

Fatigue of polymers

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ABSTRACT

The general nature of fracture in polymers, when subject to alternating loads as distinct from static or steadily increasing loads, is reviewed; and the molecular mechanisms and micromechanics aspects of the fatigue fracture process are discussed. Some attention is given to thermal fatigue, where fracture results primarily from a large specimen temperature rise due to hysteresis heating. However, primary emphasis is devoted to mechanical fatigue, in which fracture is a result of initiation and propagation of a crack, as a result of the periodic nature of the applied load.

Attention is given to the important internal, or material, variables such as polymer structure, molecular weight, crosslinking, and filler or diluent type and content; and to significant external variables such as stress or stress intensity factor amplitude, mean stress, temperature, frequency and environment. Various methods that can be utilized to provide significant degrees of enhancement in the fatigue resistance of polymers are outlined and discussed.

1. Introduction

In recent years, as the use of polymers in engineering applications has risen, an increasing amount of attention has been devoted to their performance and behavior under cyclic loading conditions. Under fluctuating loads polymers will fail at stress levels much lower than they can withstand under monotonic loading conditions; and, for a given alternating stress amplitude, they will fail in a time much less than the creep rupture time for a constant applied stress of the same magnitude. It is therefore of considerable technological interest to improve the resistance of polymers to fatigue failure. In order to do this, the mechanisms involved in the fatigue failure of polymers must be better understood. Also knowledge and understanding are needed of the influence of important external or experimental variables, such as alternating stress amplitude, stress intensity factor range, frequency, mean stress, temperature, surface condition and environment and of significant material variables, such as polymer structure, viscoelastic characteristics, molecular weight, molecular weight distribution, rubber inclusions, fillers or diluents, etc.

A comprehensive review, which discusses both experimental and theoretical developments and which covers much of the literature up to about 1973, is available [1]. Several other articles include discussions of fatigue phenomena in thermoplastics [2-5] and some aspects of polymer fatigue are reviewed in more recent articles [6, 7].

In the present paper, we discuss the general nature of fatigue behavior in solid polymers, review some of the more recent literature and give attention to both the initiation of a crack and to its subsequent propagation. The influence of experimental, material and environmental variables on fatigue performance of polymers is described. Our knowledge of this influence may be used to significantly improve the resistance of polymers and plastics to failure by fatigue.

The reader is referred to the literature for a discussion of fatigue phenomena in elastomers [8, 9], fibers [10, 11], and composites [7, 12]. Even for solid polymers, we make no attempt to be inclusive; rather we select and discuss data obtained on specific polymers to illustrate the possible, or likely, effects of a particular experimental or material variable. In a number of instances, the variable being considered may influence different polymers, depending on their composition and structure, in markedly different ways, while in other instances the effect may be quite general, although it may vary with stress amplitude, frequency, temperature, etc.

Because polymers are viscoelastic and are poor conductors of heat they are much more sensitive to the frequency of alternating loading than are metals. As a result, under cyclic loading failure may result from thermal rupture or melting. Our interest here is rather in fatigue fracture induced by crack initiation and crack propagation as a direct result of the cyclic loading. However, some attention is given to the problem of thermal fatigue both to delineate the necessary testing conditions, which will depend on the properties and structure of the polymer being tested, to be used to limit its occurrence and to outline some of the possible effects on fatigue behavior of rises in specimen, or crack tip, temperature as a result of hysteresis losses in each cycle.

Fracture under alternating loading usually involves initiation of a craze or of a damage zone, generally developing from some surface stress concentration site. This is followed by development of a cavity or microcrack in the plastically deformed region with subsequent crack propagation under the cyclic loading until some critical crack size is reached at which catastrophic fracture occurs. Both the initiation phase and the propagation phase are important even though one or the other phase may, in a particular situation, be dominant. Inhibiting or delaying crack initiation and/or strengthening the resistance of the polymer to crack propagation should improve the resistance of the polymer to fatigue-type fracture. Various illustrations will be presented herein to demonstrate these possibilities of fatigue property enhancement for both amorphous and crystalline polymers.

2. Thermal fatigue in polymers

Because polymers are viscoelastic, under cyclic loading some energy will be dissipated in each cycle. As a result the specimen temperature will rise until the heat generated per cycle is equal to the heat dissipated as a result of conduction, convection and radiation. Depending on the test temperature, the applied frequency, and the stress amplitude and on the internal friction, thermal conductivity and specific heat of the material under consideration, the temperature may quickly rise to T_g or to T_m , or it may stabilize at some particular value. The energy dissipated per second is given by [13]

$$\dot{E} = \pi f J''(f, T, \sigma) \sigma^2 \quad (1)$$

where f is the applied frequency, σ the peak stress and J'' the loss compliance; hence the resulting temperature rise, ΔT , will increase with increase of frequency, stress amplitude and internal friction.

The temperature rise under cyclic loading can be monitored by a thermocouple or by an infrared sensor. Many investigators have, for given polymers, provided data as to its magnitude and influence. Figure 1 shows that the specimen temperature, for polyethylene (PE) unnotched samples tested in uniaxial loading increases linearly with the test frequency and, for any given frequency, it increases even more rapidly with increase of the applied alternating stress [14]. For polystyrene (PS) – which has a very low internal friction – it is possible to run similar fatigue tests at 1600 cpm and with a

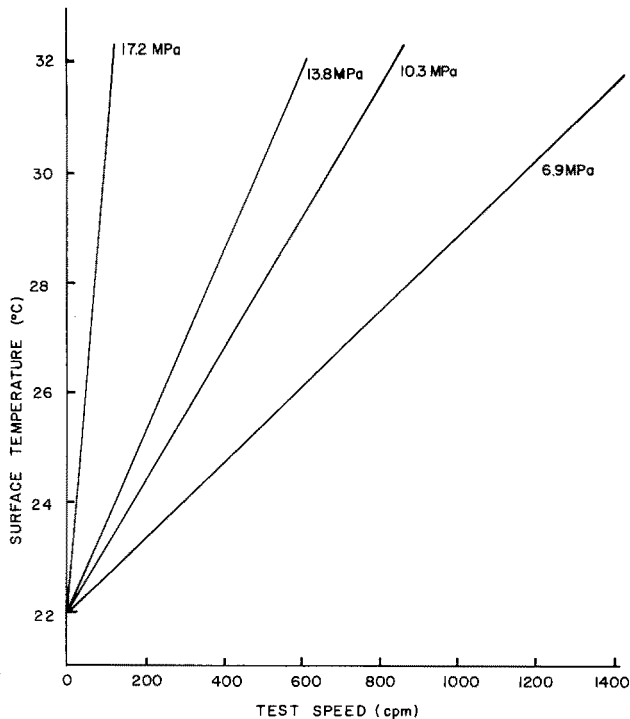


Figure 1. Specimen temperature vs. frequency for PE at various stress [14].

reported temperature rise at comparable stresses of less than 2°C [15]. Under these same conditions, PE samples quickly melt, and poly(methyl methacrylate) (PMMA), which has a sizable viscoelastic damping maximum (the β -peak due to side-branch motion) near room temperature, fails by thermal rupture, unless the applied stresses are kept very low. For PMMA tested in rotating bending at 50 Hz the measured sample temperature rose continuously with cycling and reached values close to 100°C at failure [16].

Another illustration of the important influence of stress amplitude on temperature rise under uniaxial cycling is given in Fig. 2 [17]. The data are for polyoxymethylene (POM) samples tested at 300 cpm. At an imposed stress magnitude of 22.4 MPa the temperature rises continuously and leads to thermal failure. But at stresses at or below 21.6 MPa the temperature rises slowly and then stabilizes at a final value, which is from 7° to 20°C above ambient depending on the imposed stress level. Thus, even under stable conditions, one does not obtain the desired response of the material at ambient temperature but rather its response at some higher temperature, whose value depends on frequency, stress amplitude, and material characteristics.

Many other examples of continuous temperature rises in polymers subject to cycling stressing have been noted. For example, in polytetrafluoroethylene (PTFE), thermal failure has been observed even in cantilever beam type specimens, at all stress magnitudes above 6.9 MPa (1000 psi) for tests performed at 30 Hz [18]. For this material, the $\sigma - N$ curves, and the endurance limit, fall with increasing frequency as, under these circumstances, the energy dissipated and the associated temperature rise are greater. In another investigation [19], where torsional fatigue tests were made on PMMA tubes at a shear strain of 9.4×10^{-3} , the specimen temperature rose about 6°C at 65 cpm but 27°C at 200 cpm; and, at higher speeds above 300 cpm, the temperature rose continuously until thermal failure intervened.

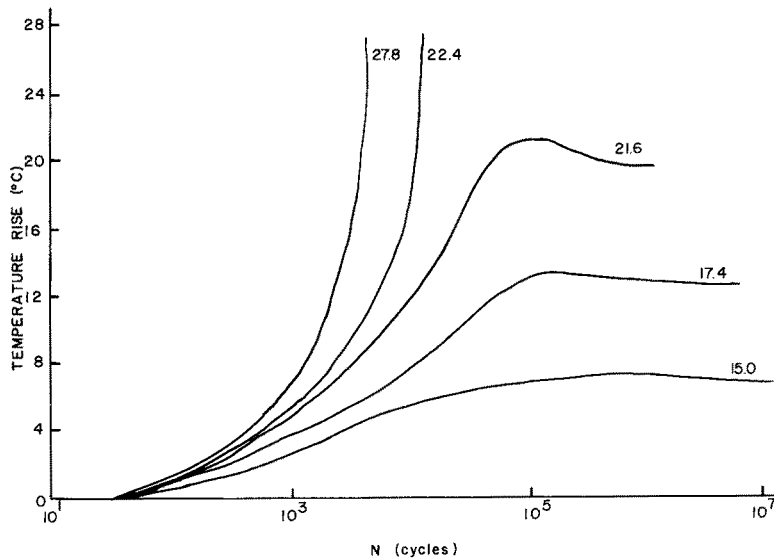


Figure 2. Temperature rise *vs.* cycles for POM at various stresses [17].

In tests on notched, rather than unnotched specimens, thermal fatigue effects are less significant as the average stress throughout most of the test specimen is relatively low. High stresses will, however, be present at the crack tip. Hence higher localized temperatures will occur at this site. For polyvinylchloride (PVC) tested at 11 Hz at 30°C temperature rise has been noted [20]. Though overall thermal failures are not encountered, these high local temperatures at and near the crack tip may approach or exceed T_g and thus strongly influence the mode of deformation. For example, in impact modified nylon 6/6, the observed temperature rise near the crack tip is over 100°C at a stress intensity factor range, ΔK , of 3.2 MPa \sqrt{m} [21].

Heat build-up in unnotched fatigued polymers can be minimized by strain cycling at a constant strain rate. For polycarbonate (PC) specimens, tested in strain-cycled fatigue at a strain rate of 10⁻² the temperature rise was reported to be less than 2°C [3]. In strain cycling, a ΔT rise causes a drop in modulus; a decrease in energy dissipation occurs and there is no thermal runaway. In stress control, a temperature rise causes both a drop in modulus and an increase in energy dissipation. Hence, unless the frequency and the stress are kept relatively low, thermal runaway, depending on the viscoelastic characteristics of the polymer, may be encountered.

Changes in wave form influence the stress level at which thermal runaway occurs. For example, under sinusoidal stresses in POM at 100 cpm, thermal runaway has been noted to occur at all stresses $\sigma > 27.8$ MPa but, for an imposed square wave, it occurs at all stresses $\sigma < 21.5$ MPa [17].

