

polymer reports

Tensile strength elevation of brittle polymers by entanglements*

D. T. Turner

Dental Research Center, University of North Carolina, Chapel Hill, NC 27514, USA

Plots of tensile strength (T) versus reciprocal number average molecular weight (M^{-1}) have been made using previously reported data for linear polymers tested in the glassy state. Over a wide range of molecular weights there is conformity to Flory's empirical equation $T = A - BM^{-1}$, in which A and B are constants. Values of M obtained by extrapolation to $T = 0$ correlate with critical values of molecular weight which are diagnostic of incipient formation of an entangled network. The entanglement thesis is developed further by reference to a model in which brittle strength is attributed to the breaking of covalent backbone bonds. Theoretical values are calculated which exceed experimental values by a factor of only three. Such close agreement is attributed to the insensitivity of glassy linear polymers to flaws.

Keywords Strength; entanglements; molecular weight; brittle fracture; critical molecular weight; glassy polymers

INTRODUCTION

Below some critical value of molecular weight the tensile strength of a polymer is negligibly small¹⁻³. Recently Gent and Thomas suggested that such a critical value corresponds to a condition in which the polymer molecules are just of sufficient length to form an entangled network⁴. Independently Bersted carried this analysis further and calculated theoretical values of tensile strength from a combination of Bueche's network theory and Orowan's theory of fracture. With the additional assumption that flaws were formed which were related in size to the distance between entanglements he obtained agreement between theoretical and experimental values of strength⁵.

The work to be reported here was elaborated independently. Broadly speaking the concepts involved were similar to those mentioned above but differences in procedures were sufficiently distinct to merit note. One difference is in the use of Flory's empirical relationship between tensile strength and molecular weight to define the critical value of molecular weight for incipient formation of an entangled network. Another difference is in the calculation of tensile strength from an extremely simple model for brittle fracture.

ANALYSIS OF MECHANICAL STRENGTH DATA

Gent and Thomas derived the maximum value of M for 'zero tensile strength', here redesignated as M_r , by extrapolation of curves of tensile strength (T) versus number average molecular weight (M). This approach has the merit of avoiding premature theoretical assumptions but places too much reliance on erratic data obtained at low molecular weights. In order to avoid the latter difficulty, the present analysis instead makes use of a plot

of T vs. M^{-1} . Flory showed that such a plot gives a straight line for data obtained with fractions of cellulose acetate (equation (1)). In equation (1), A and B are positive constants.

$$T = A - BM^{-1} \quad (1)$$

Gent and Thomas pointed out that few studies have been made of the influence of the molecular weight of a linear polymer on tensile strength in the glassy state. But, conveniently, a comprehensive coverage of the literature up to 1946 has been given by Haward⁷. Generally the earliest work is only of qualitative interest because of inadequacies in the determination of molecular weight. However, even as early as 1936, Douglas and Stoops reported data on copolymers of vinyl chloride with vinyl acetate which conform to a linear relationship for T vs.

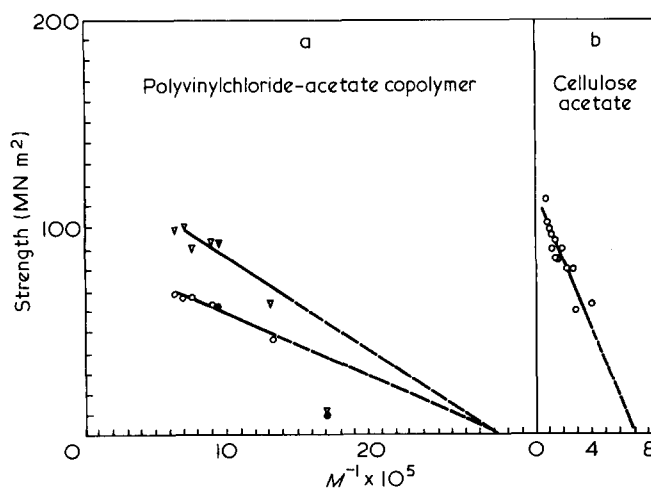


Figure 1 Strength versus reciprocal number average molecular weight. Tensile strength (○ and ●) and bending strength (△ and ▲) where the full symbols represent samples which are polydisperse and the open symbols ones which are approximately monodisperse (usually fractions). a; Douglas and Stoops (1936). b; Flory's representation (1945) of data by Sookne and Harris (1945)

