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Mechanical behaviour of poly(methyl methacrylate)

Part 3 *Activation processes for fracture mechanism*

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Poly(methyl methacrylate) (PMMA) was selected as a model material to study tensile strength, fracture toughness, and fatigue crack propagation behaviour over a wide range of temperatures (including T_β and approaching the glass transition) and cyclic frequencies. The energetic terms, including activation energy and activation volume, for the various types of fracture and their physical meaning are discussed in this paper. The activation volume for fatigue crack propagation is interpreted as the volume of the crank-shaft (eight backbone carbons) at the β transition. The apparent activation energy of fatigue fracture for a pre-cracked specimen also corresponds to the value for the β transition. For uncracked specimens in a tensile test, the values of activation energy and activation volume suggest that the glass transition process is important in governing the molecular processes involving both crack initiation and propagation. The current results also indicate that the fatigue fracture mechanism of pre-cracked PMMA is dominated by a viscoelastic process, i.e. chain disentanglement, rather than by chain breakage, although some chain breakage undoubtedly occurs.

1. Introduction

To date, analysis of polymer fracture behaviour has mostly involved evaluation of macroscopic phenomena. Less attention has been paid to development of an understanding of the fracture mechanism at the molecular level. However, several authors have examined the possibility that fatigue fracture could be modelled using reaction rate theory [1, 2], leading to the Zhurkov [4–6]–Bueche [7–9] equation.

In contrast to the continuum mechanical theories, rate process theories of fracture recognize the presence of molecular or supermolecular elements forming the material body. It is assumed that macroscopic failure is controlled by a rate process, i.e. the basic fracture events are controlled by thermally activated chain breakage or disentanglement and that the accumulation of these events in some way leads to crack formation and/or fracture. Thus, from the original concept of flow, where the thermally activated movement of molecules assists their passage across an energy barrier, various fracture theories of solids have emerged. The activation energy is that energy required to overcome this barrier and transform the material from one state to another, i.e. to lengthen the crack or produce fracture.

During deformation and fracture, a variety of events take place, including homogeneous shearing, heterogeneous shearing (shear banding), crazing, and bond rupture. The shearing and crazing may be associated with micromolecular relaxation processes. Brown *et al.* [10], Andrews and Reed [11], and Lloyd *et al.* [12] have claimed that rupture of the polymer backbone plays a central role in the fracture processes. The activation energy for bond rupture of PMMA is 85 kJ mol^{-1} [13]. On the other hand, other researchers related the fatigue processes to localized plastic deformation and associated the fracture processes with a chain disentanglement (micromolecular relaxation) process [14–20].

Recently, Wool and coworkers [21–23] applied reptation theory to crack formation and healing. The central idea is that a crack in a polymer material "heals" by chain reptation across the interface. Wool [23] has determined the effect of molecular weight on the rate of such processes, leading to a series of dynamic relationships. The inverse phenomenon would also be expected to hold, i.e. reptation across the nascent interface under stress accounts for the formation of cracks. This idea suggests that molecular diffusion, rather than chain scission, constitutes the principal mechanism of fracture.

Since the activation energy of β transition process (ranged from 71 to 126 kJ mol^{-1} [24]) is similar to the activation energy of chain rupture, both chain rupture and chain disentanglement are possibly involved in the fracture process. However, it is likely that one of

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these molecular processes should be dominant, but which one, and the degree to which it is dominant remains to be revealed.

2. Previous work

A commercial poly(methyl methacrylate) (PMMA) (Rohm and Haas Plexiglas) was selected as a model material to test the Michel–Manson (M–M) [25–28] equation over a wide range in both temperature (including β and glass transitions) and cyclic frequency. Three major series of tests, namely, stress–strain, fracture toughness and FCP, have been conducted by using both universal and servo-controlled electrohydraulic testing machines [29–31]. In the experiments, stress–strain measurements were conducted under constant strain rate, fracture toughness under constant loading rate, and FCP under constant amplitude load control with a sinusoidal waveform, and load ratio (min. load/max. load) = 0.1. The material parameters defined in the M–M equation were measured experimentally [29–31]. The physical meaning of the energetic terms, including activation energy and activation volume, will be discussed.

The previous results [29–31] show that higher loading rate and lower temperature provide greater fracture and fatigue resistance when the plane strain conditions prevail. However, when temperature approaches the glass transition region, the material is more ductile suggesting a transition to plane stress conditions, and both fatigue and fracture resistance exhibit the opposite dependence on temperature and loading rate from that at lower temperature.