In some polymers, where viscoelastic effects are large, significant temperature rises can occur even at very low frequencies. In acrylonitrile-butadiene-styrene (ABS), for example, at an imposed alternating stress of 37.5 MPa a temperature rise of 7° was observed even at the low frequency of 2 cpm [22]. Internally generated heat due to fatigue cycling can, in some instances repair microstructural damage that has occurred. In PE, electron spin resonance studies have been made on samples that were fatigued in cyclic tension at 458 cpm and then irradiated with γ -rays at liquid nitrogen temperature [23]. These studies indicate that, while the initial effects of the stress cycling is to cause a rapid decomposition of the mosaic block crystals in the PE lamellae into smaller sizes, subsequent cycling tends to repair and stabilize the mosaic

block sizes. The microstructural changes that occur are evidently on a relatively small scale as both x-ray diffraction and density show that scarcely any change has occurred in the degree of crystallinity as a result of the tensile cycling. Other examples of the beneficial effects to fatigue endurance of local temperature rises at crack tips will be given later.

The extent of the temperature rise in a given polymer will vary, as Eqn. (1) implies, with any increase in loss compliance. Thus addition of water to nylon 6, which causes a shift of the amorphous T_g transition toward room temperature, would be expected to raise ΔT for a given set of alternating stress conditions. This effect has been noted, as, at a frequency of 10 Hz, there is little change in temperature in a sample containing 0.5% moisture until near failure while in samples containing 2 or 6 percent moisture, a 40–50°C temperature rise is found after only 8000 cycles [24].

3. Mechanical fatigue in polymers

A. Cyclic softening

When metals are subject to cyclic loading they may undergo cyclic hardening or cyclic softening depending on whether the metal was initially soft or initially hard [25]. However, in many different polymers subject to cyclic strains, only cyclic softening is observed, although the extent of this is dependent upon the structure of the polymer [2, 26]. An example of cyclic softening in polycarbonate (PC) is shown in Fig. 3 [27] where, for an applied alternating strain amplitude of 5%, the peak heights of the maximum tensile and compressive stresses are displayed *vs.* time or cycles. There is an incubation stage where the stress is essentially constant, a transition stage where it reduces in both tension and compression as cyclic softening sets in, a cyclic steady state stage where the stress, though lower than the initial stress remains essentially constant, and a final crack propagation stage, prior to fracture, where the tensile stress reduces to zero while the compressive stress remains constant. It has been noted that cyclic softening can be appreciable, as much as 40% in polycarbonate and nylon 6/6. The cyclically softened state persists even after the test is stopped. Despite the softening that has occurred, the observed density of PC after testing is reported to be 1% higher [26].

It is evident from the above results that, in some polymers at least, changes in microstructure – packing rearrangements, and generation of some types of defect – may occur during cyclic straining. Recent infrared and x-ray studies [28] of cyclically stressed PS and PC films show that molecular changes, such as rearrangement of phenyl groups, changes in Bragg spacings, and overstressing and fracture of some

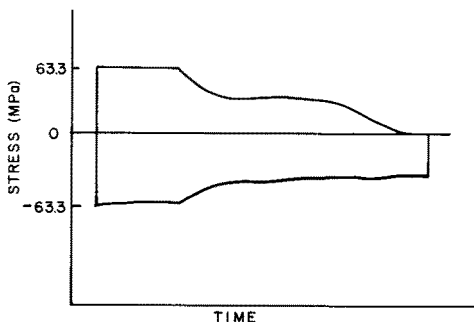


Figure 3. Variation of maximum tension and compression stress in PC at an alternating strain of 5% [27].

backbone bonds, occur. However, in these studies, no density increase was observed in fatigued PC films; rather a small decrease occurred and this was attributed to formation of chain ends and voids through bond breakage. IR has also been used to study the nature of molecular products produced by fatigue of PE [29].

B. Effects of stress amplitude and stress state

Not all polymers cyclically soften at ambient temperature. In polystyrene, there is very little indication of this phenomenon and tests on unnotched specimens in alternating strain control or in alternating stress control at 6 cpm give essentially the same $\sigma - N$ curve [30]. At high values of the alternating stresses, σ_a , which are near to the uniaxial tension fracture stress of 43.5 MPa fatigue fracture occurs within a few hundred cycles after extensive crazing and the $\sigma - N$ curve is fairly flat. The fracture surface shows smooth mirror-like facets extending over most of the cross-section. This morphology is similar to that obtained in uniaxial tensile fracture, such as that shown in Fig. 4 [31].

True fatigue failure, involving initiation of a crack and the subsequent propagation with continued cycling until fracture takes place, usually occurs at intermediate values of the alternating stress, which frequently fall between one-fourth and one-half of the tensile yield or fracture stress. In unnotched specimens, the crack generally initiates in a surface craze or in a region of localized plastic deformation that develops, upon cycling, from a surface defect or stress concentration site. In notched specimens, the craze or damage zone develops at the crack tip and failure then occurs due to rupture or fracture of fibrillar elements and to void coalescence.

In many polymers, it appears that in this intermediate stress region there is a linear relation between the alternating stress amplitude and the log of the number of cycles to failure. This type of behavior, for example, is illustrated in Fig. 5 for a commercial PS [15], of broad molecular weight distribution (MWD), and for three narrow MWD PS's of varying molecular weight value [14]. As the stress amplitude is further decreased the $\sigma - N$ curve tends to become flat and a limiting stress, the so-called endurance limit, can then be defined as that stress below which no fatigue

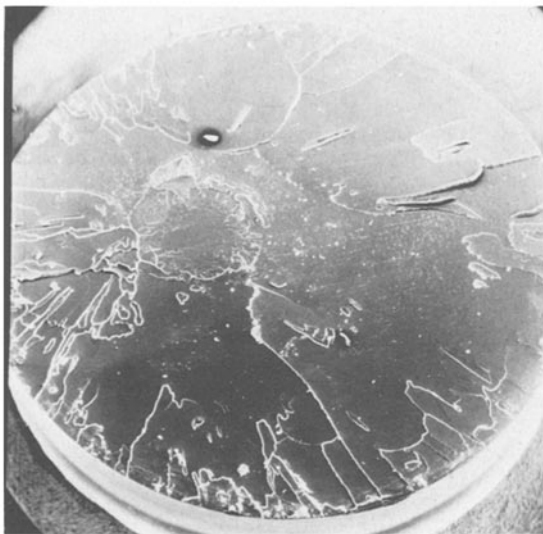


Figure 4. Scanning electron micrograph of typical tensile fracture surface in PS.

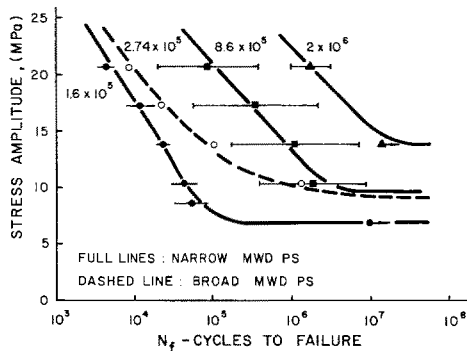


Figure 5. $\sigma - N$ curves for broad MWD PS and for 3 narrow MWD PS's.

failure occurs at least up to 10^7 cycles. The endurance limit as well as the average lifetime at any given stress amplitude, is clearly a function of molecular weight and the influence of this variable on fatigue performance will be discussed more fully in a later section. It is also a function of frequency, and in this polymer, where thermal effects are not significant, it increases with increase of frequency for the broad MWD PS from an estimated value of 7.6 MPa at 6 cpm [30] to 9.6 MPa at 1600 cpm [15].

The fatigue fracture surface in the intermediate stress - intermediate life region - is markedly different from that obtained in static fracture [30-32]. An SEM micrograph of a PS specimen fatigue fractured at $\sigma_a = 17.2$ MPa is shown in Fig. 6 [31]. Unlike the case of static fracture, where the source is frequently an internal flaw or inhomogeneity, the source of the fatigue fracture is generally a stress concentration site on the specimen surface. It has been suggested that the concentration of microcracks is higher on the surface [7] and also that interatomic bonds there are more highly stressed [33]. A smooth mirror-like region of slow growth surrounds the source. In some materials, or under certain conditions, as for high molecular weight polymer [34], more than one fatigue crack origin may be present.

The mirror-like region surrounding the surface source is usually followed by a comparatively smooth, radial-lined faster growth region, and then by a much rougher region as, with increasing stress, or stress intensity, craze bundles form at the crack tip and the crack jumps frequently from one craze plane to another and from one craze-bulk interface to another, as shown by Fig. 7 [31].

In fatigue, in contrast to uniaxial loading, one frequently observes that, in glassy polymers, a single craze develops at some surface location along the specimen gage length after some number of load cycles. Soon thereafter a crack develops within the craze and gradually propagates. In uniaxial tensile loading, extensive crazing occurs all over the gage length, even though the total strain to fracture, as for PS, may be small, 1.5 to 2%. However, if in fatigue cycling, one imposes a comparatively high mean stress and a low alternating stress then, as shown in Fig. 8, crazes may develop at various points along the gage length [31]. Surface crazes have also been observed in thin PC films tested in cycle tension [28].

Fatigue lifetime $\sigma - N$ curves for unnotched specimens of PS have also been obtained by cycling in compression from zero to some maximum stress value [35]. The $\sigma - N$ curves have a rather similar shape to those obtained under alternating tension-compression. The log of the lifetime to fracture increases linearly with decrease in σ_{\max} in the intermediate life region and there is an endurance stress limit below which no fracture occurs. One difference is that while crazes and cracks appear to develop from surface flaws, they grow parallel to the applied stress direction rather than transverse to it as in tension. Since yielding, rather than crazing, occurs in

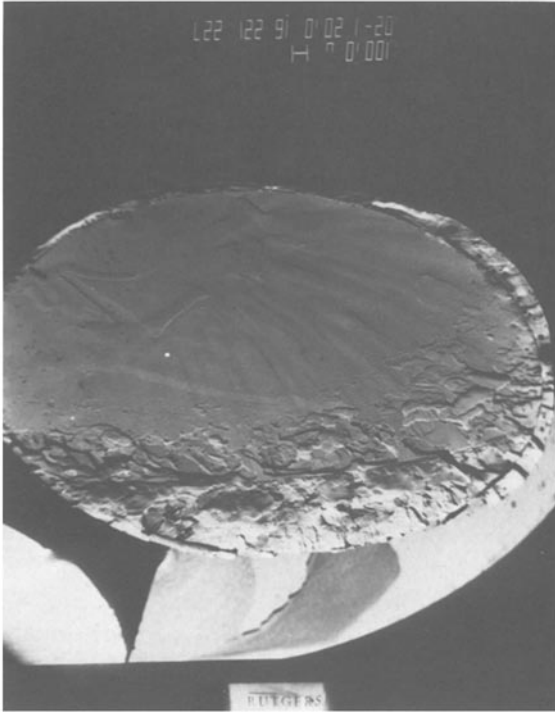


Figure 6. Scanning electron micrograph of typical fatigue fracture surface in PS tested at $\sigma_a = 17.2$ MPa, $\sigma_m = 0$.

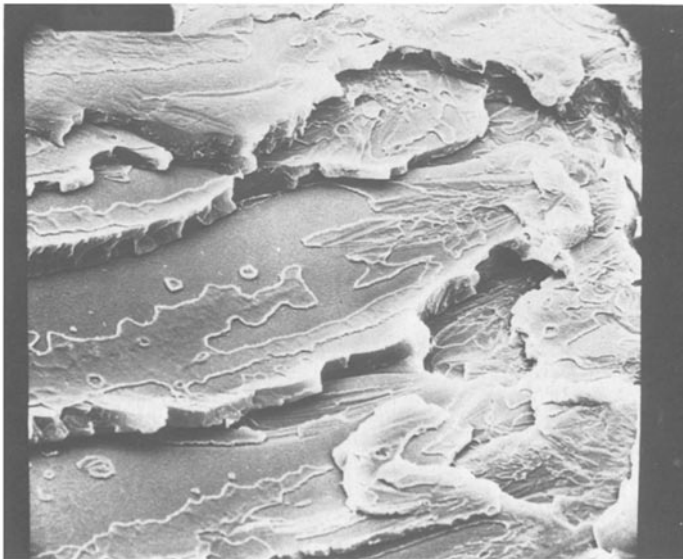


Figure 7. Scanning electron micrograph of portion of fatigue fracture surface of PS tested at $\sigma_a = 17.2$ MPa, $\sigma_m = 0$ [31].

