

Effect of CO₂ Saturation and Desorption on the Fatigue Life of Polycarbonate

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The effect of a cycle of CO₂ saturation and desorption on the yield strength, Young's modulus, and fatigue life of polycarbonate was investigated. The fatigue life of the saturation-cycled polycarbonate exceeded that of unprocessed polycarbonate by up to a factor of thirty. The fatigue life of these rough-surfaced saturation-cycled specimens was approximately equal to or greater than that of polished smooth bar specimens. The increase in fatigue life is a function of the CO₂ saturation pressure, reaching a maximum at the same saturation pressure at which there is no further reduction in static yield strength. The increased fatigue life is hypothesized to result from one or more of following mechanisms: (1) reduction of shear strength promoting slow-growing shear fatigue cracks; (2) "healing" or blunting of pre-existing flaws or microcracks by swelling strain or by stress relief strain resulting from plasticization by CO₂ during saturation.

Background

Fatigue of Polycarbonate. A considerable amount of literature has appeared over the past twenty years that relates to the fatigue of amorphous polymers. Hertzberg and Manson (1973) studying the fatigue of single-edge-notched PVC reported the continuous advance of a leading craze but the discontinuous advance of the following crack. Rabinowitz and Beardmore (1974) conducted strain controlled tension-compression tests on unnotched polycarbonate. They noted that the resistance to non-elastic deformation and the cyclic hysteresis changed prior to fatigue crack initiation and propagation under both load and strain control. Hertzberg et al. (1975) studied the frequency sensitivity of the fatigue process and found it to be greatest in polymers with a high tendency for crazing. They proposed that frequency sensitivity reflected a competition between strain rate and creep effects. They found polycarbonate to be insensitive to cyclic frequency and wave form, within their test conditions. The fracture mechanism of discontinuous crack growth was generalized to glassy polymers by Skibo et al. (1977).

Mills and Walker (1980) fatigued polycarbonate in four point bending at frequencies between 0.14 and 0.33 Hz. The maximum cyclic bending stress varied from 45 to 97 MPa. They found that craze lengths varied from 8 to 54 microns after 1000 cycles. Shear bands tended to develop at either end of a craze at 45° to its plane after the craze was 30 microns long. The shear bands opened the craze and hindered further crack growth in the plane of the craze. They observed shear planes linking series of crazes which opened into cracks.

Takemori and Kambour (1981) fatigued unnotched polished

tensile bars of LEXAN at 5 Hz. They compared profile and plan views of a discontinuous crack growth fracture surface with crack arrest bands and found that each arrest band was associated with a pair of shear bands. The shear bands depart normal to the fracture surface from both sides and bend in the direction of crack growth to an angle of 45°. They described the plastic zones at the crack tip, consisting of the leading craze and the pair of shear bands, as resembling the Greek letter epsilon in profile. They noted that the forward growth of the shear bands tends to reduce the stress at the base of the craze. Takemori et al. (1983) fatigued unnotched polished tensile bars of twelve amorphous polymers and found epsilon crack tips in four which had average or above average ratios of crazing strain to yield stress.

Takemori (1984) reported fatigue life data, later published by Matsumoto and Gifford (1985), for polycarbonate specimens with notches due to weld-lines in the middle of the gage length that revealed minimum life for maximum cyclic stresses between approximately 1/3 σ_y to 2/3 σ_y in tension-tension tests. Longer lives were measured above and below this stress range. The fracture mechanism dominate in this stress range was identified as discontinuous growth of cracks with epsilon tips. Longer fatigue life at cyclic stresses greater than 2/3 σ_y was attributed to slow growing shear fatigue cracks at 45° to the loading axis. Longer life at maximum cyclic stresses less than 1/3 σ_y was attributed to discontinuous crack growth without epsilon shaped plastic zones. Takemori (1987) coined the term "fatigue lifetime inversion" to describe the "S" shaped S-N curves that result from decreased fatigue life at intermediate stresses.

