Ductile and Brittle Behavior of Amorphous Polymers. Relationship with Activation Energy for Glass Transition and Mechanical Fracture

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Synopsis

An equation correlating the activation energy for the glass transition with T_R, a characteristic reference temperature, the fractional free volume, and the rate of change of the fractional free volume was developed. The resultant activation energies for about 30 polymers are given and favorably compare with the literature. The relationship between the activation energy and the bond-rupture energy indicates whether a polymer will fail in a ductile or brittle fashion. More accurate results are shown to be dependent on the stress, the stress concentration, molecular orientation, frequency of load application, and temperature. Equations correlating all these with the activation energies are given. These results are in agreement with the molecular domain model. Experimental observations from the literature seem to corroborate the suggestion that the molecular domain model holds in the amorphous solid, too.

DISCUSSION

A model was recently proposed[1,2] suggesting that linear, amorphous, uncrosslinked polymers exist in the glass, melt, or solution in a molecular domain form. Here the molecule is a spheroid having an internal uniform segmental density. On the "surface" of such domains, loops and strands exist and interact with the surfaces of other domains. These interactions are of both permanent and transitory nature; both affect the mechanical properties of the solid. The flow properties of the polymer are affected practically solely by the transitory interactions.

Segmental mobility dictates whether a polymer will be brittle or ductile. If the temperature of a polymer is sufficiently low to freeze out segmental mobility, or if the applied tension is so rapid that there is insufficient time for molecular motion and relaxation to take place, then the polymer will be brittle. If the temperature is high enough or the stress application is slow enough, molecular motion will take place within the time scale of the experiment and the material will be ductile.

Due to their relative segmental immobility, brittle polymers strain only slightly and fracture before they reach a yield point. That is, disengagement of transitory interdomain interactions and rupture of permanent

bonds take place soon after tension is applied, leading to a catastrophic bond rupture and fracture. When a ductile polymer is loaded, energy can dissipate by segmental motion, making the bond rupture much more gradual. Before catastrophic failure can take place, the stresses within the sample begin to shear molecular domains and stretch them in the strain direction. The shearing and stretching of the now deformable domains removes part of the stress and decreases the rate of segmental rupture in the sample. When the deformation of whole molecular domains becomes the dominant mechanism of strain, then we have reached the yield point in a stress–strain curve. This domain shearing process is manifested by the necking of the sample.[3,4]

Upon continuous loading, the sample will strain until it will finally break at a point having too few segments to bear the load without rupture. If the polymeric segments from the domains are highly oriented beyond the yield point, they might undergo strain crystallization, and higher stresses would be required to reach a given strain rate than when the orientation is poorer and crystallization absent. When the strain rate is too fast for segmental reorientation, the sample will fracture at much smaller strains than under lower strain rates; the faster the load application, the more brittle the polymer is at a fixed temperature.

Low-frequency experiments at room temperature show some polymers to be brittle and some ductile. The difference in behavior is directly linked to two activation energies: ΔH_a, the activation energy for the glass transition, and U_0, the activation energy for mechanical fracture as extrapolated to zero load.

Neglecting effects that will be dealt with later such as stress, temperature, etc., it was found that when $\Delta H_a > U_0$, the polymer is brittle; and $U_0 > \Delta H_a$, then the polymer is ductile. ΔH_a is a function of T_R and an inverse function of $\Delta\alpha \cdot \Delta T$ and $d\Delta\alpha \cdot \Delta T/dT$:

$$\Delta H_a = RT_R{}^2\tau_R/(\Delta\alpha \cdot \Delta T)(d\Delta\alpha \cdot \Delta T/dT) \qquad (1)$$

where T_R is a reference temperature characteristic of each polymer,[5–14] $\Delta\alpha \cdot \Delta T$ is the fractional free volume (FFV) at $T_g, d\Delta\alpha \cdot \Delta T/dT$ is the rate of change of FFV with temperature, R is the gas constant, and τ_R is a dimensionless constant of about 10^{-6}, probably approximating the relaxation time in seconds of long molecular segments.

T_R can be obtained by the use of the following equation[13,14]:

$$0.113 = (\alpha_L - \alpha_G)(T_R - T_g)/(T_R/T_g - 1)^{1/3} \qquad (2)$$

and then

$$\text{FFV} = \Delta\alpha \cdot \Delta T = (\alpha_L - \alpha_G)(T_R - T_g) \qquad (3)$$

Hence, a knowledge of $\Delta\alpha$ and T_g combined with the knowledge of $d\Delta\alpha \cdot \Delta T/dT$ is sufficient to solve eqs. (1), (2), and (3).