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M^{-1} (Figure 1a)⁸. Measurements were also made of bending (flexural) strength which, as usual, provide an overestimate of T although by a factor of less than two⁷. These latter data are more erratic but, on the basis of a wider experience to be given subsequently for other polymers, are also interpreted as giving a linear plot which extrapolates to the same critical value of $M_t = 3400$ (at $T = 0$) as does the tensile data. It will be noted that in making these extrapolations less reliance was placed on data obtained at low values of M .

Flory's treatment (1946)⁶ of the tensile data of Sookne and Harris⁹ is reproduced in Figure 1b. The extrapolated line gives $M_t = 14000$.

The three sets of data analysed by Gent and Thomas are due to Vincent¹⁰ (Figures 2a and b) and to McCormick, Brower, and Kin¹¹ (Figure 2c). The work on poly(methyl methacrylate), PMMA, is particularly important because it allows a more extensive check on the range of validity of equation (1). Vincent noted that only the middle range of data fit equation (1) and that a sigmoid

curve is needed to give an overall fit. The upper branch of the curve is apparent in Figure 2a while the lower one is more obvious for data obtained with polyethylene (Figure 2b) and in Wallach's data¹² for a polyimide (Figure 2d). Values of M_t are given in Table 1.

It is laborious to prepare specimens covering a wide range of molecular weights and yet avoid the intrusion of additional variables due to processing conditions^{7,13}. It is, therefore, convenient to reduce molecular weight in a controlled manner by radiation-induced degradation. Of course results obtained in this way would be misleading in cases where other critical changes, especially crosslinking, occur. PMMA is not objectionable in this respect¹⁴ and some data obtained by Bopp and Sisman on specimens exposed to pile radiation are shown in Figure 3a. Molecular weights were estimated by Charlesby and were unavoidably rough because of problems of pile dosimetry.¹⁵ Therefore, the disagreement of the value of $M_t = 11000$ with the value of $M_c = 23000$ obtained from Vincent's data (Figure 2a) is regarded with reserve. More reliance is placed on a more recent set of measurements of bending strength obtained for a polymer exposed to γ -

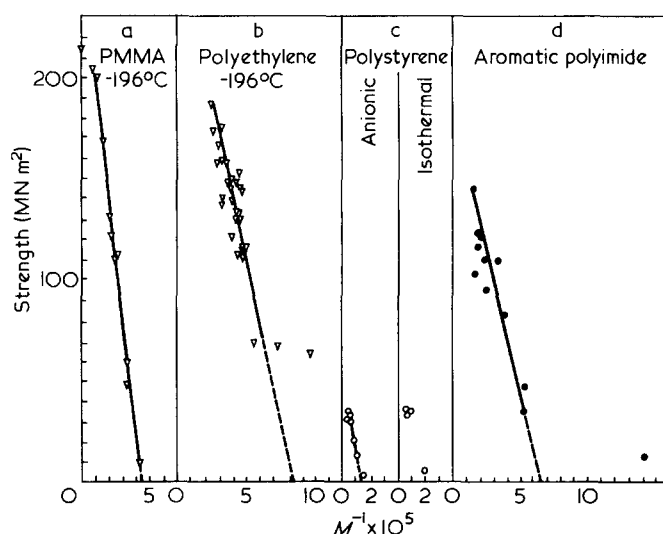


Figure 2 Strength versus reciprocal number average molecular weight. For significance of symbols see caption to Figure 1 a and b; Vincent (1960). c; McCormick *et al.* (1959). d; polyimides prepared from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether, Wallach (1968)

