Correlations between Chain Parameters and Failure Characteristics of Polymers below Their Glass Transition Temperature

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ABSTRACT: From empirical data in the literature, it is shown that the mode of failure of polymers below T_g depends on the relationship between the chain volume between entanglements, L_cd^2, and the activation volume for the glass transition, ω. When $L_cd^2 > \omega$ the failure is brittle, and when $L_cd^2 < \omega$ the failure is ductile. Depending on chain flexibility, the onset of polymeric strength occurs at chain lengths of only a few L_c, and maximum strength is reached at only slightly longer chains. The effect of entanglements frozen in the polymeric system below T_g is briefly discussed.

Introduction

There exist in the literature several molecular theories attempting to explain the deformation and failure processes of glassy polymers. The earlier theories were reviewed by Bowden,[1] Argon,[2,3] and Ward.[4] Later models appear to be heavily dependent on the reptating chain in rearranging tube theories due to de Gennes[5,6] and Edwards[7,8] or, through the phonon theory of strength,[9] on the kinetic theories of Eyring,[10,11] Lazurkin,[12,13] and Zhurkov.[14,15] In general, the above models are not sufficiently specific to explain either differences between brittle and ductile failure or variations in strength within either group of polymers. Most of these theories were tested against only a handful of polymers. Recently, a qualitative model of the stress–strain behavior of glassy polymers was introduced by Skolnick et al.[16] This model bears resemblance to the Robertson[17] model of conformational changes as the mechanism responsible for stress-induced flow in glassy polymers. Certain similarities apparently exist between the model of Skolnick et al.[16] and correlations arrived at in this work.

It is well accepted[18] that the viscoelastic response of polymeric materials changes with temperature and that the size of the entities associated with particular relaxations increases with increased temperature. Thus, in plots describing the modulus as function of temperature or frequency,[18] the narrow region where the transition interval merges into the flat plateau region is considered to be the region where motions of chain length L_c or larger start dominating the viscoelastic behavior of the polymer. Here, L_c is defined as the chain contour length between entanglements. This narrow region is at about, or right above, the glass transition temperature, T_g. Below T_g the moving entities associated with various relaxations are all smaller than L_c and may contain a few backbone bonds moving in concert, pendant groups undergoing motions independent of the chain backbone, certain rotational motions of pendant groups, and so on.[18] The range of use of most nonelastomeric polymers is substantially below T_g. In the case of many ductile "engineering thermoplastics", it can be as low as about 150 K below T_g. At these low temperatures long-range chain contortions, involving sizes of L_c and longer, are arrested, and only localized motions are expected to take place.[18]

In the following it will be shown that the brittle or ductile modes of failure of polymers below T_g, as well as their ultimate strength, appear to be strongly dependent on L_c. This indicates that the ultimate mechanical properties of polymers below T_g are not necessarily dictated by relaxational phenomena and the size of the submolecular entities undergoing these relaxations. The dependence of the above ultimate mechanical properties on L_c indicates, most likely, that entanglements that can be released above T_g are frozen into the system below T_g, and their presence is reflected in the ultimate properties of the amorphous and semicrystalline polymers below the glass transition temperature interval.

Other failure phenomena, such as fatigue response or crazing of polymers, also appear to be strongly dependent on L_c or larger chain lengths but will not be dealt with in this paper. The correlations in this work are all empirical. The development of formal molecular theory explaining them in detail will have to await future times.

Data Acquisition

A polymer may be defined as brittle when specimens in stress–strain tests fail at the maximum load at relatively low strains. Ductile polymers are those that fail after passing through a maximum load, yet at relatively low strains.[4] By its very nature, this definition excludes elastomers or other polymers at or above T_g. Under tension, the ultimate properties of most glassy polymers, especially the brittle ones, are strongly dependent on the presence or absence of impurities, inhomogeneities, minor voids, etc. Therefore, we chose whenever possible to use data of strength under compression for birttle polymers. These are usually in the range 10–15% above the strength under strain values of highly purified corresponding polymers. Most of the strength data are compiled in previous works by this author.[19-22] For room-temperature elastomers, the data were obtained in a temperature range around 50 K below T_g, where these polymers behave in a brittle fashion. Additional data necessary for the calculation of several structural parameters to be discussed in this work were tabulated by Aharoni in several papers.[23-25]

There exist in the literature empirical equations relating the macroscopic stress σ applied on a specimen and the time to failure τ. In the case of brittle polymers[14,15,18,26-29]

$$\ln \tau = \ln \tau_0 + (U_0 - \gamma\sigma)/RT \qquad (1)$$

and in the case of ductile ones[12,13,15,18-21]

$$\ln \tau = \ln \tau_0 + (\Delta H_a - \omega\sigma)/RT \qquad (2)$$

where τ_0 is a time constant of about 10^{-13} s, R is the gas constant, T is temperature, U_0 is the activation energy for mechanical or thermal bond rupture, and ΔH_a is the activation energy for the glass transition process. γ and ω are "activation volumes" or "stress concentration coefficients".

