

Influence of Molecular Weight and Molecular Weight Distribution on the Tensile Properties of Amorphous Polymers

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Synopsis

Tensile property data for polystyrene samples of varying polydispersity are correlated with various parametric measures of molecular weight. Traditional measures of molecular weight, such as \bar{M}_n , \bar{M}_w , and \bar{M}_z , are shown to be unable to account for the variation of tensile properties with molecular weight. However, a new molecular weight parameter, termed the failure property parameter, is able to provide a single relationship between tensile strength and the parameter for both the broad and narrow distribution polymers. The form of this parameter is consistent with its having origins in the view that it is the entanglement network in an amorphous polymer that provides the observed strength properties. Specifically for polystyrene, the failure property parameter results indicate that material below 60,000 molecular weight does not contribute to polymer strength. Although the results of this investigation are specifically for polystyrene, the arguments used to develop the failure property parameter are not dependent on polymer chemical structure. Consequently, we believe that both the concepts and definition of this new parameter are applicable to all amorphous polymers.

INTRODUCTION

The failure properties, such as tensile strength and impact resistance, of thermoplastics are of the utmost importance in polymers. In spite of the great importance of these properties, the effect of molecular structure on these properties is not clear at this time. The objective of this work is to clearly define the effects of molecular weight and its distribution on the tensile properties of amorphous polymers, using polystyrene as a test material. Although we believe the results reported here to be indicative of amorphous materials in general, polystyrene was chosen because of the large range in molecular weight determinations for this polymer. The effects of the chemical composition on the failure properties have been reported^{1,2} previously.

Many years ago, Flory³ suggested that a number of physical properties could be correlated with the number average molecular weight \bar{M}_n . Although such a correlation has reportedly worked for some materials, its general applicability is not certain.⁴ In actual fact, "the question of whether to correlate mechanical behavior with \bar{M}_n or \bar{M}_w , or any other type of average, has not been settled."⁵ Generally, the problem with correlations appears to be the inability of any molecular weight parameter to correlate with both very narrow and very broad molecular weight distribution (MWD) samples⁴; plots of tensile strength as a function of \bar{M}_n generally⁴ give multiple curves, depending on the polydispersity of the samples. Our goal here is to not only

TABLE I
 Characteristics of the Polymers Used for Tensile Strength Correlations

Sample ID	Molecular weight ($\times 10^{-3}$)			\bar{M}_w/\bar{M}_n	Compression molded tensile strength (psi)	Relaxed (annealed) Injection molded tensile strength (psi)	Injection molded tensile strength (psi)
	\bar{M}_n	\bar{M}_w	\bar{M}_z				
PS1	94.2	279	523	2.96	4780	4890	7830
PS1 + 3% 2000 MW	44.4	280	544	6.31	4660	4930	7530
PS1 + 3% 1.8×10^6 MW	110	326	698	2.96	4430	4800	8060
PS2	72.8	300	562	4.12	4410	4800	7880
PS3	74.6	292	552	3.91	5230	5100	7340
PS4	47.7	277	552	5.81	4870	4350	6390
PS5	68.0	213	422	3.13	5020	4280	6950
PS6	52.6	172	384	3.27	3380	3655	4990
PS7	125	292	508	2.34	6350	5460	8000
PS8	122	312	572	2.56	6040	5530	8080
Pressure chemical std.	—	498	—	< 1.20	6000	—	7500

provide an empirical parameter with which to correlate strength properties, but also to provide a reasonable theoretical model dictating the use of this parameter.

It was recognized long ago by Bueche et al.⁶ that entanglements must play a pivotal role in the interconnectiveness of amorphous polymers, and even polymers in general. However, these concepts did not gain wide popularity until Bersted¹ and Turner⁷ published papers as to the role of entanglements on tensile properties. More recently the role of entanglements has become widely recognized as holding the material together,⁸ influencing the fatigue properties of amorphous polymers,⁹ and affecting the crazing of glassy polymers.¹⁰ It is in this context that the theoretical description, leading to an effective molecular weight parameter with which to correlate to tensile properties, will be given.

EXPERIMENTAL

The samples used in this study are listed in Table I. The blends were blended in benzene and freeze-dried under vacuum. The "spiking" components were anionically polymerized standards that were obtained from the Pressure Chemical Corp.

Tensile strengths were measured on ASTM type I tensile bars at a crosshead speed of 0.2 in./min. The "relaxed" injection-molded bars were annealed in an oven at 115°C for 15 min to remove orientation. The lack of orientation in the annealed bars was confirmed by birefringence measurements.

