Decoupling the Effects of the Matrix Properties and Foam Structure on the Mechanical Properties of Microcellular Foam by Sub-T_g Annealing

KARL A. SEELER*
Department of Mechanical Engineering
Lafayette College
Easton, PA 18042

VIPIN KUMAR
Department of Mechanical Engineering
University of Washington
Seattle, WA 98195

ABSTRACT: Sub-T_g annealing microcellular polycarbonate for 100 hours at 135°C increases yield strength but decreases fatigue life and ductility. Annealing reverses the effect of CO_2 saturation-cycling on the mechanical properties of the foam matrix by decreasing the free volume created by the saturation-cycle. Consequently, annealing decouples the effects of the matrix properties and the microstructure on the mechanical behavior of microcellular foam.

KEY WORDS: microcellular, foam, polycarbonate, mechanical properties, annealing, fatigue, free volume.

INTRODUCTION

MICROCELLULAR POLYMERS ARE plastic foams with bubbles 10 μm or less in diameter. They were conceived by Suh [1] as a means to reduce the amount of plastic required to produce a part. The rational was that if voids smaller than the critical flaws pre-existing in polymers can be nucleated then material costs can be reduced without compromising the part's mechanical properties.

Microcellular foam is produced using a thermodynamic instability to cause cell nucleation, Martini et al. [2]. The process involves saturating a polymer with a non-reactive gas at a high pressure and at a temperature below the glass transition temperature. The low permeability of polymers to gases requires days for typical specimens to reach equilibrium. When the pressure is reduced to atmospheric, the specimen is supersaturated with gas. Heating the specimen softens the polymer, and the gas comes out of solution as bubbles nucleate. The polymer viscosity limits bubble growth, allowing control of the foaming so that 10 μm bubbles are created.

BACKGROUND

Mechanical Behavior of Microcellular Polycarbonate

Kumar and Weller [3,4] investigated microcellular polycarbonate (MCPC) created by saturating polycarbonate (PC) with CO_2 and found that bubble densities in the range of 1 to 10 billion per cm^3 could be achieved. Kumar et al. [5] characterized the tensile behavior of MCPC. The mechanical properties of MCPC are a linear function of the relative density, ρ_{rel}, which is the ratio the density of the foam to the density of the solid. However, there is a disproportional loss of strength and stiffness of MCPC compared to the solid, as-received PC. It was recognized, Seeler and Kumar, [6,7], Kumar and Seeler, [8] and Kumar et al. [5] that the gas saturation phase of the microcellular process alters the mechanical properties of the matrix of the polymer foam. Therefore, the tensile properties of microcellular polymers depend on both the foam microstructure and on the effect of the cycle of gas sorption and desorption on the matrix material.

Takemori and Kambour [9], Takemori et al. [10], Takemori [11,12,13], Matsumoto and Takemori [14] and Matsumoto and Gifford [15] studied the fatigue of PC. Two competing fatigue mechanisms were identified: fast growing discontinuous leading craze crack growth, which dominates at low cyclic stress, and slow growing shear fatigue cracks, which dominate at high cyclic stress. Fatigue life inversion, in which life increases with increasing cyclic stress, was observed in the fatigue of notched PC by Takemori [11] and Matsumoto and Gifford [15], who attributed the inversion to competition between the two fatigue mechanisms. Takemori [13] presented a fatigue fracture diagram which relates the fracture mechanism to temperature and normalized stress. He suggested that future work investigate the effect of thermal history and physical aging on fatigue.

Seeler and Kumar [16] reported the initial study of the fatigue of MCPC. Fatigue life increases with increasing relative density, Figure 1, and there is fatigue life inversion. The fatigue life of high relative density MCPC exceeds that of as-received solid PC, as shown in Figure 2, Kumar and Seeler [7]. Polycarbonate that was saturation-cycled but not foamed had the longest fatigue life, promoting interest in the effect of saturation-cycling on fatigue. Seeler and Kumar [6] found that the notch sensitivity of MCPC is less than that of solid PC at low cyclic stress, but exceeds that of solid PC at high cyclic stress.