According to the present results, apparent activation energies can be calculated for tensile strength, fracture toughness, and FCP (at cyclic frequency 10 Hz) which are 270, 120 and about 20 kJ mol^{-1}, respectively. The FCP activation energy was also found to be dependent on both cyclic frequency and stress intensity factor.

3. Theory

3.1. FCP activation processes

According to the current data [29, 30], the apparent activation energy, E_a, for fracture of a precracked specimen under monotonically increasing loading was found to be 120 kJ mol^{-1}. By contrast, the apparent activation energies obtained for FCP data are well below this value. The apparent activation energy for FCP increases with decreasing frequency, Table I. This finding agrees with earlier results by Phillips for PVC [20]. By plotting the apparent activation energies versus cyclic frequencies, Fig. 1, one may expect that the E_a will approach the apparent activation energy of monotonic fracture process at very low frequencies, i.e. less than 0.1 Hz.

TABLE I Influence of frequency on FCP apparent activation energy for poly(methyl methacrylate)

Frequency (Hz)	Activation Energy (kJ mol^{-1})	
	ΔK = 0.5	ΔK = 0.6
100	17	13
10	23	17
1	33	44

ΔK: Stress intensity factor range MPa (m)$^{1/2}$

An explanation for the fact that the activation energy for FCP is less than that for the monotonic fracture can be based on the Zhurkov–Bueche equation [3–9, 13] wherein the apparent E_a represents the difference between the E_a for a major process, and the work applied (the product of a stress, σ, and the activation volume, $V^{\neq}$), Equation 1.

$$E_a \text{ (apparent)} = E_a \text{ (molecular process)} - \sigma V^{\neq} \tag{1}$$

The activation volume in Equation 1 should be the activation volume for the process being considered.

For fatigue experiments conducted at room temperature and a cyclic frequency of 10 Hz, the apparent activation energy can be approximated as 20 kJ mol^{-1}. The yield strength is the maximum value that the stress could reach within the plastic zone at crack tip. When the material is brittle, tensile strength approximately equals to yield strength. Thus, it is reasonable to regard tensile strength as the stress in the Equation 1. It was found that tensile strength is nearly a linear function to the logarithmic loading rate. A tensile strength value (correlated to the FCP experimental conditions of 24° C and loading rate corresponding to cyclic frequency of 10 Hz) of 100 MPa can be obtained by extrapolating the relationship of tensile strength and log (loading rate) at room temperature. Under this circumstance, the activation volume of PMMA can be calculated from Equation 1. Alternative approaches for calculating the activation volume are given in Appendix I.

3.1.1. *Viscoelastic mechanisms*

By assuming that viscoelastic processes (e.g. glass transition of β transition process) are controlling the fracture mechanism, several values of activation volume can then be calculated based on Equation 1.

1. The activation energy for the glass transition of PMMA is about 320 kJ mol^{-1} [24]. Assuming the glass transition process is the process governing the

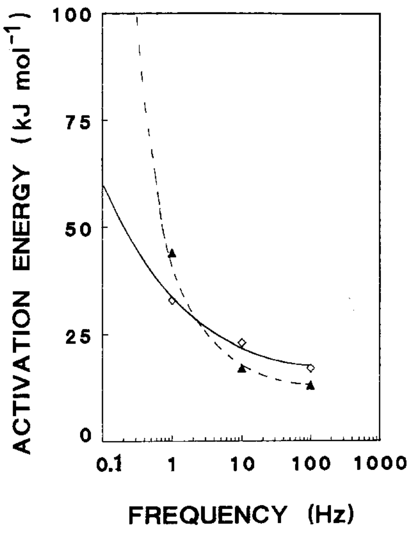

Figure 1 Activation energies of PMMA fatigue process as a function of cyclic frequencies at room temperature. (◇) 0.5 MPa m$^{1/2}$; (▲) 0.6 MPa m$^{1/2}$.

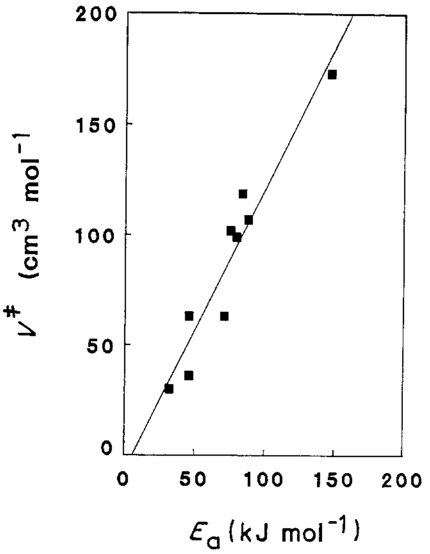

Figure 2 Activation volume as a function of activation energy of a transition. Data source: Boyer [33].

