

Microcavity Formation in Poly(Ester-carbonate) Exposed to Hot, Humid Environments

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Synopsis

The behavior of polycarbonate in hot, humid environments has been well documented in the technical literature. Poly(ester-carbonate)s based on bisphenol A connected with carbonate and tere/isophthalate units are the subject of this investigation. Poly(ester-carbonate) exhibits many similarities to polycarbonate in microcavity formation when exposed to cycling hot, humid environments. These microcavities consist of concentric bands around a central nucleation site. Scanning electron microscopy reveals that the bands consist of rings of dense material alternating with rings of material containing microvoids. Water phase separation at the nucleation site (due to cycling temperature) leads to internal pressure and thus a dilatant stress around the edge of the microcavity. It is hypothesized that this allows for the ease of further water phase separation at the periphery of the microcavity, thus yielding microvoids. The mechanical properties of poly(ester-carbonate) exposed to 96°C water immersion and 132°C steam sterilization cycling were determined and show significant loss in performance in these environments similar to that previously reported for polycarbonate.

INTRODUCTION

Transparent engineering polymers offer specific advantages in hot, humid environments, often replacing glass where ease of fabrication and greatly improved toughness are desired. These environments include medical device steam sterilization, coffee makers, sight glasses, dishwasher components, food processing equipment, dairy metering devices, etc. Most of these applications involve cyclic temperature/humidity exposure conditions. The high T_g amorphous polymers which are not distorted in boiling water, as well as under normal steam sterilization conditions, include polycarbonate, polysulfone, polyethersulfone, polyetherimide, and poly(ester-carbonate)s. The manufacturer's literature for all of these polymers suggests at least limited utility in boiling water or steam sterilization. Results of polycarbonate, polysulfone, polyethersulfone and polyetherimide exposed to hot, humid environments have been previously compared.^{1,2} Results on poly(ester-carbonate)s of various structure were compared in Ref. 2. Microcavity formation in polycarbonate has been noted to be a common occurrence in hot, humid environments.¹⁻⁴ Microcavity formation in poly(ester-carbonate)s was noted to be quite similar to polycarbonate when exposed to water at 96°C (particularly under cyclic conditions).² These results were obtained on developmental samples of poly(ester-carbonate)s obtained from various suppliers. This re-

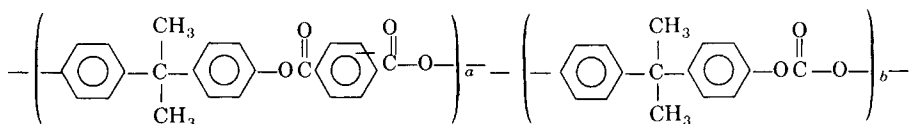
port will detail the behavior of commercial poly(ester-carbonate)s in hot, humid environments with specific emphasis on microcavity formation.

Microcavity formation in polymers exposed to boiling water was initially reported by Fedors in epoxy and silicone rubber^{5,6} containing water-soluble particulates. Fedors hypothesized that osmotic pressure created by the water-swollen particulate provided sufficient internal pressure to yield failure as observed with visual microcavities.^{5,7} This was later observed by Narkis and Bell³ in polycarbonate exposed to boiling water and then allowed to cool to room temperature. This behavior was explained by the lower water solubility at room temperature, yielding phase separation resulting in internal pressure adequate to promote failure yielding microcavity formation. Further investigation by Robeson and Crisafulli¹ of this behavior in polycarbonate, noted that microcavity formation was much more pronounced in polycarbonate exposed to cyclic hot water conditions. They hypothesized that phase separation created localized internal pressure and stress-induced hydrolysis yielded polymer failure, resulting in microcavity formation. As hydrolysis occurs, phenol end groups are created yielding an even higher level of water sorption at failure nucleation sites. This results in a further buildup in internal pressure causing a cascading effect further promoting microcavity formation.

The microcavities consist of concentric ridges and valleys emitting from the nucleus. The failure morphology is similar to the "clamshell" type topology observed in metal alloy failure as well as several polymers.⁸⁻¹² This study reveals an interesting observation not previously noted in that the ridges (of the microcavities) contain a large number of voids.

