JOURNAL OF MATERIALS SCIENCE 3 (1968) 464–470

The Inter-Relation of Some Mechanical Properties with Molecular Weight and Crystallinity in Poly(ethylene terephthalate)

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Received 28 February 1968, and in revised form 22 April

Some mechanical properties of poly(ethylene terephthalate) were determined as a function of molecular weight, temperature and crystallinity. The effect of talc, a nucleating agent, on mechanical properties was also considered.

Yield stress, initial modulus, breaking stress and elongation to break were measured over the temperature range from room temperature to 160° C. The yield strain was recorded over a smaller temperature range. The room temperature impact properties have also been studied using a Hounsfield Charpy type Impact Tester.

1. Introduction

Poly(ethylene terephthalate), PET, is a well-known commercial polymer available widely as a fibre and film. Both forms are highly crystalline and highly oriented, axially and planar respectively, crystallinity being induced from the glassy state, obtained by quenching the molten polymer. Little has been reported on the bulk properties of the unoriented polymer, crystalline or amorphous. Further, the polymer provides a unique opportunity to study the effect of incipient crystallinity on the glassy state, in contrast to other systems such as polymethylene, where crystallinity has a marked effect on mechanical properties [1] which arise where the crystalline phase coexists with a rubbery phase. The effect of crystallinity in PET on the dynamic mechanical properties have been examined by Kawaguchi [2], who showed that the glass/rubber transition temperature, T_g moved upwards in temperature with increasing crystallinity (amorphous – 80° C, 50% crystalline – 120° C at 200 cycle/sec) with a corresponding upward shift in shear modulus over the same temperature range.

Here we report measurements of some mechanical properties as a function of both molecular weight (different polymer intrinsic viscosity) and degree of crystallinity as a function of temperature. Impact properties at room temperature have also been measured.

2. Experimental

2.1. Degree of Crystallinity

The degree of crystallinity, W_c, has been calculated from the density of the samples on the usual assumption of additivity of the contributions of the amorphous and crystalline phases of the polymer, using the formula

$$W_c = \frac{\bar{V}_a - \bar{V}_p}{\bar{V}_a - \bar{V}_c} \cdot 100\%$$

where $\bar{V}$ is the specific volume and the subscripts a, c, and p refer to amorphous phase, crystalline phase and polymer sample respectively. The values used for the purely amorphous and crystalline material at 23° C were $\bar{V}_a = 0.742$ cm^3/g; $\bar{V}_c = 0.688$ cm^3/g.

The densities of the samples were measured in a density gradient column using a calcium nitrate solution as the gradient liquid. A column of density gradient range of 0.03 cm^3/g is approximately 800 mm long and the densities can easily be determined to 0.001 cm^3/g accuracy; hence the specific volume can be calculated to 0.001 cm^3/g.

A readily obtainable level of crystallinity for testing was determined by experimenting with various crystallising temperatures and annealing times. It was found that a level of 40 to 44% crystallinity was readily produced with slight variations due to difference in molecular weight of the sample annealed and the presence of a talc nucleating agent.

2.2. Preparation of Samples

The polymer used was poly(ethylene terephthalate) of three different average molecular weights obtained from ICI Fibres Ltd, Harrogate, Yorks, UK. Molecular weight was measured from solution viscosity by the usual relationship $[\eta] = K\bar{m}_n^{\alpha}$, where $[\eta]$ is the intrinsic viscosity (IV), K and α are constants depending on the solvent, and $\bar{m}_n$ is the number average molecular weight. The values of K and α used, 1.7×10^{-4} and 0.83 respectively had been derived by Ravens and Ward [3] using end-group analysis to determine $\bar{m}_n$; the solvent used was o-chlorophenol at 25° C.

From this equation, the molecular weights of the samples as received were 46000, 31000 and 21000, corresponding to IVs of 1.28, 0.92, and 0.65 respectively. After injection-moulding of the polymer into dumb-bell test specimens, typical molecular weights were found to be 29000, 22000 and 19500 corresponding to IVs of 0.86, 0.68, and 0.62, owing to degradation at the high processing temperature needed.