Table I presents the values of ΔH_a calculated by means of eq. (1) for close to 30 polymers and the corresponding values of ΔH_a obtained from the lit-

erature.   One should note the large variations in ΔH_a values found in the literature for given polymers.   The values of $\Delta\alpha \cdot \Delta T$ are also given in the table, and the values of $d\Delta\alpha \cdot \Delta T/dT$ are the slopes of the straight lines in Figure 1, in which $\Delta\alpha \cdot \Delta T$ values for all the polymers are plotted against $\Delta T - T_g (= T_R - 2T_g)$.   The low experimental activation energy, if accurate, for the higher polyalkylmethacrylates probably reflects the plasticizing effects of the large pendant groups.   Such effects will not be considered in this work.
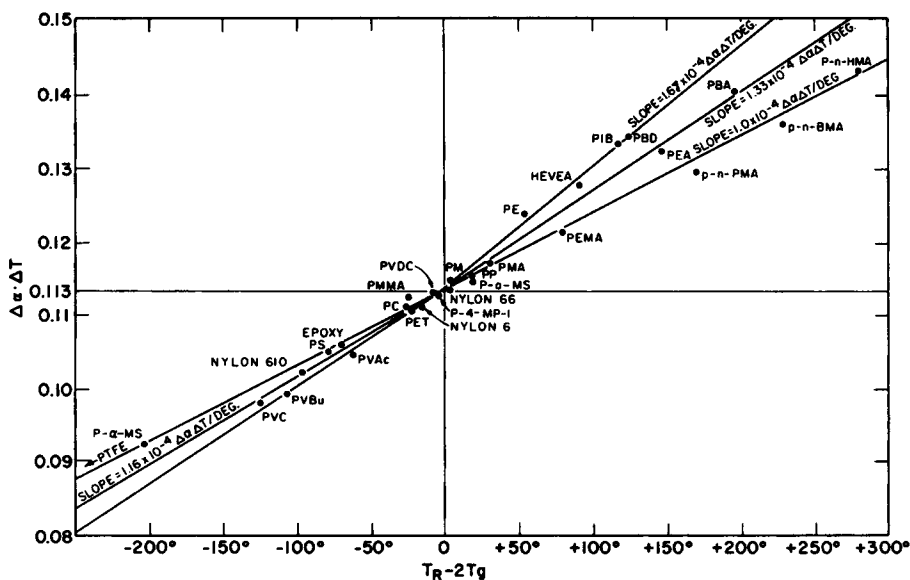

Fig. 1. Rate of change of fractional free volume with temperature.

Equation (1) indicates that the higher T_R, the larger is the activation energy for the transition at T_g.   This is counteracted by two other factors: the larger the FFV at T_g and the faster it changes with temperature, the easier it is for the molecular segments to move and relax and the lower the activation energy required for the same transition.   Hence, the ease of transition is inversely dependent not only on the magnitude of FFV but also on the rate at which the FFV changes with temperature.   This rate of change seems to be inversely related to T_R.   While T_R increases with molecular cross section or chain rigidity, the rate of change of FFV decreases with an increase in these properties and becomes larger with smaller cross section and enhanced flexibility.

Table II presents activation energy data for the processes of mechanical fracture and thermal degradation.   It is obvious that the activation energies for the two processes are the same for any given polymer.   It is also most likely that the mechanisms involved are not purely those of

TABLE I. Activation Energy for Glass Transition[a]