Under isothermal conditions, the fracture mode of amorphous polymers, or of the amorphous phase in semicrystalline polymers, depends on the relationship between

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$(\Delta H_a - \omega\sigma)$ and $(U_0 - \gamma\sigma)$. When

$$(\Delta H_a - \omega\sigma) < (U_0 - \gamma\sigma) \tag{3}$$

the fracture will be ductile, and when

$$(\Delta H_a - \omega\sigma) > (U_0 - \gamma\sigma) \tag{4}$$

the failure will be brittle.[21,22] This leads to an equation describing the brittle–ductile transition

$$\gamma + (\Delta H_a - U_0)/\sigma = \omega \tag{5}$$

Because γ is relatively small and constant,[19] the tendency of a polymer to fail in a ductile fashion will increase with an increase in $(\Delta H_a - U_0)/\sigma$. The conversion of γ or ω from units of (mm^2/kg)(kcal/mol) to units of volume is effected in accordance with Bartenev.[15,22]

Even though the mode of failure depends on the relationship between ΔH_a and U_0, we have observed in the past that the strength of both brittle and ductile polymers is related only to their respective ΔH_a values.[21,22] These values are obtainable from the temperature dependence of dynamic mechanical or dielectric loss determinations of T_g.[30] Another way to determine ΔH_a is from the knowledge of T_R, a reference temperature above T_g, the free volume at T_R, and the rate of change of the free volume in the temperature interval between T_g and T_R.[21] The agreement among results obtained by both methods is very good. Most ω values employed in this work were obtained in our previous works[21,22] from values of σ and ΔH_a that were determined, in most cases, independently. Infrequently, values of ΔH_a were used in order to derive values of ω from the relationships

$$\omega\sigma = \Delta H_a \tag{6}$$

and

$$\omega(\sigma - 7) = \Delta H_a - 70 \tag{7}$$

empirically shown in ref 21 and 22 to describe the relationship between σ and ΔH_a for brittle and ductile polymers, respectively. In eq 6 and 7 the units of σ are given in kg/mm^2, those of ΔH_a in kcal/mol, and those of ω in (mm^2/kg)(kcal/mol). The average volume of chains between entanglements, L_cd^2, and the average volume of Kuhn segments, Ad^2, were calculated, in most instances, from chain cross-sectional areas, d^2, and Kuhn segment lengths, A, listed in Tables II and III, and chain lengths between entanglements, L_c, from ref 25. Values obtained from sources other than ref 19–25 are specifically referenced in Tables I–III. Chain cross-sectional areas not in the literature were obtained by us from crystallographic data and in a few cases by analogy with available data of structurally similar polymers. The obtained d^2 estimates were checked, whenever possible, by the use of the relationship

$$d^2 = M_0/\rho L_0 \tag{8}$$

where M_0 is the weight of an average repeat unit, L_0 is its length, and ρ is the sample bulk density. When two unreferenced values of ω are shown in Table I, they were obtained according to eq 6 and 7 under the respective assumptions of brittle and ductile failure. For ease of identification, the same ordinal numbers used in ref 25 were used to denote the various polymers in the present work. In Table I, polymers experimentally observed (ref 19–22 in the text and references in Table I) to fail in a brittle or ductile manner are designated by "B" or "D", respectively. The mechanical tests were carried out below T_g on amorphous or low-crystallinity polymers.

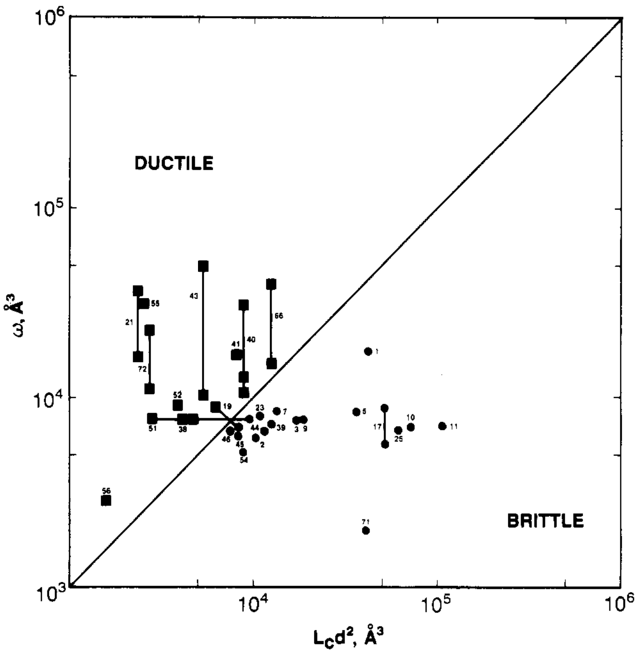

Figure 1. Dependence of polymer ductile and brittle mode of failure on the relationship between ω and L_cd^2: (●) polymers shown experimentally to fail in a brittle manner, and (■) polymers found to fail in ductile fashion. All polymers were amorphous or slightly crystalline and below T_g.

When one measures as a function of the chain length L the mechanical strength of an amorphous or semicrystalline polymer below T_g, one finds that the strength changes over a relatively narrow chain-length interval from essentially no strength at small chain lengths to a nearly constant, chain-length-independent, high strength at large chain lengths. The available experimental data, gleaned from the literature, are presented in Table IV. It seems rather clear that the points where changes in the material strength take place are strongly related to L_c.

Discussion

The data in Table I relate to the mode of polymer failure at temperatures substantially below T_g. From this table one gathers the following: (1) Brittleness or ductility is associated with the relationship between ω and L_cd^2. Substantially below T_g, polymers are brittle when $\omega \ll L_cd^2$ and are ductile when $\omega \gg L_cd^2$. When $\omega \approx L_cd^2$ the polymers are intermediate in their characteristics, semibrittle. (2) There appears to be no correlation between brittleness or ductility and the magnitude of Ad^2 or the ratio of ω to Ad^2. The first observation, graphically shown in Figure 1, is most instructive. It tells us that in the case of brittle polymers, chain lengths of the order of L_c or less are involved in carrying the applied load. In such a case, only about one entanglement is involved in the transmission of stress from one polymeric chain to another. On the other hand, in the case of ductile polymers, chain lengths substantially larger than L_c are involved in the transmission of stress. This means that the stress is being distributed among several entanglements. In the first case, the stress concentrated on a single short chain length can easily surmount the strength of that chain at its weakest point, and bond scission will occur. Such bond scissions result in brittle failure of the polymeric specimen. In the second instance, the stress is distributed along long chain lengths, each involving several entanglements. The local stress is, therefore, distributed among several L_c lengths, none of which is stressed to such a level that bond scission takes place. Under such conditions the deformation of the