Gel permeation chromatography (GPC) was used to determine the molecular weight distributions of the polystyrene samples. The GPC system consists of a Waters Model 201 ambient temperature instrument with a 6000A pump, 710A automated sample injector, and a 401 differential refractive index detector. Polystyrene solutions were prepared in tetrahydrofuran at a concentration of 0.07% (wt/vol). The column set consists of two mixed and one 100 Å nominal porosity PL gel columns from Polymers Laboratories. At a flow rate of 1.0 mL/min, these columns provide good resolution over a molecular weight range from about 7×10^6 to less than 600. The system is calibrated with narrow molecular weight distribution polystyrene standards.

RESULTS AND DISCUSSION

Correlations with Experimental Data

The list of samples in this study and their characteristics are given in Table I. Most of the data for narrow MWD polystyrene samples are from McCormick et al.¹¹ and are shown in Table II. One surprising observation from these tables is the large difference between the injection-molded and compression-molded properties. Presumably this difference is due to orientation in injection molded bars. The data in Table I show this to be the case, since the relaxed injection-molded data agree well with the compression-molded data. *This difference should caution against assuming the injection-molded physical properties necessarily reflect the intrinsic material properties.* The data from Table I, plotted in Figure 1, show a rough correlation between the different molded properties. However, for the following comparisons with

TABLE II
Molecular Weight and Tensile Strength Data for Narrow MWD Polystyrene
from McCormick et al.¹¹

Sample ID	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	Compression-molded tensile strength (psi)	Injection-molded tensile strength (psi)
s3	40,000	54,000	1.35	—	—
s4	66,300	78,100	1.18	440	1430
s5	95,700	110,000	1.16	1980	3710
s6	116,000	125,000	1.08	3000	5570
s7	131,000	141,000	1.08	4380	6540
s8	159,000	171,000	1.07	4910	7020
s9	189,000	210,000	1.11	5150	7100
s10	240,000	249,000	1.04	4660	7920

molecular weight data, only compression-molded and relaxed injection-molded tensile strengths are used.

Other data sources are sometimes referenced for physical properties of narrow MWD polystyrene, but there appear to be inconsistencies with some of the data. For example, the data from Vlachopoulos et al.¹² are probably affected by injection-molded orientation. Data from Ref. 13 were discussed in the review by Martin et al.⁴

These data appear to have consistently lower tensile strengths (by about 1500 psi) compared to similar samples from McCormick et al.¹¹ and the present a study. Because of these problems, we have not attempted to include all available data in the correlations.

Effect of Orientation on Tensile Strength in Polystyrene

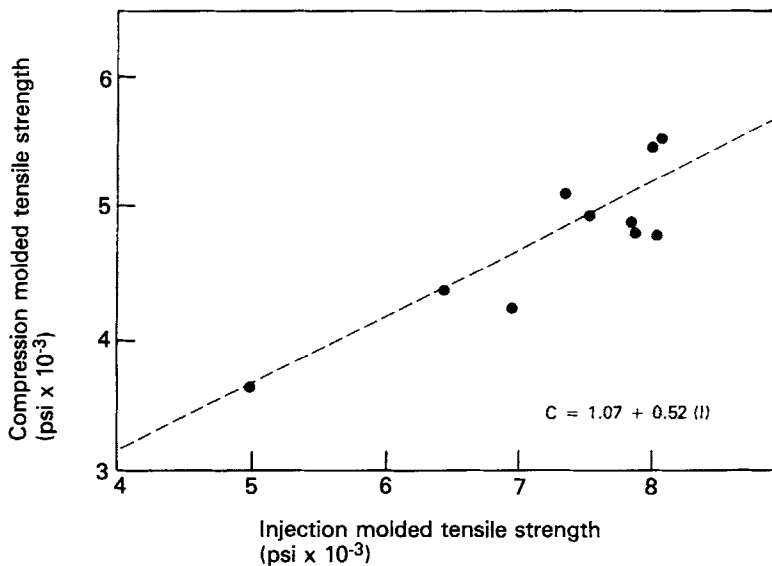


Fig. 1.

Tensile Strength (psi) Versus M_n for Compression Molded and Relaxed Injection Molded Polystyrene.

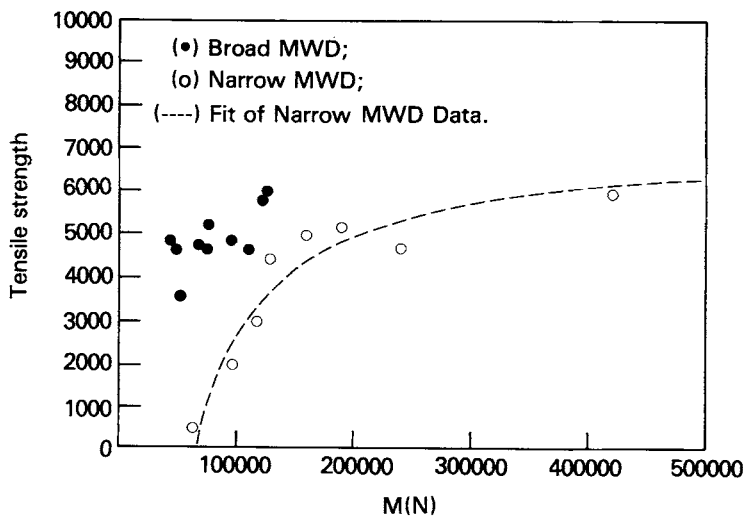


Fig. 2.

