Effects of environment and surface coatings on the fatigue properties of polystyrene

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The influence of surface condition, environmental media and surface coatings on the fatigue lifetime of polystyrene specimens has been explored. It is shown that surface flaws such as machining marks, are much more detrimental to fatigue lifetime than to static strength. The effect of alcohols on fatigue lifetime is primarily one of plasticization rather than of molecular size and mobility. Hence n-butanol is a more aggressive environment for polystyrene than is methanol. For a wide variety of organic media, a fairly good correlation was found between fatigue lifetime and solubility parameter. Highly polar media, like glycerol and water, are shown to be favourable media, rather than aggressive ones, in that they increase average fatigue lifetimes of polystyrene specimens by about one decade. It is suggested that any media that inhibit or delay crazing, either by increasing surface energy or by blunting flaws and reducing stress concentration, should also be beneficial to fatigue performance. A surface coating that performs this latter function is a 600 molecular weight polystyrene oligomer. It is shown that application of this compatible, viscous coating to polystyrene specimens increases the average fatigue life, for both polished and unpolished specimens by a decade or more.

INTRODUCTION

High polymers are being increasingly used in structural and technological applications where they may be called upon to resist either, or both, slowly applied or steady loads and dynamic or fatigue loads. Hence it is essential that the factors affecting their resistance to such applied stresses be identified and studied.

One important factor is the environment in which the polymer is stressed. Environmental stress cracking and environmental stress crazing are well known phenomena that occur in both crystalline and amorphous polymers[1,2]. As a result, the resistance of polymers to various environmental conditions has been studied both for steadily increasing stresses and for long time exposure under constant stress conditions. Reviews of much of this work are available[2,3]. However, it is not known how directly applicable the results of prior investigations on the effects of environmental media on tensile properties will be on the behaviour of polymers under alternating loading conditions. One reason is that there are significant differences in the mode of failure, and in fracture surface morphology, between fatigue fracture and static fracture of polymers[4-8].

Fatigue fracture almost invariably initiates at the surface at relatively low values of applied stress and the fracture is of the 'brittle' type with little evidence of any plastic deformation except on or near to the fracture surface. In contrast, in constant stress tests or under steadily increasing tensile loads, the source of the fracture is frequently internal and plastic deformation is present, prior to fracture, over much of the specimen gauge length[2,9-11]. In the more ductile polymers, like polyethylene (PE), polypropylene (PP), and polycarbonate (PC), necking and cold drawing occur and elongation to fracture at nominal strain rates is usually well

over 100%. Even in the so-called rigid, glassy polymers, such as polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinyl chloride) (PVC), where tensile fracture may occur at relatively low strains and without necking, there is still plastic deformation, in the form of fine crazes extending inward from the surface over most of the gauge length[2,9-15].

Environmental effects on the fatigue behaviour of polymers have hitherto received little attention[4] despite the fact that fatigue cracks usually initiate at the surface and hence are directly accessible to the surrounding medium. One objective of the present study is to acquire test data and information concerning the influence of various environmental conditions on the fatigue resistance of a particular polymer, polystyrene. For this polymer the influence of mean stress[6] and of deliberately introduced surface notches[16] on fatigue lifetimes has been reported. Also we have investigated the influence of radiation, resulting in crosslinking and increased branching, and these results will be discussed in a separate publication[17].

In this article we shall be concerned with the effects of surface condition, organic reagents, and chemical environments on the resistance of polystyrene to alternating loading. Some information is available as to the influence, under direct loading, of various environmental factors on physical properties, such as tensile strength, critical crazing strain, crack propagation rate, and fracture toughness[2,18-25]. Hence, by comparing results obtained from the present fatigue study with results obtained from these prior studies, it should be possible to assess the influence of testing mode on environmental effects and to see to what extent results obtained under steady load or creep conditions can be carried over to fatigue behaviour.

A second purpose of this study is to explore means of improving the fatigue properties of polymers, so that longer lifetimes to fracture for given alternating stress applications and higher endurance and fatigue strengths will be realized.

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Two different means of accomplishing these objectives have been investigated in our laboratory. One method is to increase the average polymer chain length, and thus the molecular weight of the polymer, and the second method is to apply appropriate coatings to the polymer surface.