Table I[a,c]
Comparison of Activation Volume for Yield with Chain Volume between Entanglements and Kuhn Segment Volume

no.	polymer	mode of failure	ω, Å^3	L_cd^2, Å^3	Ad^2, Å^3	σ, Kg/mm^2	ΔH_a, kcal/mol
1	poly(dimethylsiloxane)	B	18600	42030	445	0.65	17
2	polyethylene[b]	B	6210	10255	225	2.00	17.5
3	polypropylene	B	7610	17310	380	3.45	37
5	polyisobutene	B	8450	36210	433	2.1	25
7	*cis*-polybutadiene	B	8520	13390	157	1.75	21
9	*cis*-polyisoprene	B	7780	18540	246	2.1	23
10	polystyrene	B	6980	72300	1180	8.65	85
11	poly(α-methylstyrene)	B	7100	106300	1770	11.9 (1)	119
17	poly(vinyl acetate)	B	5710 (2)	52065	950	5.35 (2)	43
			8850 (3)			3.45 (3)	
19	poly(vinyl chloride)	D	9000 (4)	6200 (5)	323		
		B	7220	8370		6.00	61
21	poly(acrylonitrile)	D	36575 (6)	2375	509	10.3 (7)	240
			16550 (6)				
23	poly(tetrafluoroethylene)	B	8050	11020	1043	1.5	17
25	poly(methyl methacrylate)	B	6890	62000	1085	10.3	100
38	poly(ethylene terephthalate)	D	7750	4260	222	7.1	77.5
39	poly(ethylene isophthalate)	B	~7100	12400	222		70 (8)
40	poly(carbonate of bisphenol A)	D	9980	8900	908	7.65	109
			12900 (4)				
			30500				
41	poly(1:1 ester carbonate of bisphenol A + terephthalic acid)	D	17100	8780	1020	6.5 (9)	156.5 (10)
43	poly(dimethylphenylene oxide)	D	49700				
			10460	5360	874	7.6	112
44	poly(ether of bisphenol A + diphenyl sulfone)	B	6670	11560	535	7.45	70
45	poly(ϵ-caprolactam)	B	6250	8250	168	5.0	44
46	poly(hexamethyleneadipamide)	B	6910	7660	187	5.75	56
51	cellulose nitrate	B	7770	9600 (5)	13970	6.85	75
		D		4500 (11)			
				2825			
52	cellulose acetate	D	9000	3925	12560	5.05	64
54	cellulose tributyrate	B	5160	8840	15810	5.5	40
55	poly(*p*-phenyleneterephthalamide)	D	31035 (12)	2500	50010		63 (12)
56	poly(*p*-benzamide)	D	2900	1575	80790	10 (13)	41 (14)
66	poly(carbonate of tetramethylbisphenol A)	D	40340				
			15050	12425	1044	9.2 (15)	195 (16)
71	poly(oxymethylene)	B	2030	41000 (17)	253 (18)	7.0	20
72	poly(aromatic ether ether sulfone) (ICI Victrex)	D	22550 (19)				262 (19)
			11200 (20)	2730 (21)		8.25 (15, 22)	130 (20)

[a] B = brittle failure; D = ductile failure; ω = activation volume; L_cd^2 = chain volume between entanglements; Ad^2 = volume of a Kuhn segment; σ = applied stress; ΔH_a = activation energy for long-range chain motion. [b] Intermediate density PE (average value of 10 sources). [c] References are as follows: (1) Breaking stress estimated from the activation energy–stress relationship for brittle polymers in ref 20 in the text. The extreme brittleness of poly(α-methylstyrene) is well-known. (2) Lains, L. A.; Kuvshinsky, Ye. V. *Vysokomol. Soyedin* **1961**, *3*, 215. Not translated in *Polym. Sci. USSR* (*Engl. Transl.*). (3) Blaikie, K. G.; Small, M. S. In "Encyclopedia of Chemical Technology"; Kirk, R. E., Othmer, D. F., Eds.; Interscience: New York, 1955; Vol. 14, pp 691–709. (4) Bauwens, J. C.; Bauwens-Crowet, C.; Homes, G. *J. Polym. Sci. Part A-2* **1969**, *7*, 1745. (5) Porter, R. S.; Johnson, J. F. *Chem. Rev.* **1966**, *66*, 1. (6) The high activation energy places PAN among the ductile polymers, leading to ω = 36575 Å^3. Under an assumption of brittleness, ω = 16550 Å^3. Both values are much larger than L_cd^2. (7) Andrews, R. D.; Miyachi, K.; Doshi, R. S. *Polym. Prep.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1972**, *13* (2), 1168. (8) From T_g = 334 K and rate of change with frequency of measurements, in Aharoni, S. M.; Prevorsek, D. C. *Int. J. Polym. Mater.* **1977**, *6*, 39. (9) Aharoni, S. M. *J. Macromol. Sci., Phys.* **1984**, *B22*, 813. (10) Calculated from T_g = 177 °C according to: Lewis, A. F. *J. Polym. Sci., Part B* **1963**, *1*, 649. (11) Haward, R. N.; Thackray, G. *Proc. R. Soc. London A* **1968**, *302*, 453. (12) Cook, R. *Polym. Commun.* **1984**, *25*, 246. (13) Alfonso, G. C.; Bianchi, E.; Ciferri, A.; Russo, S.; Salaris, F.; Valenti, B. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 213. (14) Vettegren, V. I.; Kusov, A. A.; Korzhavin, L. N.; Frenkel, S. Ya. *Polymer Sci. USSR* (*Eng. Transl.*) **1982**, *24*, 2241. Values appear substantially lower than expected, leading to low values of ω. A more reasonable value should be close to, or the same as that of poly(*p*-phenyleneterephthalamide). (15) Kambour, R. P. *Polym. Commun.* **1983**, *24*, 292. (16) Calculated from T_g = 200 °C according to Lewis, A. F. Reference 10 above. (17) L_cd^2 was estimated from d^2 = 21.50 Å^2 by analogy with PEO, L_c = 1900 Å, l_0 = 1.43 Å, and N_c = 1330. The N_c value was obtained from M_c = 20000. The value of M_c was obtained from analysis of η_{sp}/c vs. M_v curves in: Hohr, L.; Jaacks, V.; Cherdron, H.; Iwabuchi, S.; Kern, W. *Makromol. Chem.* **1967**, *103*, 279. The large N_c value is, however, in agreement with expectations based on the large C_∞ = 10.5 value reported by Stockmayer, W. H.; Chen, L. L. *J. Polym. Sci., Part A-2* **1966**, *4*, 437 and A = 16.45 Å calculated therefrom. (18) A = 11.75 Å from σ = 1.9 (Aharoni, S. M. *J. Appl. Polym. Sci.* **1976**, *20*, 2863.), l_0 = 1.43 Å (Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969; p 159.), $C_\infty = 2\sigma^2 = 7.22$ and $A = (C_\infty + 1)l_0$. d^2 = 21.50 Å^2 by analogy with PEO (ref 25 in text). (19) Calculated from T_g = 230 °C according to Lewis, A. F. Reference 10 above. (20) Our estimate based on trends observed in ref 20 and 21 in the text. (21) From M_c = 1411 (our measurements of Victrex 300P of ICI, MW = 22400 in DMF, C_c = 6.3%), N_c = 73, l_{0a} = 1.211 Å, L_c = 88.4 Å, d^2 = 30.9 Å^2 by analogy with polymers 40 and 41 in this table. (22) ICI Technical Service Note for Victrex 300P.