EXPERIMENTAL

The commercial poly(ester-carbonate)s investigated in this study were PPC [poly(phthalate-carbonate)s] Lexan 4501 and Lexan 4701 manufactured by General Electric. The structure of these products was determined by nuclear magnetic resonance studies (obtained by L. M. Maresca and S. Y. Kang). The generalized structure of poly(phthalate-carbonate) [same as poly(ester-carbonate)] is



The structure of Lexan 4501 [hereafter referred to as poly(ester-carbonate) I] is: ester/carbonate molar ratio = 40/60; tere/iso ratio = 30/70. The structure of Lexan 4701 [hereafter referred to as poly(ester-carbonate) II] is: ester/carbonate molar ratio = 35/65; tere/iso ratio = 83/17.

Polysulfone was included in this study for control purposes, since it has been well documented to exhibit excellent hydrolytic stability.^{1,2,13} The polysulfone utilized was UDEL P-1700 (Union Carbide).

The injection molded specimens were prepared using conditions recommended by the material suppliers. As with polycarbonate, care must be taken to properly dry poly(ester-carbonate) to prevent hydrolysis during injection

molding. The poly(ester-carbonate) pellets were dried in vacuum for 24 h at 100°C prior to injection molding, and the relative viscosity was checked on molded samples to assure that significant hydrolysis did not occur.

The hot water immersion test involved 96°C water in a Markson water bath. Cyclic exposure involved 16 h at 96°C followed by cooling to room temperature for 8 h (80 h for weekend) and continuing the cycle. The exposure time noted is the time exposed at 96°C.

Two Vernitron steam sterilizer units (Models 8020 and 8080) were used for the steam sterilization experiments. All injection-molded test specimens were cleaned with isopropanol. The samples were placed on the sterilizer trays in loose stacks or criss-cross fashion to promote good steam contact. The steam pressure was raised to 27 psig (270°F) and maintained for 30 min. Pressure was released followed by removal of samples and held at room temperature for at least 30 min. Samples were removed after every 20 cycles for property determination.

Tensile properties were determined as per ASTM D-638 and tensile impact strength as per ASTM D-1822. The reduced viscosity was measured in chloroform at 25°C (0.2 g/dL). The inherent viscosity was determined on a solution of the polymer in a 60/40 mixture of phenol/1,1,2,2-tetrachloroethane. Test specimens 2.75 × 3.5 × 0.125 in. were tested by dropping a 15-lb

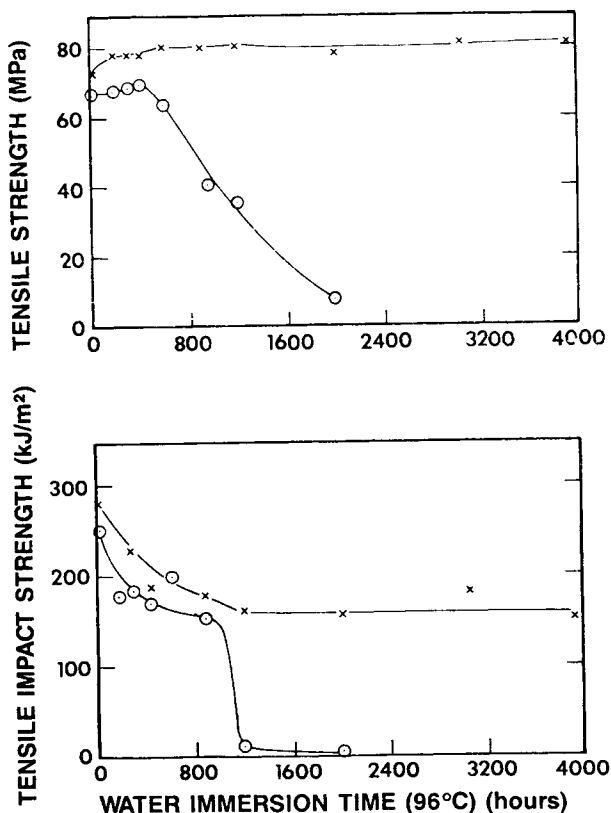


Fig. 1. Mechanical property data after continuous exposure to 96°C water immersion: (X) polysulfone; (O) poly(ester-carbonate) I.