Most authors advocate the correlation of mechanical properties with \bar{M}_n , as proposed by Flory³:

$$\text{property} = A + B/\bar{M}_n \tag{1}$$

Figure 2 shows such a correlation for both the broad and narrow MWD polystyrene samples listed in Tables I and II. The fit of the narrow MWD data, using eq. (1), is very good (see Table III). However, the data in Figure 2 clearly demonstrate that \bar{M}_n cannot be correlated for samples of varying polydispersity.

Another possible molecular weight parameter as suggested by Prentice¹⁴ is the high molecular weight tail as indicated by \bar{M}_z . Prentice suggested this on the basis of a theoretical "pullout" mechanism of entangled chains during

TABLE III
Compression-Molded Tensile Strength (psi) vs. \bar{M}_n , \bar{M}_w ,
and \bar{M}_z for Narrow MWD Polystyrenes

Std. Dev.	$\sigma = 7190$	$- 4.51 \times 10^8 (1/\bar{M}_n)$	
t	± 411	± 0.49	$R^2 = 93.36\%$
	17.5	9.18	$df = 6$
Std. Dev.	$\sigma = 7390$	$- 5.33 \times 10^8 (1/\bar{M}_w)$	
t	± 468	± 0.63	$R^2 = 92.20\%$
	15.8	8.42	$df = 6$
Std. Dev.	$\sigma = 7560$	$- 6.23 \times 10^8 (1/\bar{M}_z)$	
t	± 623	± 0.86	$R^2 = 89.79\%$
	13.4	7.26	$df = 6$

Tensile Strength (psi) Versus M_z for Compression Molded and Relaxed Injection Molded Polystyrene.

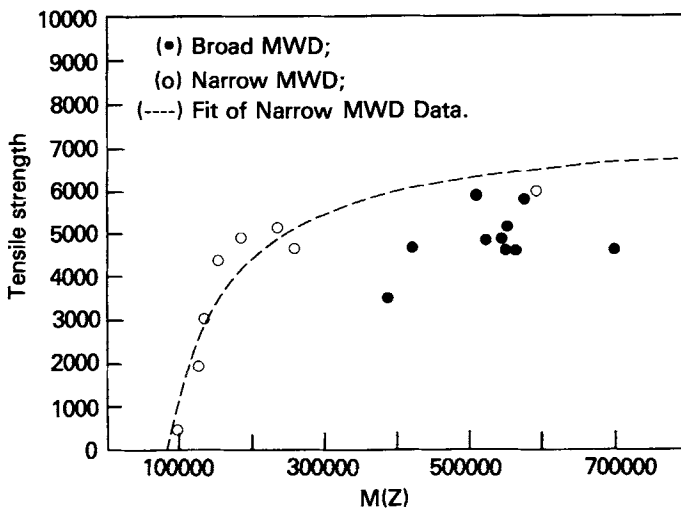


Fig. 3.

fracture. His reported correlation of failure stress with \bar{M}_z supported his ideas, although the samples used were essentially monodisperse. Figure 3 is a plot of tensile strength as a function of \bar{M}_z , as suggested by the argument of Prentice. Clearly, no single relationship is suggested by this plot, although a good correlation is again obtained for the narrow MWD samples (see Table III).

Closer examination of the data in Table I is in order. The first three samples in the table all have the same base resin, except the second and third have been "spiked" with small amounts of either low or high molecular weight material, the blends having been made from freeze-dried benzene solutions. The first unblended material was also freeze-dried and treated in the same manner as the blends. Interestingly, neither addition of the small amount of either very low or very high molecular weight material to the base material affected the tensile strengths, even though substantial changes to \bar{M}_n and \bar{M}_z resulted from the blending. This further supports the conclusion, based on the lack of a single molecular weight-tensile strength relationship as a function of polydispersity, that neither \bar{M}_n nor \bar{M}_z are correct molecular parameters to correlate with strength properties.

Comparing the relative offset between broad and narrow MWD samples in Figures 2 and 3, it appears that \bar{M}_w might provide a more consistent correlation with tensile strength. As can be seen in Figure 4, the broad and narrow MWD samples are in relatively good agreement when tensile strength is plotted vs. \bar{M}_w . However, the broad, MWD samples increase the scatter in data and result in a slightly lower quality fitted equation (see Table III).