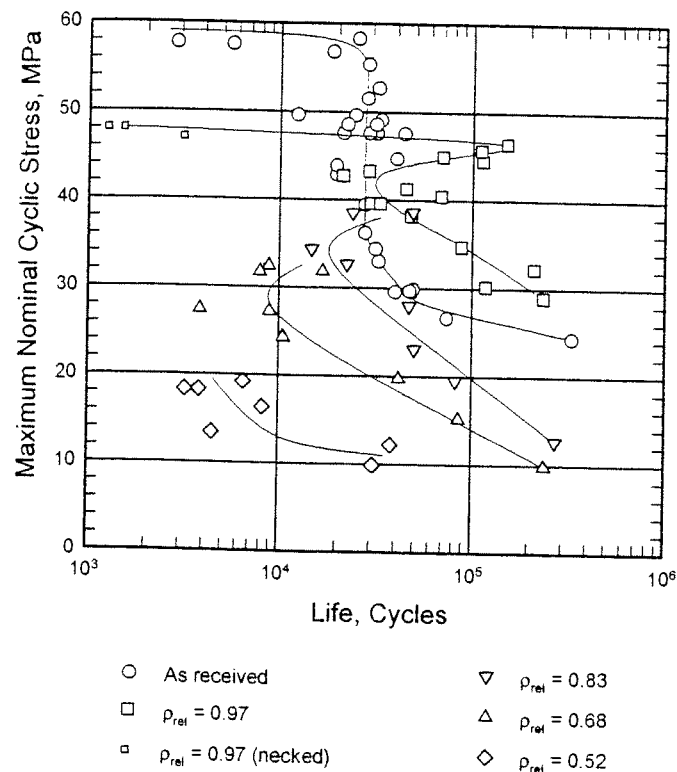*Author to whom correspondence should be addressed.

Figure 1. *Fatigue life of polycarbonate and microcellular polycarbonate from Seeler and Kumar [6]. Note the long fatigue life of* ϱ_{rel} = 0.97 *microcellular polycarbonate.*

Effect of Gas Absorption and Desorption on the Mechanical Properties of Polycarbonate

The mechanical properties of amorphous polymers are affected by dissolved gas, as reported by Hojo and Findley [17] who observed increased creep in PC tubes pressurized with CO_2. CO_2 dissolved in PC reduces its glass transition temperature. A theoretical model developed by Chow [18] 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. [19]. Wing et al. [20] investigated the effect of CO_2 on the creep of polycarbonate and found that the creep response is initiated at lower stress levels in saturated PC than in as-received PC.

Wonders and Paul [21] reported volume expansion following a cycle of saturation and desorption. A cycle of gas sorption and desorption was found to leave lasting effects on the gas sorption, thermal and static mechanical properties of amorphous polymers by Chan [22] and Chan and Paul [23] who attributed the ef-

fects to the increase in free volume of the polymer that results from a saturation cycle. Chan and Paul [24] reported that annealing, which increases the density of amorphous polymers, reverses the effect of a saturation cycle on the sorption of CO_2 in PC. They found that the yield strength of PC films exposed to 6.1 MPa CO_2 for a day is reduced 15 percent. Annealing PC at 125 and 135°C has the opposite effect, increasing the yield strength by 25 per cent.

Seeler and Kumar [7] investigated the mechanical properties of PC saturation-cycled with CO_2 at pressures ranging from 0.7 to 5.5 MPa. All specimens desorbed at atmospheric pressure for at least 500 hours before testing. (Some specimens desorbed more that 4000 hours before testing.) DSC measurements indicated that there is no reduction in the T_g following desorption. Both the tensile yield strength and the fatigue life of saturation-cycled PC are functions of the saturation pressure. Saturation-cycling decreases tensile yield strength linearly with increasing saturation pressure up to a saturation pressure of 4.1 MPa. The strength remains constant at approximately 75 percent of the as-received strength for higher saturation pressure. Significantly, saturation-cycling increases fatigue
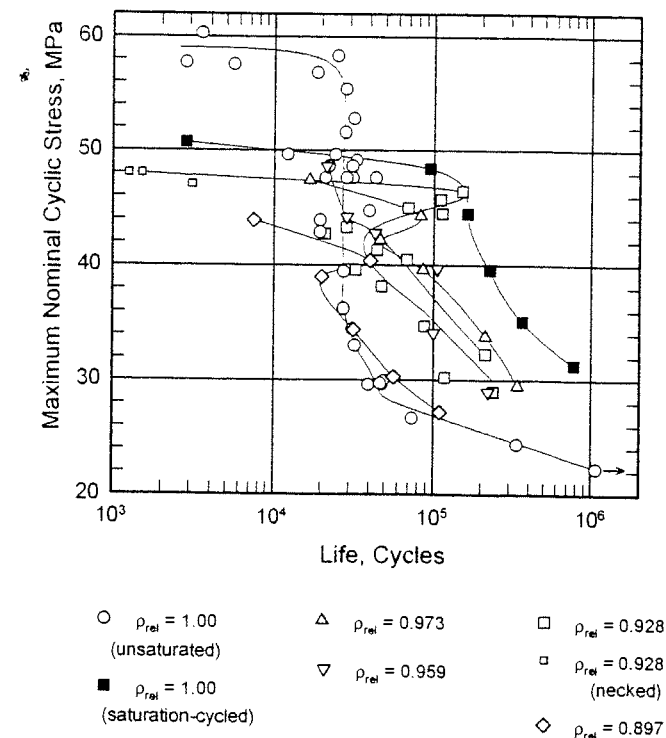

Figure 2. *Fatigue life of polycarbonate, saturation-cycled polycarbonate and microcellular polycarbonate from Kumar and Seeler [7]. Note the long life of saturation-cycled polycarbonate.*

life by up to thirty times. Seeler and Kumar proposed that the increased fatigue life results from saturation-cycling induced increased free volume, which decreases shear strength and increases creep compliance, favoring the slower shear fatigue mechanism.

