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The Tensile Behaviour of Polyethylene Terephthalate

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Measurements of the load/extension curves of polyethylene terephthalate (PET) over a wide range of temperatures showed four regions of behaviour. These were brittle fracture, ductile, cold-drawing, and uniform extension. A particular study was made of the transitions between brittle fracture and ductile failure, and between ductile and cold-drawing, since these define the limits of the three regimes of failure observed at temperatures below the glass transition and softening range.

The effects of molecular weight and crystallinity were examined. The brittle strengths measured in tension at low temperatures showed a very large scatter. There was evidence, in spite of this scatter, that the brittle strength falls with decreasing molecular weight. The yield behaviour was not affected, so that the brittle/ductile transition moves to higher temperatures.

Crystallinity affects both brittle strength and yield behaviour. The brittle strength falls with increasing crystallinity, whereas the yield stress rises. Both effects combine to raise the temperature of the brittle/ductile and the ductile/cold-drawing transitions.

Stress/temperature curves were also constructed for notched specimens. Notching raises the effective yield stress and reduces the brittle strength so that the brittle/ductile transition is moved to higher temperatures. The observed effects are in qualitative agreement with theoretical predictions of the plastic constraint at the tip of a notch, and thus the latter gives a satisfactory qualitative explanation of notch sensitivity. Notching leads to brittle failure at room temperature, and in notched specimens the brittle strength rises as the temperature is decreased. The brittle strength of the lowest molecular weight sample was again significantly less than that of the higher molecular weight samples.

1. Introduction

There is an increasing interest in the failure phenomena in polymers, whether this occurs by brittle fracture or ductile yield. It is evident that in some respects polymers behave similarly to metals. For example, brittle/ductile transitions play an important rôle in their behaviour [1]. The present investigation examines the failure of polyethylene terephthalate over a wide range of temperatures at various strain rates.

Particular points of interest are the notch sensitivity and the effects of molecular weight and crystallinity. The latter aspects have been discussed previously in an earlier publication from this laboratory, with reference to yield stress and impact strength [2].

2. Experimental

2.1. Preparation of Samples

The tensile samples of PET were prepared by injection moulding. Two samples sizes were chosen; for their dimensions see fig. 1. It was appreciated that such samples are not randomly oriented. A separate experiment was therefore undertaken to investigate this effect and this is discussed in section 3 below. Samples with different degrees of crystallinity were obtained either by varying the time in the mould and the mould

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temperature or, as in the case of the small dumbbell specimens, by using a specially heated jig to prevent distortion of the samples. This jig was mounted in a heating block oven at temperatures ranging from 150 to 180° C and for times varying from 7 to 25 min.

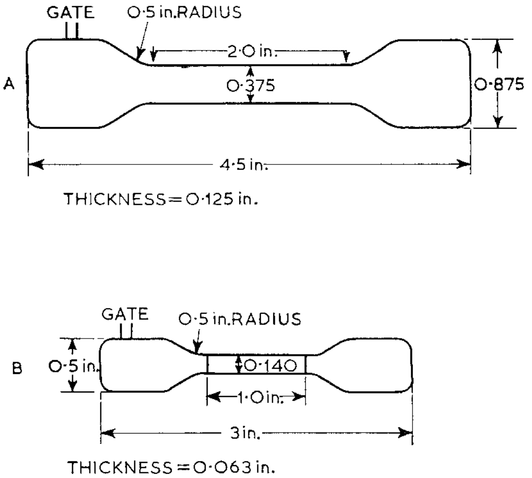

Figure 1 **Dumb-bell dimensions for tensile experiments. 1in. = 2.54 cm.**

2.2 Tensile Measurements

The tensile experiments were carried out on a Hounsfield E-type Tensometer, equipped with a variable temperature control cabinet, capable of producing temperatures in the range − 90 to + 200° C. The brittle strengths at − 196° C were obtained using a specially designed tensile rig mounted in a thermos flask containing liquid nitrogen. Temperatures between − 196 and − 90° C were obtained by passing N_2 gas through a germanium-silver coil heat exchanger immersed in a thermos vessel containing liquid nitrogen, see fig. 2.

2.3. Measurement of Crystallinity in PET Samples

The degree of crystallinity, W_C, was calculated from the density of the samples, assuming the amorphous and crystalline phases to be additive (see [2] for details). A calcium nitrate density gradient column was used to measure density.

2.4. Measurement of Molecular Weight

Values for the number average molecular weight $\overline{M}_n$ were estimated from solution viscosity measurements using the Mark-Houwinck relationship $[\eta] = K\overline{M}_n^{\alpha}$ where $[\eta]$ is the intrinsic viscosity; K and α are constants assumed, on the basis of previous work [3], to be 1.7×10^{-4} and 0.83 respectively.