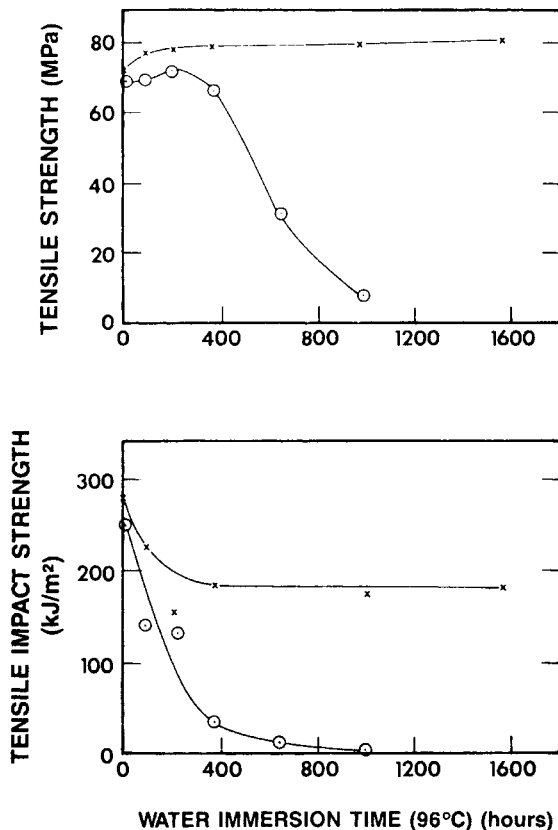


Fig. 2. Mechanical property data after cyclic exposure to 96°C water immersion: (X) polysulfone; (O) poly(ester-carbonate) I.

dart with a 1 in. diameter impact head utilizing an "Increasing Stair-Step" procedure. Using the same sample, the dart is first dropped at 0.5 ft height. If no failure occurs, the height is increased to 1 ft and retested. The procedure is repeated at increasing 1 ft intervals until failure occurs. The height reached by the dart just prior to failure is reported. This test for toughness is commonly referred to as the falling dart toughness test.

A Reichert optical microscope was utilized to obtain photomicrographs of the microcavities. Polarized transmitted illumination was used to photograph the microcavities. Fracture surfaces were coated with 200 nm of gold, then examined and photographed with the JEOL-JSM 35C scanning electron microscope.

EXPERIMENTAL RESULTS

The mechanical property data after continuous exposure to 96°C water immersion for polysulfone and poly(ester-carbonate) I are illustrated in Figure 1. A precipitous loss in both tensile strength and tensile impact strength is observed after 800 h exposure for poly(ester-carbonate) I. The results for samples exposed under cyclic conditions are illustrated in Figure 2. Poly(ester-carbonate) I exhibits a more drastic loss in properties for cyclic

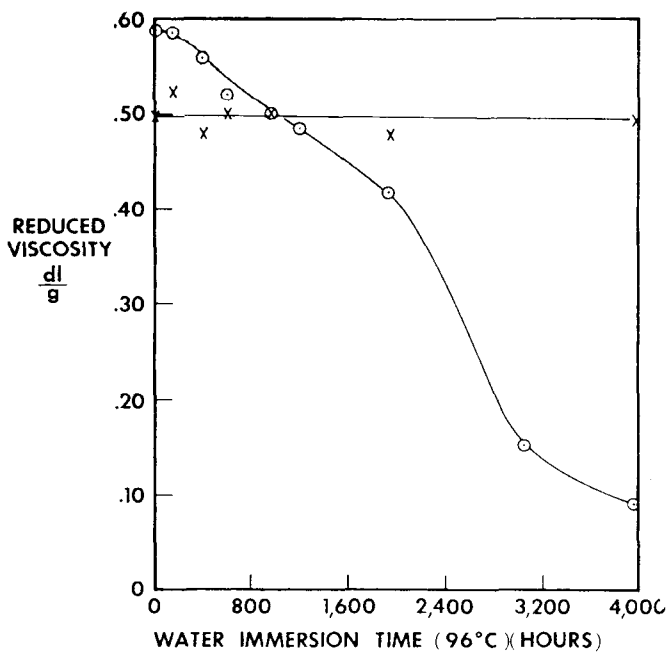


Fig. 3. Reduced viscosity data after continuous exposure to 96°C water immersion (CHCl_3 ; 25°C; 0.2 g/dL): (X) polystyrene; (O) PEC-1.