Seeler and Kumar [25] investigated the effect of saturation-cycling on the notch sensitivity of PC. Specimens were saturation-cycled with 5.5 MPa CO_2 and then notched and tested after desorbing. CO_2 saturation-cycling increases the fatigue life of notched PC by up to seventy times. Saturation-cycling also decreases yield strength and relaxation time at low stress and greatly increases stress relaxation at high stress. Seeler and Kumar proposed that the increased fatigue life of notched, saturation-cycled PC is caused by increased free volume.

Free Volume and Physical Aging

Amorphous polymers below T_g are solidified supercooled liquids whose volume, enthalpy and entropy are greater than the equilibrium state. Free volume is an intrinsic variable of this non-equilibrium state. Alfrey, Goldfinger, and Mark [26] reported that the density of polystyrene below T_g depends on both its temperature and temperature history, which they attributed to rate dependent changes in free volume. At temperatures below T_g, volume decreases isothermally towards the equilibrium volume extrapolated from the volume-temperature relationship for temperatures greater than T_g. Spencer and Boyer [27] found that isothermal volume change of polystyrene occurs on two time scales, one almost instantaneous and the other much slower. They also considered the volume-temperature relationship of quenched samples and proposed annealing schedules. McLoughlin and Tobolsky [28] reported that the stress relaxation rate of polymethyl methacrylate (PMMA) depends on the rate at which the sample is cooled through T_g. The rate of stress relaxation increases with the cooling rate. They attributed the increased stress relaxation to increased free volume which allows faster internal flow. Kovacs, Stratton and Ferry [29] studied the dynamic mechanical properties of polyvinyl acetate near T_g and found that relaxation times were essentially functions of free volume alone.

The term "physical aging" is now used to refer to isothermal changes in free volume. The mechanical properties of amorphous polymers change in the same direction during physical aging at temperatures below T_g as they do during cooling above T_g, becoming stiffer and more brittle, with less damping and a shift to longer relaxation or retardation times by approximately one decade for each tenfold increase in aging time, as summarized by Struik [30]. Struik also demonstrated that physical aging is thermally reversible. Amorphous polymers recover their initial properties upon reheating above T_g. Matsumoto [31] reported that, due to physical aging, time-temperature superposition causes large errors in long time creep prediction for PC.

Struik [30] reported that high stress can partially erase the effect of physical aging on the yield strength of PC in tests at constant deformation rates, presumably by increasing free volume. Muller and Wendorff [32] reported that cold drawing PC 100 percent decreased specific volume by 0.3 percent but increased the rate

of volume relaxation by an order of magnitude, which they attributed to increased free volume.

Cyclic loading at stresses above the endurance limit affects the mechanical properties of polymers. Beardmore and Rabinowitz [33] reported that isothermal cyclic softening of PC was a state that persisted "indefinitely" if the specimen was stored at room temperature. The density of PC was found to increase one percent due to the cycling. They noted that the densification of ductile polymers in cyclic deformation resulting in a decrease in the resistance to nonelastic deformation is difficult to account for with any free volume model of nonelastic deformation in rigid plastics. They observed cyclic softening in PMMA at temperatures above 40°C, where it is ductile, but the state did not persist after the cycling ended. Conversely, Bouda [34] fatigued PMMA and poly(n-propyl methacrylate) at 20°C and observed a slight decrease in density and an increase in stiffness due to cyclic loading. These contradictory results imply that the effect of cyclic loading on density and stiffness depends on ductility and, hence, the relaxation times. Struik [30] reported that creep is greater under cyclic loading than static loading and suggested that aging occurs under constant load but cyclic loading erases part of the aging.

Free volume theories for amorphous polymers are of current interest in the polymer physics community. Specific volume by itself does not determine the behavior of amorphous polymers. Two specimens with the same specific volume but prepared differently can exhibit very different behavior. Free volume theories reconcile this memory effect by postulating that it is not only the total amount of free volume but also its distribution that are important. Many studies have reported reduction in specific volume due to physical aging. Bubeck et al. [35] reported that annealing PC at 120°C for 380 hours reduces its density 0.13 percent. Curro and Roe [36] used small-angle X-ray scattering to observe local free volume change in PC during isothermal annealing but found no correlation with dilatometric results. Royal and Torkelson [37] used photochromic and fluorescent probes and suggest that while there is a loss in local free volume during physical aging, the average size remains constant. Kluin et al. [38] performed ortho-positronium lifetime studies and found that the hole size distribution shifted during the aging process in PC, but also reported possible artifacts due to positron irradiation.