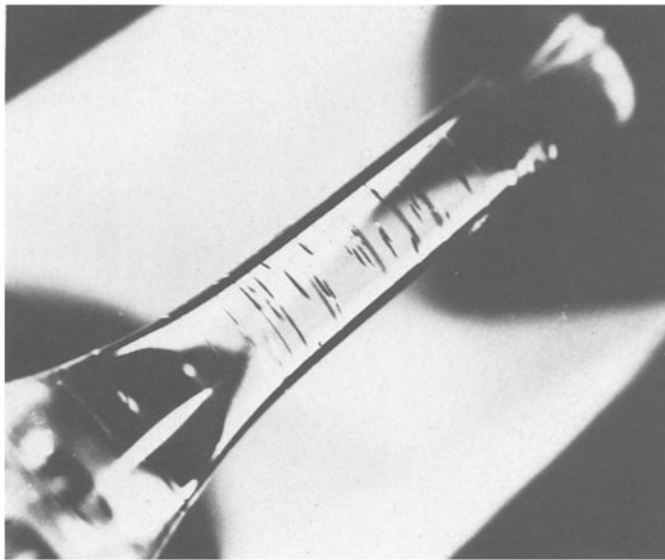


Figure 8. Scanning electron micrograph of surface of PS specimen, tested for over 13 million cycles at $\sigma_a = 4.3$ MPa, $\sigma_m = 12.9$ MPa [31].

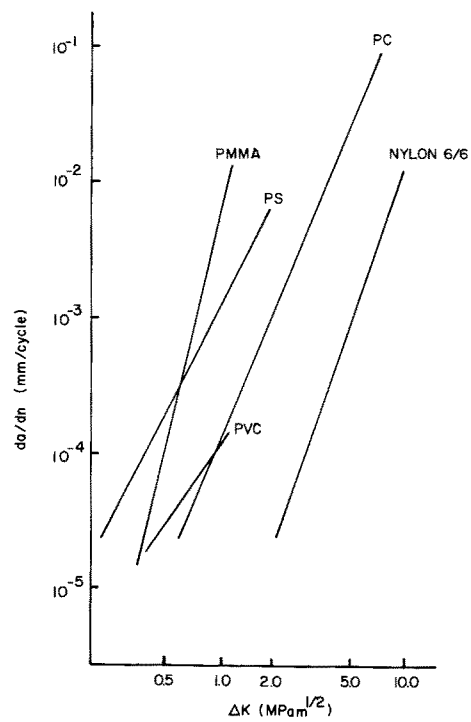


Figure 9. FCP rate vs. ΔK for several thermoplastics [39].

uniaxial compressive stressing it is evident that cyclic stressing can change the mode of deformation and thereby cause failure to occur at lower stress values than σ_y . Cyclic compression tests have also been carried out at 10 Hz in nylon 6 and, for a maximum imposed strain of 4%, fatigue failure accompanied by an 18°C temperature rise, occurred in 30,000 cycles [24].

Despite the obvious technological importance of combined stresses, few investigators of fatigue phenomena in polymers have carried out tests under such conditions. However, the endurance strength of high density polyethylene (HDPE) has been studied under biaxial tension for various ratios, σ_2/σ_1 , of the two principal stresses [36]. It is noted that the boundary lines for fatigue failure corresponding to any number of cycles from 10^2 to 10^6 could be represented by ellipses. One interesting aspect of these studies is that the data indicate that, at high stresses and low cycles to failure, imposition of a second principal tensile stress is beneficial while at low stresses and high cycles to failure, the reverse was true. This may result from a change in the fracture mechanism in the two cases; in fact, at high stresses fracture was of the ductile type with oriented strands of polymer visible while at low stresses, the HDPE tubes fractured in a brittle manner.

C. Fracture mechanics aspects

Many studies of fatigue fracture, for both glassy and crystalline polymers, have been made by fracture mechanics type experiments [1, 25]. In these tests the fatigue crack propagation (FCP) rate is determined in notched specimens for various values of the stress intensity factor range, ΔK . Tests are usually performed with single edge notched (SEN) specimens or with compact tension (CT) specimens. The stress intensity factor K is given by

$$K = Y\sigma\sqrt{a} \quad (2)$$

where a is the crack depth, σ the applied stress and Y a geometrical parameter [37], which takes the value $\sqrt{\pi}$ for the case of a central crack of length $2a$ in an infinitely large plate. Experiments are generally performed only in reciprocating tension and frequently with a minimum stress that is 0.1 of the maximum stress.

Despite the fact that polymers are highly viscoelastic and that linear fracture mechanics applies strictly only to elastic materials, it appears that crack propagation rates in many polymers can be correlated with the stress intensity factor range at the crack tip, although in some situations, as discussed in a later section, the mean stress, or mean stress intensity factor, is also an important variable. Nevertheless, in many polymers, as well as in metals, the Paris equation

$$\frac{da}{dn} = A\Delta K^n \quad (3)$$

is in accord with the experimental observations [38]. Here A and n are material constants but they will be a function of temperature and, in some cases at least, of crack speed and of other variables as frequency, environment, and the like. Data showing the dependence of FCP rate on ΔK are shown in Fig. 9 for 3 amorphous polymers, PMMA, PS, and PC and for the crystalline polymer nylon 6/6 [39]. Another crystalline polymer poly(vinylidene fluoride) (PVF₂) shows almost identical behavior to that of nylon 6/6. In all cases the FCP rate correlates with the stress intensity factor range in accord with Eqn. (3). Similar curves have been obtained for many other polymers [1, 40–42]. For PE, the parameters, A and n and the length of the

observed damage zone at the crack have been found to depend on cooling rate, on molecular weight, and on frequency [42].

D. Discontinuous growth bands and striations

Concentric growth bands have been observed on the fracture surface in many polymers subject to alternating tension-compression cycling but they are more prevalent when a mean stress is present and when cycling is done purely in the tensile mode. An SEM micrograph showing growth bands obtained in an unnotched specimen of PS tested at 1600 cpm and at a maximum stress of 17.2 MPa and a minimum stress of zero is shown in Fig. 10 [31]. Such bands have also been noted in PE [42], in PVC [43, 44], and in many other polymers [45]. It is now known that these bands represent crack arrest lines and that the size of the bands and the number of cycles/band are functions of the stress intensity factor range. Figure 11 shows how the band size varies with ΔK for PS, PVC and PMMA and Fig. 12 shows how the number of cycles/band for the same 3 polymers, and for PC, vary with ΔK [45]. It appears that the craze develops continuously with cycling but that crack growth is discontinuous with the number of cycles between jumps being of the order of 10^2 to 10^3 depending on the ΔK value and on the polymer structure. At first, it was thought that the crack jumps through the entire length of the preexisting craze but there is now evidence that it jumps only part way through the craze [40]. Fatigue striations, in which the crack jumps incrementally in each cycle, are also observed in many polymers, such as PMMA, PS and polysulfone (PSF), at high ΔK values [1, 45].

The size of the discontinuous growth bands may be related to the plastic zone dimension, R , of the Dugdale model [46]. This dimension is given approximately by [1]

$$R = \frac{\pi}{8} \frac{K_{\max}^2}{\sigma_y^2}. \quad (4)$$

One can then compute σ_y from the observed band spacing and from the known stress

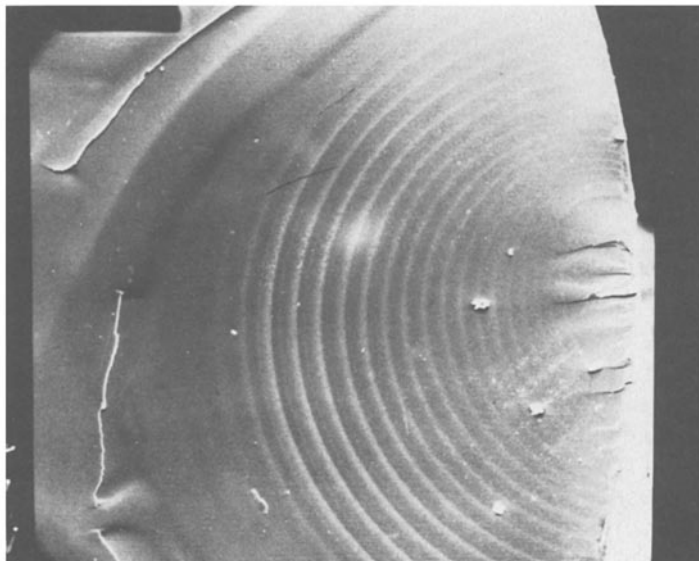


Figure 10. Scanning electron micrograph showing discontinuous growth bands on fracture surface of PS specimen tested at $\sigma_m = \sigma_a = 8.6$ MPa [31].

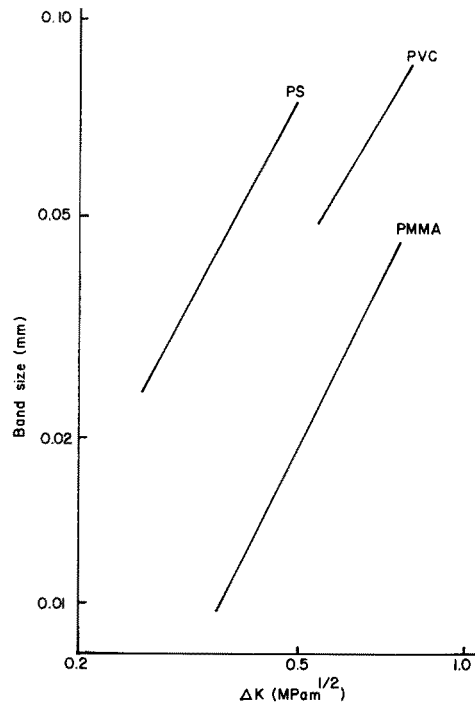


Figure 11. Discontinuous growth band size vs. ΔK for three thermoplastics [45].

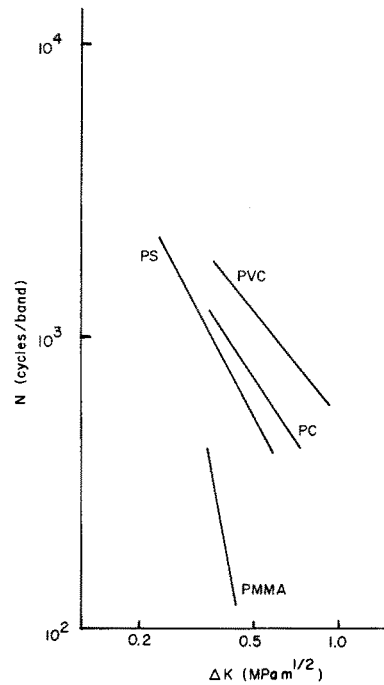


Figure 12. Cycles per band vs. ΔK for four glassy polymers [45].

and crack size, as $K_{\max} = Y\sigma_{\max}\sqrt{a}$. Computed values are found to be in fairly good agreement, for a number of different glassy polymers, with the reported craze initiation stresses, determined in simple tension [45, 46]. The crack opening displacement (COD) can be estimated from the expression (5)

$$\delta = \text{COD} = \frac{K^2}{\sigma_y E} \quad (5)$$

For PVC, it is reported to be about $20 \mu\text{m}$ or about twice the craze thickness [40]. For PE, the size of the observed damage zone at the crack tip increases as ΔK^2 , in accord with Eqn. (4), but it also increases appreciably with decrease of cyclic frequency [42].

A model for fatigue crack growth, based on a reduction in craze stress due to continued cycling, has been developed [47]. In this model it is assumed that crack growth will occur when the crack opening displacement reaches some critical value. The model is reported to give a good account of the influence of the applied stress intensity factor on FCP rate in various polymers, such as PMMA, PC, Nylon 66 and PE, and to account also for the effects of frequency and mean stress.