polymeric specimen is associated with a concerted motion of chain lengths multiply entangled with each other.[21]

It should be remarked that below T_g the volume, ω, of the motional unit according to Table I is of the size inferred in the qualitative theory of Skolnick et al.[16]

When the Kuhn segmental length values of the polymers in Tables II and III are plotted against their d values, one finds that for the 35 polymers categorized as flexible, there exists a linear dependence of the form

$$A \propto d \tag{9}$$

In Figure 2, A is plotted against d^4, but plots of A vs. d^2 and A vs. d produced identical results, naturally. Linear regression analysis of the 35 polymers resulted in r =

Table II[a]
Polymers and Their Characteristic Parameters (Appearing in Ref 25)

no.	polymer	A, Å(1)	d^2, Å^2	A/d	L_c Å
1	poly(dimethylsiloxane)	10.2	43.6 (2)	1.54	964
2	polyethylene	12.3	18.28 (3)	2.88	561
3	polypropylene	11.1	34.27 (3)	1.90	505
4	hydrogenated polyisoprene	12.0	28.5 (4)	2.25	350
5	polyisobutene	10.5	41.24 (3)	1.63	878
6	*cis,trans*-polybutadiene	9.6	19.3 (2)	2.19	485
7	*cis*-polybutadiene	7.6	20.7 (2)	1.67	647
8	1,2-polybutadiene	11.7	49.88 (5)	1.66	234
9	*cis*-polyisoprene	8.8	28.0 (4,6)	1.66	662
10	polystyrene	16.9	69.80 (3)	2.02	1036
11	poly(α-methylstyrene)	17.7	100 (7)	1.77	1063
16	poly(*N*-vinylcarbazole)	26.0	131.02 (8)	2.27	428
17	poly(vinyl acetate)	16.0	59.3 (2)	2.08	878
19	poly(vinyl chloride)	11.9	27.18 (3)	2.28	308
20	poly(acrylic acid)	11.9	45.2 (6)	1.77	200
21	poly(acrylonitrile)	16.5	30.85 (3)	2.97	~77
22	polyacrylamide	24.3	45.2 (9)	3.61	396
23	poly(tetrafluoroethylene)	38.5	27.08 (3)	7.40	407
24	poly(methyl acrylate)	21	59.3 (2)	2.73	862
25	poly(methyl methacrylate)	17	63.84 (3)	2.13	970
26	poly(*n*-butyl methacrylate)	17	93.6 (2)	1.76	1309
27	poly(*n*-hexyl methacrylate)	21	114.2 (2)	1.97	1663
28	poly(*n*-octyl methacrylate)	20	135.1 (2)	1.72	1771
29	poly(*n*-dodecyl methacrylate)	30	176.6 (10)	2.26	2256
30	poly(2-ethylbutyl methacrylate)	15.9	100 (7)	1.59	775
31	poly(ethylene oxide)	7.7	21.50 (3)	1.66	447
32	poly(propylene oxide)	9.1	24.47 (3)	1.84	596
38	poly(ethylene terephthalate)	11.1	20.0 (2)	2.48	213
40	poly(carbonate of bisphenol A)	29.4	30.89 (11)	5.29	288
41	poly(1:1 ester carbonate of bisphenol A + terephthalic acid)	33.0	30.9 (12)	5.94	284
42	poly(2-methyl-6-phenyl-1,4-phenylene oxide)	25.4	56.5 (13)	3.38	99
43	poly(2,6-dimethyl-1,4-phenylene oxide)	24.6	35.52 (14)	4.13	151
44	poly(ether of bisphenol A and diphenyl sulfone)	17.3	30.9 (12)	3.11	374
45	poly(ϵ-caprolactam)	9.4	17.86 (3)	2.22	462
46	poly(hexamethylene-adipamide)	10.6	17.60 (3)	2.53	435
49	polymeric sulfur	5.7	24.33 (10)	1.26	6180
51	nitrocellulose	178	78.5 (15)	20.09	36
52	cellulose acetate	160 ± 40	78.5 (16)	18.06	50
53	(hydroxypropyl)-cellulose	198	128.61 (17)	17.46	34
54	cellulose tributyrate	186	85.0 (16)	20.17	104
55	poly(*p*-phenylene-terephthalamide)	1300	38.47 (18)	209.6	65
57	poly(benzobis-oxazole)	1147	36.6 (19)	185.6	63
59	poly(γ-benzyl L-glutamate)	2400	85.2 (6)	260.0	308
60	poly(*n*-butyl isocyanate)	1000	76.59 (20)	114.4	198
62	xanthan polysaccharide	~7000	400 (21)	350	51