Seeler and Kumar [25] reported that saturation-cycling reduces the faster relaxation times and increasing the stress relaxation of PC. They proposed that increased free volume from saturation-cycling at room temperature persists because, although T_g is reduced to approximately 80°C during CO_2 saturation at 5.5 MPa, as estimated by Seeler and Kumar [7] using Chow's [18] model and Chiou et al.'s [19] data, the reduced T_g is still more than 50°C above room temperature. With reference to the WLF equation, the time required to establish thermodynamic equilibrium increases by a factor of ten for each 3°C increase in the temperature difference ($T_g - T$). Even if the time required to reach volume equilibrium at T_g is assumed to be only one millisecond, equilibrium would not be reached at room temperature for millennia. Wing et al. [20] found that creep compliance changes with time after saturation-cycled PC fully desorbs, indicating physically aging at room temperature.

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 PC sheets. The number average molecular weight of the PC is 10,380 and weight average molecular weight is 29,450, as determined by gel permeation chromatography. The specimens were all oriented in the same direction relative to the sheet to reduce the effect of anisotropy.

The saturation-cycled and microcellular specimens were saturated in 5.5 MPa CO_2 at room temperature for 60 hours. Some specimens warped, suggesting that the T_g reduction relieved residual stress. The specimens to be foamed were immersed in a heated glycerine bath for 30 seconds and then quenched in room temperature water. Bath temperatures of 55°C and 65°C were used, producing microcellular foams with relative densities of 0.88 and 0.82, respectively, as shown in Table 1.

The saturation-cycled and microcellular specimens desorbed at atmospheric pressure and room temperature for a minimum of 1500 hours before either an-

Table 1. Specimen characteristics.

| Relative Density $\frac{\varrho_{foam}}{\varrho_{solid}}$	Foaming Temperature °C	Annealing History	Tensile Yield Strength MPa	Ultimate Tensile Strength MPa
1.00 Not saturation-cycled	Not foamed	Not annealed	65.7	81.8
1.00 Not saturation-cycled	Not foamed	Annealed 100 hours at 135°C	76.0	69.7
1.00 Saturation-cycled	Not foamed	Not annealed	49.2	52.7
1.00 Saturation-cycled	Not formed	Annealed 100 hours at 135°C	68.1	62.5
0.88	55	Not annealed	40.8	62.2
0.90	55	Annealed 100 hours at 135°C	58.2	49.0
0.82	65	Not annealed	37.8	51.3
0.86	65	Annealed 100 hours at 135°C	55.6	44.9
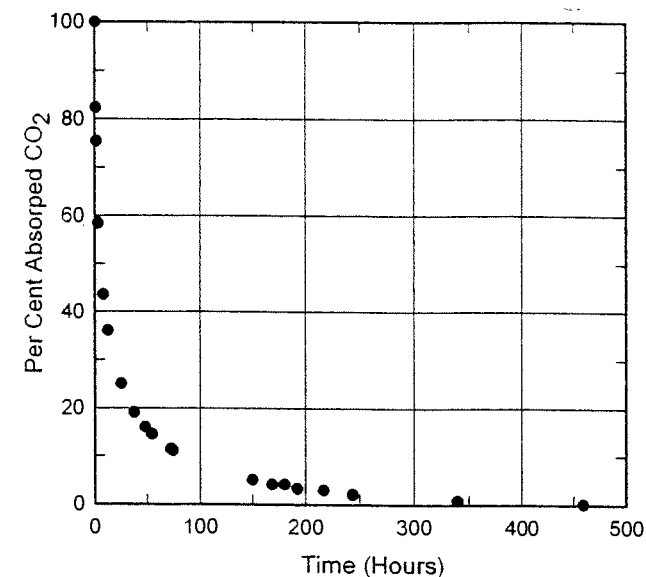
Figure 3. *Desorption at atmospheric pressure of CO_2 from a 1.5 mm thick polycarbonate plaque saturated at 5.5 MPa. From Seeler and Kumar [8].*

nealing or testing. Figure 3 is a desorption curve which shows that the specimens were completely desorbed after 450 hours at atmospheric pressure. Specimens were annealed in a convection oven for 100 hours at 135°C. The temperature was controlled to within one half of a degree. Annealing increased the relative density of the microcellular specimens from 2 to 5 percent.

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

Stress Calculations

Nominal stresses were calculated as engineering stress, using the initial macroscopic cross-sectional area, neglecting the voids in the foamed specimens and fractures or deformations in all specimens. The average stress in the polymer matrix of the microcellular foam specimens exceeded the calculated nominal stress since the voids were neglected. The ratio of nominal stress to relative density approximates the stress carried by the foam matrix because relative density is approximately inversely proportional to the increase in cross-sectional area with foaming.

Yield strength was defined as the first peak stress or, in specimens with no peak, as the breaking stress.

Tensile Test Procedure

Tensile tests were performed at room temperature using an Instron 8500 servo-hydraulic testing machine. The displacement rate was 10 mm/min.

Fatigue Test Procedure

Tension-tension fatigue tests were performed with a sinusoidally varying load at 10 Hz on Instron/Lawrence and Instron 8500 servohydraulic testing machines. The average ratio of the minimum to maximum load was 0.1. In the tests with maximum cyclic stresses greater than 45 MPa, 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 tests were conducted at room temperature.

