fracture strength, σ_f. The critical fibre length defined as the minimum length of the fibres required to insure that the fibres can be loaded to fracture is

$$l_c = r\,\sigma_f/\tau \qquad (1)$$

where τ is the shear stress along the fibre and related to either the interface strength or the matrix shear strength, whichever is smaller, and r is the radius of the fibres. In order to achieve an efficiency of 90%, compared to a continuous fibre composite, a length of the fibres of $4l_c$ is required [24]. Based on the relative values of l_c, with respect to l, two mainly simple theoretical considerations will be discussed here.

1. The fibres fracture before the matrix ($l_c < l$): in this case, the strength of the composite can be expressed as [24]

$$\sigma_c = \left(1 - \frac{l_c}{2l}\right) \sigma_f \nu_f + \sigma_m (1 - \nu_f) \qquad (2)$$

where σ_c and σ_m are the fracture strengths of the composite and the matrix, respectively, and ν_f and l are the volume fraction of the fibres and their length, respectively.

The above equation can be written in terms of tensile moduli:

$$E_c = \left(1 - \frac{l_c}{2l}\right) E_f \nu_f + E_m (1 - \nu_f) \qquad (3)$$

where E_c, E_f and E_m are the tensile moduli of composite, fibre and matrix, respectively.

2. The matrix fractures before the fibres ($l < l_c$): in this case, the strength of the composite material is given by the relation [24],

$$\sigma_c = \frac{l\tau}{2r} \nu_f + \sigma_m (1 - \nu_f) \qquad (4)$$

In order to compare the predictions of the theory with the experimental results, one needs the parameters E_m, E_f and τ. The theoretical value of Young's modulus of PB-1 crystals [25] is chosen to be $2.5 \times 10^{10}\,\mathrm{N\,m^{-2}}$. The Young's modulus of the matrix (amorphous component) is estimated to be $3 \times 10^9\,\mathrm{N\,m^{-2}}$ for the glassy state (− 196° C) and $3 \times 10^7\,\mathrm{N\,m^{-2}}$ at room temperature for the rubbery state [26]. The volume fraction, ν_f, of the fibres is 0.54 as determined from density measurements. In Fig. 3, the Young's modulus E_c of the composite is plotted against the average length l of the needle crystals. Scrutiny of Fig. 3 reveals a rapid increase in the value of E_c measured at − 196° C with needle length up to 350.0 nm. Further increases in the needle lengths do not change the values of E_c significantly. Extrapolating this curve to infinite needle length gives a value of Young's modulus, E_c, to be about $1.7 \times 10^{10}\,\mathrm{N\,m^{-2}}$. Using the isostrain model for continuous fibres

$$E_c = E_f \nu_f + E_m (1 - \nu_f) \qquad (5)$$

The calculated value of the Young's modulus, E_f, of the PB-1 needle crystal is about $3.1 \times 10^{10}\,\mathrm{N\,m^{-2}}$, which is in reasonable agreement with the theoretical value [25]. The critical length of the needle crystals calculated from Equation 3 is 135.0 nm. In glass fibre-reinforced epoxy resins [27] with similar parameters as in our material, the critical length was determined to be about ten times the fibre radius and an efficiency of 90% compared to continuous fibres was reached at $4l_c$. In the needle crystal reinforced PB-1, the critical length, l_c, is about 13 times the fibre diameter and an efficiency of 90% is obtained at $3.5l_c$.

According to Equation 1, the critical length increases with decreasing shear strength, τ, of the matrix (or interface). For the measurements of strength of the PB-1 samples at room temperature, a drastic increase in l_c is expected (the decrease of the shear strength of the amorphous matrix is much greater than the decrease of the fracture strength, σ_f, of the needle crystals. This is mainly because the amorphous matrix changes from the glassy to the rubbery state. In the case of this change of state, the decrease in E_m is of about two orders of magnitude and, hence, the needle crystals in our samples cannot be loaded to the fracture stress at room temperature. The variation of Young's modulus, E_c, of the composite with needle length is depicted in Fig. 3. In comparison to the low temperature measurements (− 196° C), values of E_c are much lower and increase almost linearly with needle length. This linear dependence is expected for composites in which the fibre length is smaller than the critical length ($l < l_c$, Equation 4).

The nature of the amorphous matrix and the interface of the composite can be characterized from the thermal studies. As seen from Fig. 4, on scanning the samples with fixed ends in the DSC experiment, the increase in melting peak temperature is about 40° C. This particular observation leads to the conclusion that most of the molecules in the amorphous parts are tightly attached to the needle crystals and form molecular networks among the needle crystals. Hence, the whole system can be visualized as being cross-linked where the needles act as physical tie-points. In conclusion, the pertinent features of the present investigations are as follows below.