[a] References are as follows: (1) All values of A, together with values of N_c, C_∞, l, and their respective references are tabulated in: Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722. The numerical order of the polymers in this table is identical with their order in the reference. (2) Boyer, R. F., Miller, R. L. *Rubber Chem. Technol.* **1978**, *51*, 718. (3) Privalko, V. P. *Macromolecules* **1980**, *13*, 370. (4) Boyer, R. F., Miller, R. L. *Polymer* **1976**, *17*, 925. (5) Our estimate from data in: Tadokoro, H. "Structure of Crystalline Polymers"; Wiley-Interscience: New York, 1979. (6) Boyer, R. F., Miller, R. L. *Macromolecules* **1977**, *10*, 1167. (7) Our estimate from space-filling molecular models. (8) From crystallographic data of: Crystal, R. G. *Macromolecules* **1971**, *4*, 379. (9) Our estimate from structural similarity to poly(acrylic acid), ref 6. (10) Our estimate from crystallographic data in ref 5 and in: Wunderlich "Macromolecular Physics"; Academic Press: New York, 1973, Volume 1. (11) Calculated by us from: Bonart, R. *Makromol. Chem.* **1966**, *92*, 149. (12) Estimated from chain cross-sectional area of poly(carbonate of bisphenol A). (13) Averaged from: Boon, J.; Magre, E. P. *Makromol. Chem.* **1970**, *136*, 267 and ref 14 below. (14) Calculated from: Horikiri, S. *J. Polym. Sci., Part A-2* **1972**, *10*, 1167. (15) Calculated from Ptitsyn, O. B.; Eisner, Yu. E. *Dok. Phys. Chem. (Engl. Transl.)* **1962**, *142*, 28. (16) Estimated from nitrocellulose. (17) Calculated from: Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1980**, *13*, 69. (18) From data of: Vitovskaya, M. G.; Lavrenko, P. N.; Okatova, O. V.; Astapenko, E. P.; Novakovsky, V. B.; Bushin, S. V.; Tsvetkov, V. N. *Eur. Polym. J.* **1982**, *18*, 583. (19) Estimated from crystallographic data of model compounds in: Wellman, M. W.; Adams, W. W.; Wolff, R. A.; Dudis, D. S.; Wiff, D. R.; Fratini, A. V. *Macromolecules* **1981**, *14*, 935. (20) Calculated from crystallographic data in: Shmueli, U.; Traub, W.; Rosenheck, K. *J. Polym. Sci., Part A-2* **1969**, *7*, 515. (21) From estimates by: Southwick, G. J.; Jamieson, A. M.; Blackwell, J. *Macromolecules* **1981**, *14*, 1728.

0.8275, a rather good correlation considering the diversity of flexible polymers, the fact that polymeric sulfur (49) and selenium (70) were included in the sample population, and the large number of independent data sources. Interestingly, all 15 data points of the polymers considered by Graessley and Edwards,[31] indicated by encircled dots, fall nicely around the line $A \propto d$, with 13 of them within one standard deviation from this line. The polymers in the semiflexible group are characterized by their high ductility at temperatures far below T_g and include the high-T_g, highly impact-resistant "engineering thermoplastics". These polymers have essentially the same chain cross-sectional area, d^2, as the flexible polymers along the line right under the semiflexible region, yet the flexible polymers are brittle in the glassy state at temperatures relatively close to T_g. Therefore, we must conclude that the brittle or ductile *mode of failure* is not dependent on d alone or, at most, is very weakly dependent on d. This is unlike the brittle or ductile *strength* below T_g, shown by Vincent[32] to be inversely dependent on d^2. An attempted correlation between the mode of failure and the presence of a relaxation below T_g was shown by Heijboer[33] to be riddled with inconsistencies.

In ref 25 it was shown that for a large number of flexible polymers

$$L_c \propto A^2 \tag{10a}$$

and

$$N_c \propto A^2 \tag{10b}$$

Combining proportionalities 9 and 10, one obtains

$$L_c \propto A^2 \propto d^2 \tag{11a}$$

and

$$N_c \propto A^2 \propto d^2 \tag{11b}$$

which indicates that in the case of flexible polymers the mode of failure may depend on any of the parameters $L_c(N_c)$, A, and d. The exact dependence of the mode of failure on any of the three chain parameters and its independence from other parameters are not known to us at present. Nevertheless, the apparent independence of the mode of failure from d in the above comparison of semiflexible and flexible polymers leads us to believe that

Table III[a]
Polymers and Their Characteristic Parameters (Not Appearing in Ref 25)

no.	polymer	C_∞	A, Å	d^2, Å^2	A/d	N_c	L_c, Å
63	poly(ethyl acrylate)	8.82 (1)	15.12	73 (2, 3)	1.77	625	960
64	poly(butyl acrylate)	9.00 (4)	15.40	94.08 (2)	1.59	460	705
65	poly(ethylhexyl acrylate)	9.15 (4)	15.63	115 (3)	1.46	315	485
66	poly(carbonate of tetramethyl bisphenol A)		29.4 (5)	35.5 (6)	4.93	280 (7)	350
67	poly(ester carbonate of 1 terephthalic acid + 2 tetramethyl bisphenol A)		33 (5)	35.5 (6)	5.54	320 (8)	315 (8)
68	poly(ester of bisphenol A + 4,4′-benzophenone dicarboxylic acid)	3.5 (9)	38.9 (9)	30.9 (6)	7.00	138 (8)	134 (8)
69	poly(ethylene tetrasulfide)	3.5 (10)	8.55 (10)	42.85 (2)	1.31	767 (11)	1457
70	polymeric amorphous selenium	1.015 (12)	4.715	18.97 (13)	1.08	447	1045