RESULTS

Specimen Dimensional Stability

Annealing increased the relative densities of the MCPC specimens from $\varrho_{rel} = 0.82$ to $\varrho_{rel} = 0.86$ and from $\varrho_{rel} = 0.88$ to $\varrho_{rel} = 0.90$.

Tensile Tests

Annealing increased the tensile yield strength of as-received PC, saturation-cycled PC and MCPC, as shown in Table 1 and Figures 4, 5, and 6. The yield strength of as-received PC, saturation-cycled PC, $\varrho_{rel} = 0.88$ and $\varrho_{rel} = 0.82$ MCPC increased 16, 38, 43 and 47 percent, respectively. The yield strength of annealed saturation-cycled PC is 10 percent less than the yield strength of annealed as-received PC.

Annealing reduced the ultimate strength between approximately 10 and 20 percent, except for the saturation-cycled PC in which it increased approximately 20 percent. Annealed saturation-cycled PC was the most brittle material, as shown in Figure 5.

Fatigue Tests

Annealing reduced the fatigue life of as-received PC for maximum cyclic stresses greater than 22 MPa, as shown in Figure 7. Significantly, fatigue life reversal seen in as-received PC was eliminated. The fatigue life of annealed as-received PC decreased continuously with increasing maximum cyclic stress.

Annealing also reduced the fatigue life of saturation-cycled PC and $\varrho_{rel} = 0.88$ and $\varrho_{rel} = 0.82$ MCPC. Interestingly, the shortest fatigue lived material was annealed saturation-cycled PC and not annealed MCPC, even though the cyclic stresses were calculated as nominal stresses which underestimate the average stress in the microcellular foam matrix.

Annealing increased the maximum nominal cyclic stress the materials could carry by at least 12 percent, except for annealed saturation-cycled PC.
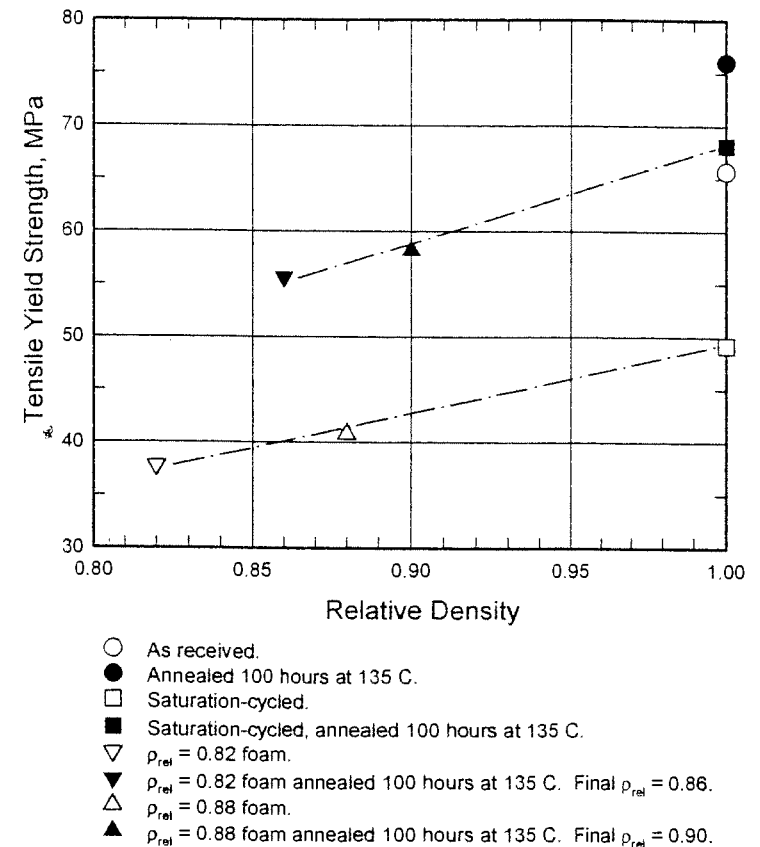

○ As received.
● Annealed 100 hours at 135 C.
□ Saturation-cycled.
■ Saturation-cycled, annealed 100 hours at 135 C.
▽ $\rho_{rel} = 0.82$ foam.
▼ $\rho_{rel} = 0.82$ foam annealed 100 hours at 135 C. Final $\rho_{rel} = 0.86$.
△ $\rho_{rel} = 0.88$ foam.
▲ $\rho_{rel} = 0.88$ foam annealed 100 hours at 135 C. Final $\rho_{rel} = 0.90$.