Matsumoto and Gifford (1985) found that tests on specimens with weld-lines and specimens that were razor notched were substantially similar. They performed tests at 1 Hz and 10 Hz to demonstrate that the fatigue life inversion was not due to

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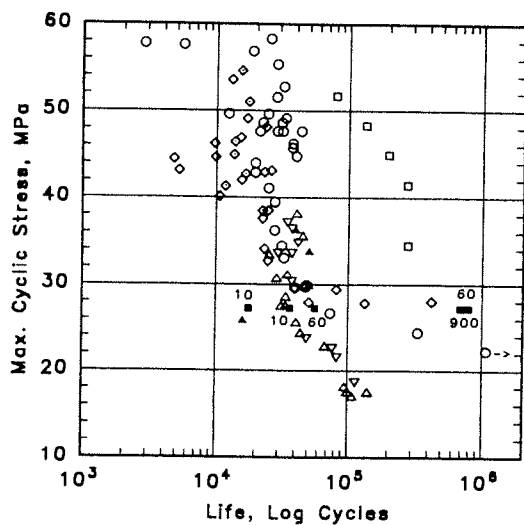


Fig. 1 Fatigue life versus maximum cyclic stress. Open symbols are unnotched polycarbonate specimens. Filled symbols are notched specimens that were creep strained before cycling. Note the long lives of Matsumoto and Gifford's polished smooth bar specimens cycled at 35 and 41 MPa.

hysteretic heating. They further demonstrated that the increased life of notched specimens fatigued at high cyclic stress was due to strain and not heat by creep loading notched specimens at 52 MPa before cycling them at 28 MPa. Fatigue life increased by up to approximately two orders of magnitude as a function of the duration of the creep loading. Finally, they found that polished smooth bar specimens, washed to remove craze producing oils accumulated during polishing, do not have fatigue life inversion. They proposed the lack of inversion was due to the time it took to initiate the fatigue crack on the smooth surface and because the specimens exhibited both discontinuous crack growth and shear band growth. Their data are shown in Fig. 1. They concluded that the fatigue lifetime of polymers that exhibit epsilon cracks can be increased by inducing the slower plane-strain shear fatigue process. Takemori (1988) published fatigue life diagrams for polycarbonate specimens with weld-lines for temperatures ranging from -25°C to 125°C . Fatigue life inversion was not observed above 50°C .

Boukhili, Gauvin and Gosselin (1989) investigated ASTM D647 Type A and B dog-bone specimens that were machined from injection molded plaques with and without weld-lines. Their data are also reproduced in Fig. 1. Boukhili et al. concluded that polycarbonate's fatigue lifetime inversion results from its notch sensitivity. They suggested the hypothesis that the lack of notch sensitivity above a maximum stress of 38 MPa results from the notch tip blunting within the first few cycles, leading to a ductile type failure involving extensive shear yielding. They tested this hypothesis by creep-loading weld-line specimens at a constant stress of 52 MPa for seven minutes before cycling them at maximum stresses from 25.9 to 36.4 MPa and increased fatigue life by up to 210 percent. They also reported that at high cyclic stresses most of the weld-line specimens did not fail at the weld-line notch and that at high cyclic stress fatigue life was independent of whether or not the specimen failed through the notch. Boukhili and Gauvin (1990) proposed that the fatigue life inversion observed in polycarbonate specimens with weld-lines could be described as a brittle-ductile transition, analogous to the behavior of notched polycarbonate in static tensile tests, with high cyclic stress blunting crack the crack tip and inhibiting craze formation.

Effect of Gas Absorption on the Mechanical Properties of Polycarbonate. Hojo and Findley (1973) reported increased creep in polycarbonate tubes pressurized with CO_2 . The glass transition temperature of polycarbonate is reduced by dissolved CO_2 . A theoretical model developed by Chow (1980) to predict the glass transition temperature of polymer-diluent systems has been shown to be in good agreement with experimental data for polycarbonate- CO_2 by Chiou et al. (1985).

Michaels et al. (1963) noted that the diffusion of CO_2 in glassy amorphous polyethylene terephthalate did not obey Henry's law and postulated two concurrent mechanisms of sorption: ordinary dissolution and "hole-filling," or dual sorption, combining Henry's law and a Langmuir expression. Previous workers reported two-stage sorption in glassy polymers below T_g , as cited by Crank and Park (1968). The solubility, permeability and diffusion time lag for CO_2 in polycarbonate has been modelled by Koros et al. (1977) who also combined Henry's law and a Langmuir expression. The hypothesis that the latter diffusion mechanism results from the excess free volume in the polymer is supported by Toi (1980) who reported pressure dependence of the diffusion coefficient for CO_2 in glassy polymers.