Polymer	T_g	T_R	ΔT	$\Delta\alpha \times 10^4$	$\Delta\alpha \cdot \Delta T$	$\dfrac{d\Delta\alpha \cdot \Delta T}{dT} \times 10^4$	ΔH_a, kcal/mole	Literature values
1. Polystyrene	373	668	295	3.565	0.105	1.00	84.3	101[16], 129[17], 86[18], 79[19,20]
2. Poly(α-methylstyrene)	445	688	243	3.80	0.0925	1.00	101.0	
3. Poly(ortho-methylstyrene)	403	825	422	2.71	0.114	1.00	118.5	
4. Polyethylene	188	430	242	5.10	0.1235	1.67	17.8	18[16], 44[17], 25[21], 28[22], 60[23]
5. Polymethylene	180	365	185	6.20	0.1145	1.67	13.8	
6. Polypropylene	256	532	276	4.18	0.115	1.33	36.7	28[16], 42[17]
7. Polyisobutylene	200	520	320	4.175	0.1335	1.67	24.0	33[16], 16[17]
8. Polybutadiene	180	485	305	4.40	0.134	1.67	20.7	30[16], 16[17], 14.4–16.1[24]
9. Natural (Hevea) rubber	201	486	285	4.48	0.1275	1.67	22.0	30[16], 16[17], 13–14.2[24]
10. Poly(4-methylpentene-1)	302	600	298	3.78	0.112	1.33/1.67	47.9/38.2	
11. Poly(methyl acrylate)	275	584	306	3.80	0.1165	1.33/1.67	43.5/34.8	35[16], 32[17], 57[25]
12. Poly(ethyl acrylate)	251	650	399	3.30	0.132	1.33	47.6	
13. Poly(butyl acrylate)	217	630	413	3.40	0.1405	1.33	42.0	
14. Poly(methyl methacrylate)	378	755	357	3.15	0.112	1.00	101.0	100[16], 121[17], 100[26]
15. Poly(ethyl methacrylate)	338	758	420	2.88	0.121	1.00	94.2	57[17], 92[26]
16. Poly(n-propyl methacrylate)	308	790	482	2.65	0.128	1.00	96.5	49[25]
17. Poly(n-butyl methacrylate)	300	830	530	2.58	0.136	1.00	98.5	33[17], 39[26]
18. Poly(n-hexyl methacrylate)	268	818	550	2.60	0.143	1.00	92.1	27[17]
19. Poly(vinyl butyral)	323	540	217	4.56	0.099	1.33	43.8	
20. Poly(vinyl acetate)	305	549	244	4.30	0.1045	1.33	43.0	44[16], 37[17], 60[27]
21. Poly(vinyl chloride)	357	590	233	4.19	0.098	1.16	60.6	70[16], 68[17], 77[28], 85[29]
22. Poly(vinylidene chloride)	256	506	250	4.50	0.1125	1.16	38.8	
23. Nylon 6	290	565	275	4.04	0.111	1.33	42.9	62[30], 48[31]
24. Nylon 66	323	649	326	3.46	0.113	1.33	55.4	35[16], 60[17], 62[30]
25. Nylon 610	323	560	237	4.30	0.102	1.16	52.5	
26. Poly(ethylene terephthalate)	340	658	318	3.48	0.1105	1.00	77.5	67[17], 65[30], 100[32]
27. Epoxy	405	740	335	3.16	0.106	1.00	102.3	43–326[17]
28. Poly(tetrafluoroethylene)	400	503	103	7.00	0.072	1.00	69.5	
29. Polycarbonate (bisphenol A)[b]	420	817	397	2.79	0.111	1.00	119.0	115[16], 333[17]

[a] Sources for T_g and $\Delta\alpha$ values are given in Appendix I of ref. 13.

[b] T_g and $\Delta\alpha$ values for polycarbonate were averaged from values in ref.15.

TABLE II
Activation Energies for Mechanical Failure and Thermal Degradation

Polymer	Mechanical failure U_0, kcal/mole		Thermal degradation E, kcal/mole		References
	U_{02}	U_{01}	E_1	E_2	
1. Polystyrene	30–35	54–55	30–35	50–56	33–37
2. Poly(α-methylstyrene)			37	65	37, 38, p. 66
3. Polyethylene	25	60–70	25	60–76	37, 38, p. 112, 39
4. Polypropylene	29	55–56	26	55–58	36, 37, 39
5. Polyisobutylene				49	38, p. 124
6. Polybutadiene				62	38, p. 207
7. Rubber, natural				54–63	38, p. 219–225
8. Poly(methyl acrylate)				34	38, p. 192
9. Poly(methyl methacrylate)	31–34	54–55, 130	30, 35	50–53	35–37, 40, 41, 38, pp. 23, 187
10. Poly(vinyl chloride)	35–36	55	32–39	38–51	36, 39, 42, 43
11. Poly(vinylidene chloride)				36	39
12. Nylon 6		45	43		36
13. Nylon 66		42	42–52		39
14. Nylon 610			42		39
15. Poly(ethylene terephthalate)			62.5–69		39
16. Poly(tetrafluoroethylene)		70–75	76–80		36, 39, 38, p. 171

cleavage of primary chemical bonds but can involve secondary interactions, especially in the light of the recent studies[44,45] connecting polymer moduli with Lennard-Jones-type of segmental interactions. Comparison of the data in Tables I and II reveals that the fracture of a polymer can proceed by two mechanisms. Under equivalent conditions, when the ΔH_a is higher than U_0, as is the case with polystyrene (PS) or poly(methyl methacrylate) (PMMA) at room temperature, then the fracture proceeds by severing segmental interactions with almost no domain deformation, shearing, or long-range segmental motion. When ΔH_a is lower than U_0, then the fracture proceeds by a ductile flow of deformed and sheared domains and subsequent rupture, as is the case with polyethylene (PE), polypropylene (PP), and nylon 6, at room temperature.