Moulding was carried out on a 60 g Stubbe injection-moulding machine. The moulding conditions used were: injection pressure 1500 kg/cm^2, clamping pressure of 150 kg/cm^2, barrel temperature 280 to 290° C; maximum feed and screw advance, 15 sec injection time, and 15 sec cooling time. A cold mould was used for tensile specimens, since previous experiments had shown that wide temperature variations across this mould tool led to variations in crystallinity of the samples. For impact specimens, a hot mould (140° C) was used. Control of level of crystallinity was achieved by annealing in the mould, and the barrel of the injection-moulding machine purged of degraded polymer before moulding subsequent samples.

In some samples, 0.5 wt % of a talc (Mistron Super Frost) has been added. It is a nucleating agent for PET and leads to a faster crystallisation of the polymer. Also a finer spherulitic texture results.

2.3. Crystallisation

For the tensile specimens a study of crystallisation of the samples as a function of annealing time and temperature was made to determine an easily reproduced level of crystallinity. By referring to published data [4] on the rate of crystallisation of the various molecular weight PET, it is found that the most rapid crystallisation occurs close to 140° C. From recently reported studies [5] of the change of crystallinity with annealing conditions it was possible to select conditions to give reproducible levels of crystallinity.

The slow rise to equilibrium of W_c with increasing annealing temperature was confirmed by experiment, the results of which are shown in fig. 1. The most consistent results were obtained at 183° C with 26 min annealing time. Only slight variations were introduced by the nucleating agent and the different molecular weights. The total spread of W_c on the samples checked after annealing was only 4%, ranging from 40 to 44%.

Attempts to produce samples of higher W_c were successful in yielding crystallinities of 57 to 61% on annealing the polymers at 225° C for 20 min, but the samples produced were too brittle for tensile testing. To produce samples of W_c significantly lower than 40% would necessitate using lower temperatures, for which the scatter of W_c was too great to obtain consistent mechanical properties. Also the rate of crystallisation is much slower in this region and the annealing times required to reach the equilibrium W_c would be higher. For instance, the half-time of crystallisation at 110° C is approximately 10 min and rises rapidly with decreasing temperature. To ensure that the equilibrium W_c was reached, a minimum of 10 half-lives or 100 min would be needed.

Early attempts to produce samples of suitable quality were thwarted by thermal distortion of samples during annealing. This was overcome by using a specially constructed brass annealing block. The block consisted of ten rectangular sections 0.3 × 3.2 × 1.25 in. (0.75 × 8.00 × 3.1 cm); along the long axis of each section a trough was milled wide enough to hold a dumb-bell tensile specimen. The depth milled out varied; in the centre of the piece enough metal had been removed to give a small clearance, whereas at the ends less had been machined away so that the sample was tightly clamped at both ends. The ten sections were then stacked together so that nine specimens could be annealed. Although the dumb-bell centres were not in actual contact

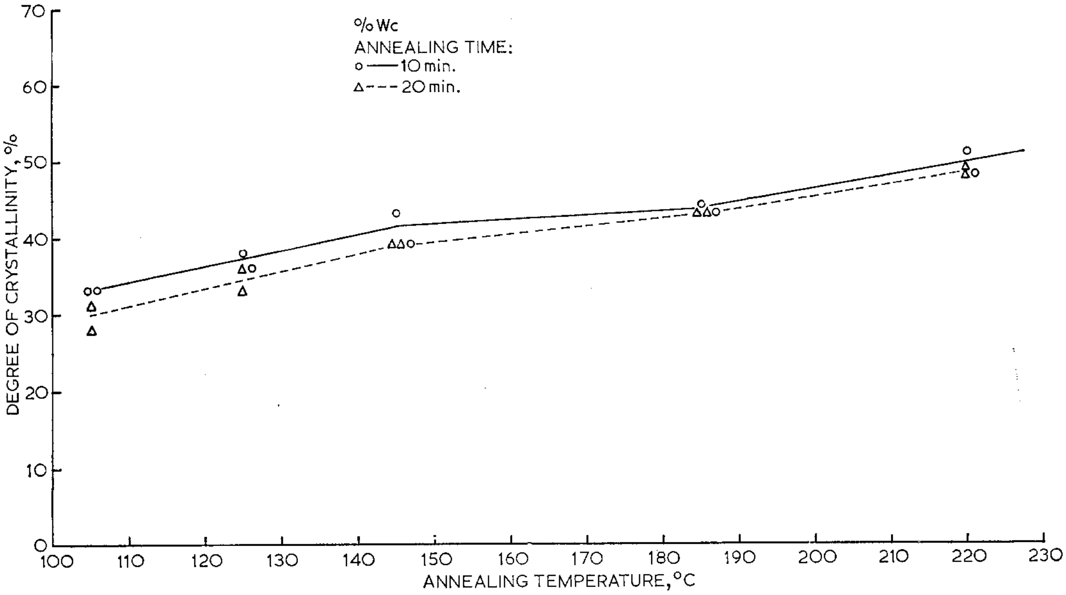

Figure 1 Variation of crystallinity with annealing temperature.