The use of \bar{M}_w in eq. (1) presents a problem when trying to develop a consistent theory to correlate both broad and narrow MWD samples. For the monodisperse or narrow MWD samples, \bar{M}_n , \bar{M}_w , and \bar{M}_z are approximately

Tensile Strength (psi) Versus M_w for Compression Molded and Relaxed Injection Molded Polystyrene.

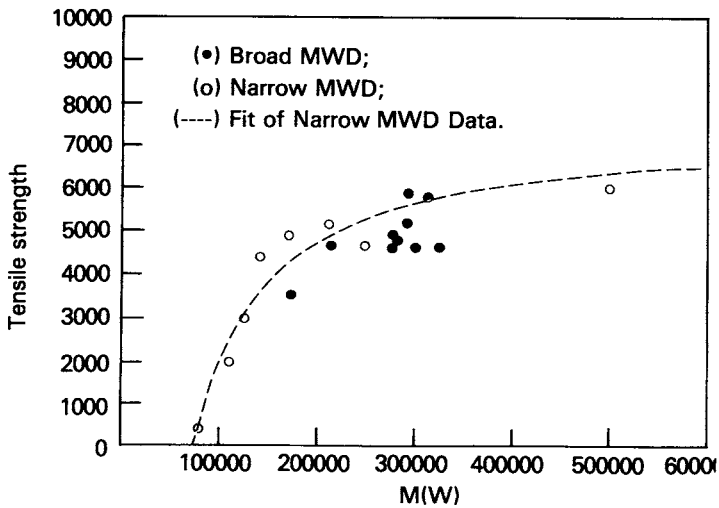


Fig. 4.

equal or have relatively constant offsets. Therefore, all of these molecular weight averages should work equally well in eq. (1). This is shown to be true by the fitted equations listed in Table III. However, the physical properties of a broad MWD sample should be calculable as the sum of contributions from individual components:

$$\sigma = \sum w_i \sigma_i = \sum w_i (A + B/M_i) \quad (2)$$

It is not obvious how such a summation, using the form of eq. (1), can result in the weight average molecular weight determining the physical property. The agreement between broad and narrow MWD samples for tensile strength vs. \bar{M}_w must be considered fortuitous. Therefore, a better theory is needed that will provide a single relationship between physical properties and molecular weight for samples of varying polydispersities, and which will be in agreement with a summation of the component contributions as in eq. (2).

It has generally been shown that the molecular weight dependence for narrow molecular weight homologs obey an equation of the form

$$\sigma = \sigma_\infty (1 - M_T/M) \quad (3)$$

where σ_∞ is the limiting tensile strength for high molecular weights, M_T the threshold molecular weight $\approx M_c$,¹⁵ and σ_∞ can be correlated to $1/M_e$.¹ In light of the increased belief that entanglements ultimately are responsible for the brittle strength in polymers, eq. (3) is consistent with a correlation of σ with entanglement density, if it is assumed that the $2M_T/M$ term is the result of the ineffectiveness of the chain ends and $M_i < M_T$ to form effective bridging chains capable of retarding crack growth.

For our model we will assume that the tensile strength is proportional to the entanglement density, and that molecules less than M_T will have no contribution to the tensile strength. Consequently, for any arbitrary polydisperse sample

$$\sigma \propto \sum n_i \cdot (\# \text{ entanglements per molecule for molecules of molecular weight } M_i) \quad (4)$$

when n_i is the number of molecules of molecular weight m_i per unit volume. It follows that

$$\sigma \propto \sum_{i=1}^{\infty} (\rho N_0 / M_i) \cdot [(M_i - M_T) / M_e] w_i \quad (5)$$

where ρ is the density, M_e the molecular weight between entanglements, and w_i the weight fraction of species i . Since the species below M_T are assumed to be ineffective in forming strength enhancing entanglements, this fraction of molecular species will be considered a diluent of fraction $(1 - \phi)$. M_T in the above for $M_i > M_T$ constitutes the ineffective portion of the chain forming entanglements.

Equation (5) becomes

$$\sigma \propto (\rho N_0 / M_e) \sum_{i=T}^{\infty} (w_i - w_i M_T / M_i) \quad (6)$$

or

$$\sigma \propto \phi (\rho N_0 / M_e) \cdot (1 - M_T / \bar{M}_n^*)$$

where

$$1 / \bar{M}_n^* \equiv \sum_{i=T}^{\infty} \bar{w}_i / M_i = 1 / \phi \sum_{i=T}^{\infty} w_i / M_i \quad (7)$$

($\bar{w}_i = w_i / \phi$, \bar{w}_i being the renormalized MWD for weight fractions not including $M_i \leq M_T$),

$$\sum_{i=T}^{\infty} \bar{w}_i \equiv 1 \quad \text{and} \quad \sum_{i=T}^{\infty} w_i = \phi$$

Equation (6) suggests the following molecular weight dependence for samples of varying molecular weight distribution:

$$\sigma = \sigma_{\infty} (1 - M_T / \bar{M}_n^*) \phi \quad (8)$$

where $\phi(1 - M_T / \bar{M}_n^*)$ will be termed the failure property parameter, embodying the molecular weight dependence of a given polymer type and σ_{∞} the limiting tensile strength at very high molecular weights.