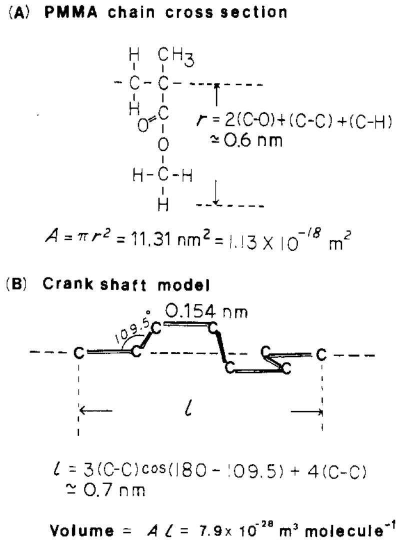

Figure 3 PMMA molecular structure. (A) Cross-sectional area of the back-bone chain. (B) Free volume estimated from the Crank-shaft model.

fracture mechanism, and the apparent activation energy for FCP is 20 kJ mol^{-1}, tensile strength is 100 MPa, the activation volume is calculated to be 3×10^{-3} m^3 mol^{-1}.

2. The β transition is also considered as possibly the governing process. The activation energy of the β transition, according to McCrum *et al.* [24], is found to range from 71 to 126 kJ mol^{-1} [24]. The apparent activation energy obtained from the fracture toughness experiments is about 120 kJ mol^{-1}, which falls within the range of E_a value for the β transition. By using 120 kJ mol^{-1} as the E_a of the β transition, the activation volume associated with the β process is calculated to be 10×10^{-4} m^3 mol^{-1}.

3. Eby [32] employed a semiempirical relationship for calculating the activation volume, $V^{\neq}$

$$V^{\neq} = 4kE_a \tag{2}$$

where k is the isothermal compressibility. k-values are 3.1×10^{-5} and 5.1×10^{-5} atm^{-1} (3.06×10^{-10} and 5.03×10^{-10} Pa^{-1}) for the β and glass transitions, respectively [33]. If the activation energies are taken as 120 and 320 kJ mol^{-1} for the β and glass transitions, respectively, the activation volumes for both transition processes can be calculated to be 1.5×10^{-4} and 6.4×10^{-4} m^3 mol^{-1}, respectively.

4. Boyer [33, 34] tabulated values of activation volume and E_a for several polymers, which shows a linear relationship between activation volume and E_a for the β process, Fig. 2 [35]. By extrapolating this plot, the activation volume corresponding to the β activation energy for current PMMA (120 kJ mol^{-1}) is about 1.5×10^{-4} m^3 mol^{-1}. Boyer and co-worker also found that the activation volume of the glass transition process increases exponentially with T_g [33, 34], and a linear relationship exists between T_g in degrees Kelvin and the logarithm of the activation volume. Again, by extrapolating, a value of 8.5×10^{-4} m^3 mol^{-1} for activation volume associated with the current PMMA (T_g = 125° C at 110 Hz, i.e. about 119° C at 10 Hz) is obtained.

5. Bershtein *et al.* [36] suggested that for temperatures at T_β and below, the activation volume is correlated to the volume of the equilibrium Kuhn segment [37]. A real polymer chain containing n chain segment units of length l' is statistically equivalent to N Kuhn chain segments of length L, i.e. $nl' = NL$ [35]. It is known that

$$L = \langle r^2 \rangle / nl' \tag{3}$$

and,

$$C_\infty = \langle r^2 \rangle / nl'^2 \tag{4}$$

where $\langle r^2 \rangle$ is the end-to-end distance of a polymer chain, and C_∞ is the characteristic ratio, a measure of the effect of short-range interactions on molecular chain dimensions (the short-range interactions include bond angle restrictions and the steric hindrances to internal rotation). Therefore,

$$L = C_\infty \times l' \tag{5}$$

and, Kuhn volume can be expressed as

$$V = AL \tag{6}$$

where A is the cross section of the polymer chain.

For PMMA, the characteristic ratio ranged from 5 to 9 [38]. Choosing the average value, 7, for PMMA and the C–C carbon bond length being 0.154 nm, the cross-sectional area of PMMA is calculated to be 1.1×10^{-18} m^2, Fig. 3, and the Kuhn volume is 7.2×10^{-4} m^3 mol^{-1}.