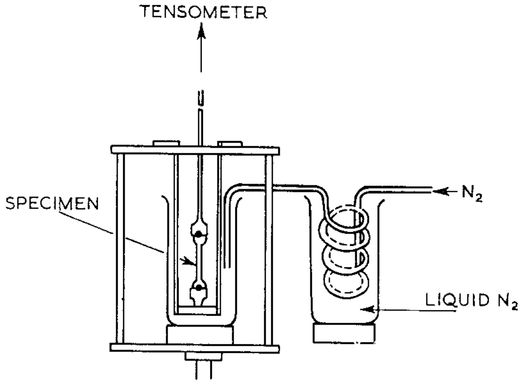

Figure 2 **Low temperature for tensile experiments.**

3. Results and Discussion; Tensile Fracture Experiments

3.1. Amorphous PET

Diagrammatic representations of the different types of failure observed in amorphous PET are shown in fig. 3. In a recent article Vincent [4] distinguishes four of the five modes of failure shown in this figure. These are brittle, necking rupture, cold-drawing and uniform extension. In PET we observe the behaviour termed "ductile" at temperatures immediately above the brittle range, but at this stage we do not see the formation of a neck as in the necking rupture case described by Vincent.

The stress-temperature plots, shown for example in figs. 4 and 5 reveal three regions of behaviour: a brittle region, a yield region (which embraces both ductile and necking rupture) and a cold-drawing region. Necking rupture is only seen in a temperature range just below the cold-drawing region. For this reason in our work we have distinguished a brittle region and two regions of yield behaviour.

It was feared that injection moulding might introduce a degree of molecular orientation which would invalidate the results. The effects of annealing the samples for 2 h at 80° C were therefore examined, and the data are included in fig. 4. No significant differences were observed between annealed and unannealed samples, either in respect of yield stress or brittle fracture stress. Annealing produced a reduction in the low

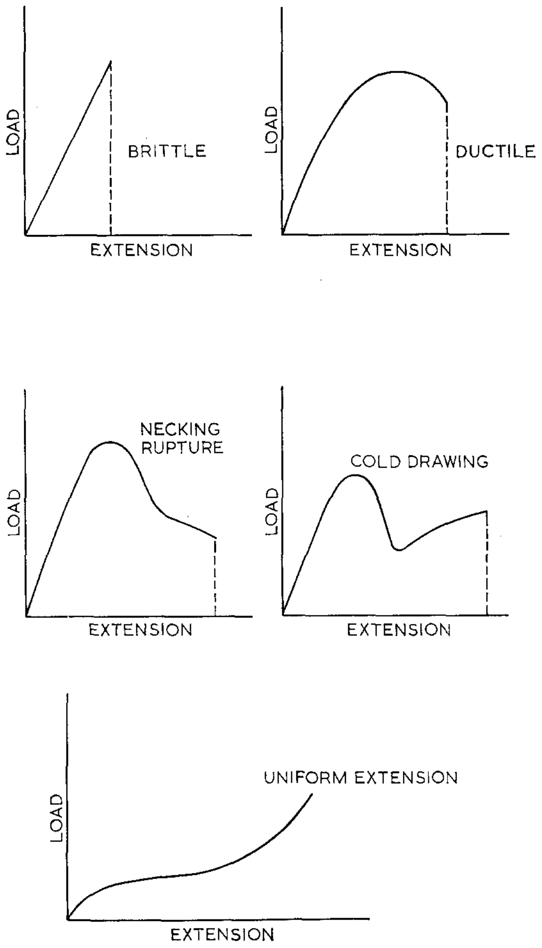

Figure 3 Diagrammatic representation of the different types of failure.

degrees of birefringence observed when the sample was viewed between crossed polarisers, and small amounts of shrinkage (~ 10% maximum). These small amounts of shrinkage in amorphous PET are consistent with the very low birefringence [5]. Previous studies of the influence of molecular orientation on yield stress [6] are consistent with this small degree of birefringence introducing a negligible increase in the yield stress above that for an isotropic sample.

The effect of molecular weight on the stress/temperature behaviour is shown in fig. 4. It can be seen that the yield stress is independent of molecular weight (over a range of molecular weight from 11 000 to 27 000). This appears to be true for both regions of yield behaviour, although it must be emphasised that very small changes in the extent of the lower region of yield i.e. the ductile region, would not be detectable. These results show that the brittle stress is not really affected by molecular weight from 16 500 to 27 000 but that the brittle stress of the 11 000 sample is very significantly lower. This result suggests that there may be a threshold in the molecular weight required for ductile behaviour at room temperature. This is an important result and will be investigated further.