[a] Values of l_0 can be obtained by the division of L_c by N_c. References are as follows: (1) Using $A = l_0 (C_\infty + 1)$ and $C_\infty = 2\sigma^2$. Data of: Birshtein, T. M.; Ptitsyn, O. B. "Conformations of Macromolecules"; Interscience: New York, 1966; pp 15, 189. (2) From crystallographic data assembled by: Miller, R. L. In "Polymer Handbook, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; pp III-1–III-50. (3) Estimated from d^2 progression in methacrylate series and from data in: Privalko, V. P. *Macromolecules* **1980**, *13*, 370. (4) Estimated by analogy to the methacrylate series in Table II from data in: Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722; Kurata, M.; Tsunashima, Y.; Iwama, M.; Kamada, K. In "Polymer Handbook, 2nd ed.; (see ref 2) pp IV-1–IV-60. (5) Estimated by analogy to polymers no. 40 and 41 in Table II. (6) Estimated by analogy to polymers no. 40 and 41 in Table II and chain cross-sectional area of poly(2,6-dimethyl-1,4-phenylene oxide) in ref 39 of Table II. (7) Calculated from plateau modulus, density, and structure given by: Wisniewsky, C.; Marin, G.; Monge, P. *Eur. Polym. J.* **1984**, *20*, 691. (8) Prevorsek, D. C.; DeBona, B. T. Allied Corp., Morristown, NJ, Dec 1982, Research Report 82-42. (9) A characteristic ratio of 3.5 was estimated from structure and hindered rotation about the aromatic carbonyl and aromatic oxygen bonds. A virtual bond of 8.65 Å, similar to poly(carbonate of bisphenol A), was assumed. (10) Calculated by assuming weighted amounts of C–C and S–S bonds from characteristic ratios of polyethylene and polymeric sulfur. Value is expected to be lower than $C_\infty = 4.2$ for poly(ethylene sulfide). See: Abe, A. *Macromolecules* **1980**, *13*, 541, 546. (11) Tobolsky, A. V.; MacKnight, W. J. "Polymeric Sulfur and Related Polymers"; Interscience: New York, 1965; pp 24–26, 46–49, 117–123. Density of amorphous selenium is 4.26 g/cm^3, acrylates estimated to be 1.2 g/cm^3. (12) Estimated from data in: Semlyen, J. A. *Trans. Faraday Soc.* **1967**, *63*, 743, using characteristic ratios of sulfur and selenium octamers and linear amorphous sulfur. Also see: Mark, J. E.; Curro, J. G. *J. Chem. Phys.* **1984**, *80*, 5262. (13) Wunderlich, B. "Macromolecular Physics"; Academic Press: New York, 1973; Vol. 1, pp 96–100. Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969, pp 157–159.

Table IV
Chain Lengths at Which Bulk Mechanical Properties Change[a,c]

polymer	length at zero tensile strength, Å	length at maximum strength,[b] Å	L_c, Å	A/d
polyethylene	780–850 (1) 1205 (2)	2130–6030 (3) 3550 (2)	461	2.88
polypropylene		1430–2380 (3)	505	1.90
polystyrene	960–1385 (1)	1540 (2) 2300–3080 (3)	1036	2.02
poly(methyl methacrylate)	420–460 (1) 500 (2)	1800 (2) 1300 (3) 2000 (4)	970	2.13
poly(oxymethylene)		≤5330 (3)	1900 (5)	2.53
poly(ethylene terephthalate)	470–520 (6)	1300 (6)	213	2.48
poly(ϵ-caprolactam)	~155 (7)	~700 (7) 540–910 (8)	462	2.22
poly(carbonate of bisphenol A)	235 (6)	610–660 (3)	288	5.29
poly(1:1 ester carbonate of bisphenol A + terephthalic acid)	353 (6)	1565 (6)	284 (9)	5.94
poly(ether of bisphenol A + diphenyl sulfone)		900 (10)	374	3.11
cellulose acetate	390 (1)	880–1470 (3)	50	18.06
cellulose nitrate		780–940 (3)	36	20.09
poly(*p*-benzamide)	460 (11)	≥1090 (11)	41	338.7
poly(*p*-phenyleneterephthalamide)	460 (12)	≥1090 (12)	65	209.6

[a] Lengths converted from molecular weight values in cited references. [b] Maximum strength values were obtained from measurements of tensile strength, elongation, yield point, and brittle point, as a function of molecular weight. Maximum strength is defined as the region where the mechanical properties below T_g become insensitive to changes in MW. Zero strength is defined as the point where the mechanical properties increase from negligible values over a rather narrow change in molecular weight. [c] References are as follows: (1) Turner, D. T. *Polymer* **1982**, *23*, 626. (2) Vincent, P. I. *Polymer* **1960**, *1*, 425. (3) Martin, J. R.; Johnson, J. F.; Cooper, A. R. *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C8*, 57 and references therein. (4) Prentice, P. *Polymer* **1983**, *24*, 344. (5) See ref 17 for Table I above. (6) Aharoni, S. M., unpublished observations. (7) Mark, H. F. *Am. Sci.* **1967**, *55*, 265. (8) Bartenev, G. M.; Zuyev, Yu. S. "Strength and Failure of Viscoelastic Materials"; Pergamon: Oxford, 1968; pp 125–160. (9) Aharoni, S. M. *J. Macromol. Sci., Phys.* **1983**, *B22*, 813. (10) Estimated from $M_w = 20000$ and $M_n = 10000$ data of: Mills, N. J. *Rheol. Acta* **1974**, *13*, 185. (11) Estimated from strength of fibers "as spun" from isotropic solutions and from their molecular weight dependence. Data extracted from: Alfonso, G. C.; Bianchi, E.; Ciferri, A.; Russo, S.; Salaris, F.; Valenti, B. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 213. (12) Values estimated from similarity of mechanical behavior of unannealed fibers to similar fibers made of poly(*p*-benzamide).

the mode of failure is more dependent on L_c and on A (a reflection of chain rigidity) than on d.