A cycle of gas sorption-desorption has been found to leave lasting effects on the gas sorption, thermal and static mechanical properties of glassy polymers by Chan (1978) and Chan and Paul (1979) who attribute the effects to the increase in free volume of the polymer that results from a saturation cycle. Wonders and Paul (1979) report volume expansion following a cycle of saturation and desorption. Chan and Paul (1980) report that annealing, which increases the density of glassy polymers, reverses the effect of a saturation cycle on the sorption of CO_2 in polycarbonate. They found that the yield strength of polycarbonate films exposed to 6.1 MPa CO_2 for a day was reduced 15 percent. Annealing polycarbonate at 125 and 135°C had the opposite effect, increasing the yield strength by 25 percent. Interestingly, neither annealing nor gas sorption affected modulus in their study. Their yield data are shown in Fig. 4. The low yield strength they reported for their unprocessed specimen could be due to notching by an extensometer.

Experimental

Specimen Preparation. ASTM test method D638 Type IV specimens with 50 mm long gage sections were milled from 1.5 mm thick LEXAN 9030 polycarbonate sheets. The specimens were all oriented in the same direction relative to the sheet to reduce the effect of anisotropy. Two different sheets of commercially obtained LEXAN 9030 were used, referred to hereafter as sheets 1 and 2. The reported weight average molecular weight for LEXAN 9030 ranges from 20,000 to 40,000.

Specimens were saturated in high pressure CO_2 at room temperature for 60 hours. The equilibrium CO_2 concentration and the corresponding T_g calculated using Chow's model are presented in Table 1. The reduction in T_g ranges from 30°C at 0.7 MPa to 70°C at 5.5 MPa. Two specimens saturated at 5.5 MPa warped, suggesting that the T_g reduction relieved residual stress.

Figure 2 is a desorption curve for a 1.5 mm thick plaque saturated at 5.5 MPa. Specimens desorbed at atmospheric pressure and room temperature for a minimum of 500 hours before testing, except for two tensile specimens noted below which were tested after desorbing 290 hours. Figure 3 shows saturation concentration of CO_2 as a function of saturation pressure. Also shown are data from Chan (1978) and Kumar and Weller (1993).

Table 1 T_g calculated using Chow's (1980) model

Saturation pressure (MPa)	Equilibrium CO ₂ concentration (mg/g)	Calculated T_g (°C)
0.7	26	120
1.2	37	112
2.8	61	99
4.1	93	87
5.5	122	80

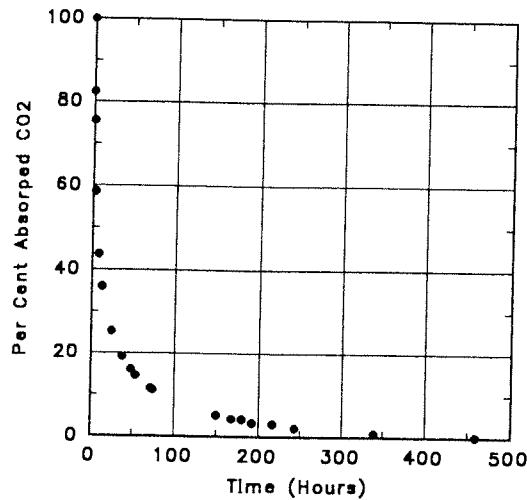


Fig. 2 Desorption of CO₂ from a 1.5 mm thick polycarbonate plaque saturated at 5.5 MPa

The milled surfaces of the specimens were sanded with 320 emery paper to remove machining marks after CO₂ desorption. The specimens were neither polished nor washed to remove oils accumulated during handling.

Differential Scanning Calorimetry Test Procedure.

Differential scanning calorimetry tests were performed on control and saturation-cycled specimens from sheet 1 that desorbed a minimum of 1000 hours using a Perkin Elmer DSC-4 at a scan rate of 10°C per minute.

Tensile Test Procedure. Tensile tests were performed at room temperature using an Instron 8500 servohydraulic testing machine with extensometer to measure modulus. An extensometer was not used in tests measuring the yield and ultimate strengths. The cross-head displacement rate was 10 mm/min.