Equation (8) is simply the usual equation for the molecular weight dependence, except the ineffectiveness of the chains shorter than some threshold molecular weight M_T has been taken into account in \bar{M}_n^* (which is the number average molecular weight for that part of the molecular weight distribution greater than M_T) and in ϕ , which takes into account the ineffectiveness of the chains of molecular weight less than M_T .

Determination of M_T

In eq. (6), the effect of MWD on strength can be predicted once M_T is known. Intuitively, one might expect that M_T should approximately equal the critical entanglement molecular weight M_c as determined by the intersection of $\eta_0 - \bar{M}_w$ melt rheology curves both below and above the onset of the entanglement region. However, based on the concept that strength is due to sample interconnectiveness from entanglements, one might expect the strength to vanish when the effects of entanglements start to vanish. Therefore, while the intersection of $\eta_0 - \bar{M}_w$ curves gives M_c , the transition¹² between the two regions is finite over a range of molecular weights. Careful examination¹⁷ of this transition region suggests that for polystyrene the change from the entanglement region (where $\eta_0 \propto \bar{M}_w^{3.5}$) to the nonentangled region starts at a molecular weight of about 60,000. Gent and Thomas¹⁵ have shown that M_T and M_c can be correlated such that

$$M_T = KM_c \quad (9)$$

where $K \approx 2-3$. Therefore, the correlation of M_T with M_c appears to represent the correlation of M_c with the onset of the entanglement region.

In general, one must determine the validity of eq. (8) by the ability to predict tensile strengths of both broad and narrow MWD samples and determine the optimum value of M_T for a particular polymer. This can be easily accomplished by calculating the failure property parameters $FP(M_T)$ for a few assumed values of M_T . The tensile strength versus $FP(M_T)$ data are then fit to either a linear or log-log relationship from eq. (8):

$$\sigma = A + K [FP(M_T)] \quad (10)$$

or

$$\log \sigma = \log K + B \log [FP(M_T)] \quad (11)$$

As M_T approaches the optimum value, the quality of the fit improves, the intercept of the linear equation approaches zero, and the slope of the log-log equation approaches 1.0.

For the samples in Tables I and II, the failure property parameter was calculated with trial values of M_T equal to 31,200, 38,000, and 59,000. The two lower values of M_T are commonly referenced M_c values,^{17,18} while the highest value is near the onset of the entanglement to nonentangled transition region of polystyrene.¹⁷ These data are summarized in Table IV. The tensile strengths vs. failure property parameter fitted equations are also shown in Table IV. The linear relationships are shown in Figures 5-7, for M_T of 31,200, 38,000,

TABLE IV
Failure Property Parameters for Selected Values of M_T and Tensile Strengths (Compression-Molded and Relaxed Injection-Molded)

Sample ID	\bar{M}_n	\bar{M}_{w0}	\bar{M}_z	\bar{M}_w/\bar{M}_n	For $M_T = 59,000$			Failure Property Parameter			Tensile strength (psi)
					\bar{M}_n^*	$\phi (< 59,000)$	$M_T = 59,000$	$M_T = 38,000$	$M_T = 31,200$		
PS1	94,000	279,000	523,000	2.96	184,000	0.133	0.590	0.700	0.740	4840	
PS1 + 3% 2000 MW	44,400	280,000	544,000	6.31	187,000	0.154	0.580	0.689	0.725	4800	
PS1 + 3% 1.8 $\times 10^6$ MW	110,000	326,000	698,000	2.96	194,000	0.117	0.616	0.722	0.760	4620	
PS2	72,800	300,000	562,000	4.12	194,000	0.135	0.603	0.708	0.748	4600	
PS3	74,600	292,000	552,000	3.91	191,000	0.140	0.595	0.700	0.740	5160	
PS4	47,000	277,000	552,000	5.81	186,000	0.168	0.569	0.673	0.714	4610	
PS5	68,000	213,000	422,000	3.13	155,000	0.182	0.509	0.634	0.682	4650	
PS6	52,600	172,000	384,000	3.27	136,000	0.273	0.414	0.584	0.605	3520	
PS7	125,000	292,000	508,000	2.34	191,000	0.090	0.631	0.739	0.778	5900	
PS8	122,000	312,000	572,000	2.56	195,000	0.103	0.626	0.734	0.772	5780	
PS Standard		498,000		< 1.20			0.882	0.924	0.937	6000	
S3	40,000	54,000		1.35			—	—	—	—	
S4	66,300	78,100		1.18			0.110	0.430	0.530	440	
S5	95,700	110,000		1.16			0.380	0.600	0.670	1980	
S6	116,000	125,000		1.08			0.490	0.670	0.730	3000	
S7	131,000	141,000		1.08			0.550	0.710	0.760	4380	
S8	159,000	171,000		1.07			0.630	0.760	0.800	4910	
S9	189,000	210,000		1.11			0.690	0.800	0.830	5150	
S10	240,000	249,000		1.04			0.750	0.840	0.870	4660	

Tensile Strength (psi) Versus Failure Property Parameter for $M_T = 31,200$.