3.1.2. Chain rupture mechanism

As mentioned previously, polymer backbone rupture might play an important role in governing the fracture mechanism. According to Kausch [13], the activation energy of the PMMA bond rupture process is about 85 kJ mol^{-1}. In order to calculate the activation volume by Equation 1, it is necessary to choose a stress for the bond breaking process. Although the tensile strength which was used for the viscoelastic mechanisms could be used here as well, it is more realistic to use the stress required to break a C–C bond. Based on the consideration of C–C bond breakage, a theoretical stress to break has been calculated to be 6.74×10^{11} dyne cm^{-2} (6.74×10^{10} Pa) (Appendix 9.1 in [37]). The activation volumes are calculated to be 6.5×10^{-4} and 9.6×10^{-7} m^3 mol^{-1} for tensile strength and the stress to break a C–C bond, respectively.

3.1.3. *Plastic zone size*

It is known that the plastic zone size at the crack tip of a fatigue specimen increases as ΔK increases. It is also known from current work that the apparent activation energy of fatigue fracture process decreases as ΔK increases. According to Equation 1, for constant activation energy of the process governing fracture mechanism and constant σ, the activation volume should increase when the apparent activation energy of the fatigue process decreases as is the case for increasing ΔK level. Based on this analysis, it seems that the activation volume and plastic zone have the same dependence on ΔK.

The plastic zone volume can be estimated by Equation 7,

$$V = r_y t B \tag{7}$$

where

$$r_y = \text{plastic zone size} = (\pi/8) \times (K_{\max}/\sigma_{ys})^2 \tag{8}$$

$$t = \text{crack opening displacement (COD)}$$

$$= (K_{\max})^2/(E \times \sigma_{ys}) \tag{9}$$

B = specimen thickness,

and

E = Young's modulus.

The detailed calculation is described in Appendix I. The plastic zone volume was calculated to be 8300×10^{-4} m^3 mol^{-1}.

3.1.4. *Crank-shaft free volume*

One other important physical volume of a polymer is its free volume. The Schatzki crank-shaft model [37, 39–41] offers a theoretical way to calculate the free volume of a polymer, especially PMMA. According to Fig. 3, the crank-shaft type polymer segment is considered as a cylinder consisting of four consecutive monomeric units. A theoretical free volume for PMMA is then calculated to be 4.8×10^{-4} m^3 mol^{-1}.

All the values of activation volume calculated using various approaches are listed in Table II.

3.2. Fracture toughness activation processes

Three molecular processes which could control the thermal activation of fracture toughness are the viscoelastic mechanism, β and glass transitions, and bond breakage. Using Equation 1, it is possible to calculate the activation volume associated with each process.

3.2.1. *Viscoelastic mechanisms*

The apparent activation energy for fracture toughness of PMMA under monotonically increasing loading was found to be 120 kJ mol^{-1} [29]. The tensile strength is 100 MPa. First, considering the β transition as the controlling process for this mode of fracture, the true E_a ranged from 71 to 126 kJ mol^{-1} [24], as described previously. Choosing 120 kJ mol^{-1} as the true E_a value, according to Equation 1, the activation volume is calculated to be zero m^3 mol^{-1}.

When the glass transition is considered as the governing process, and the value of the activation energy for PMMA glass transition is 320 kJ mol^{-1} [24], the activation volume is calculated to be 20×10^{-4} m^3 mol^{-1}.

3.2.2. *Bond rupture mechanism*

For the bond rupture mechanism, the value of E_a is 85 kJ mol^{-1}, and the theoretical C–C bond breaking stress is 6.74×10^{10} Pa [37]. According to Equation 1, the activation volume is calculated to be -5.2×10^{-7} m^3 mol^{-1}.

The values of activation volumes for the fracture toughness process are listed in Table III.

3.3. Uniaxial tensile activation processes

The thermal activation processes for the uniaxial tensile failure mechanism is also considered. In this

TABLE II Activation volumes for fatigue crack propagation

	Activation volume ($\times 10^{-4}$ m^3 mol^{-1})				
	Current$^{(1,2)}$ FCP data	Crank-shaft model	Kuhn volume	Eby $V = 4k\,E_a$	Boyer's approach
β-transition$^{(5)}$	10*	4.8	7.2	1.5	1.5
Glass transition$^{(6)}$	30	–	6.4	6.4	8.5
Bond rupture$^{(7)}$	(2) 6.5 (3) 0.0096	1.2	–	–	–
Plastic zone volume	8300	–	–	–	–

1(1) The calculations are based on E_a (apparent) = E_a (control process) $- \sigma V^{\neq}$.
(2) Based on σ = yield strength = 100.8 MPa = 1.0×10^8 Pa.
(3) Based on σ = stress to break C–C bond = 6.74×10^{10} Pa.
(4) The apparent activation energy for FCP = 20 kJ mol^{-1}.
(5) The activation energy for β transition of PMMA = 120 kJ mol^{-1}.
(6) The activation energy for glass transition for PMMA = 320 kJ mol^{-1}.
(7) The activation energy for C–C bond breakage = 85 kJ mol^{-1}.
(*) To obtain activation volume, $V\neq$, multiply tabulated values by 10^{-4}.

case, the apparent activation energy for the tensile strength measurements is 270 kJ mol^{-1} [29]. Again, the tensile strength of 100 MPa is used in Equation 1 to determine the activation volume.