Figure 4. *Tensile yield strength of saturation-cycled and annealed polycarbonate and microcellular polycarbonate. The extension rate was 10 mm/min.*
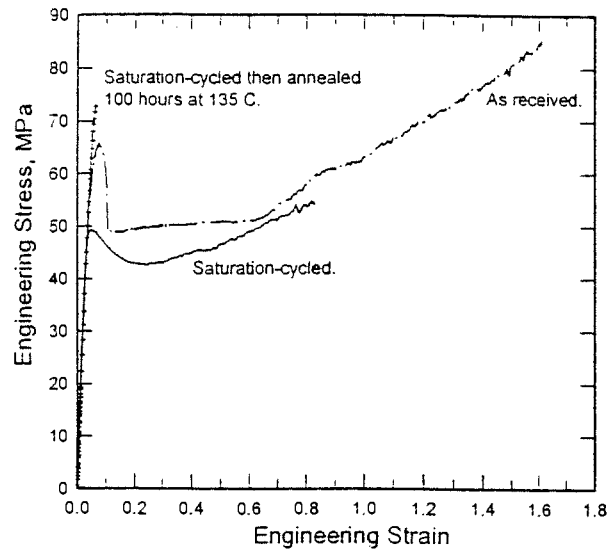
Figure 5. Engineering stress vs. engineering strain for as-received, saturation-cycled and annealed saturation-cycled polycarbonate. The extension rate was 10 mm/min. Strain was computed from crosshead displacement.
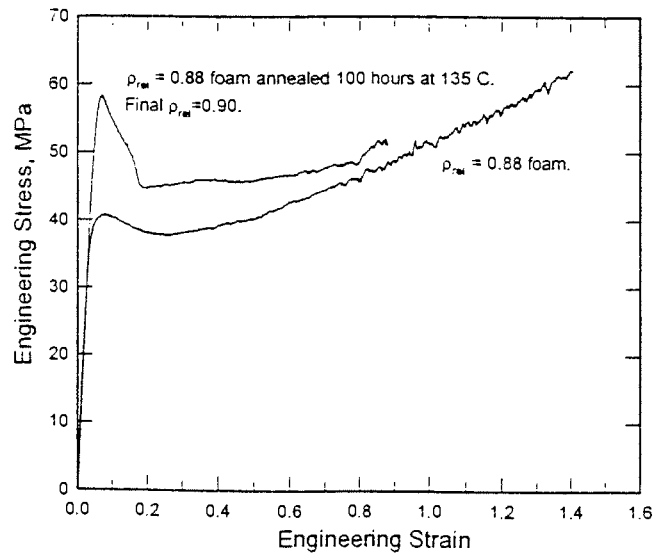

Figure 6. Engineering stress vs. engineering strain for microcellular and annealed microcellular polycarbonate. The extension rate was 10 mm/min. Strain was computed from crosshead displacement.
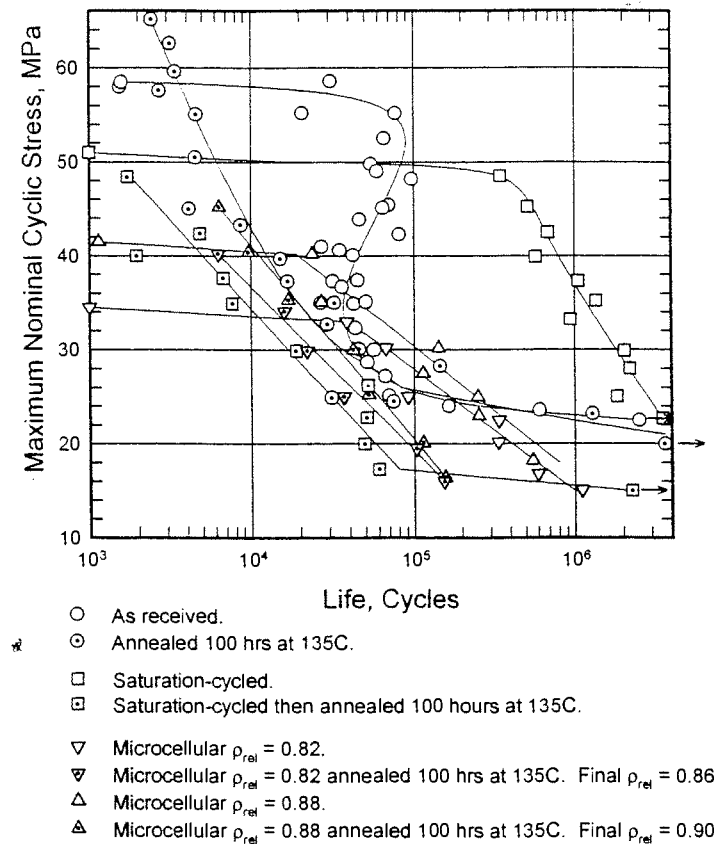

O   As received.
⊙   Annealed 100 hrs at 135C.
▢   Saturation-cycled.
⊡   Saturation-cycled then annealed 100 hours at 135C.

▽   Microcellular $\rho_{rel} = 0.82$.
▼   Microcellular $\rho_{rel} = 0.82$ annealed 100 hrs at 135C. Final $\rho_{rel} = 0.86$.
△   Microcellular $\rho_{rel} = 0.88$.
▲   Microcellular $\rho_{rel} = 0.88$ annealed 100 hrs at 135C. Final $\rho_{rel} = 0.90$.