with the brass, crystallinity measurements were uniform throughout the samples, indicating that there had been good heat transfer.

2.4. Test Procedure

2.4.1. Tensile Testing

The samples, half-size standard tensile specimens to BS 2782 method 301E, having a gauge length of 1 in. (2.5 cm), were tested on a Hounsfield type E tensometer at a nominal strain rate of 160%/min. Elevated temperature testing was conducted in a heated chamber enclosing the sample and tensometer jaws, controlled to ±1° C. The temperature range covered was 23 to 160° C at 10° C intervals. From the load/elongation curve, yield stress, initial modulus, breaking stress and elongation to break were determined.

It was realised that initial moduli determined from the initial slope of the load/elongation curve give low results owing to incorrect strain measurement for high modulus materials; consequently after preliminary experiments an extensometer was used for accurate modulus determinations.

Samples were checked for uniformity and slight variations in thickness were found. A check of twenty of each batch of samples showed that the samples in each batch were consistent. A constant cross-sectional area was calculated for each batch with the standard deviation expected from the variation of thickness of samples within each batch. We moulded specimens under constant machine conditions and the testing involved large numbers of specimens for the various points on our curves. Since the observed variations between specimens was small, we felt justified in taking a mean value.

2.4.2. Impact Testing

Testing was conducted on a miniature Hounsfield Charpy Impact testing machine using a $\frac{1}{16}$ lb (22.1 g) pendulum weight [6]. The samples, bars of dimensions $2 \times \frac{3}{8} \times \frac{1}{8}$ in. ($5.1 \times 0.95 \times 0.32$ cm), were notched prior to testing with the Hounsfield notching machine. The dimensions of the notch used throughout are 0.110 in. (2.75 mm) deep, 45° angle, notch tip radius 0.010 in. (0.25 mm). The impact strength for notched samples has been calculated from the formula: $\text{impact strength} = \dfrac{\text{energy absorbed}}{\text{cross-sectional-area}}$. All testing was conducted at room temperature. One group of samples was tested immediately after moulding; a second batch was tested after a week's exposure to the atmosphere to determine the effect of moisture on the impact strengths.

3. Results

The effect of the various parameters is most readily appreciated from graphic presentation. Figs. 2 and 3 show the variation of yield stress with temperature for different samples. As can

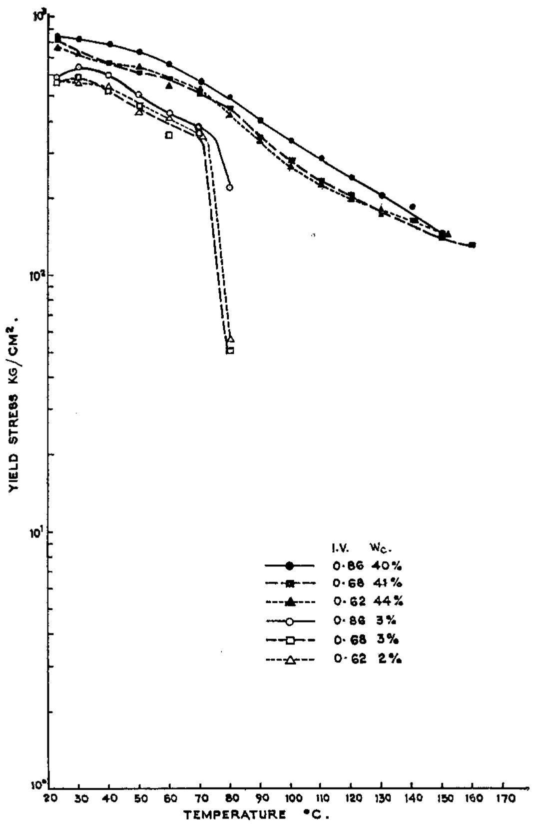

Figure 2 Variation of yield stress with temperature; effect of crystallinity.

be seen, IV (intrinsic viscosity) has little effect on the level of yield stress obtained, the greatest difference as anticipated being between amorphous and crystalline material above T_g, the glass transition temperature. Below 70° C the change of yield stress with crystallinity at constant temperature is relatively small. A similar series of results for initial modulus is seen in figs. 4 and 5, and again similar trends are followed.