1. Oriented films of PB-1 composed of needle crystals embedded in an amorphous region with varying aspect ratios (l/d) ranging from 8.5 to 57

can be easily prepared by the strain induced crystallization technique.

2. The mechanical properties of the films can be described in terms of the fibre composite theory for short aligned fibres. At low deformation temperature ($T < T_g$), a fibre length of 350.0 nm (aspect ratio of 35) is sufficient in order to achieve an efficiency of 90% of that predicted by the continuous fibre-reinforced theory of composite. At an elevated deformation temperature ($T > T_g$) about 100 times longer fibrillar crystals would be needed for achieving the same efficiency assuming that the matrix does not behave as a cross-linked system.

3. The amorphous matrix contains tie molecules bridging the side and end surfaces of the needle crystals (see the inserted schematical representation in Fig. 1).

The present study suggests an alternative means for the generation of a typical inherently reinforced thermoplastic polymeric composite via crystal growth processes, to the conventional glass or carbon fibre-reinforced thermoplastic polymeric materials.

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References

1. A. J. PENNINGS, *Macromol. Chem. Suppl.* 2 (1979) 99.
2. J. PETERMANN, R. M. GOHIL, M. MASSUD and D. GÖRITZ, *J. Mater. Sci.* 17 (1982) 100.
3. J. SMOOK, J. C. TORF, P. F. von HUTTEN and A. J. PENNINGS, *Polym. Bull.* 2 (1980) 293.
4. A. KELLER and P. J. BARHAM, *Plast. Rubber Int.* 6 (1981) 19.
5. A. KELLER and J. A. ODELL, *J. Polym. Sci., Polym. Sym.* 63 (1978) 155.
6. P. J. BARHAM and A. KELLER, *J. Polym. Sci., Lett. Ed.* 17 (1979) 591.
7. P. SMITH and P. J. LEMSTRA, *Macromol. Chem.* 180 (1979) 2983.
8. R. G. C. ARRIDGE and P. J. BARHAM, *J. Polym. Sci., Phys. Ed.* 16 (1978) 1297.
9. A. G. GIBSON, G. R. DAVIES and I. M. WARD, *Polymer* 19 (1978) 683.
10. W. T. MEAD, C. R. DESPER and R. S. PORTER, *J. Polym. Sci., Phys. Ed.* 17 (1979) 859.
11. W. WU, P. G. SIMPSON and W. B. BLACK, *ibid.* 18 (1980) 751.
12. J. RAU, R. M. GOHIL, J. PETERMANN and J. M. SCHULTZ, *Colloid Polym. Sci.* 259 (1981) 241.
13. A. J. OWEN, *J. Mater. Sci.* 16 (1981) 2324.
14. A. J. OWEN and I. M. WARD, *ibid.* 6 (1971) 485.
15. M. TAKAYANAGI, *Mem. Fac. Eng. Kyushu Univ.* 23 (1963) 1.
16. W. GRAY and N. G. McCRUM, *J. Polym. Sci. A-2* 7 (1969) 1329.
17. T. S. CHOW, *J. Mater. Sci.* 15 (1980) 1873.
18. F. R. EIRICH, *Pure Appl. Chem.* 46 (1976) 115.
19. A. KELLY, *Metall. Trans.* 3 (1972) 2313.
20. J. PETERMANN and R. M. GOHIL, *J. Mater. Sci.* 14 (1979) 2260.
21. R. M. GOHIL and J. PETERMANN, *J. Macromol. Sci. Phys.* B18 (2) (1980) 217.
22. J. PETERMANN, R. M. GOHIL, J. M. SCHULZ, R. W. HENDRICKS and J. S. LIN, *J. Mater. Sci.* 16 (1981) 265.
23. A. KELLY, "Strong Solids" (Clarendon Press, Oxford, 1966).
24. D. HULL, "An Introduction to Composite Materials" (Cambridge University Press, Cambridge, 1981).
25. I. SAKURADA and K. KAJI, *J. Polym. Sci., Part C* 31 (1970) 57.
26. J. M. G. COWIE, "Polymers; Chemistry and Physics of Modern Materials" (International Text Book Company Ltd, Bucks, 1973) p. 272.
27. P. HANCOCK and R. C. CUTHBERTSON, *J. Mater. Sci.* 5 (1970) 762.
28. J. PETERMANN and R. M. GOHIL, *J. Polym. Sci., Lett. Ed.* 18 (1980) 781.

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