Fatigue Test Procedure. Specimens were tested in tension-tension with a sinusoidally varying load at 1 and 10 Hz in an Instron 8500 servohydraulic testing machine. The average ratio of the minimum to maximum load was 0.1. In the 10 Hz tests, the initial cyclic load ratio of minimum to maximum load was 0.5. The ratio was decreased uniformly over the first 800 to 1000 cycles to 0.1 to avoid compressive stress and buckling of the specimen. The potential controller overshoot into compression at the beginning of the 10 Hz tests is presumably due to the relative high compliance of the specimen, which decreases over the first few hundred cycles, as observed by Raninowitz and Beardmore (1974), and to particular response of the controller. The tests were conducted at room temperature.

Results

Differential Scanning Calorimetry Tests. Saturation-cycling at room temperature did not effect the T_g . The enthalpy at T_g was unchanged, except for the specimen saturation-cycled at 5.5 MPa. The results are presented in Table 2.

Table 2 Differential scanning calorimetry data, sheet 1

Saturation pressure (MPa)	Desorption time (Hours)	Measured T_g (°C)	Enthalpy at T_g (Cal/(g°C))
Unprocessed	Not Applicable	147.8	3.72×10^{-2}
Unprocessed	Not Applicable	146.5	4.39×10^{-2}
2.1	1450	147.6	4.63×10^{-2}
4.1	1280	147.2	4.08×10^{-2}
4.1	1280	145.9	4.43×10^{-2}
5.5	1090	147.0	6.20×10^{-2}

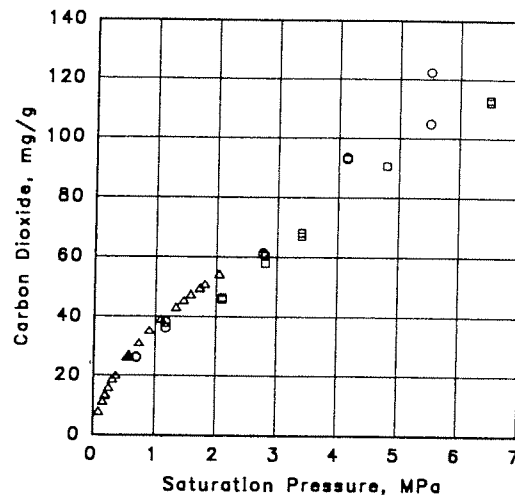


Fig. 3 CO₂ concentration versus saturation pressure. The circular symbols are from this study. The square symbols are from Kumar and Weller (1993). The saturation temperature for both of these data sets was ambient. The triangular symbols are from Chan (1978). The saturation temperature was 35°C.

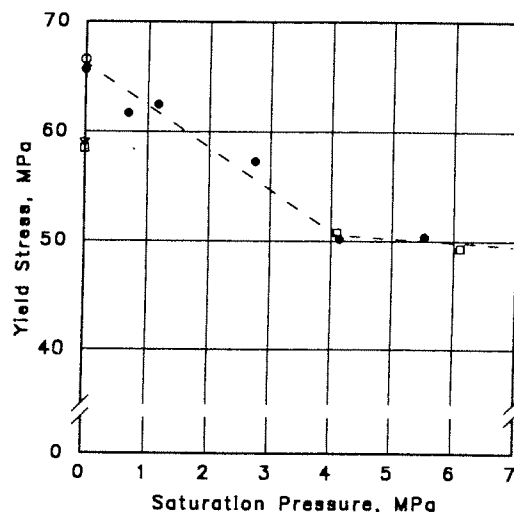


Fig. 4 Tensile yield strength of saturation-cycled polycarbonate. The specimens from this study desorbed a minimum of 500 hours before testing. Chan's (1978) specimens were 0.19 mm thick film

Tensile Tests. The tensile data are summarized in Tables 3 and 4. The tensile properties of sheets 1 and 2 were similar. The yield strength data are plotted in Fig. 4. Yield strength is a function of CO₂ saturation pressure. The yield strength of specimens saturation-cycled at 2.8 MPa is approximately 87 percent that of the unprocessed polycarbonate. The yield

Table 3 Tensile Properties, sheet 1

Saturation pressure (MPa)	Yield stress (MPa)	Young's modulus (GPa)
Unprocessed Control	65.7	2.5
0.7	61.7	2.7
1.2	62.5	2.8
2.8	57.3	2.2
4.1	50.2	2.2
5.5	50.4	2.3

Crosshead speed was 10 mm per minute. Moduli were calculated using a least squares fit of the initial portion of the load displacement curve.