The inclusion of talc has no apparent effect on either yield stress or initial modulus. Table I shows the variation observed in yield strain.

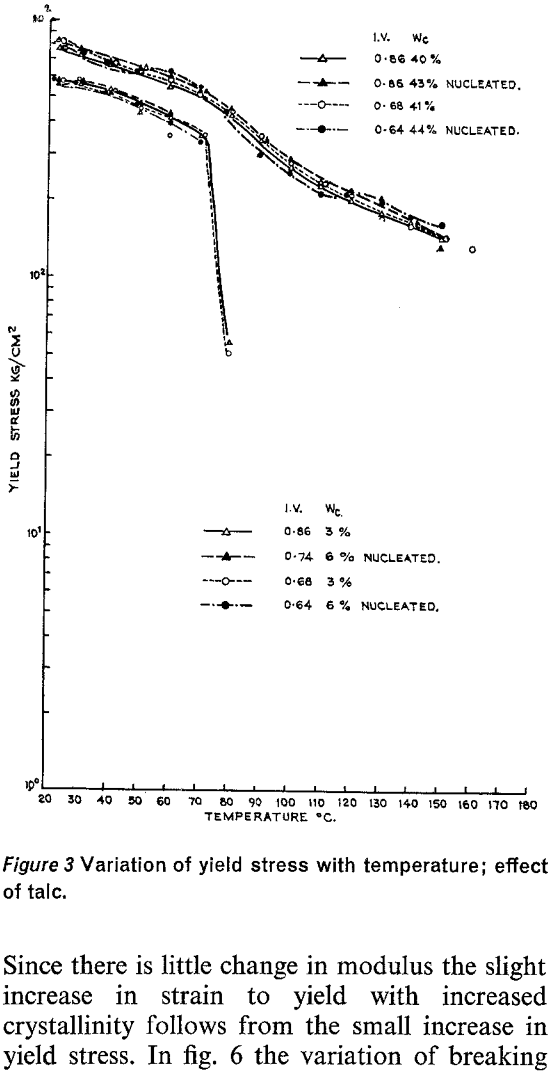

Figure 3 Variation of yield stress with temperature; effect of talc.

Since there is little change in modulus the slight increase in strain to yield with increased crystallinity follows from the small increase in yield stress. In fig. 6 the variation of breaking stress with temperature is shown. This is remarkably independent of temperature and is not markedly affected by crystallinity. Purely

TABLE I Yield strain (%) for various IV samples as a function of temperature.

Sample no.	IV of moulding	Amorphous 23° C	30° C	40° C	40% Crystalline 23° C	30° C	40° C
1	0.62	6.7	7.0	6.0	8.9	8.9	7.9
2	0.68	5.7	5.7	5.7	7.9	—	7.6
3*	0.67	5.7	5.7	5.7	7.6	7.6	7.0
4	0.86	5.7	6.0	5.7	7.9	7.0	6.7
5†	0.75	6.0	5.7	5.1	8.3	8.3	7.6