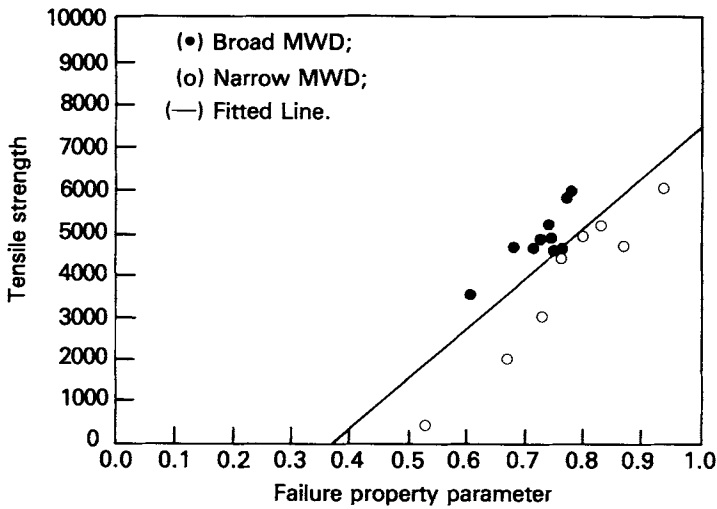


Fig. 5.

Tensile Strength (psi) Versus Failure Property Parameter for $M_T = 38,000$.

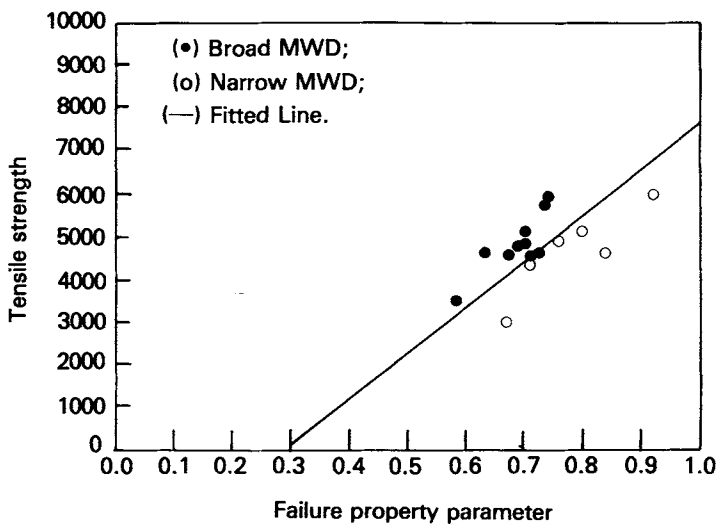


Fig. 6.

Tensile Strength (psi) Versus Failure Property Parameter for $M_T = 59,000$.

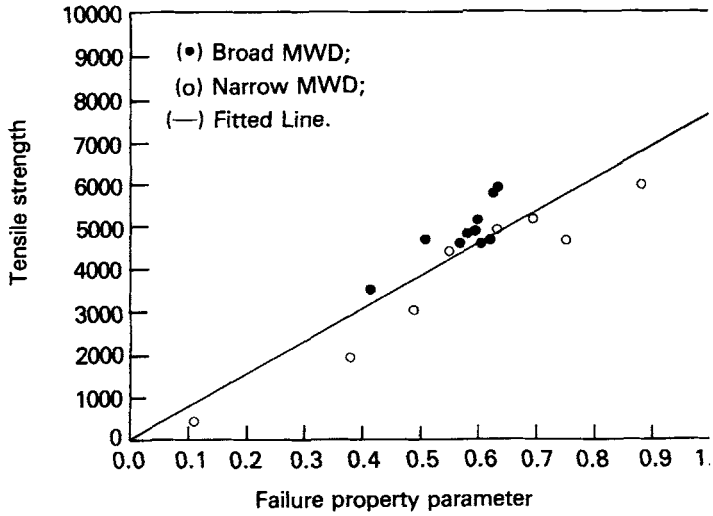


Fig. 7.

Tensile Strength (psi) Versus Failure Property Parameter for $M_T = 31,200$.