The effect of strain rate on the behaviour is shown in figs. 5 and 6. At crosshead speeds from 0.5 to 15 in. min^{-1}* no change in the brittle stress is observed, whereas the yield stress in both regions increases uniformly. Fig. 5 shows that the brittle stress is temperature and strain rate independent to a very good approximation. The brittle/ductile transition and the ductile/cold-

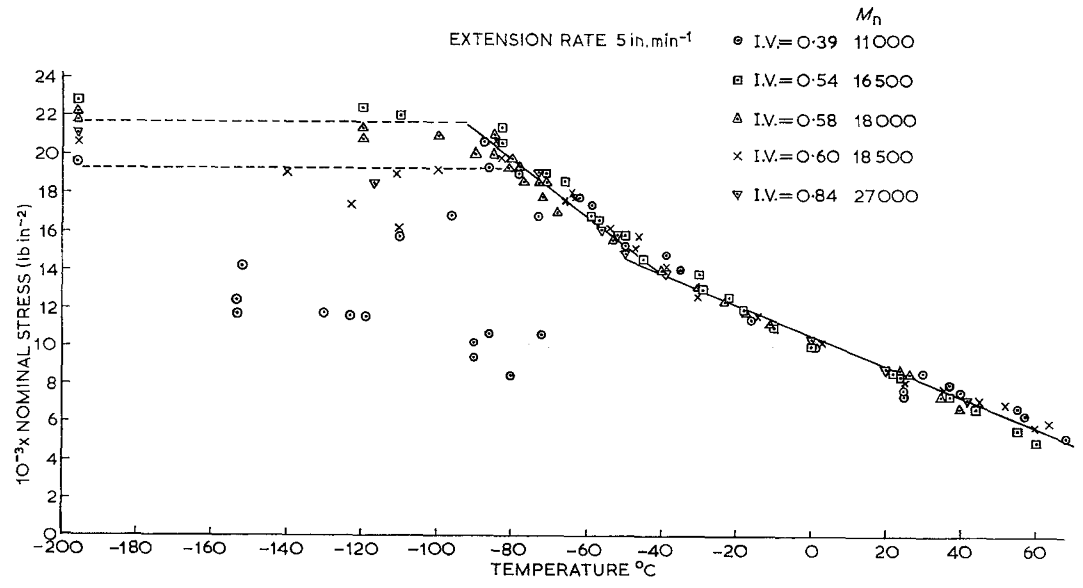

Figure 4 Effect of molecular weight on amorphous PET. 1 in. min.$^{-1}$ = 2.54 cm min^{-1}.

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*1 in. min.$^{-1}$ = 2.45 cm min^{-1}.

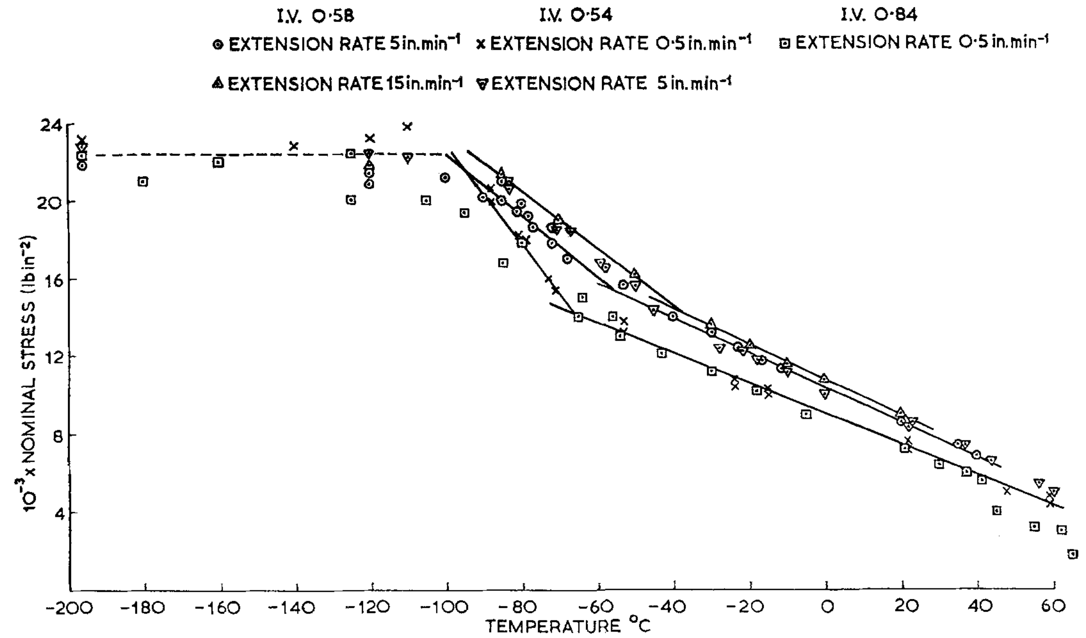

Figure 5 Effect of strain rate on amorphous PET. 1 in. min^{-1} = 2.54 cm min^{-1}.

