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Fatigue characteristics of high impact polystyrene

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INTRODUCTION

The greatly increased toughness of rubber modified or high impact polystyrene, (HIPS), as compared with the unmodified polystyrene (PS) has resulted in a rapid growth in demand for this material in various technological applications[1,2]. However, since most engineering components are subject during their lifetime to alternating stress as well as to impact loads, it is somewhat surprising that the fatigue behaviour of HIPS, and other rubber modified polymers, has not been more extensively studied. Bucknall in his recent book[1] cites a few references which bear on fatigue crack propagation (*FCP*) from notched specimens under tensile cycling[3,4]. These tests show that for PS, HIPS, and acrylonitrile–butadiene–styrene (ABS) there is a linear dependence on a log–log scale, between the *FCP* rate and the stress intensity factor range, ΔK. They also show, that for any given ΔK value, the *FCP* rate is slightly lower for HIPS than PS, and still lower for ABS. Thus, under alternating tension, it appears that the effect of dispersed rubber particles is to improve fatigue fracture resistance, presumably through the generation of multiple crazes ahead of the crack tip. More recently, Skibo *et al.*[5] have studied the specific effects of concentration of a methacrylate–butadiene–styrene (MBS) modifier on the *FCP* rate of poly(vinyl chloride) (PVC). They also found that fatigue crack propagation resistance increased with addition of the rubber component but that the effect was less pronounced as the molecular weight of the PVC was increased.

The present study was undertaken to provide knowledge of the fatigue behaviour of unnotched samples of HIPS and to determine how rubber modification influences lifetime under alternating load conditions. The results obtained are compared with average fatigue lifetime values determined on an unmodified PS homopolymer tested under similar conditions.

EXPERIMENTAL

Specimens for both tension and fatigue testing were machined from 1/2 in. diameter extruded HIPS rods. These were threaded at the ends to engage the grips and carefully polished over the gauge section to eliminate machine marks and surface scratches. The specimen geometry, and the polishing techniques, were similar to those adopted for studying the fatigue behaviour of a polystyrene homopolymer[6,7].

When tests were made in tension at a deformation rate of 5.08×10^{-2} cm min^{-1}, the yield stress of the HIPS material was 17.8 MPa and the deformation to fracture exceeded 30%. Under similar test conditions, the PS homopolymer developed a craze yielding stress of 43.4 MPa and the strain to fracture was about 1.5%. From the ratio of the yield stresses for the two materials, it is possible to estimate the rubber phase volume[2]. The value obtained is about 30% and this is indicative of appreciable PS occlusions within the second phase particles. Examination of the tensile fracture surface by scanning electron microscopy (*SEM*) was used to estimate the particle size of the rubber phase. The average size was a little above 2 μm and the range of sizes extended from about 0.5 to 4 μm.

The PS homopolymer had an $\bar{M}_w$ value of 2.74×10^5 and an $\bar{M}_n$ value of 1.0×10^5. The matrix molecular weight of the rubber modified HIPS polymer is not known. It is not, however, unusual for the matrix molecular weight of rubber modified polymers to be less than values for the unmodified polymer[1].

For investigation of the fatigue properties of HIPS, five separate specimens were tested at each of 6 stress amplitudes varying from 17.2 MPa (2500 p.s.i.) to 9.65 MPa (400 p.s.i.). In addition, one sample was tested at 8.62 MPa (1250 p.s.i.) and this sample endured for 10^7 cycles without fracture. All of the fatigue tests were carried out in a tension–compression mode, at a frequency of 31 Hz, in a Tatnall–Krouse fatigue apparatus.

RESULTS AND DISCUSSION

The results of these tests are shown by the full line in *Figure 1*. The data points represent the mean value of the log of the number of cycles to fracture, N_f, while the bars indicate the mean deviation about the average. As expected for fatigue tests, there is scatter in the results obtained from individual samples, and the spread increases as stress amplitude is lowered. This scatter is a reflection of the importance of surface condition in fatigue failure and is due to unavoidable variations in surface geometry from specimen to specimen. On the same Figure is shown, for comparison purposes, the variation of the mean fatigue life of PS specimens with applied stress[8]. The S–N curve of HIPS is generally similar in shape to that of PS, with essentially a linear variation of stress with log$N$ over the intermediate stress region, followed by a flattening of the curve at low stress amplitudes. However, for