3.3.1. Viscoelastic mechanism

When β transition is considered, the activation energy of the governing process is 120 kJ mol^{-1} [29]. Substituting the $E_a = 120\,\text{kJ mol}^{-1}$ into Equation 1, the activation volume is calculated to be $-1.5 \times 10^{-3}\,\text{m}^3\,\text{mol}^{-1}$.

On the other hand, when the glass transition is considered, the activation energy of the governing process is 320 kJ mol^{-1}. For the apparent activation energy of 270 kJ mol^{-1} [29], the activation volume is found to be $5 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}$.

3.3.2. Bond rupture mechanism

Considering the C–C bond breakage as the controlling process, the activation energy is 85 kJ mol^{-1} [13]. For the C–C bond breakage stress of 6.74×10^{10} Pa, the activation volume is $-2.7 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$.

The values of the activation volumes for the uniaxial tensile moelcular processes are also listed in Table III.

4. Discussion

Since the volume of the plastic zone is so much larger than either the theoretical estimates or measured values of the activation volume (e.g. Eby, Boyer and Kuhn segment considerations), Tables II and III, it is unlikely that the plastic zone volume exerts a controlling influence on the thermal activation of the fracture mechanism of fatigue crack growth, fracture toughness or uniaxial tension. This result suggests that the thermal activation of the fracture process is localized to a microscopic region rather than being distributed throughout the plastic zone.

If one uses the macroscopic stress at break (tensile strength) with the bond rupture mechanism, the activation volume for fatigue fracture that is computed is in reasonable agreement with the theoretical estimates. However, it is more likely that the microscopic stress for C–C bond breakage should be applied to the bond rupture mechanism. Accordingly, the activation volume obtained is much smaller than the theoretical estimates. This finding suggests that the bond rupture process is not the dominant mechanism governing fatigue fracture in amorphous PMMA, although some bond reupture undoubtedly exists. For fracture toughness and uniaxial tensile failure, the activation volumes computed for bond rupture are both negative. This indicates that either bond rupture process is not applicable for these failure modes or Equation 1 is not valid.

If Equation 1 is valid, the information in Tables II and III, showing that the calculated activation volumes agree with the theoretical values within a reasonable range, suggest that the fracture mechanism is governed by a viscoelastic process, either the glass or β transition. The apparent activation energy measured from the fracture toughness studies (120 kJ mol^{-1} with a precracked specimen) is in the range of reported values for the β transition. Also, all the experiments using precracked specimens were conducted at temperatures below T_g. The current findings support the arguments of Boyer [16], Williams [15], and Hertzberg and Manson (section 2.7 in [14]) that the β transition is the viscoelastic process governing the fracture behaviour of a cracked specimen.

An explanation for the fact that $V^{\neq}$ for FCP calculated from Equation 1 exceeds the theoretical values may stem from the choice of stress level in Equation 1. The tensile strength was used in these calculations. However, it is possible that the crack tip stress field and the stretch hardening associated with molecular alignment could elevate the effective stress that activation volume experiences, thereby decreasing the activation volume. Another interesting observation, confirming earlier work by Phillips for PVC [20], is that the activation energy for FCP in PMMA increases as cyclic frequency decreases. This result is consistent with decreasing tensile strength as the cyclic frequency decrease. According to Equation 1, when σ decreases, the product of σ and $V^{\neq}$ decreases, and thus, the apparent E_a at the left hand side of Equation 1 increases.

Only a few researches have addressed the physical meaning of activation volume. Among them, Boyer and Kumler [3, 4] found that activation volume at T_g bore a simple relation to T_g, but there was no such

TABLE III Activation volume for tensile strength and fracture toughness

	Activation volume ($\times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}$)			
	Current(1,2) σ_{UTS} data	Current(1,3) K_c data	Eby $V = 4k\,E_a$	Boyer's approach
β-transition(4)	-15*	0	1.5	1.5
Glass transition(5)	5	20	6.4	8.5
Bond rupture(6,7)	-0.027	-0.0052	–	–