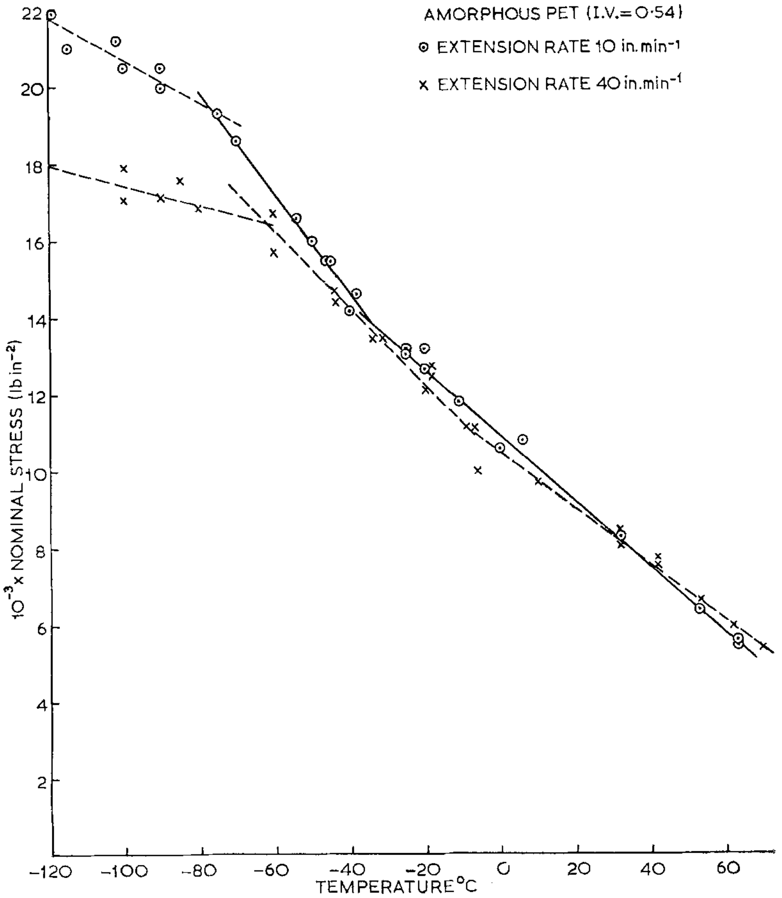

Figure 6 Effect of high strain rates. 1 in. min^{-1} = 2.54 cm min^{-1}.

drawing transition both move to higher temperatures with increasing strain rate.

At the higher rates of extension the stress values had to be measured from an oscilloscope response because of the lag on the recorder pen. Three regions of failure were evident, but at the highest rate of strain the ductile/cold-drawing transition was not very clearly defined. At the highest crosshead speed of 40 in. min^{-1} the yield stress values fell below those for 10 in. min^{-1} (see fig. 6), which suggests that adiabatic heating occurs.

The experimental results show that there are two well defined regions of yield behaviour. As well as differing in the nature of strain hardening i.e. in post-yield behaviour, the regions differ in the nature of the yield process, as revealed by the strain-rate sensitivity. A possible explanation for this is as follows. At high temperatures, cold-drawing occurs and this has been described [6] as the stretching of a molecular network. In this region it was shown by the effects of cross-linking that the yield process involves freeing the molecular chains between entanglement points. At lower temperatures, the polymer ruptures i.e. the strain hardening associated with the orientation of the molecular network does not occur. It is therefore proposed that at these temperatures the yield process involves the pulling out of entanglements. This yield process would be expected to have a higher activation energy than the high temperature yield process. The data tend to confirm this, although the range of strain rates is not sufficiently great to allow a detailed interpretation.

The change in behaviour at ~ -60 to -40°C could be associated with the γ-relaxation transition in this polymer [7].

3.2. Crystalline PET

The effect of crystallinity on the stress/temperature behaviour is shown in fig. 7. It can be seen that up to 35% crystallinity there is little influence on the brittle stress, but the yield stress is much increased. The brittle/ductile and ductile/cold-drawing transitions therefore move to higher temperatures. Increasing the crystallinity from 35 to 44% (see fig. 8) has a dramatic effect on the brittle stress, reducing it from about 20000 to 15000 psi.* This could be due either to annealing faults or to a change in the morphological structure. The transition points are still evident, and there is a further increase in the yield stress in both the ductile and the cold-drawing regions. These results show that both yield mechanisms are affected by crystallinity. This is an acceptable result, in terms of our tentative proposals for these yield mechanisms. The presence of crystallites is likely to make it more difficult either to disrupt the structure entirely, or