Results obtained by the first method, that of increasing molecular weight, have been very encouraging. For example, it has been observed that significant improvements in fatigue resistance are achieved both in an amorphous polymer, PS, and in a crystalline polymer, PE, on increasing the molecular weight and these improvements continue even for molecular weight values $>10^6$ [26,27]. Additional support for the concept that increases of molecular weight will give rise to improved fatigue properties also come from results of recent studies on other glassy polymers, such as PMMA and rigid PVC. For PMMA, it has been noted that a continued reduction in fatigue crack propagation rate occurs with increase of molecular weight from 10^5 to 4.8×10^6 [28]; and for PVC films, it has been found that at a molecular weight of 51 000, fatigue life is only a few seconds but when the molecular weight was increased to 2.28×10^5 no failure took place even after 1600 min[29]. It has been shown that the most important molecular weight parameter from the point of view of both fatigue and static strength is the number-average molecular weight, $\bar{M}_n$, although the molecular weight distribution also plays a role[8,17]. The greatly improved resistance to alternating loading which has been noted in these recent studies, upon increase of molecular weight, is attributed to a greater resistance to craze breakdown, and to formation of microcracks in the craze, as the number of chain ends are reduced and as the average chain length, and hence also the degree of chain entanglement, increases.

The second method suggested for improvement of the fatigue behaviour of polymers, viz. application of suitable surface coatings, has been little explored. This is rather surprising in view of the fact that fatigue behaviour is so greatly affected by surface condition, and that surface coatings are a well known means of improving the durability of many different materials, ranging from wood products to metals. It will be shown here, for a particular polymer, polystyrene, that several different types of surface coatings or environmental media, can lead to appreciable improvements in the fatigue resistance of this polymer. Possible reasons for the effectiveness of these surface coatings and/or environments will be discussed. Application of these ideas to other polymers, particularly to glassy polymers which have a strong tendency to respond to applied stress by craze yielding, should also result in improved fatigue performance.

The general nature of fatigue fracture in glassy polymers, such as PS, PMMA, and PVC, has been studied by various investigators, some of whom were concerned primarily with the initiation phase and some with the crack propagation phase[4-8,26-37]. From the results of these investigations, it is known that crazing plays an important role in fatigue crack initiation and growth, just as it does in the tensile or creep fracture processes of glassy polymers.

Because of the close assocation between crazing and fracture, it is a plausible hypothesis that environmental media which accelerate crazing in glassy polymers under direct stressing will also be deleterious to fatigue behaviour; and, secondly, that media or coatings that hinder or delay the inception and development of crazing (relative to observed effects in ambient air) will be beneficial to fatigue behaviour. To explore the first hypothesis, a series of fatigue tests have been carried out on polystyrene specimens exposed to the action of various organic media, some of which are known

to be weak or strong crazing agents for PS. These media have solubility parameter values that fall both above and below that of polystyrene; hence, from the test results, the influence of solubility parameter difference on the fatigue resistance of PS can be assessed.

To explore the second possibility, that of increasing fatigue lifetime by applying coatings that are retarders of crazing rather than promoters, it is of interest to cite an early literature reference pertaining to creep deformation and crazing in PS[10]. In this article it was noted that surface crazing could be inhibited or delayed by use of appropriate low molecular weight coatings; and also that the extent of crazing could be considerably reduced if the creep tests were conducted in a water environment. While this latter finding appears to be in contrast to a recent literature reference[24], in which water is included in a list of various organic media that are considered to be deleterious to the mechanical properties of PS, it should be noted that actual test measurements of the stress intensity factor for crack initiation, K_i, of PS specimens tested in a water environment show that $K_i = 2.53$ MPa $(m)^{1/2}$ as compared to a lower value of 2.0 when tests were carried out in air[38].

In view of reported results of creep studies on PS[9,10,14], it is appropriate to investigate effects of water and of other highly polar environments, as well as effects of organic agents and of flexible low molecular weight coatings on the fatigue resistance of polystyrene. This has been done and some of the results of these studies will be presented and discussed.

EXPERIMENTAL

The polymer used in the present studies was a heat-resistant grade of polystyrene made by Foster Grant and known by the name Fosterene 50. It was obtained in the form of extruded rods having a diameter of 1.27 cm. The fatigue specimens, cylindrical in nature and with threaded raised ends for attachment to the testing machine grips, were machined from the extruded rods. The specimens had a reduced gauge length of 1.27 cm and a reduced diameter of 5.08 mm. Most specimens, before testing, were carefully polished by a standard procedure[26,27] to eliminate surface flaws, scratches, or machining marks. However, some specimens were also tested in the machined condition without further polishing.

G.p.c. analysis of the test specimens indicated that the extruded PS had a weight-average molecular weight of 2.74×10^5 and a number-average molecular weight of 1.0×10^5 (ref 17).