Table 4 Tensile Properties, sheet 2

Saturation pressure (MPa)	Yield stress (MPa)	Young's modulus (GPa)
Unprocessed Control	64.4	2.8
5.5	50.9	2.8

Crosshead speed was 10 mm per minute. Moduli were calculated using a least squares fit of the initial portion of the load displacement curve.

strength of specimens saturation-cycled at 4.1 and 5.5 MPa is approximately 77 percent that of unprocessed polycarbonate. Young's modulus is not a function of saturation pressure. It is noted that yield strength and Young's modulus are only useful in comparing the strength and stiffness of viscoelastic materials tested at the same strain rate temperature.

Yield strength is dependent on the degree of desorption. Specimens saturation-cycled at 5.5 MPa and tested after desorbing for 290 hours, when they retained approximately 1.5 mg of CO₂ per gram of polycarbonate, had yield strength of 47.7 MPa, approximately 95 percent of the strength of specimens that desorbed a minimum of 500 hours before testing.

Fatigue Tests. The fatigue test results for sheet 1 are shown in Fig. 5. Saturation-cycling increases fatigue life of similarly prepared specimens. The greatest increase observed for sheet 1 was a factor of twenty for the specimens saturation-cycled at 4.1 MPa. Matsumoto and Gifford's (1985) data for polished and washed smooth bar specimens are also shown on Fig. 5. Figure 6 shows fatigue data for sheet 2 specimens that desorbed five and a half months before testing.

Discussion

Tensile Properties. Saturation-cycling does not affect Young's modulus but it does reduce the yield strength of polycarbonate. Figure 5 shows that tensile yield strength decreases with increasing saturation pressure from 0 to 4.1 MPa. The tensile yield strength of specimens saturated at 4.1 and 5.5 MPa are approximately equal. This is consistent with the results reported by Chan (1978) and Chan and Paul (1979), which they found to be a function of the saturation history. They attribute the decreased yield strength to an increase in free volume. Residual stress relief from the CO₂ plasticization would be expected to increase yield strength without affecting Young's modulus, if the polymer is modelled as ideally elastoplastic. The test results are the opposite, implying that the effect of increased free volume on yield strength is greater than the effect of residual stress relief.

Fatigue Properties. It is noteworthy that the fatigue life data reported by Matsumoto and Gifford (1985) and Boukhili et al. (1989) for creep-strained weld-line data, reproduced in Fig. 2, fall within the control data of this study. It is also noteworthy that the lives of Matsumoto and Gifford's (1985) polished smooth bar specimens, which were handled to prevent craze formation, fall within the upper bound of the saturation-

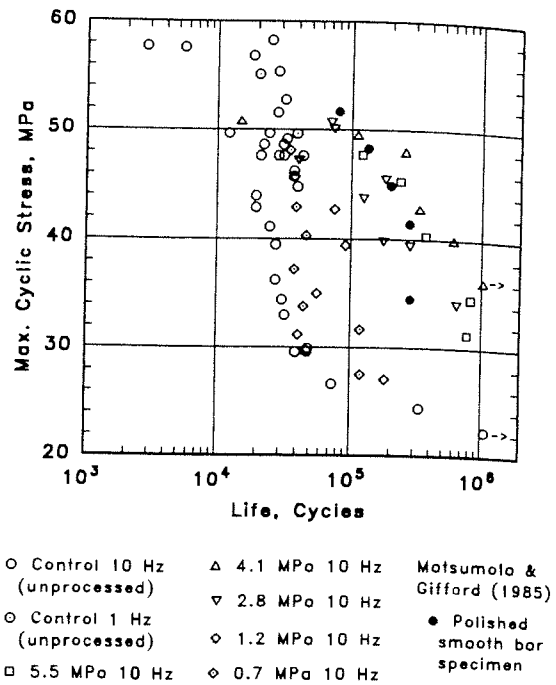


Fig. 5 Fatigue life saturation-cycled polycarbonate and Matsumoto and Gifford's (1985) polished smooth bar specimens versus maximum cyclic stress. The specimens were cut from sheet No. 1. The machined surfaces were sanded with No. 320 emery after the CO₂ desorbed. They were not washed to remove oil accumulated during handling.