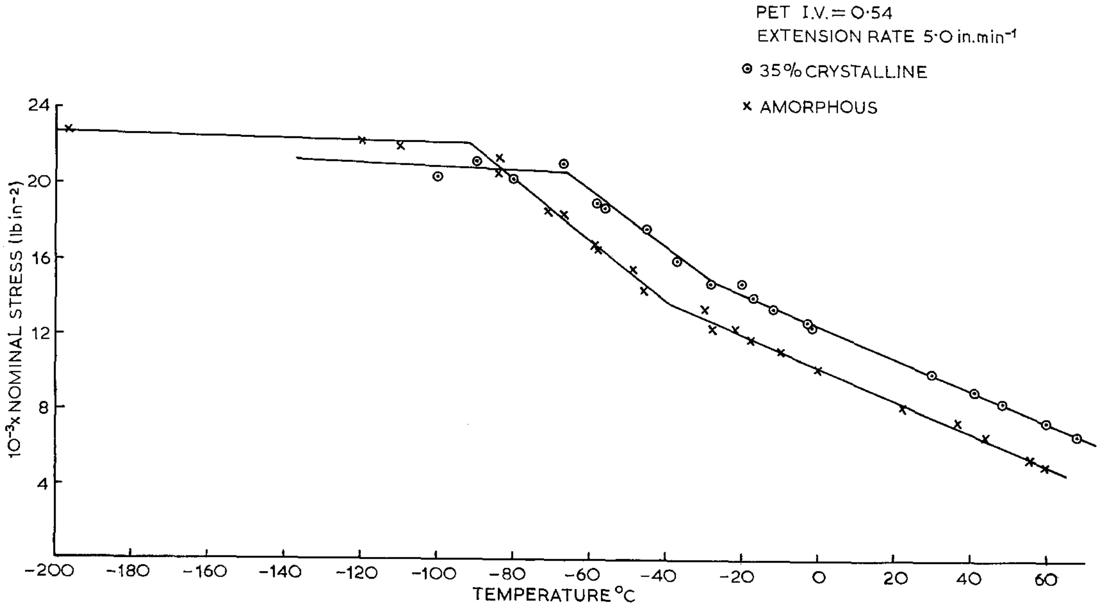

Figure 7 **Effect of crystallinity. 1 in. min^{-1} = 2.54 cm min^{-1}.**

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*1 psi = 6894.76 N m^{-2}.

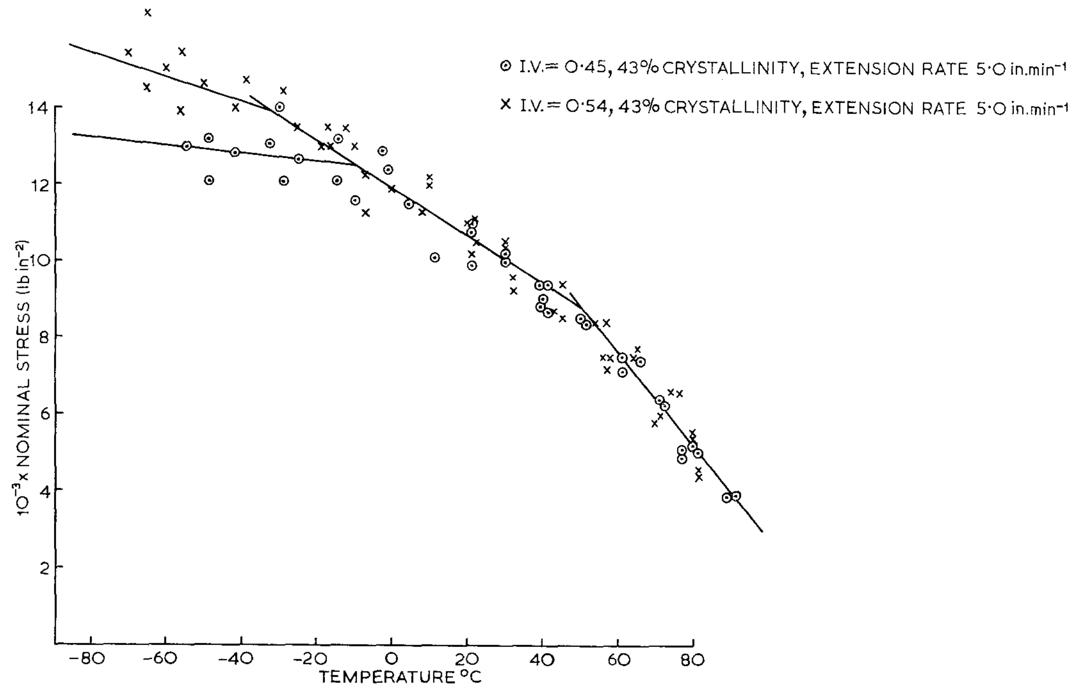

Figure 8 Effect of molecular weight on crystalline PET. 1 in. min^{-1} = 2.54 cm min^{-1}

to allow chain sliding which is the essence of the high temperature yield process.