The fatigue tests were made on a Tatnall–Krouse fatigue apparatus in the tension–compression mode with zero mean stress. The apparatus is equipped with a hydraulic load maintainer to compensate for any dimensional changes due to creep and a recorder for giving the number of cycles, N_f, to fracture. Unless otherwise indicated, all tests were performed at a fequency of 1250 cpm and an alternating stress amplitude of 17.2 MPa (2500 p.s.i.). Under these conditions polished specimens tested in air at room temperature (23 ± 2°C) give an average fatigue life of about 24 000 cycles. This corresponds to an average lifetime to fracture of about 19 min. This is a very much smaller time to fracture than would be expected, based on creep studies carried out at a constant stress amplitude of the same magnitude, viz. 17.2 MPa[9,10]. This much lower value in the alternating stress case is an indication of the effectiveness of alternating loading in accelerating craze breakdown and reducing craze stability.

Table 1 Effects of surface condition and thermal treatment on fatigue lifetime of PS

Specimen condition	Thermal treatment	No. samples tested	Average no. cycles to failure
Machined	–	5	4400
Polished	–	10	24 000
Polished	24 h at 90°C rapid quench	3	7400
Polished	24 h at 90°C slow cooling	3	23 400

Because polystyrene has very low values of internal friction, there is little rise in specimen temperature due to the stress cycling. Even at test frequencies of 1600 cpm the estimated rise is less than $2°C$[26]. To supplement the fatigue data, some static stress–strain tests were made in a Instron apparatus at a controlled crosshead speed of 5.08 × 10^{-2} cm/min. Under these conditions, the tensile strength was found to be 43.5 MPa (6300 psi), a value in good agreement with reported measurements of tensile strength at comparable test speeds[6]. Fracture surfaces were examined by optical microscopy and, after coating with a thin layer of gold–palladium, by scanning electron microscopy *(SEM)*, using an Etek apparatus.

All chemical reagents used in this study were laboratory grade. For the case of known stress crazing environments, such as kerosene and volatile liquid reagents, as the alcohols, the liquid was applied on the external surfaces of the specimens while they were mounted ready for testing in the fatigue apparatus, and the machine was then started. For the more viscous coatings such as glycerol and caster oil, the coating was usually applied to the test specimen about ½ to 1 h before testing. For coatings of the non-volatile polystyrene oligomers, fatigue tests were made after various times had elapsed after application of the coating. This was done to test the long time effectiveness of the surface treatment. Some fatigue tests were made on PS specimens that were fully immersed in water. In this particular series, the test frequency was 1600 cpm. At this frequency, the average lifetime of specimens in air is increased from an average of 24 000 cycles to 31 000 cycles[16].

RESULTS AND DISCUSSION

Effect of surface condition and thermal treatment

The influence of surface condition on fatigue behaviour of polystyrene is readily apparent from tests carried out in air on highly polished specimens and on machined, but unpolished, specimens. The results of such tests are shown in *Table 1*. The average lifetime of the unpolished specimens is seen to be only 1/5 of that of the carefully polished specimens. This effect is attributed to the presence on the machined surface of more severe stress raisers. Hence under load, surface crazes, in response to high localized stresses, initiate sooner on the machined but unpolished surfaces. From inspection of the fatigue fracture surfaces it appears that the crazes propagate inward only a small distance before cavities form within a craze and craze breakdown begins. The resulting microcrack grows slowly at first and there is a mirror-like region around the fracture source. With increasing number of fatigue cycles, the crack propagates more rapidly and the fracture surface morphology is similar to that previously described[6]. There is much evidence of mul-

tiple crazing ahead of the crack tip and of crack jumping from one craze–bulk interface to another.

In the polished specimens, where there are less severe surface flaws, a longer time is required for crazes to initiate, to grow, and to break down. Hence the average fatigue lifetime of these specimens under a constant applied alternating stress is considerably extended compared to lifetimes achieved for unpolished specimens. Polishing has much less effect on static fracture stress than on fatigue lifetimes, as the observed tensile fracture stress of the unpolished specimens was within 3% of that of the polished specimens. Surface condition was also found to have little effect on the tensile fracture behaviour of PS tested under high pressure conditions[25]. The greater effect of surface condition on fatigue behaviour is because in alternating loading craze breakdown occurs more readily[5,6]. Also, in static fracture, higher stress values are present and these can lead to debonding and microcrack formation at internal inhomogeneities. Even in filled polymers with many internal particles and interfaces, fatigue life is greatly decreased by surface scratches[39].

A greater sensitivity of surface condition to alternating loads rather than to slowly applied loads is also evident from comparison of data obtained on notched PS specimens. Thus Berry[40] found that any surface flaw less than 1 mm in depth had no effect on the static strength of PS whereas McMaster *et al.*[16] found that surface notches as small as 0.025 mm, or some 40 × smaller, had a deleterious effect on the average fatigue life.

To examine effects of residual stresses on fatigue behaviour, two sets of polished specimens were fatigue tested after being given different thermal treatments. The fatigue data obtained on these samples are shown in *Table 1*.