Slight changes in structure can affect the fatigue fracture surface morphology. For example, in pure POM (Delrin) discontinuous growth bands have been observed at high test frequencies and striations at low frequencies; but in the copolymer (Celcon), frequency had little effect and only discontinuous growth bands were noted [48].

E. Kinetic concept of fatigue fracture

Several investigators have adapted the kinetic concept of fracture developed by Zhurkov and coworkers [49, 50] to the fatigue failure process [7]. According to the kinetic concept, thermofluctuation events, activated by stress, lead to fracture of

interatomic bonds and the fracture process can be characterized by either the number of bonds broken per unit time or by the time-to-break under a given applied stress. The usual expression for the lifetime, τ , under an applied stress, σ , is:

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{kT}\right) \quad (6)$$

where τ_0 ($\sim 10^{-12}$ sec) is characteristic of the period of atomic vibrations, U_0 is the activation energy and γ a structure-sensitive coefficient. This equation is in general accord with data on static fatigue of many different materials investigated at various temperatures and stresses [5, 49] but various modifications have been proposed to take account of the stress distribution on the bonds near to the crack tip [51].

For comparison of lifetime data under static or cyclic loading conditions, it is necessary because of the variation of the load during cyclic tests, to determine an equivalent cyclic time, τ_{cy} . This time will be less than the actual fracture time and it will depend on the nature of the load variation. For some materials, such as polyacrylonitrile fibers or PMMA films good agreement has been reported between the variation with stress of both the static lifetime and the cyclic lifetime under sinusoidal loading [52]. However, in other materials, differences arise and these have been attributed to changes of the structure-sensitive parameter γ with temperature and stress and also to changes produced by the hysteresis self-heating effect. Thus in applying Eqn. (6) to the case of fatigue failure, the ambient temperature T should be replaced by the specimen temperature, T_s , and γ may also change due to structural changes produced by the cyclic loading [7].

4. Effects of various experimental variables

A. Test frequency

The influence of test frequency depends to a great extent on the viscoelastic nature of the polymer in the temperature region of investigation. Where hysteresis losses are significant, an increase of frequency will cause greater energy dissipation. A significant temperature rise may then ensue and deleteriously affect fatigue lifetimes.

In some materials, or under appropriate conditions where thermal effects are not dominant, an increase of frequency leads, in many polymers, to an increase in fatigue lifetime. One reason for this is that higher frequencies mean higher strain rates and hence there will be an increase in modulus and yield strength. Another reason, especially for fracture mechanics type specimens, is that localized heating at the flaw tip may blunt the crack somewhat, lower the effective stress intensity factor and thus decrease FCP rates [53]. In PS, for example, marked decreases in da/dn have been observed on raising frequency from 1 Hz to 10 Hz and again on raising frequency from 10 Hz to 100 Hz [54].

Another glassy polymer, PMMA, also shows a strong frequency sensitivity. In one study [55] it has been observed that the FCP rate decreased almost one decade upon increasing the frequency from 7 cpm to 17 cpm. In another study, made at -60°C , the rate of increase of crack length with time decreased noticeably, as shown in Fig. 13, as the frequency increased from 5 Hz to 100 Hz [56].

The effect of frequency can be described in terms of a frequency sensitivity factor (FSF) defined as the change in crack growth rate per decade change in frequency. It has been suggested that this factor will be relatively large for those polymers, such as PMMA, in which the frequency of molecular motions associated with the β viscoelastic damping peak is comparable to the test frequencies [57].

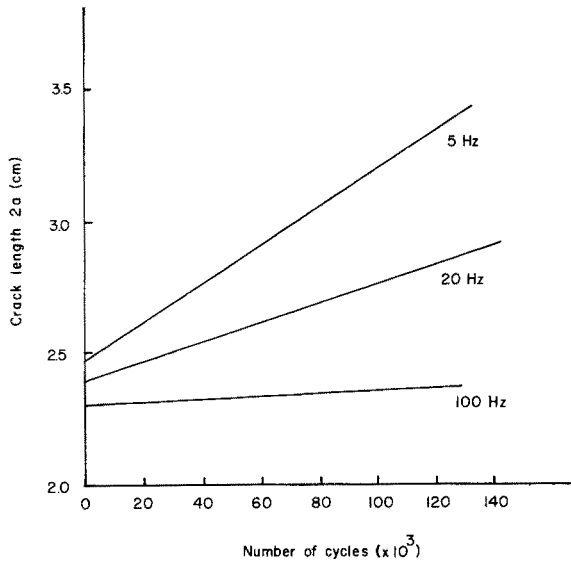


Figure 13. Crack length vs. cycles for PMMA tested at -60°C , with $K_{\max} = 0.66 \text{ MPa}\sqrt{m}$ and $K_{\min} = 0.22 \text{ MPa}\sqrt{m}$, and at several different frequencies [56].

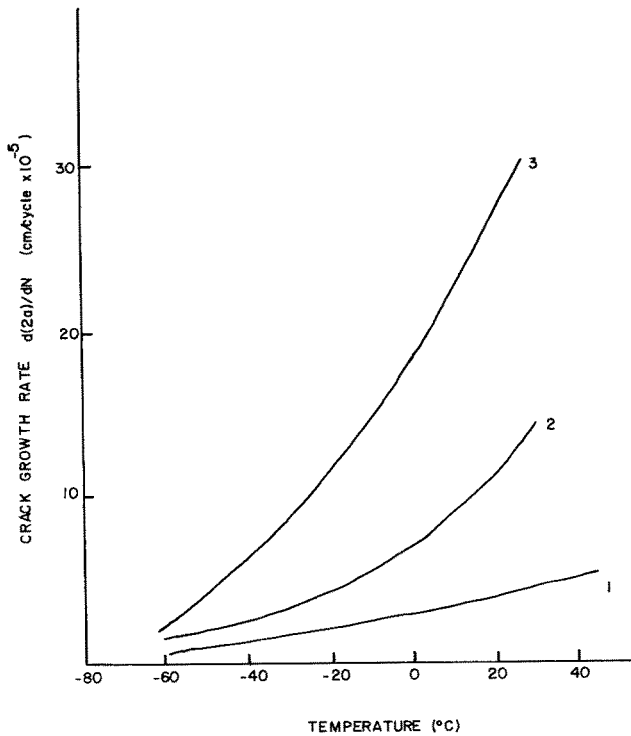


Figure 14. FCP rate vs. temperature for PMMA for various values of λ [56].

However, for those polymers where this condition is not met, as for nylon 6/6, PC and PSF, experimental observations made at ambient temperature indicate little or no frequency sensitivity [39]. Greater frequency sensitivity of FCP rates can be induced in these latter materials by lowering the temperature so as to bring the molecular jump frequencies closer to the applied test frequencies [58].

On the Williams' model of fatigue crack growth in polymers the influence of frequency on FCP rate is attributed to the strain rate sensitivity of the modulus, E , and hence of the fracture toughness parameter, $K_c = E\sqrt{\delta\epsilon_y}$, where ϵ_y , the strain at yield, is considered insensitive to strain rate effects [47]. However, it has been shown that in many polymers, as PVC, PS and poly(2,6-dimethyl-p-phenylene oxide) (PPO), the modulus is not particularly sensitive to strain rate effects and changes by only about 1% for each of several decades change in frequency [59].

Frequency also affects the stress level at which thermal runaway occurs. In POM, in uniaxial fatigue at 300 cpm, thermal runaway occurs at $\sigma > 21.6$ MPa, but at a test frequency of 100 cpm, the threshold stress for thermal runaway is 27.8 MPa [17].

B. Temperature

The effects of temperature on fatigue behavior have not been widely studied. In several polymers, lifetimes to fracture decrease and FCP rates increase with increasing temperature. For the case of polystyrene, tests made at a series of temperatures from 5°C to 75°C on unnotched specimens in cyclical compression indicate that, with increasing temperature, the $\sigma - N$ curve retains its general shape but shifts to lower stress values and to shorter fatigue lifetimes [35]. Analysis of these results in terms of an Arrhenius equation for the reciprocal of the time to failure at 1 Hz, together with a Coulomb-Navier yield criterion, permits determination of the temperature dependence of activation energy and activation volume. A change in dependency of activation energy, and of the limiting endurance stress, is noted near 50°C and this suggests a correlation between the β -molecular relaxation process and the fatigue behavior.

For PMMA, studies have been made at 5 Hz of fatigue crack extension at four different temperatures ranging from -60°C to 40°C [56]. These tests were made at constant values of λ where $\lambda = 2\Delta K \cdot K_m$ and K_m is the mean stress intensity factor. The test results, shown in Fig. 14, indicate that FCP rates decrease with decreasing temperature, and, for a given temperature, they decrease with decreasing values of λ and hence of either K_m or ΔK . Other tests on PMMA made at 1 Hz, and at temperatures to -120°C show little effect of temperature on da/dn between -120°C and -70°C but then a rapid rise of a decade or more in FCP rate occurs as the temperature rises from -70°C to room temperature [58].

The effects of temperature on FCP rates in PC are complex. One study suggests FCP rates decrease with decreasing temperature to -60°C [56]. Another study, carried out at 1 Hz and over a much wider temperature range, suggests that the highest FCP rates are obtained at a temperature of -50°C [60]. In this latter study, for a given FCP rate, a linear relation is found between the stress intensity amplitude and the fracture toughness parameter K_{Ic} ; as K_{Ic} also shows a minimum value at -50°C and then rises as temperatures are raised or lowered. Rather similar conclusions can be drawn from a third study of PC wherein the FCP rate, at a test frequency of 1 Hz, was determined as a function of temperature [58]. Here, the highest rates were recorded at about -60°C and enhanced fatigue resistance encountered as temperatures were either decreased or increased.

Prior exposure to elevated temperature may increase the fatigue resistance of crystalline polymers. To illustrate, tension-compression cycling tests at 320 cpm have been made on nylon 6 annealed in two different ways [61]. Upon heat-treating in water at 100°C, the endurance limit rose from about 22 MPa to 25 MPa; and upon annealing in oil at 180°C, the endurance limit increased to about 32 MPa. The enhancement in fatigue performance is attributed to several effects: to release of residual stresses and to development of more uniform crystal structure.

C. Mean stress

In cyclic loading, if the mean stress, σ_m , is increased while keeping the alternating stress component the same, then fatigue resistance is reduced. This is shown in Fig. 15 for unnotched specimens of PS tested at an alternating stress of 17.2 MPa and at various mean stress values ranging from 0 to 17.2 MPa [31]. At zero mean stress, the average life is about 30,000 cycles but $\log N$ decreases linearly as σ_m rises. There are also changes in the fracture surface morphology. For low mean stress values, the morphology is similar to that of Fig. 6 but for high mean stress values, crack initiation occurs at several closely spaced surface defects or crazes and the smooth slow growth region surrounding the source changes its character and takes on a step-like appearance.

If, however, the mean stress is increased while maintaining a constant maximum stress of 17.2 MPa the fatigue resistance of PS is increased rather than diminished. Under these circumstances, multiple crazes may be seen on the surface of the specimen and, at a σ_{\max} of 17.2 MPa and a σ_m of 12.9 MPa, it is possible to exceed 10^7 cycles without fracture (Fig. 8). Evidently the alternating component of stress is here too small to produce significant energy dissipation or to induce craze breakdown.

Fracture mechanics type experiments also show the importance of mean stress and of the mean stress intensity factor K_m of FCP rate. In extensive experiments, carried out on PMMA, it was suggested that the best fit to the data was given by the following expression [62]

$$\frac{da}{dN} = \frac{AK_m^{2.13}\Delta K^{2.39}}{f^{0.43}} \quad (7)$$

where f is the applied frequency.

Thus, both mean stress and stress intensity factor range are important variables governing crack growth; and an increase of frequency, as noted in the data of Fig. 13 will decrease fatigue crack growth. The effect of mean stress intensity factor is also apparent in Fig. 14 as increases in λ , which can be accomplished by increasing either K_m or ΔK , clearly lead to higher FCP rates at any temperature.