Unlike the data in Table I, the data in Table IV relate to the strength of polymers and not to their mode of failure. The data in Table IV are not as many as those in Table I. Even so, some points can tentatively be made: (1) Flexible and semiflexible polymers start developing strength at chain lengths comparable to L_c. These polymers reach their ultimate strength at chain lengths 2–4 times the length of L_c. (2) Semirigid and rigid polymers, in an isotropic bulk, develop strength at about 5–10 times L_c. Both families reach ultimate strength at about $20L_c$. A graphic description of these observations is presented in Figure 3.

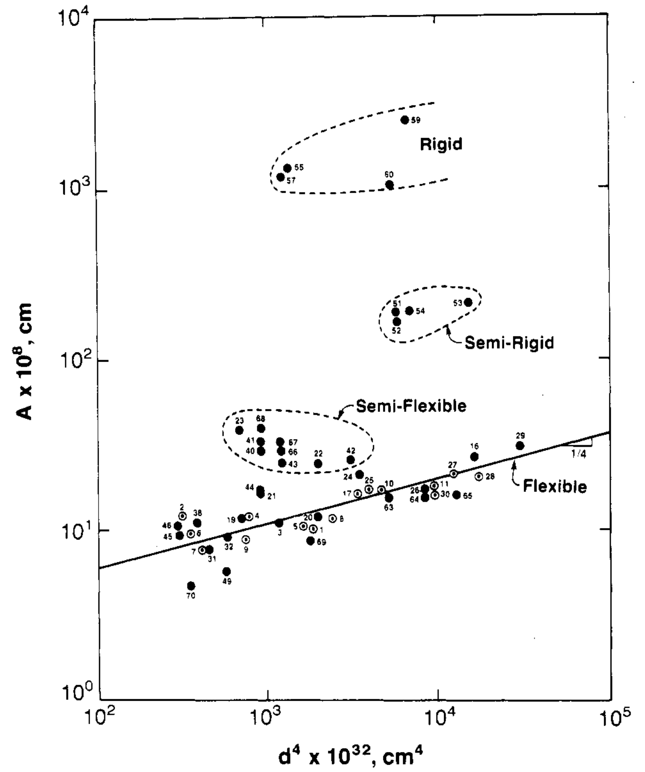

Figure 2. Relationship between A and d for polymers of varying flexibility.

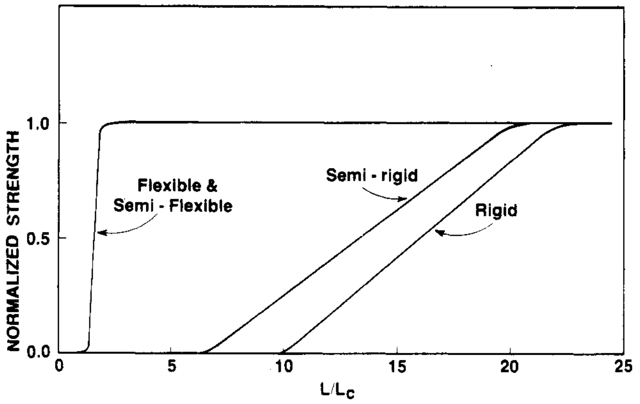

Figure 3. Normalized strength below T_g vs. chain length in L_c units.

It is well-known that for polymeric melts above T_g or the melting point but below the region of spontaneous flow the plateau modulus $G_N{}^\circ$ is inversely dependent on the length, L_c or L_e, or molecular weight, M_c or M_e, between the entanglements of polymeric chains. The correlations of the mode of failure or of the ultimate strength below T_g with L_c, observed in this paper, appear to indicate that the molecular configurations of polymeric chains in the melt remain essentially unchanged in the frozen glass and, most likely, in the isotropic amorphous phase of semicrystalline polymers below T_g. The chain entanglements, which are relatively transitory above T_g, are frozen in and rendered more permanent below T_g. Under these conditions the entanglements cannot unravel within the time spans of most common mechanical experiments and as a consequence become the loci of stress transmission from one chain to the other once the specimen experiences stress. Mechanical experiments that are very long in nature, such as slow crack growth, creep deformation, and fatigue crack propagation, are expected, therefore, to show a dependence on the total length of the polymeric chain, much more so than on the length L_c alone. This, indeed, was found to be the case.[34,35]

Finally, we recall the γ is relatively small and rather constant. The value of U_0 is also about constant within given families of polymers. From the T_g and ΔH_a data tabulated in ref 21, we observe that within each such family, i.e., polyolefins, polyacrylates, etc., the value of ΔH_a increases with T_g. This means that in eq 5, for a given value of σ, the magnitude of ω will increase with the T_g of the polymer. That is, with increased T_g the polymer will show stronger and stronger tendency toward ductile behavior.

Conclusions

It is shown that the mode of failure of polymers below T_g depends on the relationship between the chain volume between entanglements, L_cd^2, and the activation volume for the glass transition, ω. When L_cd^2 is larger than ω the failure is brittle, and when L_cd^2 is smaller than ω the failure is ductile. Depending on backbone flexibility, the onset of polymeric strength occurs at chain lengths of only a few L_c and the attainment of maximum strength occurs at only slightly longer chains. The evident strong dependency of these mechanical properties on L_c apparently indicates that entanglements frozen in the system below T_g play a major role in the distribution of stress throughout the bulk polymer. The connection between the mode of failure and ω seems to indicate that when stress is applied to polymeric specimens below T_g, chain movements take place over distances encountered around T_g in the absence of applied stress, even in polymers that fail in a brittle fashion.