Both sets of samples were annealed at 90°C for 24 h in order to eliminate residual stresses. One set was then allowed to cool slowly in the oven chamber. For this set, the average fatigue lifetime was comparable to that of the polished control sampes. This is an indication that no appreciable residual stresses are present in the control samples or are introduced as a result of the machining and polishing operations.

The second set of samples, after annealing, were rapidly quenched into ice–water. This procedure tends to introduce frozen-in stresses and/or surface voids or defects due to the non-equilibrium thermal conditions existing during the quenching operation[4]. As a result, crazing would be expected to develop sooner. Our test results are in agreement with this as they show that quenching leads to a considerably lower average fatigue lifetime. It has also been observed that quenching of polystyrene into ice–water inhibits or shifts to higher pressures the pressure-induced, brittle–ductile transition that normally occurs in the tensile elongation properties in unsheathed samples at a pressure of about 2.8 kbar[25].

Effect of alcohols

To study possible environmental effects of alcoholic agents on polystyrene, fatigue tests have been run on four different groups of samples. The external surfaces of the specimens in each group were wetted with one of the lower molecular weight alcohols immediately prior to fatigue testing. The alcohols, as a class, are known to be active media for polystyrene and when stressed specimens are in contact with these liquids crazing will occur more rapidly than when the specimens are tested in air[2,22,41]. The data obtained after testing these four groups of samples at an alternating stress of 17.2 MPa are summarized in *Table 2*. Here we show, for

Table 2 Influence of alcohols on fatique lifetime of PS

Environmental medial	Molecular weight	Molecular volume (cm^{3}mde)	Solubility parameter δ_s (cal/cm^3)$^{1/2}$	Solubility parameter difference ($\delta_s - \delta_p$)	Number of samples tested	Average no. cycles to failure
Air	–	–	–	–	10	24 000
n-Butanol	74	91.8	11.4	2.3	3	1170
n-Propanol	60	74.8	11.9	2.8	4	1230
Ethanol	46	58.4	12.7	3.6	3	7530
Methanol	32	40.2	14.5	5.4	3	11 900

each of the four alcohols investigated, the average fatigue lifetime prior to fracture. In addition, in separate columns, there are listed the nominal molecular weight, the molecular volume, and the value of the solubility parameter of the media[42-44]. The Table also lists values of the differences in solubility parameter between the environmental fluid and of the polymer. These values have been obtained using the reported solubility parameter value for PS of 9.1 (cal/cm^3)$^{1/2}$ (ref 43).

It is evident from the test results shown in *Table 2* that the fatigue resistance of the polymer has been lowered by the presence of the alcohol. The greatest reduction in lifetime occurs for n-butanol, which on the basis of the solubility parameter difference with the polymer, is the most compatible alcohol. As the molecular weight and the size of the alcohol molecule are increased, conditions which might be expected to lead to decreased penetration of the fluid, the fatigue lifetime falls. Thus mobility of the liquid environment does not appear to play an important role in the resultant fatigue behaviour, although it does have an effect on tensile fracture properties measured under high pressure[25].

The fatigue data obtained here on PS specimens exposed to different alcohols seems to be in contrast to the findings of other investigators, who studied the creep deformation behaviour of high impact polystyrenes (HIPS) in different alcoholic environments[44]. These authors noted that, at comparable stress levels to that used in the present study, the delay time for inception of accelerated creep was lowest for methanol and highest for n-butanol. They therefore concluded that, under their test conditions, mobility of the liquid was more important than its ability to plasticize.

The observed difference in behaviour in these two studies may be a result of the testing mode, alternating stress in our case *versus* constant stress in their case. Thus we find surface treatment with n-propanol to have a drastic effect on average fatigue life while others have noted that it had very little effect on the critical strain for onset of crazing under tensile loading[14]. Other factors, though, are also involved. The magnitude of the applied stress is much closer to the yield stress in HIPS than it is to the fracture stress in PS; and secondly, PS is a homogeneous polymer while HIPS is a non-homogeneous two-phase polymer. As a result, penetration of the more mobile and smaller alcohol molecules, as in methanol, may be facilitated in the HIPS material.

The data of *Table 2* suggests that a correlation may exist between fatigue lifetime and solubility parameter of the environmental fluid. As δ_s becomes closer to δ_p the average lifetime is reduced. Hence the ability of the environmental fluid to plasticize appears to be the controlling factor rather than the size or mobility of its molecules. The most aggressive alcohol is thus n-butanol, because it permits localized flow of the polymer chains, in the vicinity of surface defects or other stress concentration sites, to take place more easily;

and also, by plasticization, it reduces the rupture strength, and therefore the stability, of the crazes that do form.