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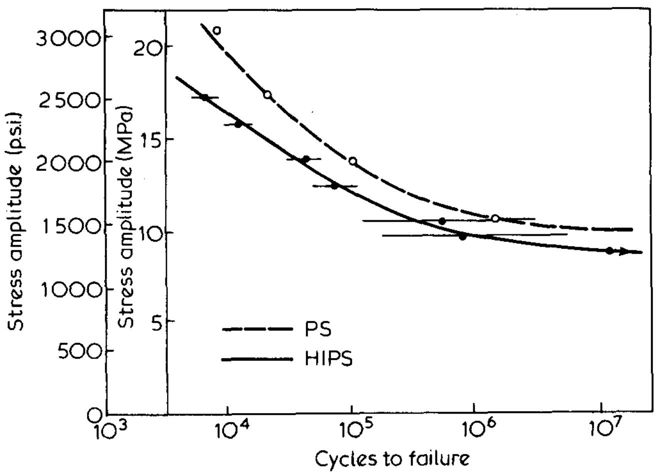

Figure 1 Stress amplitude vs. cycles to failure for HIPS and PS

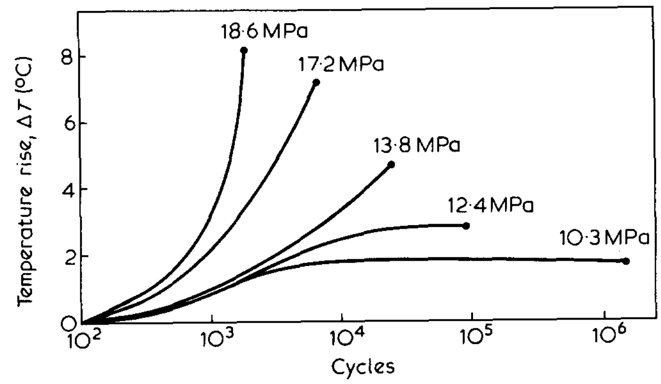

Figure 2 Specimen temperature rise in HIPS vs. number of fatigue cycles for various alternating stress amplitudes

HIPS the S–N curve falls to the left of the PS curve; hence, in these tests conducted on unnotched specimens at zero mean stress, the rubber toughened, graft-copolymerized polymer is inferior to PS in fatigue endurance. Its endurance strength, i.e. the stress below which no failure occurs in 10^7 cycles, is also less. We estimate the endurance strengths from the data of *Figure 1* to be 9.65 MPa (1400 p.s.i.) for PS and 8.62 MPa (1250 p.s.i.) for HIPS.

It is evident that the fatigue properties of HIPS do not correlate with impact strength. HIPS shows a much greater ductility than PS in tension tests and superior toughness in impact tests. Yet our data show that it is less resistant to fatigue fracture under alternating tension–compression loading than unmodified PS. Under alternating loading, the potential capability of the dispersed rubber particles to generate multiple crazing throughout the matrix, and thus increase the energy to fracture, is not realized. Instead, the fatigue crack generates from a surface craze and, in contrast to specimens fractured under uniaxial tension, there is no evidence of stress whitening except possible for some of the most highly stressed specimens in the immediate vicinity of the fracture surface. The importance of crazing in unnotched samples of HIPS subject to alternating tension–compression is also attested by the asymmetrical nature of recorded hysteresis loops[9].

The fatigue fracture surface develops at right angles to the applied stress direction and optical and *SEM* examination of the fracture surface shows a somewhat different morphology than is found for PS specimens. Although, in both cases, the fracture crack appears to develop from breakdown of a surface craze, there is no smooth mirror area surrounding the fracture source in HIPS, as in PS. Instead, most of the fracture surface, including the area in the vicinity of the surface source, is slightly textured, and, at higher magnification, many dispersed second phase particles are visible on the fracture plane. The fatigue crack propagates through equatorial crazes surrounding the rubber phase particles and generally passes through the particles themselves. As a result, the composite nature of these second phase particles is clearly revealed.

The question arises as to why the rubber modified HIPS appears to give improved fatigue crack resistance compared with PS in the fracture mechanics type of experiments of Manson and Hertzberg[3,4] and yet gives poorer fatigue performance in our experiments. In the current experiments, carried out on unnotched specimens, the recorded fatigue lifetimes are a result of both a crack initiation phase and a crack propagation phase. Hence it is conceivable that in HIPS, once a crack has formed in a surface craze, the *FCP* rate could be lower due to impediments to crack propagation produced by the dispersed rubber particles — and this would be consistent with the rougher nature of the fatigue fracture surface — but that the precursor craze, and subsequent crack generation in this craze, develops sooner in time, for a given alternating stress amplitude, than in PS.