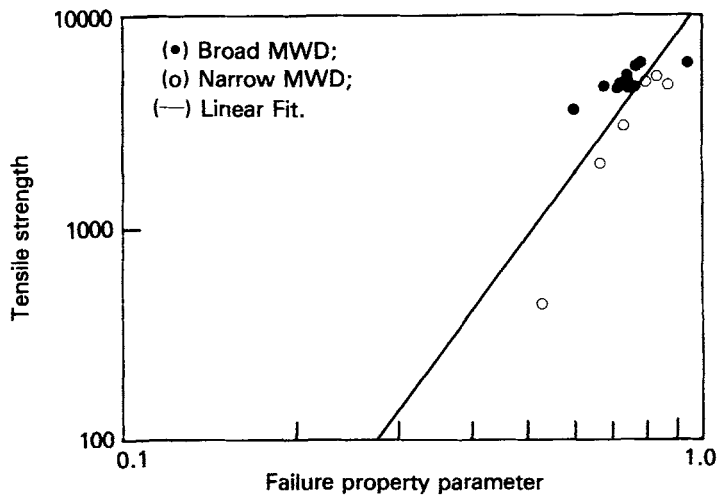


Fig. 8.

Tensile Strength (psi) Versus Failure Property Parameter for $M_T = 38,888$

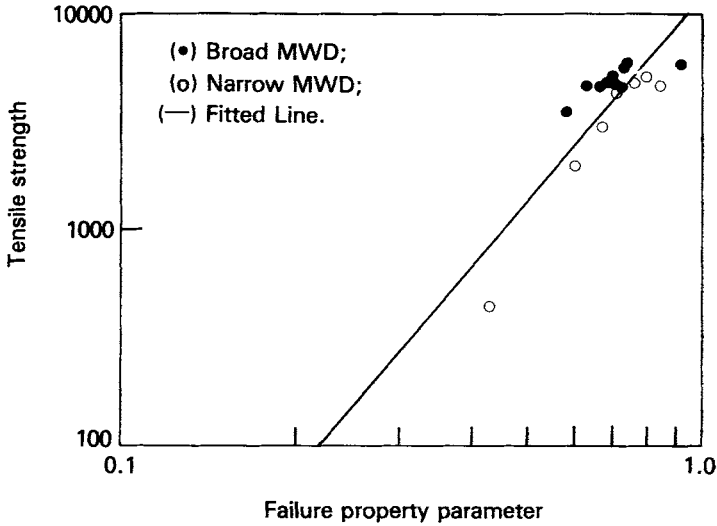


Fig. 9.

Tensile Strength (psi) Versus Failure Property Parameter for $M_T = 59,000$

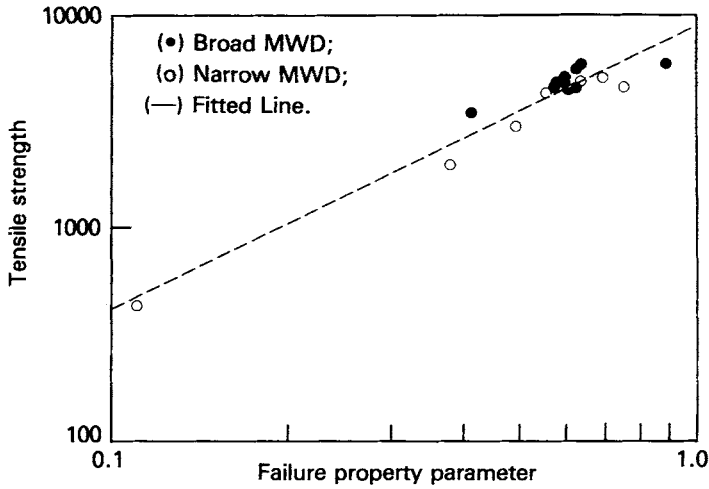


Fig. 10.

M (T) Vs Intercept (Lin Fits)

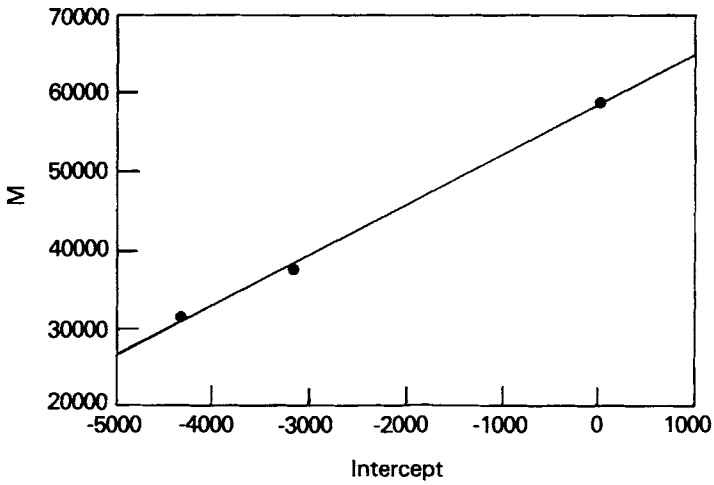


Fig. 11.