In some instances such as PS, PMMA, and poly(vinyl chloride) (PVC), there exist two activation energies for mechanical fracture and thermal degradation.[33–35,37,39,41,43 pp. 23,187]. These are in the ranges of 30–35 kcal/mole and 50–55 kcal/mole. Because of the similarity of these values to the activation energy for melt flow of these polymers below and above a melt transition point $T_{l,l}$,[9,16,46–49] these activation energies can probably be associated with two distinct mechanisms: the lower energy at lower melt temperature is connected with disengagements of interdomain transitory and permanent interactions, while the higher energy at higher melt temperature is connected with deforming and shearing whole domains and rupture of intradomain segments. The difference in the activation energies is probably due to the intradomain segments being forced out of one meta-

stable energy level and into another with the concomitant rupture of bonds, while the interdomain disengagement consisted mostly of the elimination of transitory interactions. Also, there is a significantly higher free energy associated with the bulk domain segments than with the domain's surface segments.[2]

The transition from brittle to ductile failure is frequency and temperature dependent. There are, therefore, four parameters governing the brittle-ductile transition: ΔH_a, U_0, frequency, and temperature. In the brittle state, these parameters are correlatable through the phenomenological equation of "time to fracture," proposed by Tobolsky and Eyring[50] and developed by Bueche,[51] Robertson,[4] and Kramer,[52,53] and especially by Zhurkov and co-workers,[36,42,54-60] Ivanov,[6,61] and Slonimskii and Askadskii[62-64]:

$$\ln\tau = \ln\tau_0 + (U_0 - \gamma\sigma)/RT \tag{4}$$

In the ductile state, an equation giving the time to yield and the onset of necking is

$$\ln\tau_r = \ln\tau_{0r} + (\Delta H_a - III\sigma)/RT \tag{5}$$

where τ and τ_r are the lifetime and yield time; τ_0 and τ_{0r} are material constants of the same magnitude, about 10^{-12} to 10^{-13} sec; ΔH_a and U_0 are activation energies for the glass transition and for mechanical bond rupture, respectively; σ is the stress; γ and III are "stress concentration coefficients"; R is the gas constant; and T is the temperature at which the stress is applied. The coefficient γ was shown[6,59,60,65] to be orientation and temperature dependent. We believe that the coefficient III, in addition to being orientation and temperature dependent, is also dependent on the frequency · of the load application. The shorter the load cycle, the lesser the ability of molecular segments to relax and dissipate stress. This frequency dependence is probably a weak one, but nevertheless we believe it exists. It is because of this added dependence that we chose to replace γ by III.

A comparison of eqs. (4) and (5) tells us what type of fracture is to be expected from a given polymer. When $\tau > \tau_r$, yield and ductile flow will precede the fracture; and when $\tau_r > \tau$, the failure will be brittle. These equations, therefore, introduce stress, temperature, orientation, and frequency dependence to our initial and simpler relationship between activation energies and brittle-ductile fracture. Equations (4) and (5) not only predict the type of fracture but also explain, at least macroscopically, the ductile behavior of certain polymers[63,66] below their T_g. Without the perturbations of these two equations on the simple relationship between ΔH_a and U_0, no plausible explanation is known to us.

The parameter γ is a measure of the relationship between the bulk stress and the stress at a given unit volume within the sample. This unit volume is of atomic scale and is considered to be a fixed unit.[67,68] We believe that this volume should be variable since under ductile flow there is a

higher probability that a weak bond within a segment will enter such a unit volume and will break. Under brittle conditions, such a probability is much smaller. Unlike the frequency and volume independence of γ, the frequency dependence of III is linked with its volume dependence through the change in segmental mobility upon changing from brittle to ductile conditions.