(1) The calculation are based on E_a (apparent) $= E_a$ (control process) $- \sigma V^{\neq}$.
(2) The apparent activation energy is 270 kJ mol^{-1}.
(3) The apparent activation energy is 120 kJ mol^{-1}.
(4) The activation energy for β transition of PMMA = 120 kJ mol^{-1}.
(5) The activation energy for glass transition of PMMA = 320 kJ mol^{-1}.
(6) The activation energy for C–C bond breakage = 85 kJ mol^{-1}.
(7) Based on σ = stress to break C–C bond = 6.74×10^{10} Pa.
(*) To obtain activation volume, $V^{\neq}$, multiply tabulated values by 10^{-4}.

relation between the activation volume at T_β transition temperature [34]. Bershtein *et al.* [36] suggested that the activation volume characterized the kinetic flexibility of the macromolecular chains during the deformation and related to the chemical structure of the polymeric materials. Eskin *et al.* [41] found that the length of the statistical Kuhn segment of polystyrene corresponded to 8–10 monomeric links. Keyes [42] found that activation volume is often of the order of magnitude of the volume of the relaxing unit. From these observations, the activation volume of the fracture (deformation) process is likely to be a volume which is related to the chain dimensions associated with a major viscoelastic process. In the current case, the $V^{\neq}$ of the fatigue process is very likely to be the free volume associated with the β transition. The value of crank-shaft type free volume is found to agree with other estimates of the activation volume. This agreement is encouraging and suggests that the fatigue fracture process of a cracked specimen is not only governed by the β transition but also relates to the free volume of the β transition.

The above analysis suggests that the Schatzki crankshaft motion [43] plays an important role in the viscoelastic motions resulting in the propagation of cracks in PMMA, and perhaps other linear, amorphous polymers. The Schatzki crankshaft motion involves eight backbone carbon atoms, or four mers which are displaced along the chain in a helical or corkscrew type motion, now elegantly described by deGennes [44, 45] as a reptation motion. In reptation, the chain is assumed to have certain "defects", each with a stored length assumed in this case to be the size of the Schatzki crankshaft unit. These defects migrate along the chain in a type of defect current. When the defects move, the chain progresses, causing self diffusion motion of the chain relative to its neighbours.

When external forces are present, the motions are no longer random, but tend to be in a direction that relieves the applied stress. Thus, under the cyclic motions imposed on the plastic specimen, the chains undergo directed reptation motion separating them one from another. The total effect is the propagation of the crack with little or no chain breakage.

However, when no crack is present in the specimen, e.g. uniaxial tensile experiments, the failure mechanism is more closely related to molecular processes associated with the glass transition. According to Table III, assuming the glass transition as the controlling process, the calculated values of activation volume agree very well with the estimated values of $V^{\neq}$ by the approaches of Eby and Boyer. This suggests that when the initiation of a crack is required, a higher degree of molecular chain motion is necessary than when the crack is already present. The greater chain movement facilitates chain slippage which creates the cracks and assists their propagation.

The interrelationships between viscoelastic motions, bond breakage, and crack propagation can be further clarified. The bulk of the work in failure processes of this nature comes from the reorganization, flow, and orientation of chain portions, probably via a β-process. The actual chain rupture, which takes place (together with chain slippage) as the final step in crack propagation absorbs only a few per cent of the total energy, and is "not seen" by the analysis of the data via activation energies. Of course, the resulting free radicals can be seen via electron spin resonance [12].

The foregoing discussion has presented a logic frame which intended to show that the molecular viscoelastic processes, either β or glass transition, can account for the FCP behaviour of amorphous PMMA. However, since the activation energy for the bond rupture (85 kJ mol^{-1}) is in the region of that for β transition, one cannot rule out bond rupture as making no contribution to the fracture process. In any case, present work plus other evidence, namely the extent of free radical formation during FCP [10], support the contention that bond rupture is not the dominant molecular process contributing to FCP.

5. Conclusions

An analysis of the thermal activation of several failure modes, i.e. uniaxial tension, fracture toughness, and fatigue crack propagation, of PMMA was undertaken in order to identify the types of molecular motions which contribute to the failure processes. Based on this analysis, the conclusions are:

1. The Zhurkov–Bueche equation [3–9] is found to be a useful representation of thermal activated failure processes since values of the activation volume, $V^{\neq}$. This equation decribes the decrease in FCP activation energy with increasing cyclic frequency.
2. The range of apparent activation energy for fatigue crack propagation, 13 to 44 kJ mol^{-1}, is consistent with the view that molecular movements occurring during this type of failure are essentially those of the β transition with the activation volume represented by the crank shaft model. Consequently, FCP appears to be controlled mainly by viscoelastic processes, i.e. chain disentanglement, although some chain breakage undoubtedly occurs.
3. The apparent activation energy for fracture toughness, 120 kJ mol^{-1}, falls within the range of observed values for the β transition in PMMA.
4. The apparent activation energy for failure under uniaxial tension, 270 kJ mol^{-1} for PMMA, suggests that when both crack initiation and propagation contribute to the failure process, the molecular movements which are involved are those associated with the glass transition.