*as sample 2 + 0.5 wt % talc
†as sample 4 + 0.5 wt % talc

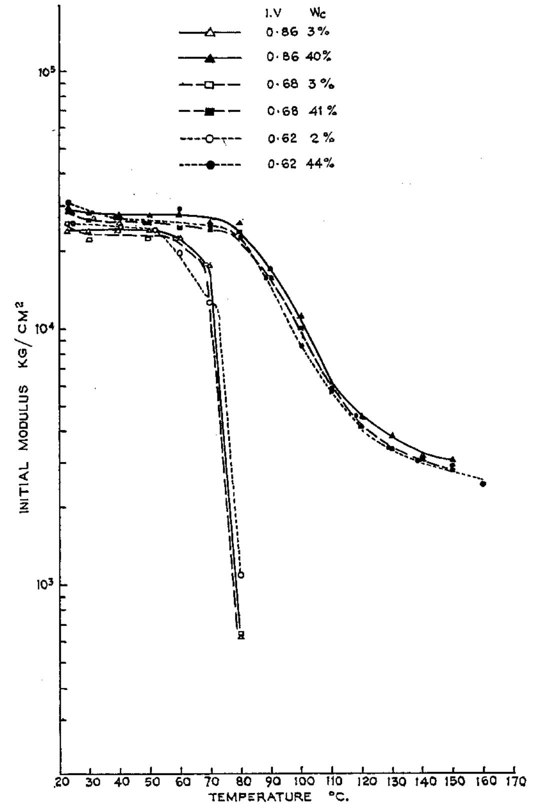

Figure 4 Variation of initial modulus with temperature; effect of crystallinity.

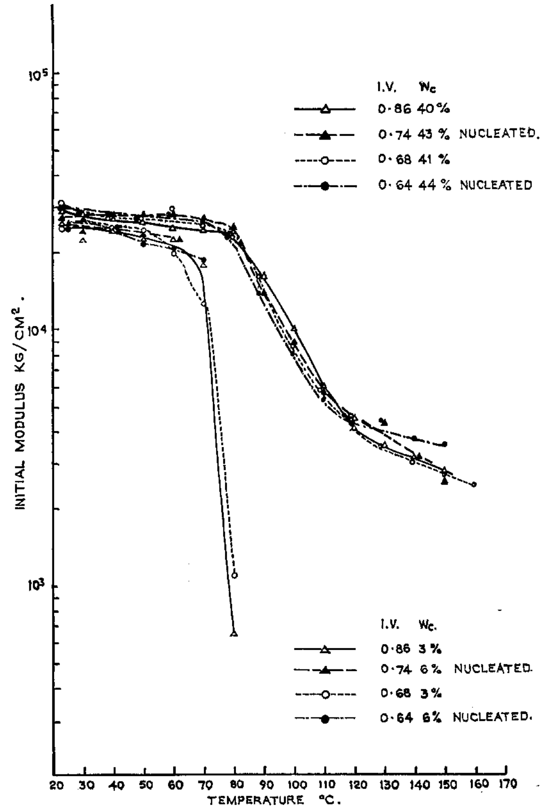

Figure 5 Variation of initial modulus with temperature; effect of talc.

amorphous samples, above T_g, behave as rubbers and failure occurs at low stress.

The variations of mean impact strength with both IV and crystallinity, with and without talc, for dry and exposed samples are presented in fig. 7 where the overall trends can be seen.

4. Discussion

The main points of the results may be briefly summarised as follows.

(i) For a fixed temperature and at a given level of crystallinity, yield stress and modulus show little dependence on molecular weight, but they do show an increase with increasing crystallinity.

(ii) For purely amorphous samples properties fall off as expected at T_g (70° C).

(iii) Yield stress and modulus show the expected decrease with increasing temperature.

(iv) Yield strain shows an increase with crystallinity but no dependency on molecular weight.

(v) The increase in intrinsic viscosity (i.e. molecular chain length) gives a correspondingly higher impact strength in both amorphous and crystalline samples.

(vi) Crystallisation of the polymer causes impact strength to decrease.

(vii) The use of talc leads to an increase in the impact strength of the crystalline samples but has no detectable effect on that of amorphous material.

(viii) Exposure to the atmosphere causes a decrease in the impact strength of amorphous samples but has little effect on the crystalline sample.

The tensile results illustrate that below T_g, there is little reinforcement of the glassy phase by introduction of crystallinity, only small increases being observed. However above T_g the effect is much more marked, the amorphous material showing poor mechanical properties whereas the crystalline phase strongly reinforces the rubbery phase of PET.