D. Flaw size and surface notches

The rate of crack growth, particularly in rubbers, has frequently been expressed [5, 8] in terms of a surface work parameter, J , as

$$\frac{da}{dn} = BJ^n \quad (8)$$

where B , referred to as the dynamic cut-growth constant, and n are constants. The exponent has a value close to 2 for natural rubber but may increase to about 4 for a noncrystallizable SBR rubber. Attempts have been made to apply a similar equation to polymers [63, 64]. For a single edge notched specimen of the type frequently used

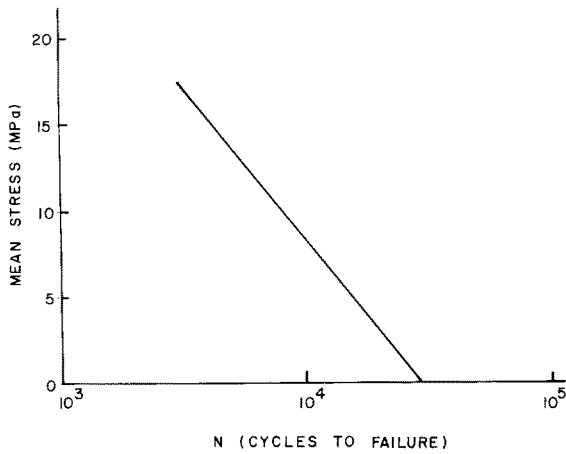


Figure 15. Effect of mean stress on lifetime for PS specimens tested at $\sigma_a = 17.2$ MPa [31].

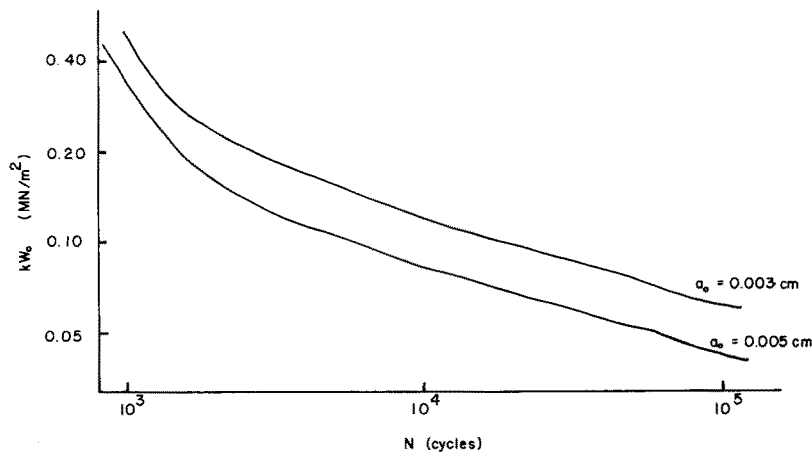


Figure 16. Stored energy vs. cycles in LDPE for two assumed values of flaw size [65].

in fatigue experiments one can relate J directly to the energy density, which for a completely elastic material, is

$$J = \pi a W_0 = \frac{\pi a \sigma^2}{2E} \tag{9}$$

or more generally, $J = kaW_0$, where W_0 is the stored energy density, E is the modulus, and k is a constant, that may depend on the material being considered. Upon placing this expression for J into Eqn. (8) and integrating from $N = 0$ cycles at $a = a_0$ to $N = N_f$ at $a \rightarrow \infty$, one obtains the following equation for the fatigue life

$$N_f = (Bk^n W_0^n a_0^{n-1})^{-1} \tag{10}$$

where a_0 is the initial crack length. This equation is reported to give good agreement with data on elastomers [5].

One can also use Eqn. (10) together with observed values of N_f , to estimate the inherent flaw size, a_0 , of unnotched polymers. Figure 16 shows how N_f depends on energy density (hence on stress squared) for LDPE for two assumed values of a_0 , vis. 3×10^{-3} cm and 5×10^{-3} cm [65]. The experimental data points (now shown) fall essentially in the band shown. Thus the intrinsic flaw size for LDPE, by this method

of estimation, is about 4×10^{-3} cm, a value probably comparable to the depth of surface scratches or to size of spherulites.

The intrinsic flaw size of a glassy polymer, PS, has been estimated from fatigue tests carried out on sharply notched samples at 1600 cpm at an alternating tension compression stress of 17.2 MPa. The average lifetime *vs.* the notch depth is shown in Fig. 17 [66]. The estimated inherent flaw size of unnotched specimens is about 2×10^{-3} cm; with imposed notches smaller than this, the fracture is not controlled by the notch but may occur anywhere in the gage length. This value for the intrinsic flaw size in PS is much smaller than that determined in static fracture experiments where an unrealistically high value of about 1 mm is obtained [67]. The value of the exponent in the dynamic cut growth equation can also be estimated from a plot of $\log N_f$ *vs.* $\log a_0$. It is found to be 1.84 for PS [68] as compared to a reported value of 2.5 for PMMA [63].

The effects of surface flaws, such as fine scratches, are not only detrimental to the fatigue resistance of many homogeneous polymers but they are also reported to result in a drastic reduction in fatigue life of even filled polymers [69]. The effect of notch geometry on the fatigue performance of fracture mechanics type specimens has been investigated. In one report, little difference is noted in the FCP behavior of PVC whether the notch is made by a sharp razor blade or induced by fatigue [40]. However, in another study involving PS, marked differences in behavior for these two situations was reported [70], with razor notching leading to craze bunches near the crack tip and a high fracture toughness while fatigue-induced cracks led to a single craze at the tip and a lower K_c value.

5. Effects of various material variables

A. Polymer structure

In general, crystalline polymers are considerably more fatigue resistant than are the glassy amorphous polymers. One reason for this is that their two-phase structure, consisting of a rigid crystalline phase imbedded in a compliant amorphous phase offers greater impedance to crack propagation. Another reason is that the crystallite deformation modes can absorb some of the fracture energy. Thus many of the crystalline polymers, like nylon and POM, have both high yield strengths and high toughness and this combination of factors leads to comparatively high endurance limits under cyclic loading. In fact, POM has a fatigue resistance superior to metals if one normalizes the FCP rate data by plotting da/dn *vs.* $\Delta K/E$ [48].

Many of the amorphous polymers, like PS, PMMA, PC, PPO, and cellulose acetate (CA) have a reported endurance limit that is only about 1/5 of the fracture stress, but this ratio rises to about 0.3 for nylon 6/6 and, for polymers or copolymers of poly(oxymethylene), it is about 0.5 [71]. It is also close to 0.5 for PTFE provided tests are carried out at a low frequency so that significant thermal effects are not present.

For linear polyethylene, the FCP rate, for the same ΔK value, is much lower than for the branched, less-crystalline variety (LDPE) but this difference largely disappears if one plots the data *vs.* $\Delta K/E$. Although fatigue resistance is generally higher for the crystalline polymers than for amorphous ones, as Fig. 9 indicates, there are few, if any, detailed studies of the relationship between crystallinity and fatigue endurance for any given polymer. Recent data obtained on PE indicate that FCP rates are generally lower for quenched samples than for slow cooled ones [42].

Unnotched PE specimens show outstanding fatigue endurance. In one study carried out at a low frequency of less than 2 Hz so that thermal effects would not be a serious problem, it was observed [14] that, for all specimens having a molecular weight of 50,000 or over, no fatigue failures occurred in less than 5 million cycles, even though the applied alternating tension-compression stress was 20.6 MPa, a value only about 10% less than the yield stress in simple tension. For comparison, under similar stress condition, the glassy polymer PS—even though its tensile strength is almost double the yield strength of PE—develops fatigue fracture in about 10^4 cycles [15]. In another study, it was noted that, under the conditions imposed, fatigue cracks could not be grown at all in POM, PP and PTFE, all highly crystalline polymers [41].

There are considerable differences in crack propagation rate among the amorphous polymers themselves, as is evident from the data presented in Fig. 9 as well as from various literature references [1, 40, 45]. Those polymers which craze in preference to shear yielding, as PS and PMMA, show the highest FCP rates. In those, like PVC and PC, which show shear yielding and necking, in addition to some crazing, in tension, the FCP rate, at a given ΔK value is much lower than for PS and PMMA. This behavior may also be related to the greater backbone chain mobility, as manifested particularly for PC by a large low temperature damping peak [72]. Increased chain flexibility should aid in providing a more uniform stressing of the macromolecules under cyclic loading conditions. This condition has in fact been noted for PC, in comparison with the behavior of PS, from studies of the distortion introduced in IR bands by cyclic loading [28].

Another interesting observation is that for PMMA and PS, the FCP rate curves cross one another as shown by Fig. 9. Thus, at low ΔK (as for very small notches or for unnotched specimens), PMMA is more fatigue resistant than PS but at high ΔK (as for specimens with large notch size) PS is the more fatigue resistant of the two polymers. This situation with regard to fatigue behavior is rather similar to that for fracture strength where it has been found that PMMA is stronger than PS in unnotched specimens but PS is stronger than PMMA in most notched specimen [67]. It may be that a greater degree of crazing and of craze bundle generation near the crack tip in PS accounts for its superior fracture strength and fatigue resistance when notched specimens are tested.

Flexible polymers, like vinyl urethane, appear to behave differently under cyclic loading than do the polymers with greater rigidity, such as PMMA and PC. For example, in vinyl urethane a change in waveform from triangular to square reduced the FCP rate by a factor of 6 [73]. But in PC, square, triangular and sinusoidal wave forms all give essentially the same response and, in PMMA, the FCP rate was somewhat higher with the square waveform than the triangular [39]. It has been suggested that at least two different factors are involved. One, which is helpful to fatigue response, is the higher strain rate associated with square wave loading and this appears dominant in the vinyl urethane. The other is the associated creep deformation that is always present, especially in tensile loading with a square waveform; and this relaxation mechanism, which one would expect to lead to lower fatigue resistance, is probably the dominant one in PMMA.

FCP rates have been measured in vinyl urethane resins, having increasing concentrations of styrene [73]. The compositions with higher styrene content exhibited about the same static tensile yield stress but under cycling loading, they developed higher FCP rates. This effect is probably due to a decrease in craze stress with increasing styrene content.

B. Molecular weight

It has been noted earlier that fatigue fracture in glassy polymers is preceded by crazing and, in crystalline polymers, by formation of a damaged zone at the crack tip. After some number of cycles, a microcrack initiates in the craze or damaged zone due both to fracture of highly stressed molecular chains or fibrils and to void coalescence. With subsequent cycling, the crack propagates, generally in a discontinuous manner, through the crazed or damaged zone. As the stress intensity factor rises, incremental crack growth may also occur prior to catastrophic fracture. Evidence for both types of crack growth in a number of different polymers, has been obtained [45].

In view of the above, if craze strength and stability could be enhanced and chain rupture or fracture inhibited, then more fatigue cycles could be endured at a given stress or stress intensity factor, and a higher stress, for a given number of cycles, could be realized. One promising means of doing this is to increase molecular weight (M.W.). It is frequently stated that physical properties of polymers, such as its glass transition temperature, increase markedly with molecular weight in the low M.W. region, but tend to approach a constant value as M.W. reaches a value somewhere between 100,000 and 200,000. While this may be true for some properties, such as T_g or possibly modulus, it does not hold for ultimate properties such as fatigue endurance [14, 15, 74–76]. Also, various literature references indicate that increasing molecular weight also increases craze strength, creep resistance, and endurance under long-time steady loading [3, 77].

The large effect of molecular weight on performance of PS specimens has already been illustrated in Fig. 5. The $\sigma - N$ curves shown on this figure for the narrow MWD polymers were obtained from tests made on anionically polymerized PS standards of three different molecular weights [14, 78]. A dramatic improvement in fatigue lifetime, at any given stress level, is evident with the increase between the low M.W. sample (1.6×10^5) and the high M.W. sample (2.0×10^6) being more than 2 decades.