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Appendix I: Calculations of activation volumes for FCP

Most of the calculations are based on Equation 1,

$$E_a \text{ (apparent)} = E_a \text{ (governing process)} - \sigma V^{\neq} \quad (1)$$

where E_a (apparent) is the Arrhenius type activation energy obtained from fatigue crack propagation (FCP) experiments; E_a (governing process) is the activation energy of the molecular process which is assumed to govern the fatigue mechanism; $V^{\neq}$ is the activation volume; and σ is the stress applied to the activation volume.

Viscoelastic mechanism

1. The glass transition is assumed to be the governing process:

The activation energy for the glass transition of PMMA is about 320 kJ mol^{-1} [15]. The tensile strength at room temperature and loading rate corresponding to a cyclic frequency of 10 Hz is estimated to be 100 MPa. The apparent activation energy of FCP for these conditions is found to be about 20 kJ mol^{-1}. Thus,

$$\begin{aligned} 20\,\text{kJ mol}^{-1} &= 320\,\text{kJ mol}^{-1} - (100\,\text{MPa}) \times V^{\neq} \\ V^{\neq} &= (300 \times 10^3\,\text{J mol}^{-1})/(100 \times 10^6\,\text{Pa}) \\ &= 30 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} \end{aligned}$$

2. The β transition is assumed to be the governing process:

The range of activation energy values reported for the β transition is from 71 to 126 kJ mol^{-1} [15], and 120 kJ mol^{-1} was chosen as the activation energy of the β transition for current PMMA. Thus,

$$\begin{aligned} 20\,\text{kJ mol}^{-1} &= 120\,\text{kJ mol}^{-1} - (100\,\text{MPa}) \times V^{\neq} \\ V^{\neq} &= 9.9 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} \end{aligned}$$

3. Eby's equation, $V^{\neq} = 4kE_a$:

The variable k in the Eby equation is the isothermal compressibility which is 3.1×10^{-5} and 5.1×10^{-5} atm^{-1} (i.e. 3.06×10^{-10} Pa^{-1}) for the β and glass transitions, respectively. Thus, the activation volumes can be calculated according to the following, (i) glass transition:

$$\begin{aligned} V^{\neq} &= 4 \times (5.03 \times 10^{-10}\,\text{Pa}^{-1}) \\ &\quad \times (320 \times 10^3\,\text{J mol}^{-1}) \\ &= 6.4 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} \end{aligned}$$

(ii) β transition:

$$\begin{aligned} V^{\neq} &= 4 \times (3.06 \times 10^{-10}\,\text{Pa}^{-1}) \\ &\quad \times (120 \times 10^3\,\text{J mol}^{-1}) \\ &= 1.5 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}. \end{aligned}$$

4. Volume of Kuhn segment:

According to the discussion in the text, the Kuhn segment length, L, is the product of the characteristic ratio, C_∞, and C–C bond length, l'. The characteristic ratio for PMMA is taken to be 7. Thus,

$$\begin{aligned} L &= C_\infty \times l' = 7 \times (1.54 \times 10^{-10}\,\text{m}) \\ &= 1.1 \times 10^{-9}\,\text{m}. \end{aligned}$$

The cross-sectional area of PMMA can be estimated by assuming that the radius, r, is composed of two (C–O) bonds, one (C–C) bond, and one (C–H) bond (see Fig. 3).

Thus the cross-sectional area, A, can be calculated by

$$\begin{aligned} A &= \pi r^2 = \pi(6 \times 10^{-10}\,\text{m})^2 \\ &= 1.1 \times 10^{-18}\,\text{m}^2 \end{aligned}$$

The Kuhn volume can be calculated by

$$\begin{aligned} V &= A \times L = (1.1 \times 10^{-18}\,\text{m}^2) \times (1.1 \times 10^{-9}\,\text{m}) \\ &= 1.2 \times 10^{-27}\,\text{m}^3\,\text{molecule}^{-1} \\ &= 7.2 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}. \end{aligned}$$

Chain rupture mechanism

The activation energy for C–C bond rupture of PMMA is 85 kJ mol^{-1} [7]. The apparent activation energy for fatigue fracture process is still 20 kJ mol^{-1}. Two cases for bond rupture mechanism have been considered according to Equation 1.