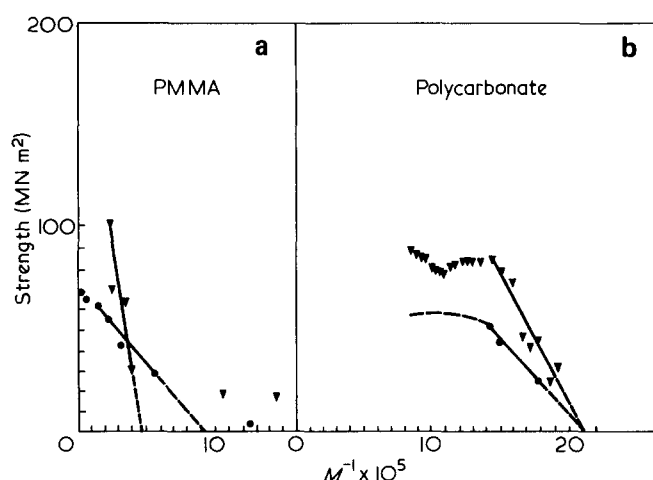


Figure 3 Strength versus reciprocal number average molecular weight for polymers exposed to high energy radiations. PMMA; tensile data of Bopp and Sisman (see Charlesby, 1960), bending strength (Kusy and Turner, 1977). Polycarbonate, poly[2,2-propane bis(4-phenyl carbonate)]: Golden *et al.* (1964)

Table 1 Critical values of molecular weight

	Figure	Tensile strength	M_t		M_c	M_e	M_g
				Bending strength			
PVC-acetate	1a	3400		3400			
PVC					5800		5000-7000
Cellulose acetate	1b	14000					
PMMA	2a		23000		11000*	6000	
			22000				
	3a	11000		21000	27500	10000	7000-13000
Polyethylene	2b		12000		4000*		
			11000*				
Polystyrene	2c		72000		30000-35000*	18100	10000-20000
			50000*				
Aromatic polyimide	2d	16000					

* Values cited by Gent and Thomas

rays which gives $M_t = 21\,000$ (Figure 3a)¹⁴.

Polycarbonate is another polymer which predominantly degrades on exposure to high energy electrons. The findings of Golden, Hammat, and Hazell¹⁶ are reproduced in Figure 3b. The most striking aspect of their data is the marked departure from equation (1) at high molecular weights.

COMPARISON OF CRITICAL VALUES OF MOLECULAR WEIGHT

Values of M_t are compared in Table 1 with other critical values derived from previous analyses of viscosity (M_v) and elasticity (M_e) data. These values are generally accepted to depend on entanglements^{17,18}. Values of M_g were obtained from an analysis¹⁹ of the dependence of glass transition temperature on M^{-1} . These have been interpreted also as being due to entanglements but there has not yet been time for independent evaluation of this view.

The results in Table 1 may be summarized by saying that critical values of molecular weight agree within a factor of about four. Thus, in a broad sense, tensile strength is recognized as another property of linear polymers which is influenced by entanglements. However, when values of M_t are compared in finer detail, then uncertainties are brought into focus. For example, Gent and Thomas suggested the approximate relationship $M_t = 2M_c$. In making this comparison they referred to a value of $M_c = 11\,000$ derived from measurements on concentrated solutions of PMMA (c.f. Table 1). In a commentary on this choice, Moon and Barker suggested that a value of $M_c = 27\,500$ would appear more appropriate on the grounds that this was obtained from experiments on the bulk polymer, i.e. without solvent²⁰. This commentary already casts doubt on experimental justification for the relationship $M_t = 2M_c$ and the results in Table 1 further caution a suspension of judgement on this rather fine discrimination. Obviously carefully designed experiments will be needed and such detailed comparisons will prove difficult judging by the problems encountered previously in making a case for another relationship between critical molecular weights *viz.* $M_c = 2M_e$ ^{17,18}.