The results of impact strength testing are gene-

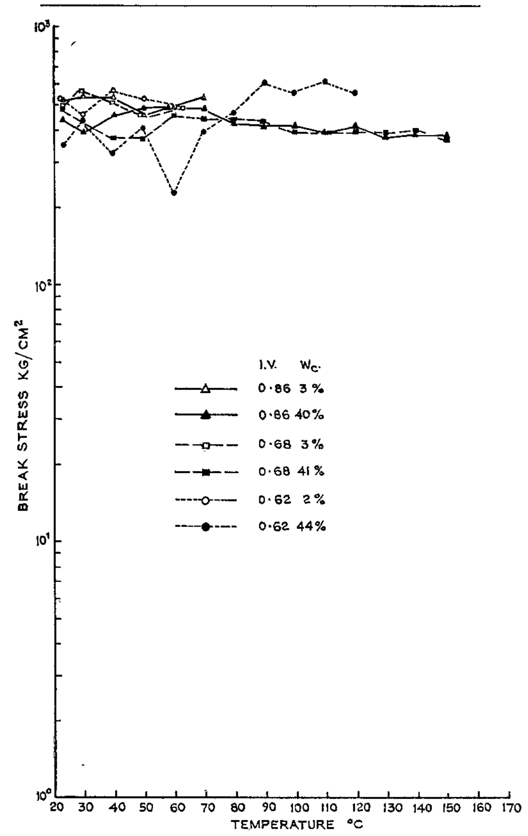

Figure 6 Variation of breaking stress with temperature.

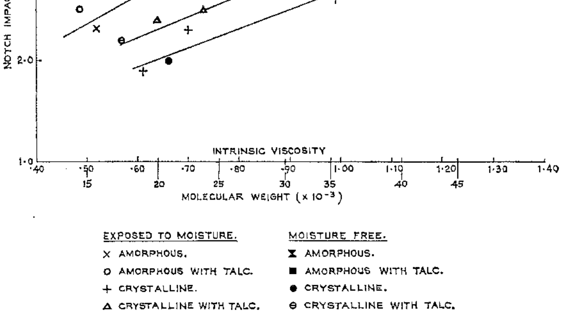

Figure 7 Variation of impact strength with crystallinity and intrinsic viscosity.

rally in line with expected material behaviour. The amorphous material shows better impact behaviour than crystalline polymer but improved impact strength can be achieved in the crystalline system by increasing the molecular weight. The effect of talc is interesting. No change is seen in the amorphous material but a significant difference is observed in the crystalline system. Without talc present, on microscopical examination of crystalline samples a spherulitic morphology can be seen with spherulites in the range 20 to 50 μm. However, when talc is used there is a reduction in the average spherulite size to the range 1 to 10 μm. The crystallinities with and without talc are similar, though those with talc present tend to be slightly higher. This would generally lead to a lowering of impact values. Thus we conclude that this must be a genuine effect which can be attributed to a textural change in the presence of talc. It is proposed to investigate this suggestion further.

We have some ideas concerning the interpretation of the effect of crystallite size on impact strength and, while not wishing to pursue them in this paper, we have some work in hand to examine this concept.

The comparative results for amorphous polymer exposed and dry (stored in a dessicator and tested shortly after moulding) is unexpected. The rate of adsorption of water at room temperature is low and it appears that a surface phenomenon is involved. However, the mechanism of surface embrittlement is not obvious. Presumably in the crystalline samples, any surface defects produced by exposure are obscured by effects due to the presence of crystallinity.

5. Conclusions

It is concluded that below T_g (70°), both crystallinity and molecular weight have little effect on the yield stress and initial modulus. Above 70° C, crystallinity reinforces the rubbery phase of PET but again molecular weight effects are small.

For improved impact resistance, high molecular weight is essential. Crystallinity lowers impact strength but providing a high enough molecular weight is used, deleterious effects are nullified.

Acknowledgements

We would like to thank Dr D. W. Woods of Research Department, ICI Fibres Ltd, Harrogate, Yorks, UK, for supplying the polymers used.

References

1. J. B. JACKSON, P. J. FLORY, R. CHIANG, and M. J. RICHARDSON, *Polymer* **4** (1963) 237.
2. T. KAWAGUCHI, *J. Polymer Sci.* **32** (1958) 417.
3. D. A. S. RAVENS and I. M. WARD, *Trans. Faraday Soc.* **57** (1961) 150.
4. F. D. HARTLEY, F. W. LORD, and L. B. MORGAN, *Phil. Trans.* **A247** (1954) 23.
5. K. G. MAUGHAN, W. J. JANES, and W. BOSCH, *J. Appl. Pol. Sci.* **9** (1965) 3605.
6. See, for example, L. E. NIELSON, "Mechanical Properties of Polymers" (Reinhold, New York, 1962) p. 123.