It is interesting to note a direct effect of molecular weight. Fig. 8 shows that decreasing the molecular weight from 16 500 to 11 000 moves the brittle/ductile transition from − 30 to − 10° C. This appears to be due entirely to a reduction in the brittle stress. The ductile/cold-drawing transition does not move significantly. This confirms that crystallinity is more important than molecular weight in determining the yield behaviour, a result to be deduced from the data of figs. 4 and 7. The data for the crystalline material is summarised in table I.

3.3. Effect of Notching and Notch Sensitivity

Notched samples were examined for stress/strain behaviour at various temperatures.

3.3.1. Preparation of Samples

A mould was constructed for producing samples that could be effectively notched and the dimensions of this mould are shown in fig. 1a. A Charpy 0.010 notching tool was mounted in a specially constructed holder and cutting of the notches was carried out on a milling machine. Two notch depths were used, 0.075 in. and 0.110 in.

3.3.2. Amorphous PET

Experimental results for PET show that notching can drastically alter the pattern of the characteristic behaviour for a given polymer. In fig. 9 the notched and unnotched stress/temperature curves for amorphous PET at a cross-head speed of 0.1 in. min^{-1} are shown. The notched sample has two notches diammetrically opposed, cut to a

TABLE I Summary of results from the stress-strain temperature experiments carried out on crystalline PET.

Cross-head speed in./min	Mol wt	% crystallinity	Brittle/ductile transition temperature °C	Ductile/cold-drawing transition temperature °C	Brittle strength psi (− 80° C)
5.0	16 500	35	− 65	− 30	21 000
5.0	16 500	43	− 30	50	15 500
5.0	11 000	44	− 10	50	13 500

1in min^{-1} = 2.54 cm min^{-1}; 1psi = 6894.76 N m^{-2}.

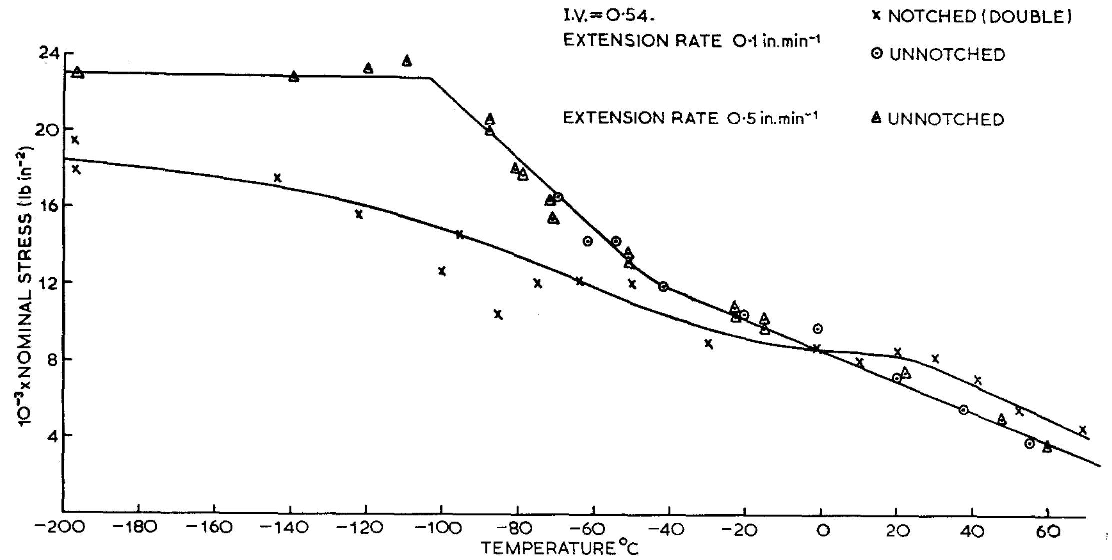

Figure 9 Notched and unnotched amorphous PET. 1 in. min^{-1} = 2.54 cm min^{-1}.

depth of 0.110 in. In the cold-drawing region the average yield stress has been raised by notching by a constraint factor, but not to the extent that the calculations for such notch dimensions predict (see appendix).

Notching also affects the brittle stress, reducing this so that when the stresses are calculated on the basis of the remaining cross-sectional area the notched brittle stress curve undercuts that for the unnotched sample.

These effects taken together increase the temperature of the brittle/ductile transition very appreciably so that notched PET shows brittle behaviour at room temperature. The brittle strength is temperature dependent, rising with decreasing temperature to a value close to the unnotched brittle strength. The fracture surfaces indicated brittle behaviour over this temperature range.

The notched brittle strengths are molecular weight dependent, as shown in fig. 10.