It is of interest to compare the effects of M.W. on fatigue behavior of polymers with its effects on strength under monotonic loading. For 3 PS standards, Fig. 18 shows how the static tensile strength and the fatigue strength at 10^7 cycles vary with number average molecular weight [79]. While the tensile strength increases about 25% from the low to the high M.W. sample the fatigue strength increases by about 100% and the ratio of tensile strength to fatigue strength rises from about 0.2 to 0.3. These striking increases in both fatigue lifetimes and in fatigue strength with increasing M.W. are attributed to several factors [14, 74, 79]. First, with increase in molecular weight and in the chain entanglement density, there is an increase in craze strength and stability and in orientation hardening of the craze fibrils. Recent measurements of craze fibril extension ratios in thin films of PS support these ideas [80]. Secondly, as has been noted, the decrease in the number of chain ends is also an important factor [74], as chain ends can act as sources of submicron cracks and thereby effect fracture strength or lifetime under stress [81]. Thus if one irradiates PS specimens to obtain higher values of \bar{M}_w and then tests these irradiated specimens in fatigue, it is noted that no increase in fatigue endurance occurs, presumably because the number of chain ends has not been reduced [79].

Some studies have been reported concerning the effects of M.W. on fatigue performance of several glassy polymers obtained under pulsating compressive stresses [82]. One advantage of such studies is that they allow test data to be acquired on relatively low M.W. samples of glassy polymers that are too brittle to investigate in tension. Low molecular weight samples of PE, with M.W. of 5000, have been tested in alternating tension-compression [14]. The $\sigma - N$ curve for these samples did not

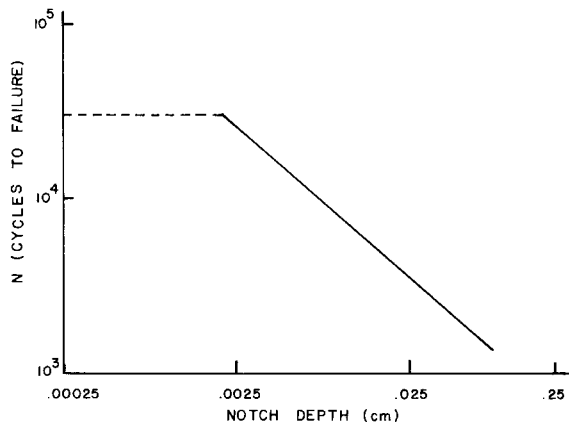


Figure 17. Influence of notch depth on fatigue lifetime of PS specimens tested at $\sigma_a = 17.2$ MPa, $\sigma_m = 0$ [66].

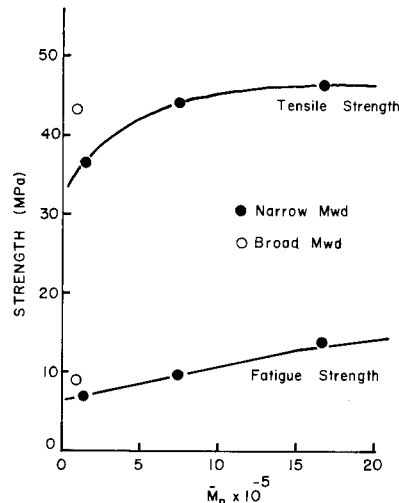


Figure 18. Tensile strength and fatigue strength vs. \bar{M}_n for various PS specimens [79].

exhibit the knee that is evident for PS specimens in Fig. 5 but did show an approximate linear relation between σ_a and $\log N$. The importance of M.W. to crystalline polymers, as well as to amorphous ones, is evident from the fact that, in this same study, and at a comparatively high alternating stress level of 20.6 MPa, no fatigue failures occurred in a 50,000 M.W. polymer until about 5×10^6 cycles and none at all occurred in higher molecular weight samples (6.85×10^5 and 2.1×10^6) even after 10^7 cycles.

The important role of M.W. has been noted from fracture mechanics type experiments. For example, it has been observed that FCP rates in PMMA decrease by two orders of magnitude on increasing \bar{M}_v from 10^5 to 4.8×10^6 [75]; and the number of alternating cycles per growth band in PVC increases by more than one decade as the M.W. increased from 9.7×10^4 to 2.3×10^5 [45].

Molecular weight distribution might also be expected to play an important role in developing fatigue resistance in polymers as it is known that in PS, addition of even 1% of a high M.W. component (6.85×10^5) to a low M.W. component (10^4) increases the resistance to fracture and produces crazes and craze fibrils under tensile loading whereas only fracture cracks appeared before the addition of the high M.W. component [83]. Thus the high M.W. components in any broad MWD polymer give increased craze stability and this should lead to increased fatigue resistance. In Fig. 18, for example, it may be noted that the broad MWD commercial polymer shows both a higher fatigue strength and a higher tensile strength than would be expected based on the trends for the three narrow MWD polystyrenes.

MWD has also been shown to play an important role in fracture mechanics type studies of FCP rate [84]. These fatigue studies have been carried out on specially prepared PMMA specimens containing either high-M.W. tails or low M.W. tails. It was noted that, whereas the polymer with the low M.W. tail gave essentially equivalent FCP rates to the standard polymer of the same \bar{M}_n value, the polymer with the high-M.W. tail showed considerably lower FCP rates. This improvement in fatigue resistance is another manifestation of the importance of molecular entanglements in developing increased craze stability in amorphous polymers subject to cyclic loading.

C. Rubber modification

It is now well established that incorporation of a rubber phase, particularly in glassy polymers, will greatly increase impact resistance and toughness [85, 86]. Its effect on fatigue resistance while present, is generally not as striking. For example, ABS shows FCP rates about one-third of that of PS over the ΔK range from 1–2 MPa \sqrt{m} [21] but it is inferior to both rigid PVC [41, 87] or to PC [88] over wide values of the stress intensity factor range. The rubber toughened PS grade, HIPS, shows a slightly lower FCP rate than PS, although it has a much higher impact strength, but a slightly higher FCP value than ABS [89].

Some fatigue test data on unnotched samples of ABS and HIPS, taken at the very low speed of 2 cpm, and in a tension compression square wave loading pattern, have recently been reported [22]. Hysteresis loop areas recorded after various number of cycles are shown in Fig. 19. The loops for ABS tend to be symmetrical. This is attributed to shear yielding being the dominant deformation mode fatigue in this polymer. In HIPS, in contrast, the hysteresis loop area is much greater for the tension half-cycle than for the compression half-cycle and, after remaining essentially constant for some number of load cycles, it begins to significantly increase. This effect is attributed to the production and growth of crazes after some induction period. For ABS, with increase of stress amplitude the energy dissipated per half-cycle, as well as the temperature rise in the specimen, increase significantly, while the effective secant modulus decreased. Thus it appears that a cyclic softening effect occurs in the rubber modified polymers as well as in homopolymers like PC or nylon 6/6.

It may be concluded from these results that the incorporated rubber phase is less effective in enhancing fatigue performance than impact strength because, at high stress amplitude, the increasing hysteresis losses and the associated temperature rises lead to strong thermal influences on fracture; while, at low stress amplitudes, where brittle crack propagation is encountered, the rubber particles, due to the triaxial strain conditions prevailing at the crack tip, are not as effective for producing crazes as under tensile loading [22].

Some attention has been given to the fatigue performance of other rubber-toughened polymers. PVC's of different molecular weights, and with varying percentages of a methacrylate-butadiene-styrene (MBS) modifier, have been studied [90]. A reduction in FCP rate was realized upon addition of MBS with the relative effect depending on the molecular weight. For $\bar{M}_w = 67,000$ and for 14% MBS, the FCP rate reduces one decade or more. At higher \bar{M}_w values about 200,000 the FCP rate was still reduced by incorporation of 14% MBS but the relative effect was smaller. For a given MBS constant, as 10%, a reduction in rate of about 1 decade was observed with increase of \bar{M}_w for 67,000 to 210,000. Thus, as noted in a preceding section, an increase of average chain length and a reduction in number of chain ends is beneficial to the fatigue behavior of rubber toughened polymers as well as to homopolymers.

Under some circumstances, incorporation of a rubber phase can be effective in improving fatigue resistance while ineffective in increasing impact strength. For example, with methacrylate-butadiene modified PVC's, it has been noted that for low molecular weight resins, fatigue crack propagation rates decrease about 7X upon incorporation of 6 phr of rubber while the impact strength is unchanged [89]. Furthermore, upon increasing rubber content to 10% the fatigue durability is unaffected while the impact strength falls by a factor of 5. However, for high M.W. resins, the situation changes. Here an increase in fracture toughness, in fatigue resistance, and in impact resistance of 6 phr of rubber is observed; but, on further increase in rubber content, the relative impact strength increases greatly while the fatigue performance remains about the same.

Attempts have been made to correlate damping and fatigue properties of HIPS using a controlled amplitude torsional pendulum [91]. For an applied tension stress of 11.8 MPa and for an alternating angular displacement of 0.03 radians or greater, crazing and amplitude dependent damping occurred even though no crazing is observed for much longer times at the same tensile stress in a static creep experiment. It was also noted, from examination of the fracture surfaces of specimens cycled for 16,000 cycles, and then fractured at liquid nitrogen temperatures, that the fracture passed through the fatigue-induced crazes and, frequently, through the rubber particles as well; also the rubber particle boundaries were much easier to delineate than under simple static fracture.

Even in rubber modified polymers, surface condition is important to fatigue performance, as fatigue fracture generally starts at the surface and then propagates inward with time. For example, it has been noted that in HIPS the fatigue lifetime, for a rotating bending specimen stressed to a maximum value of 13.8 MPa, was about one decade higher for specimens with smooth molded surfaces than for specimens with scratched surface [69].

D. Fillers and reinforcement

Fillers are frequently used in polymers to increase stiffness and to reduce cost. When improved strength and better fatigue performance are needed, fillers are usually replaced by fiber-type reinforcement.

Some fatigue data have been obtained on both thermoplastic matrices, like the nylons, and on thermosetting matrices, like the epoxies, containing inert fillers such as glass beads, silica powder or clay particles. In one study of such systems, an effort was made to monitor the extent of damage produced by fatigue cycling by following the changes in modulus and damping as a function of stress or strain amplitude and of number of cycles [69]. In tests carried out at high stresses, a drop in modulus and a rise in damping was observed and attributed primarily to heat build-up.

However, unlike the situation in unfilled thermoplastic [26], cyclic softening did not appear to set in until near the end of the specimen lifetime. For example, in tests carried out at 3.6 Hz on nylon 6 rotating-beam type specimens containing 70 wt. % glass beads, no significant changes were noted in the dynamic mechanical properties up to 22,000 cycles, even though the lifetime at the imposed maximum stress of 13.8 MPa was only 200–500 cycles longer [69]. Thus monitoring of mechanical properties during fatigue of filled polymers does not appear to be a promising method for estimating fatigue lifetimes.

The fatigue strength of polymers, and the ratio of the fatigue strength to the tensile strength, can be increased by fortifying the polymer with short glass fibers. Some $\sigma - N$ curves obtained on 3 thermoplastics containing 40 wt. % glass fibers ($\frac{1}{2}$ " long) are shown in Fig. 20 [92]. The data was acquired in fluctuating tension at a test frequency of 600 cpm. In all three cases, the fatigue strength at 10^7 cycles has been raised by the inclusion of the glass fibers. For the glass fortified PS, the endurance strength is 0.39 of the tensile strength while for PE and nylon, the ratios are 0.32 and 0.36 respectively. This compares to values obtained from alternating tension-compression tests of about 0.20 for unreinforced glass polymers and to values in the range of 0.25 to 0.45 for laminated and reinforced polymers [71].