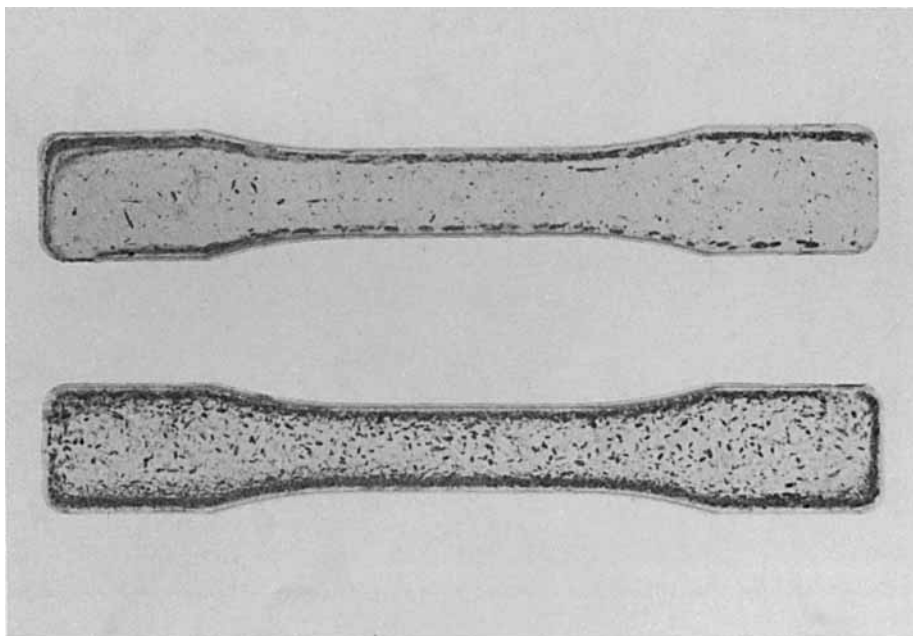


Fig. 4. Tensile specimens of poly(ester-carbonate) I after water immersion at 96°C: (top specimen) 1976 h continuous exposure; (bottom specimen) 992 h cyclic exposure.

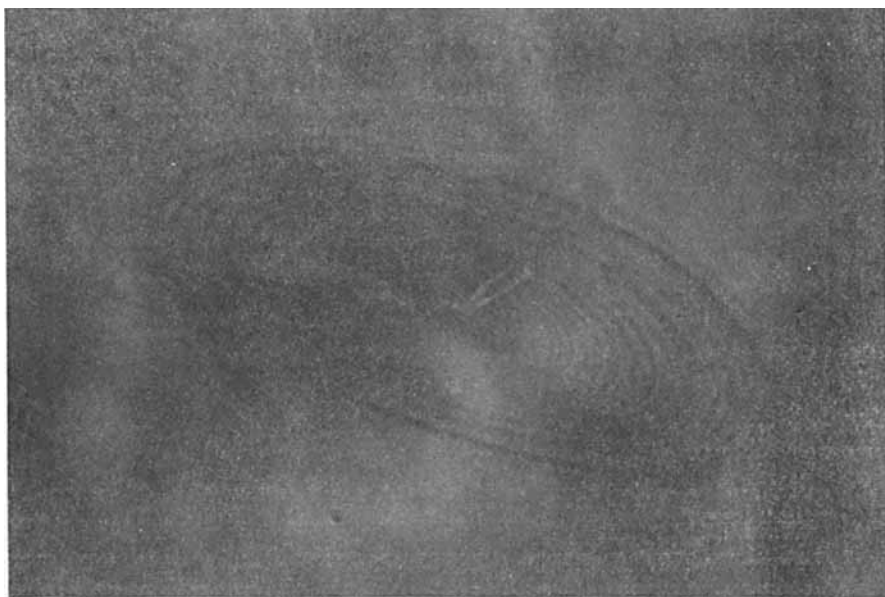


Fig. 5. Photomicrograph of typical microcavity observed in poly(ester-carbonate) I (992 h cyclic exposure) ($450\times$).