and 59,000, respectively. With $M_T = 59,000$, a better fit of the data is obtained with an intercept near zero (see Fig. 7):

$$\sigma = 19 + 7700 \times FP_{59}$$

$$(\pm 580) \quad (\pm 980)$$

Similar results are obtained for the log-log relationships, as shown in Figures 8-10. Again, for $M_T = 59,000$, a better fit is obtained and the slope is

M (T) Vs Slope (Log Fits)

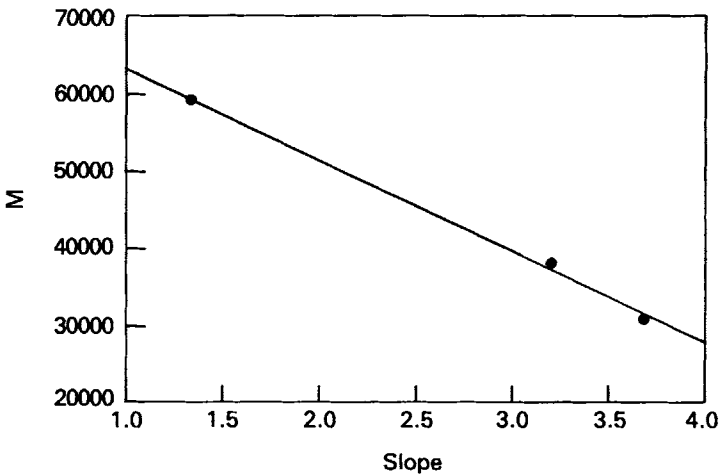


Fig. 12.

approaching 1.0 (see Fig. 10):

$$\log \sigma = 3.96 + 1.33 \times \log(\text{FP}_{59})$$

(±0.03) (±0.09)

Although the choice of $M_T = 59,000$ appears to be very close to the optimum value, it is not necessary to make numerous trial-and-error adjustments of M_T . As shown in Figures 11 and 12, the linear fit intercepts and the log fit slopes can be plotted vs. trial value of M_T to obtain an optimum M_T value. At zero intercept (linear fits) the optimum M_T is 58,800 and at a slope of 1.0 (log fits) the optimum M_T is 63,000. These are very close when considering the overall uncertainty in the data and regression coefficients. It is also encouraging that the linear failure property relationship for both broad and narrow MWD samples predicts about the same limiting tensile strength, 7700 psi, as was obtained from $1/\bar{M}$ fits of only the narrow MWD data, 7200–7600 psi. If the optimum M_T of 63,000 is used to recalculate the failure property parameter, the log–log relationship yields a similar value for the limiting tensile strength.

General Applications

The data reported on here are all for crystal polystyrene, since for polystyrene widely varying MWDs are available and the molecular weight data are easily obtained (calibration procedures are well defined). However, the concept, involving the strength of amorphous polymers being due to an entanglement network, are believed applicable to all essentially amorphous polymers. As such, the failure property parameter is expected to be a useful measure to account for observed variations in tensile properties for other amorphous polymers. It is conceivable that even high molecular weight polycrystalline materials can also be described by such ideas, since presumably the entanglements should remain intact. However, this is at present an actively debated subject and beyond the scope of this study.

The general application of the failure property parameter concept for amorphous engineering polymers is not straightforward, since neither M_c nor M_T , which are necessary to calculate the failure property parameter, is generally known for most amorphous engineering resins. The following suggests a method to make use of these ideas. For a series of samples, the tensile strength can be measured, and the failure property parameter FP calculated for various assumed M_T values. From a plot of the slope of the logarithm of tensile strength near $\log(\text{FP})$, we get a series of slopes corresponding to each assumed M_T . The M_T corresponding to a slope of 1 should from the foregoing analysis be the correct one.

From this type of analysis, an M_T , which is characteristic of the material, can be determined and used in future calculations for that particular type of polymer.

CONCLUSIONS

A new molecular weight parameter, the failure property parameter, has been shown to be capable of accounting for the variation of tensile strength in

polystyrene with molecular weight distribution; the ability to correlate both broad and narrow MWD materials with tensile properties by means of a single relationship has hitherto not been possible for any polymer system. The definition of the failure property parameter is shown to follow rather naturally from the assumption that the strength of a polymer arises primarily from its forming an entanglement network.

Although the results reported here deal specifically with polystyrene, the concepts, calculations, and use of this new molecular weight parameter is believed generally applicable to all essentially amorphous polymer systems, including amorphous engineering polymers.

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