The nature of the crack growth process in reinforced polymers is quite complex. It involves crack initiation usually at the interface of the fiber and the matrix, propagation along the fibers, debonding, fiber pull-out, and crack propagation in the matrix material itself. Thus in nylon, $1/8$ " glass fibers give improved fatigue resistance,

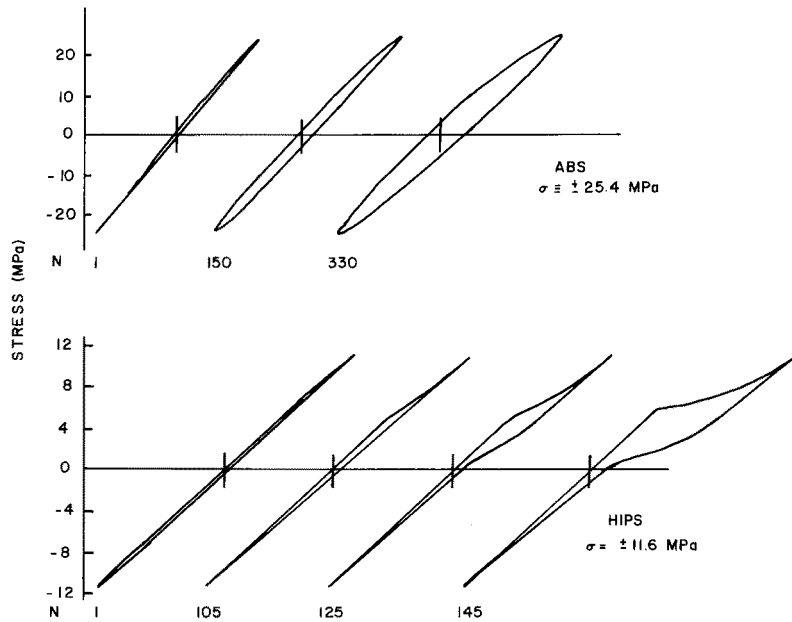


Figure 19. Hysteresis loops after various cycles in ABS tested at $\sigma_a = 25.4$ MPa and in HIPS tested at $\sigma_a = 11.6$ MPa [22].

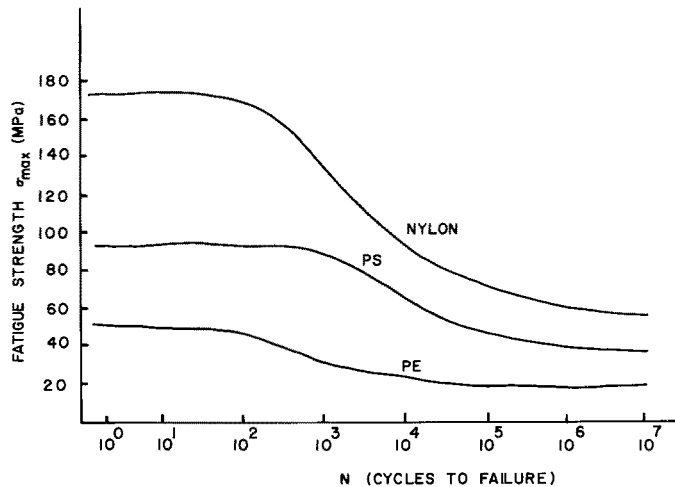


Figure 20. Fatigue strength vs. cycles for three glass fiber reinforced plastics [92].

and higher endurance ratios (0.50 vs. 0.36) compared to $\frac{1}{2}$ fibers, presumably because the longer fibers provide better channels for fatigue-induced crack growth [92].

A rather unusual filled polymer, designated Simplex P, which is used as a bone cement and is prepared by mixing in the ratio of 2:1 a PMMA powder with MMA liquid monomer, has been studied in fatigue by monitoring the FCP rate of SEN specimens as a function of ΔK [93]. For any given ΔK value the filled polymer has somewhat lower FCP rates than a pure PMMA material and the resistance to crack growth is further improved by introducing microvoids during the kneading operation. The enhanced FCP resistance is attributed to pinning of the crack tip by the constituent particles and to crack bifurcation and increased energy absorption caused by the presence of the microvoids.

Some additional fatigue tests have been made on rotating beam type specimens of acrylic cements [94]. One interesting result is that the average fatigue lifetime was increased 5 times when tests were run in bovine serum at 37°C, rather than in ambient air, in order to simulate *in vivo* conditions. Other examples of fatigue enhancement in pure polymers through control of environment and surface treatments will be given in a later section.

Studies have been made of FCP rates in nylon 66, reinforced with short graphite fiber, as a function of both the maximum stress intensity factor and the stress intensity factor range [95]. The test results could not be correlated with Eqn. (3) but could be correlated by the Erdogan equation [96]

$$\frac{da}{dt} = \beta [K_{\max}^{1-\gamma} \Delta K^\gamma]^r \quad (11)$$

where β , γ and r are constants for fixed values of frequency and temperature. Hence, as already noted for homopolymers, the ΔK value, though important, is not the only controlling factor for fatigue crack growth behavior in reinforced polymers. The mechanism of crack propagation in these short fiber reinforced polymers involved matrix deformation and cavitation, as well as fibre pullout and breakage, and, in some respect, was analogous to that involved in growth and fracture of crazes in thermoplastics [95].

It appears that submicroscopic flaws can nucleate early in the fatigue life of composites and then grow with continued cycling. For example, in polyester reinforced with glass cloth many cracks were already observed at only 2% of the specimen lifetime [97]; and in the graphite reinforced nylon 66, the flaw propagation rate remained constant for almost the entire lifetime, until it accelerated during the last several cycles [95].

E. Diluents

The possible influence of diluents or plasticizers on fatigue behavior has been little studied to date. To the extent that the added plasticizer reduces T_g and increases bulk mobility, one would expect that it would act rather like an increase in temperature and thus increase FCP rates. However, under some conditions, it may lead to crack tip blunting and this should be helpful to fatigue resistance.

In one study of FCP rates in PVC at a low frequency of 15 cpm it was observed that, as the plasticizer content (DOP) increased, so too did the fatigue crack rate [98]. In another study, however, with 13% DOP, no change in FCP rate was found in tests at 600 cpm with a low molecular weight polymer ($\bar{M}_v = 6.1 \times 10^4$) but a slight increase for the plasticized material was reported for a high molecular weight polymer ($\bar{M}_v = 2.3 \times 10^5$) [75].

Some observations have been reported of FCP rates in PMMA internally plasticized (copolymerized) with butyl acrylate (BA) [75]. The results were complex. Poorest results were obtained with 20% BA; better results with 30% BA, with behavior analogous to commercial PMMA; and still lower FCP rates, especially at lower ΔK values below $1.0 \text{ MPa}\sqrt{m}$, for the sample with 10% BA and whose behavior was rather similar to that of the pure PMMA. It thus appears that several mechanisms are operative. As the % BA is increased the material becomes softer and more ductile and FCP rates increase. But at BA contents over 20%, localized heating probably leads to crack tip blunting and thus rates decrease again.

In both externally plasticized PVC and internally plasticized PMMA, it is possible to reach conditions where stable crack growth cannot be obtained at all. This

occurs in PVC with 20% added DOP [58] and in PMMA at BA contents above 30% [75].

The influence of water on FCP rate in nylon 6/6 has received some attention [1, 99]. Again, it appears that more than one mechanism is operative. At water contents to about 3%, FCP rates decrease but at 8% water content FCP rates are higher than for the dry polymer. At low water contents, molecular mobility increases and there is an improvement in molecular packing as *H*-bonds are disrupted. These factors appear to toughen the polymer; but, at high water contents, there is a significant plasticizer effect, T_g falls, the modulus decreases appreciably, and growth rates rise. Moisture effects have also been noted in fabric polyester laminates and in glass epoxy unidirectional laminates [100]. Water was found to increase FCP rates under cyclic loading but to decrease crack propagation rates under constant loading. In this latter case, it increased the size of the damage zone and reduced local stresses while in the cyclic tests, where the damage zone was already large, it simply weakened the material and thus increased FCP rates.

F. Cross-linking

Cross-linking of amorphous polymers, whether carried out by chemical or irradiation means, generally increases rigidity, and reduces ductility. It may thus inhibit or reduce creep or crazing and, by embrittling the polymer, inhibit local plastic deformation and possible crack tip blunting. Thus lower fatigue crack resistance is expected.

Studies of FCP rates in notched samples of cross-linked PS (CLPS) have been made [25, 89]. The test results show that CLPS is generally inferior to regular PS, and that it exhibits less frequency sensitivity, probably because molecular mobility has been restricted. Fatigue lifetimes have been reported for a series of unnotched, branched PS samples produced by exposure to γ -radiation [79]. In tests made at an alternating stress level of 17.2 MPa and at a test frequency of 1250 cpm, it was found that the average lifetimes of the irradiated specimens, for doses up to about 70 Mrad, did not increase despite a large increase in \bar{M}_w . Additional irradiation to 200 Mrad (well beyond the gel dose of 83 Mrad) also gave no improvement in fatigue resistance [101].

The effect of cross-link density on FCP rates and on fracture toughness has been studied for a series of epoxy resins by altering the ratio of amine hardener to epoxy resin [58]. With increasing ratios from 1:1 to 2:1, it is found that FCP rates decrease for a given ΔK by almost 2 orders of magnitude. This is attributed to an increased molecular weight (M_c) between cross-links and to greater capacity for plastic deformation at the crack tip as a result of the increased mobility.

6. Effect of environment and surface coatings

Since fatigue fractures in most polymers develop from surface sources, fatigue behavior will be sensitive to the environment and enhancement, or deterioration, of fatigue resistance should be possible by use of appropriate surface environments.

It has been noted that, if polyamide samples are fatigue tested in certain liquids, such as petroleum ether, water and alcohol, the fatigue strength at a given number of cycles is raised as compared to results obtained in air [102]. However, this effect, which was observed at a relatively high frequency of 3000 cpm, was essentially a thermal one and attributed to a cooling of the specimen as the volatile media evaporated from the surface. In fact, in non-volatile liquids, as transformer oil, results were similar to those obtained in air.

Atmospheric oxygen can, in some polymers, deleteriously affect fatigue performance. This has been shown for nylon 6 where the endurance ratio increased from 0.23 for specimens tested in moving air to 0.27 for specimens tested in flowing N_2 [102]. As another example, it has been recently shown that a factor of 2 increase in fatigue life of unnotched PS specimens can be realized by testing in N_2 [78]. A similar increase is realized by testing in air, provided the specimens have first been coated with a very thin layer of ductile aluminum or gold [68]. Since the degree of enhancement is approximately the same for all three sets of test specimens, it is suggested that the primary effect is the exclusion of oxygen during the fatigue cycling. Although PS is not particularly sensitive to oxygen under ambient conditions fatigue fracture in this material is preceded by crazing, large localized plastic deformation, and possibly some bond fracture as craze fibrils rupture. The free radicals present can then interact with oxygen in the air to produce oxidative degradation.

For those polymers that show a propensity for crazing, it is to be expected that fatigue endurance will probably be lowered if known crazing agents are in contact with the specimen surface; while, if one can hinder the development of crazes, without sacrificing any existing molecular mobility that the polymer possesses, then fatigue endurance should be enhanced. As already noted, fatigue endurance can be significantly enhanced by increasing craze strength, as by increase of molecular weight. In this section, we present several examples to illustrate how fatigue endurance can be enhanced by surface treatment. First, however, let us look at the effects of known crazing (or cracking) agents.

A. Crazing or cracking agents

Various investigators have deliberately utilized liquid or vapor crazing agents as an active environment in order to accelerate the acquisition of fatigue data on polymers. In one instance, PVC specimens were fatigue tested in ethanol vapor, at 3.5 Hz and at 9.8 MPa, in order to study the influence of molecular weight [103]. Although ethanol is a non-solvent for PVC and does not significantly plasticize it, it will cause specimens to craze. Its use enabled the authors to readily observe the important effects of molecular weight on craze stability and fatigue lifetime, as at $\bar{M}_w = 51,000$, the specimens fractured in a few seconds but, at $\bar{M}_w = 228,000$, no fatigue failure occurred in 1600 min.