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Registry No. Polyethylene (homopolymer), 9002-88-4; polypropylene (homopolymer), 9003-07-0; polyisobutene (homopolymer), 9003-27-4; polybutadiene (homopolymer), 9003-17-2; polyisoprene (homopolymer), 9003-31-0; polystyrene (homopolymer), 9003-53-6; poly(α-methylstyrene) (homopolymer), 25014-31-7; poly(vinyl acetate) (homopolymer), 9003-20-7; poly(vinyl chloride) (homopolymer), 9002-86-2; poly(acrylonitrile) (homopolymer), 25014-41-9; poly(tetrafluoroethylene) (homopolymer), 9002-84-0; poly(methyl methacrylate) (homopolymer), 9011-14-7; poly(ethylene terephthalate) (SRU), 25038-59-9; poly(ethylene isophthalate) (SRU), 26948-62-9; (isophthalic acid)·(ethylene glycol) (copolymer), 26810-06-0; poly(carbonate of bisphenol A) (SRU), 24936-68-3; (bisphenol A)·(carbonic acid) (copolymer), 25037-45-0; (bisphenol A)·(terephthalic acid)·(carbonic acid) (copolymer), 31133-78-5; poly(2,6-dimethylphenylene oxide) (SRU), 24938-67-8; poly(2,6-dimethylphenol) (homopolymer), 25134-01-4; poly(ether of bisphenol A + diphenyl sulfone) (SRU), 25135-51-7; poly (ϵ-caprolactam) (SRU), 25038-54-4; poly (hexamethyleneadipamide) (SRU), 32131-17-2; cellulose nitrate, 9004-70-0; cellulose acetate, 9004-35-7; cellulose tributyrate, 39320-16-6; poly(p-phenyleneterephthalamide) (SRU), 24938-64-5; (terephthalic acid)·(p-phenylenediamine) (copolymer), 25035-37-4; poly(p-benzamide) (SRU), 24991-08-0; poly(p-aminobenzoic acid) (homopolymer), 25136-77-0; poly(carbonate of tetramethylbisphenol A), 38797-88-5; (tetramethylbisphenol A)·(carbonic acid) (copolymer), 52684-16-9; Victrex 100P, 25667-42-9.

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Effects of Polydispersity on the Linear Viscoelastic Properties of Entangled Polymers. 1. Experimental Observations for Binary Mixtures of Linear Polybutadiene

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ABSTRACT: Viscoelastic effects of polydispersity for linear polymers in the entanglement regime were studied with binary mixtures of nearly monodisperse polybutadiene. Five series of mixtures (7–10 compositions in each) were investigated for component molecular weight ratios, $R = M_L/M_S$, from 2.5 to 10.7. Storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, were measured for each composition over a wide range of frequencies at several temperatures and reduced to master curves at 25 °C. Viscosity η_0 and recoverable compliance J_e° were obtained and compared with a variety of proposed mixing laws. The peaks in $G''(\omega)$ were used to estimate relaxation times and weighting factors for the individual component contributions. The compositional dependence of these quantities was in fairly good agreement with the tube model and constraint lifetime ideas applied to mixtures.

Introduction

The viscoelastic properties of polymer melts and solutions are strongly influenced by molecular weight distribution. In dilute solutions the effect of polydispersity is straightforward. If the chains do not interact, the polymeric contribution to stress is obtained by simple addition. In concentrated solutions and melts the chains overlap extensively; if they are long enough the behavior is dominated by entanglement interactions. How polydispersity affects linear viscoelastic behavior in such strongly interacting systems is a subject of longstanding interest.[2]

The shear stress relaxation modulus $G(t)$ contains all information on the linear viscoelastic behavior of a liquid and is a convenient property for discussion purposes. The dynamic shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ is more commonly measured and is related to $G(t)$ by Fourier transformation:

$$G^*(\omega) = i\omega \int_0^\infty G(t) \exp(-i\omega t)\, \mathrm{d}t \tag{1}$$

The values of steady-state viscosity at zero shear rate η_0 and steady-state recoverable shear compliance J_e° can be obtained from the moments of $G(t)$ or from the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ at low frequencies:

$$\eta_0 = \int_0^\infty G(t)\, \mathrm{d}t = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{2}$$

$$J_e^\circ = \frac{1}{{\eta_0}^2} \int_0^\infty tG(t)\, \mathrm{d}t = \lim_{\omega \to 0} \frac{G'(\omega)}{|G^*(\omega)|^2} \tag{3}$$

The relaxation spectrum $H(\tau)$ is an equivalent expression of linear response which can be derived from data on $G(t)$ or $G^*(\omega)$ by an integral inversion, e.g.

$$G^*(\omega) = \int_{-\infty}^{\infty} \frac{i\omega\tau}{1 + i\omega\tau} H(\tau)\, \mathrm{d} \ln \tau \tag{4}$$

Extensive measurements have been made on highly entangled systems of nearly monodispersed linear chains. The response at long times or low frequencies is found to assume a universal form.[2-4] Thus, in the plateau and terminal regions

$$G(t) = G_N^\circ U(t/\tau_0) \tag{5}$$

where $U(t/\tau_0)$ is a universal function, normalized to give $U(0) = 1$, G_N° is the plateau modulus, and τ_0 is a characteristic time:

$$\tau_0 = \eta_0 J_e^\circ \tag{6}$$

The terminal spectrum is quite narrow, and this, together with its large separation from the transition region for long chains ($M \gg M_e$), results in a prominent and well-defined peak in the loss modulus, G_m'' at ω_m, and a rapid approach of $G'(\omega)$ to G_N° beyond ω_m. The dimensionless products

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