It is of interest to compare these fatigue results with reported effects of alcohols on other physical properties of polystyrene, and of similar glassy polymers. It has been noted, for both PS[21] and a rubber modified styrene acrylonitrile (SAN)[23], with rubber content varying from 0 to 50%, that the critical strain for crazing in a methanol environment was higher than in ethanol; and, in both PS and glass-filled PS, the stress intensity factor for crack initiation was found to be higher for methanol than for ethanol[24]. Thus here too, as in the fatigue tests, the least aggressive medium is the one whose solubility parameter is the highest and which has the least ability to plasticize.

The influence of a wide range of alcohols on solvent crazing in PS and PMMA has been reported[22]. Here too it was observed that, as the ability of the alcohols to plasticize increased, the resistance to crazing decreased. Rather similar conclusions were drawn from studies of the delay time for accelerating creep, at low applied stresses, for HIPS tested in various alcohols[44]. Thus in so far as the effect of alcohols is concerned, the conclusions drawn from the fatigue studies are in general agreement with expectations based on experiments performed under steady or increasing, tensile stress or strain.

Effects of organic media and water

To investigate further the relation between solubility parameter and fatigue resistance, additional fatigue tests have been carried out on PS specimens placed in contact with various organic media having solubility parameter values ranging from $\delta_s = 7.4$ (cal/cm^3)$^{1/2}$ (n-heptane) to $\delta_s = 23.4$ (cal/cm^3)$^{1/2}$ (water). Most of these tests were made on polished specimens but a few tests were also made on machined, but unpolished specimens. For the polished specimens the number of samples tested for each given medium ranged from 3 to 6. The results obtained, including data for the alcohols, are presented in *Figure 1* in the form of a plot of the log of the fatigue lifetime *versus* the solubility parameter of the medium[42]. Typical values for log N_f for specimens tested in air are also shown for comparison. The filled circles represent average values for polished specimens and the vertical lines through the data points represent the range of values obtained for each medium. For media having lower solubility parameter values than that of PS only a few tests were run and these were made on unpolished specimens. The data for these tests are represented by crosses. Somewhat higher values for log N_f would be expected if polished specimens had been used.

Figure 1 shows that there is a fairly good correlation between fatigue lifetime and solubility parameter of the environment, with an apparent minimum in lifetime occurring for media with solubility parameter values near to that of PS.
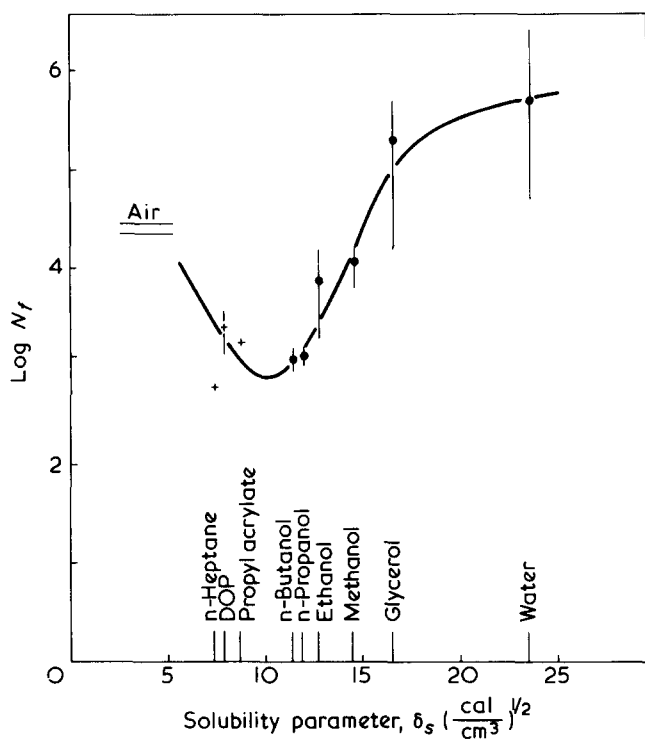
Figure 1 Log (fatigue lifetime) plotted *vs.* solubility parameter

Fatigue resistance rises as the solubility difference with PS increases. Although some of the previous investigators of environmental effects on mechanical properties of glassy polymers have not covered as wide a range of δ_s values as shown in *Figure 1*, curves of the same general form have been found for the effects of organic liquids on other physical properties. For example, in PS, Mai and Atkins[24] noted a minimum near δ_p in a plot of the stress intensity factor for crack initiation *versus* δ_s and Henry[23] found a similar minimum in a plot of crazing strain *versus* δ_s. In PMMA, a minimum in the plot of surface work for crack propagation *versus* δ_s was noted by Andrews and Bevan[20] and Vincent and Raha[19] found a minimum at $\delta_s \approx \delta_p$ in a plot of critical crazing strain *versus* solubility parameter for eight different non-hydrogen-bonding liquids. Also in poly(dimethyl phenylene oxide), (PPO), a curve of similar shape to *Figure 1* was obtained on plotting the critical stress for onset of crazing *versus* the solubility parameter of the medium[18].