The above macroscopic description is in agreement with the molecular domain model.[1,2] Accordingly, the load bearing parts of the molecules are mostly the interdomain segments. These can be classified under two headings: (1) segments forming transitory interactions such as loop–loop, loop–strand, and strand–strand interactions, and (2) segments forming permanent bonds or interactions. The separation between transient and permanent interactions is frequency and temperature dependent.[17] An interdomain segmental interaction that is disengageable within the time scale of the experiment is of transitory nature, while an interaction that is not disengageable within such a period is of permanent character. With cooling, and especially under the low mobility conditions below T_g, disengagement becomes slower and slower. Hence, the ratio of the permanent to the transitory interactions increases with the frequency of the applied load and with the decrease in temperature. In the melt or solution, the high segmental mobility makes almost all the interdomain interactions transitory ones.

Upon straining a solid, the stress will be a direct function of all the effective interdomain segments. The transitory ones will resist the strain but will gradually disengage. The permanent ones will first stretch taut and pull parts of segments from within the domains but will ultimately rupture. Hence, upon subjecting a sample to a constant strain, it will show an immediate stress developing in it which is a function of all effective interdomain segments. Segmental rupture will take place only later and from a slow start will accelerate over a small strain into a catastrophic rupture and failure. Under a constant stress rate the behavior should be about the same. When constant stress creep (and not constant stress rate) is applied, a constant strain and a constant segmental rupture should take place. In cyclic stress loading, under small loads, the transitory interactions will disengage first in such a manner that a loading cycle will be reached at which most of the transitory interactions are already gone and a sudden and very sharp increase in segmental rupture will take place. Subsequent cycles will yield only small incremental increases in the number of ruptured segments. This description is in excellent agreement with the recent observations of DeVries et al.[69,70] and Zhurkov et al.[71] combining EPR techniques to measure the number of ruptured bonds with tensile measurements.

The relatively small number of interdomain permanent interactions leads to a small number of ruptured segments upon brittle fracture. This is reflected in a low spin concentration in EPR fracture experiments. The measured values are about one hundredth the values calculated on the basis of randomly entangled amorphous linear polymer. This fact has been ob-

served over and over,[69,72−78] but no plausible explanation was available hitherto.

Not only the interdomain permanent interactions are relatively small in number, but the effectivity of the transitory interactions is rather low. The combination of these two facts is manifested in the low strength of polymeric amorphous solids relative to the computed strength assuming a uniform segmental density throughout the sample.[39,79] Density-wise, when the sample is not strained or stressed, the interdomain segmental density approximates the uniformly distributed intradomain segmental density. Upon straining, the intradomain segments are affected much less than the interdomain ones, the latter being stressed and "give," such that the segmental density in the interdomain regions falls with increased local stress. Also, the stress concentration coefficients of eqs. (4) and (5) increase in magnitude as a function of the local stress on the interdomain segments, making the total rate for the respective process faster than the rate for the lower stress region within the domains.

The fact that low molecular weight PMMA showed brittle fracture while high molecular weight PMMA showed ductile fracture[80] indicates that the low molecular weight domains have very little interdomain interactions while the high molecular weight domains show heavy interactions. It was recently shown that the tensile breaking stress of glassy polymers is weakly dependent on their molecular weight above a certain minimum.[60,81,82] This, as well as the former observation, is in agreement with the molecular domain model[1,2] in which interdomain interactions are molecular weight dependent. The observed differences between "zero strength molecular weight" and "entanglement molecular weight," always in favor of the former, are in agreement with the proposed model in which both the permanent and transitory interactions count in the glassy state, while under flow or viscoelastic conditions the transitory interactions dominate in both effect and number.

Recent observations of microfibrils within crazes in amorphous PS showing them to be composed of molecular domains or nodules interconnected by regions of low material density[83] seem to be in perfect agreement with the model. Similar features were noted also in crazed PMMA.[84]

CONCLUSIONS

The relationship between ΔH_a and U_0 gives a means of determining whether a polymer under zero load will fail in a brittle or ductile manner. When loaded, the stress, load frequency, and temperature affect the results, and a comparison of eqs. (4) and (5) will reveal whether the polymer will fail in a ductile or brittle fashion.

ΔH_a can be calculated according to eqs. (1), (2), and (3) if the values of T_g and $\Delta\alpha$ are known. Conversely, a knowledge of T_g, the chemical structure, ductility, or brittleness of the polymer, combined with position-

ing it according to its structure in Figure 1, will yield a ballpark approximation of both its $\Delta\alpha$ and T_R.

On the molecular level, these conclusions are in agreement with the molecular domain model. This was corroborated by numerous recent observations reported in the literature.

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