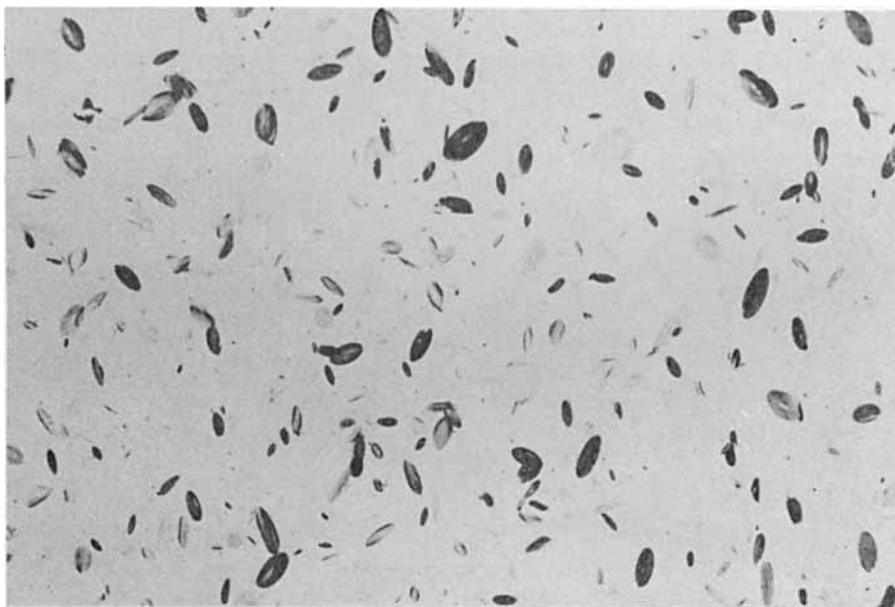


Fig. 6. Microcavities observed in extruded poly(ester-carbonate) II (416 h cyclic exposure) ($10\times$).

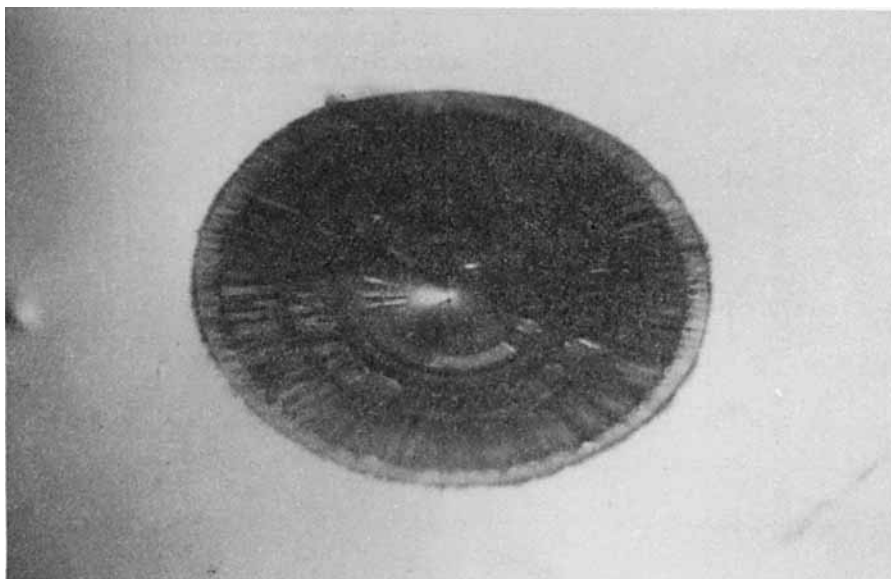


Fig. 7. Photomicrograph of typical microcavity, observed in extruded poly(ester-carbonate) II ($290\times$).