Figure 7. Effect of annealing on the fatigue life of polycarbonate, saturation-cycled polycarbonate and microcellular polycarbonate.

DISCUSSION

Tensile Tests

Annealing MCPC recovers the yield strength lost in the gas saturation phase of the microcellular process. There is a linear relationship between relative density and the yield strengths of MCPC and saturation-cycled PC. There is a corresponding linear relationship between relative density and the yield strengths of annealed MCPC and annealed saturation-cycled PC. Note that the yield strengths of as-received PC and annealed as-received PC do not fall on these lines. This indicates that the yield strength of MCPC and annealed MCPC depend on both the microstructure structure of the foam and on the effects of saturation-cycling and annealing on the yield strength of foam matrix.

Annealing saturation-cycled PC increases its yield strength, but not to that of annealed as-received PC. This can be explained in terms of free volume if the reduction in free volume during the anneal was less than the increase in free volume during the saturation-cycle. Annealed saturation-cycled PC is also the more brittle than annealed as-received PC, which is inconsistent with the free volume explanation for the lower yield strength, if physical aging of the saturation-cycled PC proceeds at the same rate of that of the as-received PC but starts at a larger free volume. One possible explanation for the combination of lower yield strength but increased brittleness is the development of flaws in the material during the cycle of expansion and contraction. A second explanation is a memory effect in the absence of flaws.

The stress vs. strain curve for annealed MCPC, Figure 6, shows that annealing embrittles MCPC, but it remains more ductile than annealed saturation-cycled PC. Both the properties of the matrix material and the microstructure of the foam may be factors in its greater ductility. The properties of the annealed MCPC matrix and the annealed solid PC may be different because, even though the materials had the same anneal, they have different thermal and deformation histories. The thermal histories differ because the polymer is heated in the microcellular process to soften it and drive gas out of solution to create bubbles. The free volume of the foam matrix would exceed the free volume of saturation-cycled PC when the gas pressure rises as the temperature is increased. Some of the free volume created by the increased pressure in the softened polymer would be retained after the material is quenched. Strain has also been shown to increase free volume, [30,32]. Therefore, the strains associated with foaming may also increase the free volume of the matrix material. Finally, molecular orientation created by the bubble growth may also be a factor.

One factor that suggests the microstructure plays a role in the ductility of annealed MCPC is a comparison of yield strains, Figures 5 and 6. The yield strain of annealed saturation-cycled PC is greater than that of saturation-cycled PC but the yields strains of annealed MCPC and MCPC are approximately equal. The microstructure may increase the ductility by impeding the propagation of fracture surfaces normal to the applied load or by promoting shear deformation.

Fatigue Tests

The relationship between free volume and fatigue life in PC is revealed by the fatigue lives of saturation-cycled PC and annealed PC. Saturation-cycling, which increases free volume, increases fatigue life. Annealing, which decreases free volume, decreases fatigue life. The PC and the annealed PC data over lap for maximum cyclic stresses less than approximately 35 MPa. The divergence for greater stresses is due to the fatigue life reversal in the PC data. With reference to the work of Takemori, Matsumoto and Gifford, the lack of fatigue life stress insensitivity or fatigue life reversal at high cyclic stress in annealed PC suggests that the slower growing shear fatigue mechanism does not compete successfully with the faster leading craze crack growth mechanism when free volume is reduced. Conversely, the long lives of saturation-cycled PC suggest that the slower growing shear fatigue mechanism dominates the leading craze crack growth mechanism when free volume is increased.

The fatigue life of $\varrho_{r,i} = 0.90$ annealed MCPC is approximately twice that of annealed saturation-cycled PC. The increase in life of annealed MCPC over annealed saturation-cycled PC is even greater if the materials are compared using the average stress in the polymer rather than nominal stress, since the nominal stress was calculated neglecting the voids in the foam. It is possible that both the microstructure of annealed MCPC and the free volume of the matrix are factors in extending its fatigue life. If the free volume of the foam matrix material is greater than that of annealed saturation-cycled PC then the fatigue life of the annealed foam may be increased by the dominance of the slower growing shear fatigue crack mechanism. The microstructure may increase fatigue life by either promoting the shear fatigue mechanism or by hindering the growth of a leading craze crack, possibly by forcing it to create a larger surface area.

CONCLUSIONS

The gas saturation-cycle stage of the microcellular manufacturing process affects the properties of the foam matrix by increasing its free volume. Annealing MCPC increases its yield strength and decreases its fatigue life and ductility by reducing the free volume. The fatigue life of annealed MCPC exceeds that of annealed saturation-cycled PC at high cyclic stress. Conversely, the fatigue life of MCPC is less than that of saturation-cycled PC.