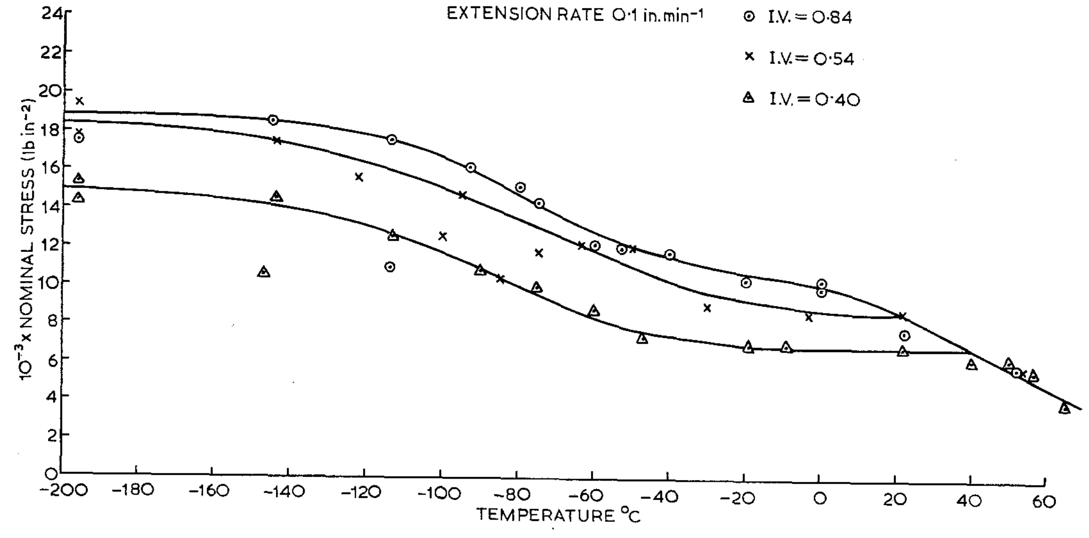

Figure 10 Effect of molecular weight on double notched amorphous PET. 1 in. min^{-1} = 2.54 cm min^{-1}.

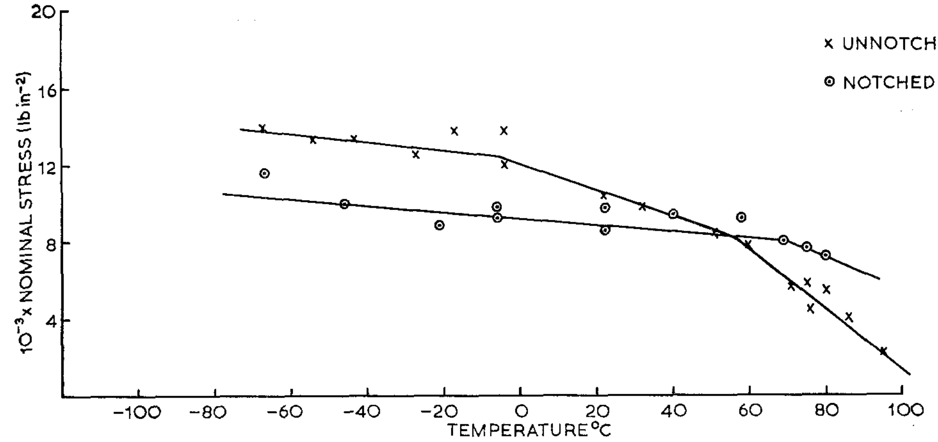

Figure 11 Notched and unnotched crystalline.

3.3.3. *Crystalline PET*

The increase in yield stress on notching (in the cold-drawing region) appears to be greater in the case of the crystalline samples, and the transition shifts to a higher temperature region, in keeping with the result observed with the unnotched samples. In fig. 11 the notched and unnotched stress/temperature curves for a 43% crystalline PET sample are shown. The undercutting of the ductile region of the unnotched curve due to notching is quite substantial, but again the brittle stress as measured at — 196° C is not lowered very greatly (see table II). Increasing crystallinity, as in the unnotched case, causes a shift in the brittle/ductile transition to higher temperatures as can be seen in fig. 12.

4. Conclusion

This survey of fracture in PET provides a number of guide lines for understanding the failure of this polymer.

(i) There is some similarity between brittle/ductile transitions in polymers and those in metals (as proposed by Vincent [1]). The brittle stress is almost temperature and strain rate independent, whereas the yield behaviour is markedly sensitive to these parameters. Notch sensitivity, i.e. embrittlement due to notching, relates to the effective raising of the yield stress due to the plastic constraint at the tip of the notch.