In view of the above similarities in behaviour, it may be concluded that the environmental effect of aggressive media is primarily one of plasticization whether the applied stress is static or alternating. These active media, through absorption, lower the T_g of the stressed material, increase chain mobility, and permit crazing to occur at lower stress, or for a constant applied stress, to occur sooner.

An interesting feature of the data of *Figure 1* and a direct consequence of the fatigue studies, is that not all media are aggressive. Unfortunately, this condition is frequently taken for granted and the very words, environmental stress cracking and environmental stress crazing, practically imply that the effects of an environment are deleterious. As *Figure 1* shows, this is clearly not the case for the highly polar environmental media like glycerol and water. In fact, the fatigue lifetime of PS in these environments is about a decade higher than it is in air. The implication of this is that the polar media act as craze retarders rather than as craze promotors. Both glycerol and water not only have high values of solubility

parameter but also very high values of surface tension, viz. 63.4 and 72.8 dynes/cm respectively. Although contributions of surface energy to the work of fracture are generally considered to be small compared to the viscous energy dissipation involved in craze propagation[2], the surface energy term is probably important in the initiation of a craze. Also the greater the surface tension, the higher is the stress to grow cavities that tend to form at the interfaces with impurity particles[11].

It has been suggested that surface contact with volatile liquids might increase lifetimes of polymer specimens subject to alternating loads through a cooling effect[45]. The evaporation of the liquid slightly lowers the temperature of the specimen and, since strength rises with decreasing temperature, a rise in fatigue strength, or an increase in fatigue life for a given applied stress, might be expected. It is doubtful if this mechanism is an important one in our experiments. First, because of the low internal friction of PS, the temperature rise of our specimens due to repeated cycling is very small; secondly, the evaporation rate of the alcohols is high and yet they lowered fatigue lifetimes; and thirdly, the evaporation rate of the viscous glycerol is much smaller than that of water and yet both were effective in increasing fatigue life. It is concluded that highly polar liquids, which do not plasticize polystyrene, are effective in raising average fatigue lifetimes because they hinder or delay craze initiation and inhibit cavity growth and coalescence in crazes that do form.

A close examination of available literature data indicates that there is additional evidence, from other than fatigue lifetime measurements that support this conclusion, viz. that liquids of high surface tension and high solubility parameter inhibit or delay crazing, in polystyrene and other glassy polymers. For example, in one study[46] of the effect of various media on onset of crazing in PS, the test data show that the stress for craze initiation was highest when the medium was water; and for other highly polar media, like ethylene glycol, the observed craze strength was higher than for the less polar alcohols or for non-polar media. In another study[47] the critical crazing strains for styrene—acrylonitrile copolymer, exposed to several different media of high solubility parameter values, are higher than the observed critical crazing strain for air. In yet another study[23], it was observed that the critical crazing strain for polystyrene exposed to the polar liquid, formamide, was 0.8%; this value is higher than recorded values for media of lower solubility parameter and is also higher than the value reported for PS tested in air[2]. Vincent and Raha[19] noted that, in addition to the solubility parameter, the dipole moment and the hydrogen bonding parameter of the environmental media also played a part in the development and growth of crazes in glassy polymers. For both PMMA and rigid PVC, they found that the highest critical strains occurred when the medium was water or glycerol; and, in both cases, their reported values for the strain for onset of crazing after 1 h immersion are above reported values of the critical crazing strain for testing in air[47].

The influence of testing mode on environmental effects is evident from comparison of the fatigue behaviour of polystyrene in a water environment (*Figure 1*) with results obtained by others[25] on the influence of water on the static tensile properties of PS. It was found in the latter study that the stress—strain curve and the fracture strength of PS were almost identical whether the test was performed in an air or water environment; on the contrary, we obtain, as *Figure 1* shows, much higher average fatigue lifetimes for tests done in a water environment rather than in air. Our

Table 3 Effects of Kerosene and Castor oil on fatigue lifetime of PS

Specimen condition	Environmental media	Surface tension (dynes/cm)	No. samples tested	Average no. cycles to failure
Polished	Air	—	10	24 000
Polished	Kerosene	23–32	3	700
Polished	Castor oil	39	5	47 000
Unpolished	Air	—	5	4400
Unpolished	Caster oil	39	5	20 600

fatigue results, implying that water is a retarder of crazing in PS, are more in keeping with the results of creep studies[10]. In general, static tensile tests are much less sensitive to surface condition, as noted in the previous section. However, under conditions of high hydrostatic pressure, environmental effects especially for mobile liquids of low molecular weight, can be severe even for simple tensile loading[25].