In another study, liquid ethanol and carbon tetrachloride were used to investigate FCP phenomena in PMMA with the crack rate being investigated as a function of ΔR where $R = K^2/E$ for the plane stress case [104]. For intermediate values of ΔR , the FCP rate was found to be a function of both the stress and of the absorbed solvent at the crack tip while for higher ΔR values, where crack speeds were large, the solvents had less influence. One interesting feature of these studies is that, at very low values of ΔR , there appeared to be an inverse effect, possibly associated with fine crazing acting to blunt the crack tip, with the FCP rate decreasing with increasing ΔR .

The influence of various crazing agents, such as heptane, kerosene and the alcohols up to *n*-butanol, on the fatigue durability of PS has received some attention [105]. In fatigue tests carried out on unnotched samples whose external surfaces were wetted with the active organic media just before the test was started, the average fatigue lifetimes as compared to that of the untreated specimens were lowered. For the alcohols and some other reagents there appeared to be a fair correlation between fatigue lifetime and solubility parameter with the lifetimes decreasing as the solubility parameter of the solvent, δ_s , became closer to that of the polymer, δ_p . Thus methanol with a δ_s value, highest of the alcohols, of $29.7 \text{ (MJ/m}^3)^{1/2}$ lowered fatigue lifetime

about a factor of 2; while butanol, whose δ_s value of $23.4 \text{ (MJ/m}^3\text{)}^{1/2}$ is closer to that of polystyrene, viz. $\delta_p = 18.6 \text{ (MJ/m}^3\text{)}^{1/2}$, lowered fatigue lifetime by about a factor of 20.

Many factors other than solubility parameter, such as the size of the molecule, its diffusion constant, its *H*-bonding index, time of contact, stress level, frequency, etc. probably play a part in this environmental phenomena; but in the fatigue tests on PS samples treated with the alcohols and tested in alternating tension-compression at a stress level of 17.2 MPa, the most important factor governing behavior appeared to be the degree of compatibility between the liquid and the polymer. Other investigators, who have studied the influence of a liquid environment on some physical properties of polymers, have also noted the important influence of solubility parameter. For example, a minimum value of the property at $\delta_s \approx \delta_p$ and a rise in value as the difference $|\delta_s - \delta_p|$ increased has been noted in studies of the influence of liquids on crazing strain in PS [106], on crazing stress in PPO [107], on the stress intensity factor for craze initiation in PS [108], on the surface work for crack propagation in PMMA [109] and on the crazing strain in PMMA in the presence of non-hydrogen bonding liquids [110].

B. *H*-Bonding liquids

There is some indication in the literature, particularly for glassy polymers, that the presence of *H*-bonding liquids can affect mechanical behavior. Thus when PMMA and rigid PVC are strained while immersed in *H*-bonding liquids, a simple correlation between the measured physical property, as crazing strain, and solubility parameter of the environmental liquid breaks down; and more complex plots, taking into account both the solubility parameter and the *H*-bonding index, are then needed [110]. In this same study, the highest values of crazing strains were found when water and glycerol were present. It has also been observed, from creep studies carried out on PS, that crazing can be hindered or suppressed by carrying out the tests in a water medium [111]; and, in another study of the influence of organic reagent on crazing stress in PS, the highest value was obtained when the medium in contact with the specimen was water [112]. Since fatigue failure in glassy polymers such as PS is precipitated by crack initiation within a surface craze, it may be conjectured that if the testing is done in a water environment, or with the specimen surfaces coated with other *H*-bonding liquids, that the fatigue resistance could be enhanced.

This hypothesis has been explored by carrying out a series of fatigue tests, at an alternating tension-compression stress of 17.2 MPa, on unnotched specimens of PS that were in contact with various *H*-bonding liquids. The test results are shown in Table 1. The mean fatigue life, based on average values of $\log N$ rather than N itself, has increased in all instances with, in general, the degree of enhancement increasing

TABLE 1
Effects of *H*-bonding liquids on fatigue behavior of PS

Treatment	No. of specimens tested	Surface tension (10^{-3} N/M)	Solubility parameter ($\text{MJ/m}^3\text{)}^{1/2}$	Mean life (cycles)	Degree of enhancement
Control	10	33-36	18.6	18,100	-
Ethylene glycol	4	47.7	29.9	49,300	2.7
Formamide	4	-	36.3	43,400	2.4
Glycerol	6	63.4	43	79,200	4.4
Water	5	72.8	47.9	157,000	8.7

as the surface tension and the solubility parameter of the liquid has increased. It appears that the *H*-bonding liquids hinder or delay the development of surface crazes and, by so doing, increase the number of alternating cycles prior to crack initiation and propagation. In a water environment, which gives the greatest degree of fatigue enhancement, some reorientation of the phenyl side chains in the PS molecules adjacent to the surface may occur [113].

Surface energy effects are small compared to the energy involved in plastic deformation and rupture of the craze in specimens fractured under simple tension [3]. However, it has been suggested that *H*-bonding liquids, by exerting surface tension forces across interfaces and surface flaws, may inhibit or delay craze initiation due to fatigue cycling [78, 105]. In static tension tests, where applied stresses are high enough to generate multiple crazes throughout the gage length and where the fracture source is frequently an internal flaw, the stress-strain response of PS specimens tested in air or water is essentially the same [114].

C. Surface plasticizing agents

As noted in the section on "Diluents", incorporation of a plasticizer has the effect of lowering the glass transition temperature, and thus increasing molecular mobility. It has been found that, in many systems, the drop in T_g at least for small additions of diluents, is proportional to the weight fraction of diluent, w_2 ,

$$T_g^0 - T_g = kw_2 \quad (12)$$

where T_g^0 is the glass transition temperature of the pure polymer and the coefficient k depends on the diluent and polymer under consideration [115]. Similarly, if one "plasticizes" a polymer by lowering its molecular weight and increasing the number of chain ends, then the same equation can be used to describe the extent of T_g lowering. In this case k is given by [115]

$$k = \frac{2N\phi}{\alpha M_2} = \frac{N\phi}{\alpha M_0} \quad (13)$$

where N is Avagadros number, ϕ the free volume per chain end, α the difference in thermal expansion coefficient above and below T_g , M_0 the monomer molecular weight, and $M_2 = 2M_0$ the molecular weight associated with the plasticizer (here the chain ends).

Thus bulk plasticization, either by addition of external plasticizer or by addition of chain ends (lowering of molecular weight) should increase chain mobility, reduce craze and yield strength, and thus lower the number of cycles required to break down a craze and produce a fatigue crack and eventually fatigue failure. Examples of both of these effects have already been given.

However, if plasticization can be produced locally, particularly in regions where flaws are present, then it need not be detrimental to mechanical properties but could be helpful. One example of property improvement by incorporation of a surface plasticizing agent is given in the literature for PMMA [116]. This polymer was exposed to a high molecular weight stable plasticizer at elevated temperature and the exposure time was kept very short so that only a thin surface region was plasticized. The sample was then cooled to ambient temperature. On testing in tension it was noted the specimens showed greatly increased ductility and toughness as the more mobile surface layer permitted greater plastic deformation without development of a crack.

TABLE 2
Effect of low molecular weight PS oligomers on fatigue lifetimes of PS

Surface condition	Nature of coating	No. of samples	Mean life cycles	Degree of enhancement
Polished	None	15	18,800	–
	600 MW PS	9	91,500	4.9
	900 MW PS	6	13,900	0.74
Unpolished	None	15	7,560	–
	600 MW PS	6	55,100	7.3
	600 MW PS	5	71,500*	9.5

* Tests made 6 months after applying coating.

Considerable enhancement in fatigue endurance of polymers is also possible through surface plasticization. This has been demonstrated for PS by coating both polished and unpolished specimens with a compatible 600 molecular weight PS oligomer, whose T_g is below 0°C [78, 105]. Table 2 presents results of these tests made at an alternating tension-compression stress of 17.2 MPa and at a frequency of 1250 cpm. For both sets of specimens, the average fatigue lifetime has been considerably extended. Furthermore, tests made on specimens that were tested 6 months after coating gave equivalent performance. The greatly increased fatigue lifetimes are attributed to a surface swelling that blunts flaws, redistributes high stresses, and retards development of surface crazes.

The data of Table 2 show that if the surface is coated with a 900 molecular weight oligomer, fatigue lifetime is reduced. The reason is that the 900 M.W. oligomer has its T_g above room temperature; hence it acts rather like a brittle lacquer and develops cracks soon after start of fatigue cycling. This causes increased surface stress concentration, rather than crack and flaw blunting as obtained with the more flexible 600 M.W. oligomer.

Other means of surface plasticization, including short time exposure of PS specimens to the vapors of various solvents, such as benzene, chloroform and acetone, have also been investigated [117, 118]. In each instance, there was a noticeable improvement in surface finish and the average fatigue lifetimes increased by factors of from 1.5 to 4.

The decrease in FCP rate, which has been observed to occur upon increase of frequency in notched specimens of PMMA, PS, and PVC [54–56], can also be considered to result from localized surface plasticization. In these tests, energy dissipation under cyclic loading raises the temperature of that part of the specimen near the crack tip while the bulk of the specimen, not so highly stressed, remains cool. Thus the material at the crack tip is closer to T_g and possesses greater molecular mobility. The net effect is to blunt the crack tip, reduce the effective stress intensity factor range, and thus lower the FCP rate.

D. Elastomeric coatings

Although little published research is available on the subject another approach to improving the fatigue lifetime of polymers is to coat them with a flexible rubber coating. The rubber coating appears to serve several purposes. First, it protects the specimen, and especially the critical surface, from attack by oxygen or other pollutants in the air. Secondly, it provides a comparatively smooth and highly flexible

TABLE 3
Effect of flexible rubber coatings on fatigue lifetimes of PS

Surface condition	Nature of coating	No. of samples	Mean life cycles	Degree of enhancement
Polished	None	15	18,800	–
	Vulc. N.R.	4	37,700	2.0
	N.R.	4	70,200	3.7
	Nitrile rubber	4	225,000	12.0
Unpolished	None	15	7,560	–
	Vulc. N.R.	4	30,000	4.1
	N.R.	4	57,000	7.5
	Nitrile rubber	4	82,100	10.9

surface coating that, at least on specimens of PS, delays the onset of surface crazing and thus significantly enhances average fatigue lifetimes.

Test data have been acquired using various types of rubber coating applied both to polished PS specimens and to unpolished ones [78, 119]. Some of the results of this study are presented in Table 3. In all cases, the average fatigue lifetimes, measured at an alternating stress of 17.2 MPa and at a frequency of 1250 cpm, are higher than the observed values for the uncoated samples. The natural rubbers and the nitrile rubber were applied in the form of a rubber latex by a simple dipping operation and the coatings were then dried by heating for a short time at 50°C. The nitrile rubber, possibly because of better adherence to the PS surface, gave the greatest degree of fatigue enhancement. However, all the flexible rubber coatings delay the onset of surface crazing, and hence of crack initiation, and thus extend the number of alternating cycles that either polished or unpolished specimens can withstand prior to fracture.

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RÉSUMÉ

On passe en revue la nature générale de la rupture dans les polymères lorsqu'ils sont sujets à des contraintes alternées en contraste par rapport à des contraintes statiques ou croissantes de manière régulière. On discute également les mécanismes moléculaires et les aspects micromécaniques qui prennent place dans le processus de rupture par fatigue. Une attention particulière est accordée à la fatigue thermique où les résultats de fatigue résultent principalement d'une élévation sensible de la température de l'éprouvette en raison du chauffage par hystérèse. Cependant, l'accent est principalement consacré à la fatigue mécanique dans lequel la rupture est le résultat d'un amorçage et d'une propagation d'une fissure tels qu'ils résultent de la nature périodique des charges appliquées.

On accorde une attention particulière à des variables importantes internes ou caractéristiques du matériau telles que la structure du polymère, le poids moléculaire, les liaisons et le type et contenu des agents de dilution. Des variables externes significatives telles que la contrainte ou l'amplitude du facteur d'intensité de contrainte, la contrainte moyenne, la température, la fréquence et l'environnement sont également pris en considération. Des méthodes variées susceptibles d'être utilisées en vue d'accroître de manière significative la résistance à la fatigue des polymères sont mis en avant et sont discutés.