Another possibility is that in HIPS there may be a significant heat build-up due to hysteresis. In the case of PS, it is known that at the highest stress employed in our study the ΔT rise due to this effect is less than 2°C even for frequencies up to 1600 cpm[8]. To investigate the possibility that our test results on HIPS have been influenced by thermal effects, an infra-red sensor was utilized to determine the specimen temperature during the course of a fatigue test as a function of both stress magnitude and cycles. The results obtained are shown in *Figure 2.* For the highest stress of 18.6 MPa, the specimen temperature continues to rise with cycling until failure and there is a maximum temperature increase of about 8°C. At lower stresses, the temperature rise is less and the specimen temperature tends to stabilize a few degress above ambient. The recorded temperature rises do not appear to be large enough to account for the lowered fatigue resistance of HIPS relative to PS demonstrated by the data in *Figure 2* but they probably are a contributing factor.

Another difference between the fatigue tests reported here and those carried out by Hertzberg *et al.*[3] is that our fatigue tests were carried out at zero mean stress in a tension–compression mode while their tests were done in cyclic tension, with the minimum stress being 1/10 of the maximum stress. To see whether this difference in testing mode is significant, we ran a new series of fatigue tests on 5 specimens of HIPS, in which the maximum stress was 17.2 MPa and the minimum stress was 3.45 MPa. The mean lifetime for 5 such specimen tested under these conditions was 36 300 cycles. This may be compared with a mean lifetime of 78 900 cycles for five PS specimens, tested under similar conditions[6,10]. Thus, differences in the mode of testing do not appear to be a significant factor as, both for tests performed in cylic tension and for tests performed under alternating tension–compression unnotched samples of HIPS are, on average, less fatigue resistant than unmodified PS.

Still another factor that may be involved is molecular weight. The resistance ot fatigue fracture of glassy polymers, whether notched or unnotched, is greatly increased by increase of molecular weight[7,8,11–13]. Hence, a lower matrix molecular weight may be a contributing factor to the observed lower fatigue resistance of HIPS compared with PS.

Although HIPS is inferior to PS when fatigue lifetimes are compared on a basis of absolute stress magnitude, the rubber modified polymer shows up favourably if comparison of fatigue lifetimes is made against relative stress magnitude, based on ratio of the applied stress amplitude to the observed maximum stress in a tensile test. This is because the tensile fracture stress is much higher for PS than HIPS. At an elongation rate of 0.02 in $\min^{-1}$, the tensile strength of HIPS was observed to be 19.5 MPa (2830 p.s.i.) vs. 43.4 MPa (6300 p.s.i.) for PS. Hence the ratio of endurance strength to tensile strength, a parameter of significance to designers, is 0.22 for PS and 0.44 for HIPS.

It has been reported that blends of glassy polymers with a nitrile elastomer lead to a lower fatigue resistance than that of the unmodified polymer[14]. From the present study, it appears that fatigue resistance is also reduced even when the rubber component is grafted to the glassy matrix and rubber phase volume is high. Thus greater toughness, as assessed from tensile data on unnotched specimens or from impact data on notched specimens, does not necessarily imply greater resistance to fatigue fracture when the material is exposed to alternating stresses. Another conclusion is that in rubber modified polymers subject to alternating loads, craze and crack initiation occur sooner than in unmodified polymers and appear to have a greater influence on fatigue life than a possibly reduced fatigue crack propagation rate due to presence of the dispersed rubber phase.

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Annealing of nodular linear polyethylene crystallized from the glass

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Since Yeh and Geil reported the presence of nodular structures of the order of 10 nm in diameter in amorphous polyethylene terephthalate[1], there have been several reports of similar size nodular structures in amorphous samples of polycarbonate[2], isotactic poly(methyl methacrylate)[3] and polypropylene[4]. Smaller nodules have also been reported for atactic polystyrene[5]. Based primarily on dark field diffraction contrast observations of polyethylene terephthalate[1] and polystyrene[5] the nodules were suggested to represent domains of local order. There has, however, been considerable debate as to whether the nodules represent a bulk structural feature, a surface structure or are merely an artifact. For instance, Thomas and Roche recently reported[6] that apparent structures of several nm in diameter could be caused by defocus fringes and/or noise; they showed such size structures even in evaporated carbon film, which is expected to be structureless above the 0.5 nm level.

In this report, we will show the presence of nodular-like crystallites with dimensions of the order of 10 nm in samples of ultraquenched polyethylene warmed to room temperature and their growth with annealing at elevated temperatures; these nodular crystallites can be considered as an extreme morphology for crystalline polymers.

EXPERIMENTAL

The polyethylene used was Marlex 6015. Xylene solutions of 0.5 ~ 0.2% polyethylene were heated to 120°C and a carbon-coated glass slide dipped into the solution and then removed; thin polyethylene films from less than 100 nm to several hundred nanometers in thickness were obtained. The thickness was estimated from the interference colour of the films. The polyethylene–carbon film was floated on a water surface and picked up on an electron microscope grid. The grid with specimen was heated to 175°C for 5 min in an oven flushed with dry nitrogen and ultraquenched into isopentane cooled by

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