THEORETICAL BRITTLE STRENGTH

The tensile strength (T) of an ideal brittle material can be calculated on the assumption of simultaneous fracture of all the load bearing bonds in the plane of fracture (equation (2)):

$$T = nf \quad (2)$$

In equation (2), n is the number of load bearing bonds per unit area and f the force required to break each individual bond. More generally there may be contributions to the product nf from both primary and secondary (Van der Waals) bonds²¹ but in the present case the latter will be neglected on the grounds that negligible strength is observed experimentally below M_t . In order to calculate a value of n for primary backbone bonds, the number of load bearing chains per unit area, reference will be made to the simple model of a crosslinked network treated by Bueche²². This envisages a grid of uniform network chains which resembles a simple cubic lattice, the junction points being hexafunctional crosslinks. Bueche's

expression for tensile strength is adopted but with reference to the chain molecular weight between entanglements, M_e (equation (3)):

$$T_\infty = nf = \left(\frac{\rho N}{3M_e} \right)^{2/3} f \quad (M = \infty) \quad (3)$$

In equation (3), ρ is the density of the polymer, N Avogadro's number, and f the force required to break a backbone chain. The expression refers to a fully entangled network with primary²³ molecules of infinite molecular weight ($M = \infty$). A theoretical value of strength was calculated for PMMA of 400 MN^{-2} using the following values: $\rho = 1 \text{ g cm}^{-3}$; $M_e = 10^4$; $N = 10^{23}$; and $f = 5.6 \times 10^{-4} \text{ dyne}$. The value taken for f is de Boer's estimate for the strength of a C-C bond; other estimates are $6.1 \times 10^{-4} \text{ dyne}$ ²⁴ and $1.9 \times 10^{-4} \text{ dyne}$ ²⁵. At the present stage of development, the choice of an appropriate value for f is of secondary importance in comparison with the problem of how to estimate a value of n .

A dependence of strength on molecular weight can be introduced by reducing the fraction of load bearing network chains by exclusion of those which are bounded by only one entanglement. In an analogous treatment of the influence of finite molecular weight on the modulus of rubber elasticity various refined treatments are recognized^{26,27}. However, in a simple treatment of tensile strength it will suffice to use Flory's end correction factor²³ and modify equation (4) as follows:

$$T = nf = \left(\frac{\rho N}{3M_e} \right)^{2/3} f \left(1 - \frac{2M_e}{M} \right) \quad (M \text{ infinite}) \quad (4)$$

An equation of the same form as Flory's empirical equation (1) is obtained from equations (3) and (4):

$$T = T_\infty - 6.8 \times 10^{15} \rho^{2/3} M_e^{1/3} f \left(\frac{1}{M} \right) \quad (5)$$

DISCUSSION

Qualitatively it seems clear that entanglements are mainly responsible for the strength of linear polymers. As a first step towards a quantitative treatment, initial values of molecular weight have been estimated from Flory's equation. However, in a refinement of this step, further work is needed to ensure that use of the number average molecular weight is appropriate²⁸ and to account for discrepancies from Flory's equation at both high and low molecular weights. As a second step the physical structure of polymers²⁹ needs to be elucidated taking account of entanglements. At present the best that can be done is to invoke a hypothetical structure for some selected polymer, such as PMMA. In this regard Bueche's model network has been chosen for its tractability rather than for its close correspondence to physical reality. For example, it would seem more realistic to consider a close-packed network with tetrafunctional, rather than hexafunctional, entanglements.

Perhaps the most drastic simplification which has been made is in limiting attention to ideal brittle fracture. In a macroscopic sense, a case for a brittle regime of fracture has been detailed for PMMA at low temperatures by Beardmore³⁰. However, in a microscopic sense it seems

likely that evidence of plastic deformation (crazing) can always be detected in the vicinity of the fracture plane³¹. Therefore it might be objected that the ideal case is never encountered in practice. This objection is valid but should be put into perspective by recognizing that it could also be made of theoretical treatments of the strength of inorganic glasses which, notwithstanding, have proved instructive in understanding these materials^{7,32}.

The theoretical value of the strength of PMMA, of 400 MN m⁻², only exceeds experimental values^{30,33} of brittle strength, ca. 135 MN m⁻², by a factor of three. This is in contrast to discrepancies of two orders of magnitude generally found for other brittle materials such as silicate glasses. It is known that such large discrepancies are caused by flaws which act as stress concentrators and that when extreme care is taken to prepare flawless specimens experimental values of strength actually approach theoretical estimates. In order to account for the remarkably close agreement found between theoretical and experimental values of tensile strength of PMMA, the suggestion^{34,35,30} is adopted that specimens of glassy organic polymers, as commonly prepared for testing, are relatively insensitive to adventitious flaws.

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