Effects of kerosene and castor oil

The possible environmental influences of kerosene and of castor oil on the mechanical behaviour and fracture of polystyrene are of considerable interest, as both of these fluids have been used for hydrostatic extrusion of PS and other polymers[48-53] and also as the pressure fluid for study of properties of thermoplastics under high pressure conditions[54-59]. Also, since fatigue fracture is so sensitive to surface condition, environmental effects of the surrounding fluid should be more readily detectable from fatigue studies than from measurements of tensile properties. The results of fatigue tests obtained with these environmental fluids are given in *Table 3* along with, for comparison purposes, the fatigue data obtained on testing uncoated specimens in air. Some tests were done using polished specimens and some with machined, but unpolished surfaces. Reported surface tension values for the environmental media are also given in the Table together with the average fatigue lifetimes[60].

Kerosene has a dramatic effect on fatigue behaviour, even though it was only applied to the surface of the test specimens shortly before the test was begun. It reduces the average lifetime to less than 1/25 of the value for air. The static strength is also affected. For a kerosene treated specimen, it was found to be about 50–60% of the tensile strength of the control samples.

In both modes of testing, onset of crazing was accentuated by the presence of the kerosene, and craze breakdown and fracture caused early failure. In creep tests too, kerosene reduces the critical strain for crazing as compared to values obtained for PS tested in air[14]. It may be noted from *Table 3* that the reported values of surface tension for kerosene cover a wide range. This is because kerosene does not have a fixed composition. Nevertheless, the reported values all lie below the critical surface tension of PS, which is 33–36 dynes/cm[43-61]. Thus kerosene readily wets polystyrene and reduces its resistance to crazing and crack formation. Hence one finds the drastic reduction in fatigue properties is but another indication of the more important role of the surface under alternating loading than under static, or creep loading where, as previously noted, the actual source of the fracture is frequently an internal flaw or inhomogeneity.

Castor oil, unlike kerosene, does not readily wet polystyrene nor is it absorbed to any appreciable extent. Our tests show that coating PS specimens with castor oil pro-

duces little change in static tensile strength but does provide a modest improvement in fatigue resistance. For 5 polished test specimens, the average fatigue life was found to be about double that of the control samples.

As a further check on these results, it was decided to coat an additional 5 unpolished specimens with castor oil and then fatigue-test these at the usual alternating stress magnitude. The test results, also given in *Table 3*, indicate that the average lifetime of the coated samples has again increased compared to uncoated ones, in this instance by about four times. In view of these results, it seems evident that a castor oil coating on the test specimens is helpful rather than harmful to fatigue performance. The results are thus rather like those attained with the highly polar environmental media like water and glycerol, except that the extent of the improvement is not as large. This is perhaps to be expected as the surface tension of castor oil, while higher than the critical surface tension of PS, is much less than that of glycerol or water. Thus coating with castor oil may raise the surface energy of polystyrene and, to some extent, delay onset of crazing or of cavity growth and crack development within the craze. However, under high pressure conditions, where a large pressure gradient is available to drive the medium into flaws or pores, castor oil, like water also, can become a stress cracking medium and induce earlier failure[58].

Effect of low molecular weight PS coatings

As noted in the Introduction, it has been reported[10] that a low molecular weight compatible compound, applied to the surfaces of polystyrene specimens, could reduce the extent of crazing that ordinarily would develop at the imposed stress level. To explore this matter further, we have coated two sets of fatigue specimens of polystyrene with compatible low molecular weight oligomers of polystyrene itself. These materials or standards, available from the Pressure Chemical Company, have molecular weights of 600 and 900 respectively and a narrow molecular weight distribution. The 600 MW standard is a viscous liquid, as its T_g is below room temperature; the 900 MW standard is available as a powder, as its T_g is above room temperature[27].

The lower molecular weight material was applied as a surface coating to 5 polished and 5 unpolished specimens of polystyrene. To apply the 900 MW standard, it was first heated to 50°C in order to convert it into a liquid. Then it was applied to fatigue specimens that had also been warmed to the same temperature. As the specimens slowly cooled down to ambient temperature, the coating gradually solidified into a thin solid film. At this stage, the coating appeared homogeneous and there were no visible cracks.