1. Tensile strength:

By using the tensile strength, 100 MPa, as the stress term in Equation 1, then

$$\begin{aligned} 20\,\text{kJ mol}^{-1} &= 85\,\text{kJ mol}^{-1} - (100\,\text{MPa}) \times V^{\neq} \\ V^{\neq} &= (65 \times 10^3\,\text{J mol}^{-1})/(100 \times 10^6\,\text{Pa}) \\ &= 6.5 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} \end{aligned}$$

2. Theoretical C–C bond breaking stress:

The theoretical C–C bond breaking stress is calculated to be about 6.74×10^{10} Pa (Appendix 9.1 of [25]). Thus,

$$\begin{aligned} 20\,\text{kJ mol}^{-1} &= 85\,\text{kJ mol}^{-1} - (6.74 \times 10^{10}\,\text{Pa}) \\ &\quad \times V^{\neq} \\ V^{\neq} &= (65 \times 10^3\,\text{J mol}^{-1})/(6.74 \times 10^{10}\,\text{Pa}) \\ &= 9.6 \times 10^{-7}\,\text{m}^3\,\text{mol}^{-1} \end{aligned}$$

Plastic zone volume

To calculate the plastic zone volume, both yield strength, σ_{ys}, and Young's modulus, E, need to be known. Both quantities for the experimental conditions of room temperature and a cyclic frequency of 10 Hz can be determined from the current tensile experiments. For these conditions, yield strength is approximately the same as tensile strength, i.e. 100 MPa. The Young's modulus is also estimated to be 3.78×10^9 Pa.

The plastic zone volume can then be calculated according to

$$V = r_y t B$$

where B is the specimen thickness and t is the crack opening displacement. The plastic zone size, r_y, is calculated according to the Dugdale model,

$$r_y = (\pi/8)\,(K_{max}/\sigma_{ys})^2$$

The stress intensity factor range, ΔK, associated with the apparent activation energy of 20 kJ mol^{-1} is about 0.558 MPa m$^{1/2}$. Since the minimum to maximum load ratio for this work is 0.1, K_{max} equals to

$\Delta K/0.9$. Thus,

$$r_y = (\pi/8) \times [(0.558/0.9)/100]^2 = 1.48 \times 10^{-5}\,\mathrm{m}$$

The crack opening displacement, t, is calculated from

$$\begin{aligned} t &= (K_{\max})^2/(E \times \sigma_{ys}) \\ &= (0.558 \times 10^6/0.9)^2/(3.78 \times 10^9 \times 100 \times 10^6) \\ &= 1.01 \times 10^{-6}\,\mathrm{m} \end{aligned}$$

Therefore, plastic zone volume is

$$V = r_y t B = 9.5 \times 10^{-14}\,\mathrm{m}^3.$$

Assuming the density of PMMA, ϱ, for bulk and within the plastic zone to be the same ($1.188\,\mathrm{g\,cm}^{-3}$), the mass of the plastic zone is

$$\begin{aligned} M &= \varrho V = (9.5 \times 10^{-8}\,\mathrm{cm}^3) \times 1.188 \\ &= 1.1 \times 10^{-7}\,\mathrm{g} \end{aligned}$$

The weight average molecular weight for this PMMA is $987\,000\,\mathrm{g\,mol}^{-1}$. The number of moles of molecular chains in the plastic zone is,

$$\begin{aligned} N &= M/M_w = (1.1 \times 10^{-7})/(994\,000) \\ &= 1.1 \times 10^{-13}\,\mathrm{mol} \end{aligned}$$

Therefore, the plastic zone volume corresponding to a mole polymer chains is

$$\begin{aligned} V' &= V/N = (9.5 \times 10^{-14}\,\mathrm{m}^3)/(1.14 \times 10^{-13}\,\mathrm{mol}) \\ &= 8300 \times 10^{-4}\,\mathrm{m}^3\,\mathrm{mol}^{-1}. \end{aligned}$$

Crank-shaft model

The cross-sectional area of PMMA main chain is estimated to be about $1.1 \times 10^{-18}\,\mathrm{m}^2$ (see Fig. 3). The theoretical chain length of eight carbon atoms is estimated to be about $6.68 \times 10^{-10}\,\mathrm{m}$ (also see Fig. 3). Consider the Crank-shaft volume as a cylinder, for which the volume equals the product of chain cross-section area and chain length, l,

$$\begin{aligned} V &= A \times l = (1.1 \times 10^{-18}\,\mathrm{m}^2) \times (7 \times 10^{-10}) \\ &= 7.9 \times 10^{-28}\,\mathrm{m}^3\ \mathrm{molecule}^{-1} \\ &= 4.8 \times 10^{-4}\,\mathrm{m}^3\,\mathrm{mol}^{-1}. \end{aligned}$$

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