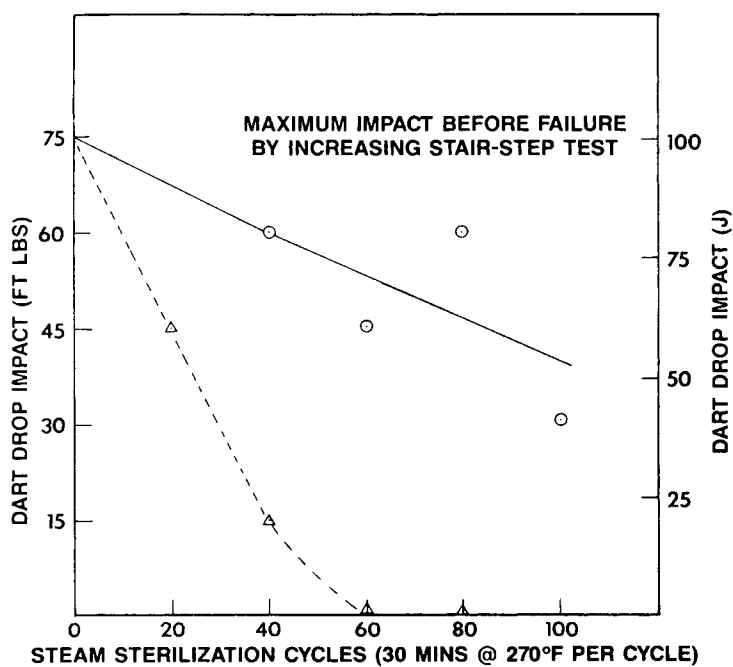


Fig. 8. Falling dart impact strength after steam sterilization cycling (\odot) polysulfone; (Δ) poly(ester-carbonate) I.

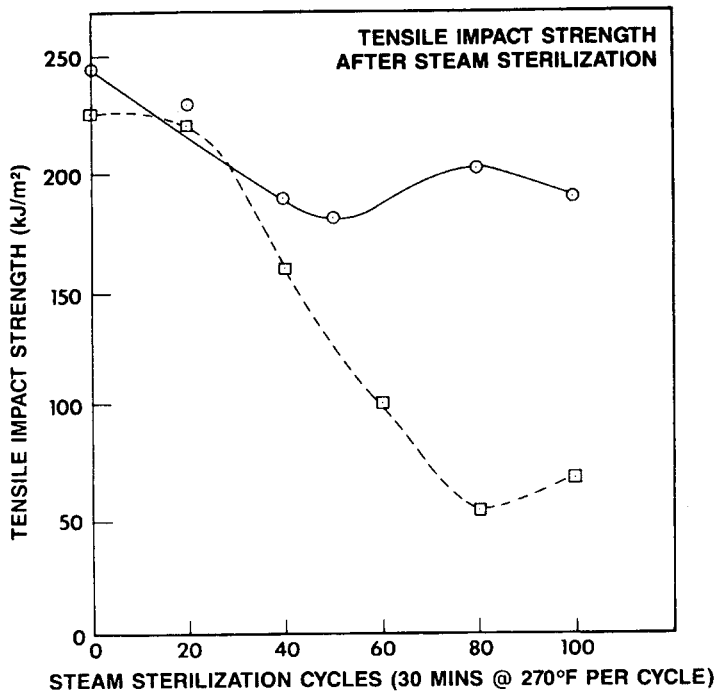


Fig. 9. Tensile impact strength after steam sterilization cycling: (○) polysulfone; (△) poly(ester-carbonate) I.

exposure than for continuous exposure. The reduced viscosity for the samples exposed to continuous water immersion at 96°C is illustrated in Figure 3. Polysulfone (as expected) shows no loss in molecular weight. Poly(ester-carbonate) I, however, illustrates decreasing molecular weight with hot water exposure as previously reported for polycarbonate.¹⁴⁻¹⁸

The samples of poly(ester-carbonate) I after both cyclic and continuous exposure exhibit microcavity formation. The cyclic exposure condition is much more severe than continuous exposure as illustrated in Figure 4. A microcavity typically formed in poly(ester-carbonate) I is illustrated in Figure 5. An extruded sample of poly(ester-carbonate) II gave large, uniform microcavities as illustrated in Figure 6 with photomicrograph of a typical microcavity shown in Figure 7.

The falling dart impact strengths for polysulfone and poly(ester-carbonate) I after steam sterilization cycling are illustrated in Figure 8. The tensile impact strengths after steam sterilization cycling for the same materials are illustrated in Figure 9. Molecular weight reduction for poly(ester-carbonate) I is observed as shown in Figure 10. Polysulfone was not tested since it has been previously shown to be resistant to molecular weight reduction when exposed to hot water and steam sterilization under even more severe conditions (see comparison of Fig. 3).