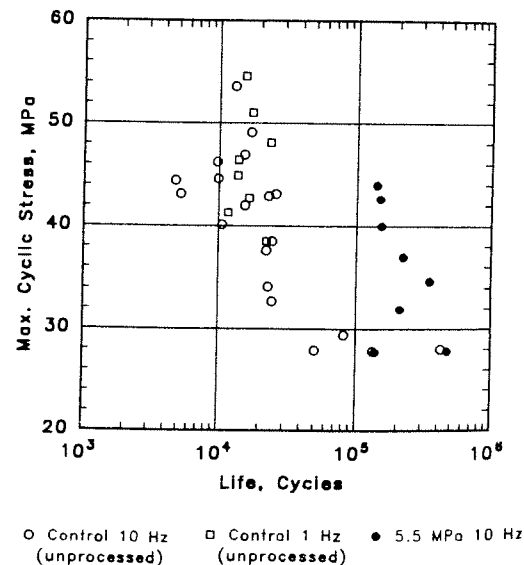


Fig. 6 Fatigue life of saturation-cycled polycarbonate versus maximum cyclic stress. Specimens were cut from sheet No. 2. The saturation-cycled specimens desorbed approximately 4000 hours prior to testing. The machined surfaces were sanded with No. 320 emery after CO₂ desorption.

cycled data of this study shown on Fig. 5. Let it be restated that the saturation-cycled specimens were sanded with No. 320 emery after the CO₂ had desorbed. Saturation-cycling increases the fatigue life of rough-surfaced specimens, even if the rough surface is created after the saturation-cycling.

Saturation-cycling increased the fatigue life of polycarbonate by as much as factors of twenty and thirty, as shown in Figs. 5 and 6. Figure 5 shows data for specimens saturated between 0.7 and 5.5 MPa. The specimens saturated at 4.1 MPa are the longest lived, but that could be coincidental and all of the saturation-cycled data above 1.2 MPa may belong to the same population. Figures 7 and 8 show the fatigue data nor-

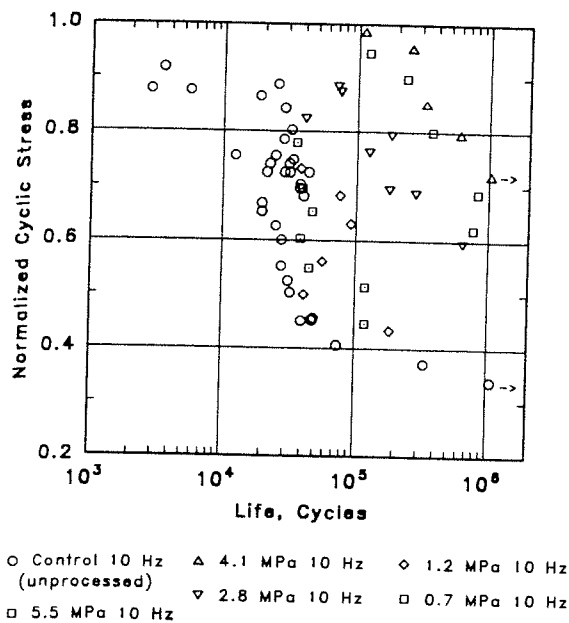


Fig. 7 Fatigue life saturated-cycled polycarbonate versus maximum cyclic stress divided by yield strength

malized by yield strength. Figure 7 shows that saturation-cycled polycarbonate maintains greater fatigue life at maximum cyclic stress close to yield than does unprocessed polycarbonate. Figure 8 shows an increase in fatigue life of approximately a decade on the log scale for equal normalized maximum cyclic stress.

The fatigue lives of specimens saturated at 4.1 and 5.5 MPa, desorbed a minimum of 4000 hours and tested at high normalized cyclic stress at 1 Hz were in the range of the results of the 10 Hz tests. It does not appear that hysteretic heating was a factor in the increased lives of the specimens tested at 10 Hz. However, significantly more creep was observed in the saturation-cycled specimens than in the control specimens in tests at 1 Hz. Saturation-cycling appears to increase the creep compliance of polycarbonate.