The results of the fatigue tests, again carried out at an alternating stress level of 17.2 MPa, are given in *Table 4*. For the polished specimens, all of which were tested within 5 days after application of the coatings, a dramatic improvement of almost a decade has occurred in the fatigue lifetime of the specimens coated with the 600 MW oligomer; and a reduction in average lifetime has occurred for the samples coated with the 900 MW standard. Thus, although both of these coatings materials are equally compatible with the polymer and have comparable solubility parameters, their effect on fatigue performance are strikingly different.

The reason for the drop in average fatigue lifetime for the PS specimens coated with the 900 MW material is thought to be that it is acting rather like a brittle lacquer. The solid 900 MW surface film is more brittle than the polymer itself. Under stress and repeated cycling it soon develops cracks.

Table 4 Effects of low molecular weight PS coatings on fatigue lifetime of PS

Nature of coating	Surface condition	No. samples tested	Average no. cycles to failure
None	Polished	10	24 000
600 MW PS	Polished	9	227 000
900 MW PS	Polished	6	15 500
None	Unpolished	5	4400
600 MW PS	Unpolished	6	58 500
600 MW PS	Unpolished	5	78 500*

* Tests made approximately 6 months after coating was applied

These produce severe stress concentration sites on the specimen surfaces from which crazes can develop and grow sooner than if the flaws were not present. Hence the final fracture, due to crack formation in the craze, and subsequent crack propagation, also occurs sooner.

For the unpolished PS specimens, fatigue tests were made only on samples coated with the 600 *MW* PS oligomer. These tests were conducted to see whether the improvement resulting from the presence of the flexible, compatible coating would still be realized even when the initial specimens contained many stress risers in the form of machine marks and surface ridges. The test results of *Table 4* show that, compared to uncoated, unpolished specimens, the extent of improvement in fatigue performance on coating with the 600 *MW* standard was as great as for the polished specimens, with the average lifetime being increased by more than one decade.

The efficiency of surface treatment with the 600 *MW* viscous liquid is also evident from a comparison of the average lifetime of the polished and uncoated PS, viz. 24 000 cycles, with that of the unpolished but coated samples, viz. 58 800 cycles. Thus, treatment of the polymer surfaces with the flexible, 600 *MW* polystyrene oligomer is an even more effective means than careful polishing in reducing surface stress concentration sites.

Another interesting feature of the data of *Table 4* is that it shows that the beneficial effects produced by application of the 600 *MW* standard are not merely temporary effects. This is evident from the fact that the average fatigue lifetime for one set of fatigue specimens that was stored in the laboratory for over 6 months after the coating operation, was actually slightly higher than that of the first set which were tested within a few days after the coating application.

The question arises as to the cause of the large increase in fatigue durability that is attained by use of the flexible, compatible coating. On a solubility parameter argument, one would expect that environmental media with comparable solubility parameter values, would soften the polymer and diminish its resistence to crazing and to fracture. Clearly, this has not happened with the 600 *MW* PS coating; hence other factors must be considered.

Some of the possible factors that are involved are as follows. First and perhaps most important, the 600 *MW* compatible coating is believed to blunt surface flaws and reduce stress concentration by a mechanism of surface plasticization. Hence a longer time is required, for a given alternating stress value, for surface crazes to initiate and develop from flaws, machine marks, surface notches, etc. Secondly, the compatible liquid may swell a thin surface layer of the material and these swelling stresses could produce residual tensile stresses in the core and favourable compressive stresses in the surface

layers. In some instances, as discussed by Alfrey[62], swelling stresses can become large enough actually to cause tensile fracture of the core material. Favourable residual stresses on the surface would delay crazing and increase the time before craze breakdown and crack formation occurred.

Another factor is that while the 600 *MW* viscous liquid is compatible with the polymer its size and molecular weight are so much larger than that of low molecular weight organic reagents like heptane and the alcohols, that it does not produce volume plasticization and thus cause crazing to be accentuated. Other possibilities are: the compatible but non-volatile coating may permit some localized shear flow and thereby blunt flaws; and it may increase the size of the plastic zone in front of the craze or crack tip and thus increase the resistance to fracture[63]. The latter process has also been invoked to account for the fact that PMMA has a higher failure stress when broken in n-propanol than when broken in air[64].

It is concluded that some surface coatings, such as the 600 *MW* PS oligomer, can be instrumental not only in providing an immediate improvement in fatigue durability of polystyrene but also in giving long-time improvement. However, if the compatible coating is a brittle solid at ambient temperature, like the 900 *MW* PS standard, then no fatigue benefit is achieved by its application. It is suggested that improvements in fatigue performance of other glassy polymers that have a tendency to craze under applied stress could be achieved by use of similar methods and secondly that other types of flexible surface coatings, including polymeric ones could also be effective in extending fatigue life. This latter possibility is being currently explored and the results will be presented in a future publication.

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