Water sorption and diffusion data were obtained on both poly(ester-carbonate) I and II. The sample of poly(ester-carbonate) I was an injection-molded 0.125 in. plaque and poly(ester-carbonate) II was an ex-

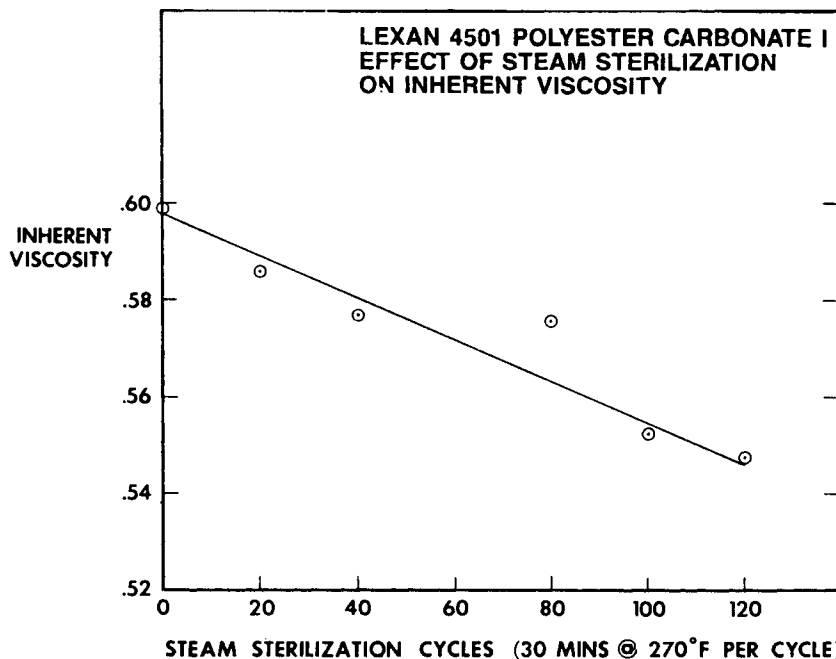


Fig. 10. Inherent viscosity for poly(ester-carbonate) I after steam sterilization cycling.

truded 0.250" thick sheet. The results are listed in Table I. The diffusion coefficients were calculated from q_t/q_∞ data determined by direct weight measurements (q_t = quantity of water sorption at time = t ; q_∞ = equilibrium water sorption). The q_t/q_∞ data were obtained under the following initial and boundary conditions¹⁹:

$$C = C_0, \quad x = 0, \quad t \geq 0$$

$$C = C_0, \quad x = l, \quad t \geq 0$$

$$C = 0, \quad 0 < x < l, \quad t = 0$$

TABLE I
Diffusion Coefficient and Water Sorption Data

Polymer	Temperature (°C)	Diffusion coefficient D (cm ² /s)	Equilibrium water sorption (wt %)
Poly(ester-carbonate) I	23	4.3×10^{-8}	0.48
Poly(ester-carbonate) I	96	7.4×10^{-7}	0.78
Poly(ester-carbonate) II	23	6.0×10^{-8}	0.52
Poly(ester-carbonate) II	96	8.5×10^{-7}	0.78
Polycarbonate ^a	23	6.5×10^{-8}	0.41
Polycarbonate ^a	96	1.0×10^{-6}	0.63
Polysulfone ^a	23	3.8×10^{-8}	0.86
Polysulfone ^a	96	5.9×10^{-7}	1.0

^a Data from Ref. 1.