Takemori (1984) and Matsumoto and Gifford (1985) identified the competition between leading craze crack growth and shear fatigue crack growth in the fatigue of polycarbonate. The increased fatigue life from saturation-cycling may result from reduction of the shear strength, proportional to the observed reduction in tensile yield strength, favoring the shear fatigue crack growth mechanism. However, if that were the only effect increasing fatigue life then the specimens saturated at 4.1 and 5.5 MPa would have the same fatigue life because they have the same yield strength. It is possible that the decreased fatigue life at 5.5 MPa is a result of a change in the state of the polymer because only the specimen saturation cycled at 5.5 MPa showed a change in the enthalpy at T_g . However, this could be a spurious result, as Chan and Paul (1979) have demonstrated the importance of the saturation history on the CO_2 sorption in polycarbonate.

The increased fatigue life may also result from strains during saturation "healing" or blunting pre-existing flaws or microcracks. Matsumoto and Gifford (1985) demonstrated that creep strain increases fatigue life. There are strains associated with saturation-cycling from swelling of the polymer and creep during stress relief. Loss of surface residual compressive stress would be expected to reduce fatigue life. Consequently, there must be a compensating improvement in the material properties or the geometry or stress-state of pre-existing flaws or microcracks. The pre-existing flaws or microcracks affected by the saturation-cycling must be internal because the machined surfaces of the specimens are sanded after desorption.

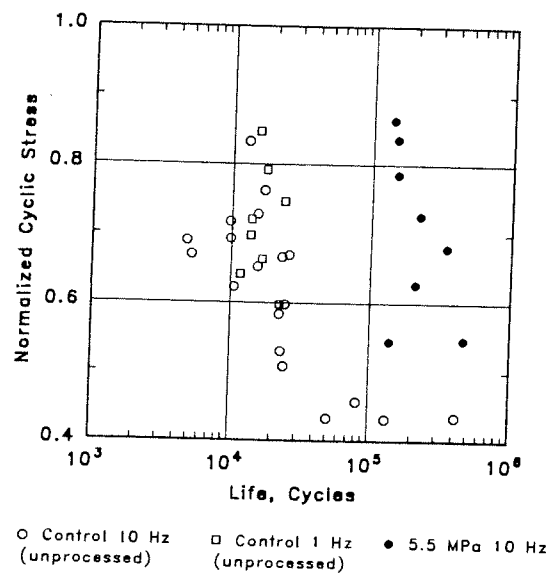


Fig. 8 Fatigue life of saturation-cycled polycarbonate versus maximum cyclic stress divided by yield strength. The saturation-cycled specimens desorbed approximately 4000 hours prior to testing.

Finally, the increased fatigue life could be due to residual plasticization by retained CO_2 because of the low mobility of the gas sorbed by a Langmuir mechanism. If there is sorbed gas after 500 hours of desorption, the quantity is below the limit of the precision of the measurements. It would also be apparently "permanently" sorbed because the increase in fatigue life of saturation-cycled polycarbonate persists after 4000 hours of desorption.

Conclusions

Saturation-cycling polycarbonate with CO_2 greatly increases fatigue life and decreases yield strength but does not affect Young's modulus of rough-surfaced polycarbonate specimens. The increased life of the saturation-cycled specimens occurs even though the surfaces were roughened after the CO_2 desorbed. The increase in fatigue life is related to the saturation concentration of CO_2 and, consequently, the yield strength. These effects may be due to changes both in the properties of the polymer and the state of pre-existing internal flaws or cracks. CO_2 saturation swells polycarbonate and plasticizes it, relieving residual stress. The lives of the rough surfaced specimens saturation-cycled at 4.1 MPa were approximately equal or greater than the lives of Matsumoto and Gifford's (1985) polished smooth bar specimens. This implies that saturation-cycling retards crack growth because the sanded surfaces provided an abundance of crack initiation sites.

Loss of residual stress alone would be expected to increase yield strength and decrease fatigue life. The observed decreased yield strength implies that loss of residual stress is not responsible for the observed change in the mechanical properties. The reduction in yield strength is likely due to an increase in the free volume of the polymer.

The increase in fatigue life is possibly due to change in both the polymer properties and the internal pre-existing flaws or microcracks. Reduction in the shear strength of the polymer favors slow growing shear fatigue cracks. Local strains due to change in the free volume and creep strain during stress relief could affect pre-existing flaws or microcracks and retard crack growth. The relative importance of these mechanisms depends on the cyclic stress magnitude. The lives of the saturation cycled specimens exceeded that of the polished smooth bar specimens for maximum cyclic stresses greater than 42 MPa.

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