Annealing as-received PC reduces its high cyclic stress fatigue life by promoting leading craze crack growth relative to the competing slower shear fatigue crack growth. Conversely, saturation-cycling PC increases its high cyclic stress fatigue life by promoting shear fatigue crack growth relative to leading craze crack growth. Therefore, the dominant fatigue mechanism, and, consequently, the fatigue life of PC, is a function of free volume.

Annealing has a far greater effect on the mechanical properties of MCPC than it does on the foam microstructure, as evidenced by the large changes in tensile strength and fatigue life and the small change in relative density. Consequently, annealing decouples the effects of the microstructure and matrix properties and will allow investigation of the effect of the microstructure on the mechanical behavior of microcellular polymers.

REFERENCES

1. Suh, N. P. 1979. *Private Communication.*
2. Martini, J. E., N. P. Suh and F. A. Waldman. 1984. *U.S. Patent No. 4,473,665.*
3. Kumar, V. and J. E. Weller. 1991. *SPE Technical Papers,* 37:1401–1405.
4. Kumar, V. and J. E. Weller. 1994. *J. Engineering for Industry,* 116:413–420.

5. Kumar, V., J. E. Weller, M. M. VanderWel and K. A. Seeler. 1994. *J. Engineering Materials and Technology*, 116:439–445.

6. Seeler, K. A. and V. Kumar. 1992. *ASME Materials Division*, 38:93–108.

7. Seeler, K. A. and V. Kumar. 1994. *J. Engineering Materials and Technology*, 116:451–466.

8. Kumar, V. and K.A. Seeler. in review. *J. Engineering Materials and Technology*.

9. Takemori, M. T. and R. P. Kambour. 1981. *J. Materials Science*, 16:1108–1110.

10. Takemori, M. T., R. P. Kambour and D. S. Matsumoto. 1983. *Polymer Communications*, 24:297–299.

11. Takemori, M. T. 1984. *Annual Review of Material Science*, 14:171–204.

12. Takemori, M. T. 1987. *Polymer Engineering and Science*, 27:46–54.

13. Takemori, M. T. 1988. *Polymer Engineering and Science*, 28:641–647.

14. Matsumoto, D. S. and M. T. Takemori. 1985. *J. Materials Science*, 20:873–880.

15. Matsumoto, D. S. and S. K. Gifford. 1985. *J. Materials Science*, 20:4610–4616.

16. Seeler, K. A. and V. Kumar. 1993. *J. Reinforced Pastics and Composites*, 12:359–376.

17. Hojo, H. and W. N. Findley. 1973. *Polymer Engineering and Science*, 13:255–265.

18. Chow, T. S. 1980. *Macromolecules*, 13:362–364.

19. Chiou, J. S., J. W. Barlow and D. R. Paul. 1985. *J. Applied Polymer Science*, 30: 2633–2642.

20. Wing, G. T., A. Pasricha, V. Kumar, M. E. Tuttle and K. A. Seeler. in review. *J. Engineering Materials and Technology*.

21. Wonders, A. G. and D. R. Paul. 1979. *J. Membrane Science*, 5:63–75.

22. Chan, A. H. 1978. Ph.D. thesis, University of Texas at Austin.

23. Chan, A. H. and D. R. Paul. 1979. *J. Applied Polymer Science*, 24:1539–1550.

24. Chan, A. H. and D. R. Paul. 1980. *Polymer Engineering and Science*, 20:87–94.

25. Seeler, K. A. and V. Kumar. in review. *Polymer Engineering and Science*.

26. Alfry, T., G. Goldfinger and H. Mark. 1943. *J. Applied Physics*, 14:700–705.

27. Spencer, R. S. and R. F. Boyer. 1946. *J. Applied Physics*, 17:398–404.

28. McLoughlin, J. R. and A. V. Tobolsky. 1951. *J. Polymer Science*, 7:658.

29. Kovacs, A. J., R. A. Stratton and J. D. Ferry. 1963. *J. Physical Chemistry*, 67:152–16.

30. Struik, L. C. E. 1978. *Physical Aging in Amorphous Polymers and Other Materials*, Amsterdam, Elsevier.

31. Matsumoto, D. S. 1988. *Polymer Engineering and Science*, 28:1313–1317.

32. Muller, J. and J. H. Wendorff. 1988. *J. Polymer Science: Part C: Polymer Letters*, 26:421–427.

33. Rabinowitz, S. and P. Beardmore. 1974. *J. Materials Science*, 9:81–99.

34. Bouda, V. 1976. *J. Polymer Science: Polymer Physics Edition*, 14:2313–2323.

35. Bubeck, R. A., S. E. Bales and H.-D. Lee. 1984. *Polymer Engineering and Science*, 24:1142–1147.

36. Curro, J. J. and R.-J. Roe. 1984. *Polymer*, 25:1424–1430.

37. Royal, J. S. and J. M. Torkelson. 1992. *Macromolecules*, 25:4792–4796.

38. Kluin, J.-E., Z. Yu, S. Vleeshouwers, J. D. McGervey, A. M. Jamieson, R. Simha and K. Sommer. 1993. *Macromolecules*, 26:1853–1861.