(ii) The yield stress is not sensitive to molecular weight. It is, however, increased by increasing

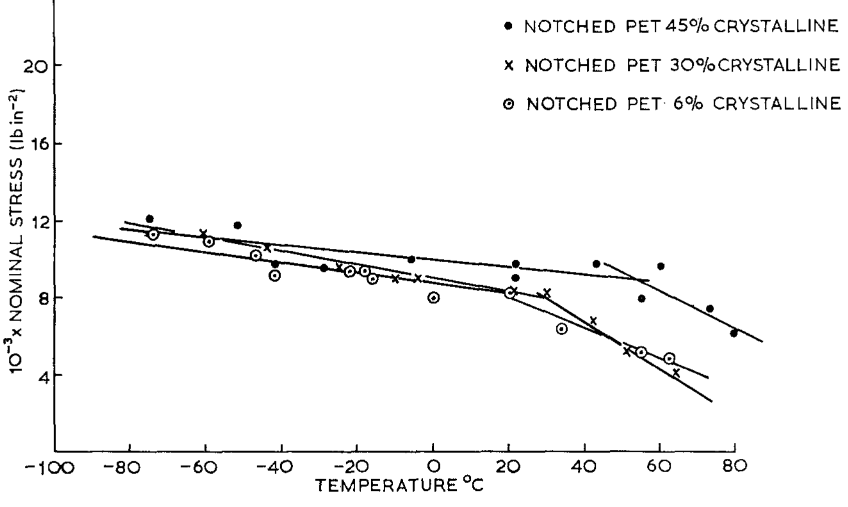

Figure 12 Effect of crystallinity on notched PET.

TABLE II Summary of notched tensile date.

Mol wt	% Crystallinity	Ductile/cold-drawing transition temperature °C	Brittle strength, unnotched, − 196° C psi	Brittle strength, notched, − 196° C psi
16 500	0	25	23 000	22 000
16 500	43	64	18 000	17 250

*1 psi = 6894.76 N m^{-2}.

crystallinity and this can lead to brittle behaviour if this yield stress exceeds the fracture stress, which is reduced by crystallisation.

(iii) The brittle stress is comparatively insensitive to molecular weight at high molecular weights but falls rapidly at low molecular weights. The brittle/ductile transition therefore moves to higher temperatures as the molecular weight of the polymer falls and can even lead to brittle behaviour at room temperature for a very low molecular weight.

Appendix

Constraint Factor for Deep Wedge-Shaped Notches with Circular Roots [8]

From the longitudinal tensile stress distribution across the minimum section of a long notched bar, use of Hencky's theorem leads to a yield point load (L) per unit thickness of,

$$L = 4\,ka\left[(1+\alpha) - \frac{r}{a}(e^{\alpha} - 1 - \alpha)\right]$$

if $a/r \geqslant e^{\alpha} - 1$. Here r is the radius of the circular root, of angular span 2α. $2a$ is the width of the minimum section of the bar and $2k$ is the tensile yield stress.

The constraint factor is the ratio of the yield point load to the yield point load for tensile yield of the same thickness of width $2a$ and equals $L/4ka$.

(i) For a 0.075 in. notch and $r = 0.010$ in. the constraint factor is 2.09.

(ii) If r is 0.005 in. then the constraint factor is 2.12.

(iii) For a 0.110 notch and $r = 0.010$ in. the constraint factor is 2.04.

Acknowledgement

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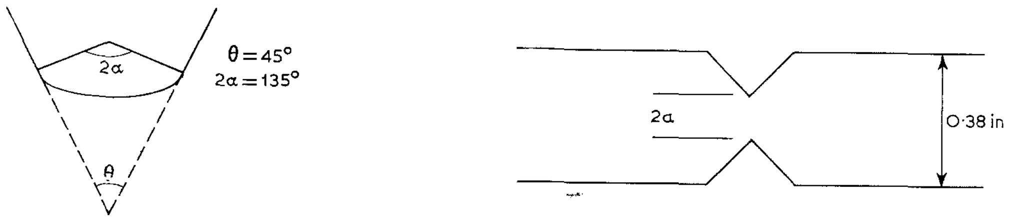
References

1. P. I. VINCENT, *Polymer* **1** (1960) 425.
2. J. B. JACKSON and E. R. DIXON, *J. Materials Sci.* **3** (1968) 464.
3. D. A. S. RAVENS and I. M. WARD, *Trans. Faraday Soc.* **57** (1961) 150.
4. P. I. VINCENT, Encyclopedia of Polymer Science and Technology Vol. 7 (1967) p. 292.
5. P. R. PINNOCK and I. M. WARD, *Trans. Faraday Soc.* **62** (1966) 1308.
6. S. W. ALLISON and I. M. WARD, *Brit. J. Appl. Phys.* **18** (1967) 1151.
7. A. B. THOMPSON and D. W. WOODS, *Trans. Faraday Soc.* **52** (1956) 1383.
8. R. HILL, "Plasticity" (Clarendon Press, Oxford, 1950) p. 250.



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