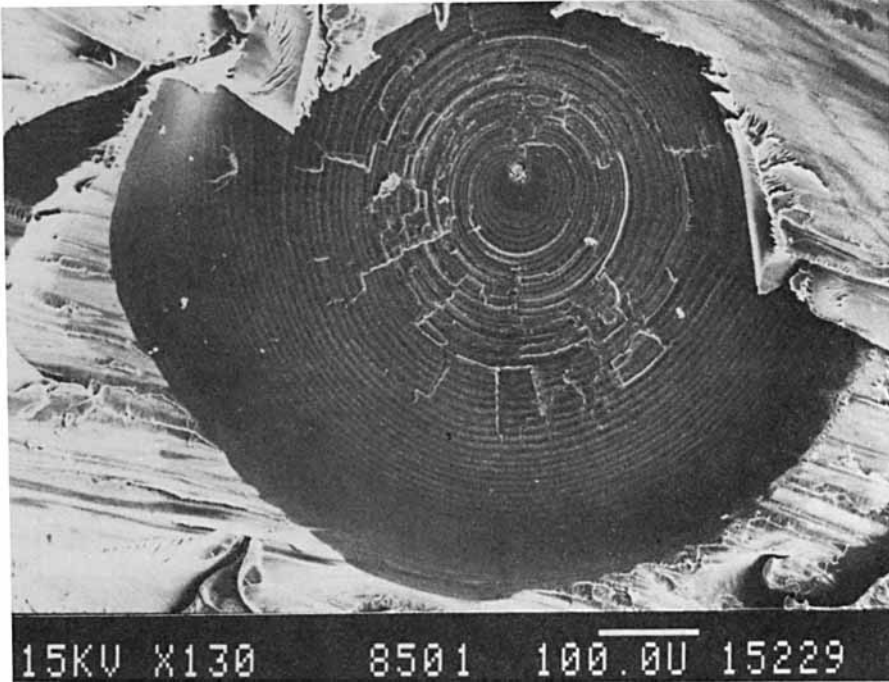


Fig. 11. Microcavity on fracture surface of poly(ester-carbonate) I.

The diffusion coefficient can be calculated from the following solution of q_t/q_∞ for the above conditions¹⁹:

$$q_t/q_\infty = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(2n+1)^2 \pi^2 t/l^2}$$

Another procedure for calculating D involves using the value of (t/l^2) when $q_t/q_\infty = 0.5$ in the following equation:

$$D = 0.049 / (t/l^2)_{1/2}$$

This approach assumes a diffusion coefficient which is not concentration dependent. For comparative purposes, this is a reasonable assumption.

A sample of poly(ester-carbonate) I (~ 1300 h cyclic exposure) was fractured by bending a flexure bar. The brittle failure exposed the surface of various microcavities; one of which is illustrated in Figure 11 obtained with the scanning electron microscopes. A closer view of this same microcavity reveals the ring structure contains microvoids in each band (ridge) (Figures 12 and 13).

A sample of bisphenol A polycarbonate (Lexan 101) (~ 1500 h cyclic exposure) was also fractured by bending a flexure bar. The brittle failure yielded microcavity surfaces as illustrated in Figure 14. A closer view of this microcavity (Fig. 15) illustrates microvoid formation except that the fracture plane went through the individual microvoids.

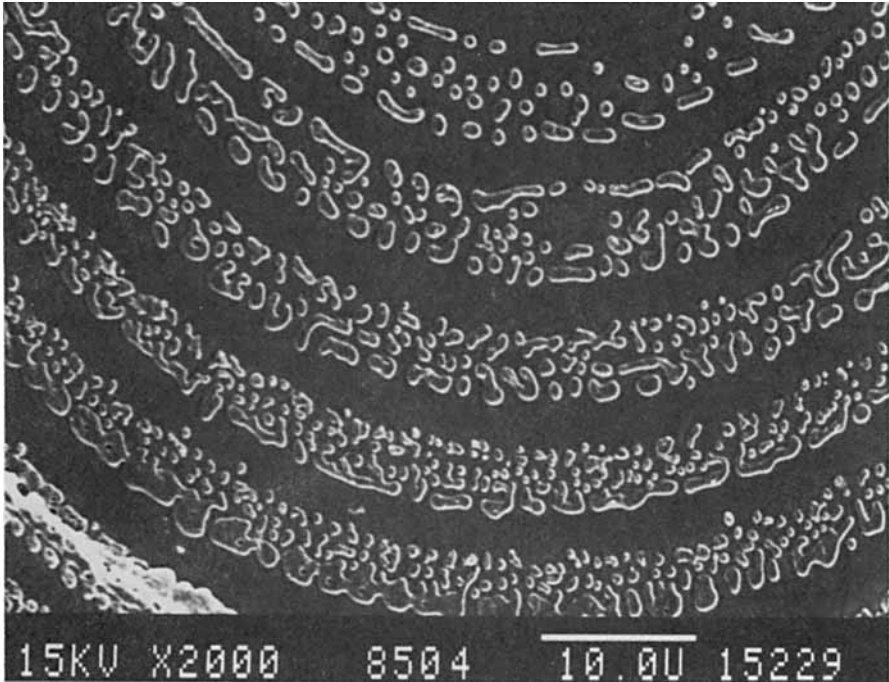


Fig. 12. Closer examination of ring structure of poly(ester-carbonate) I microcavity of Figure 11 (near nucleation site).

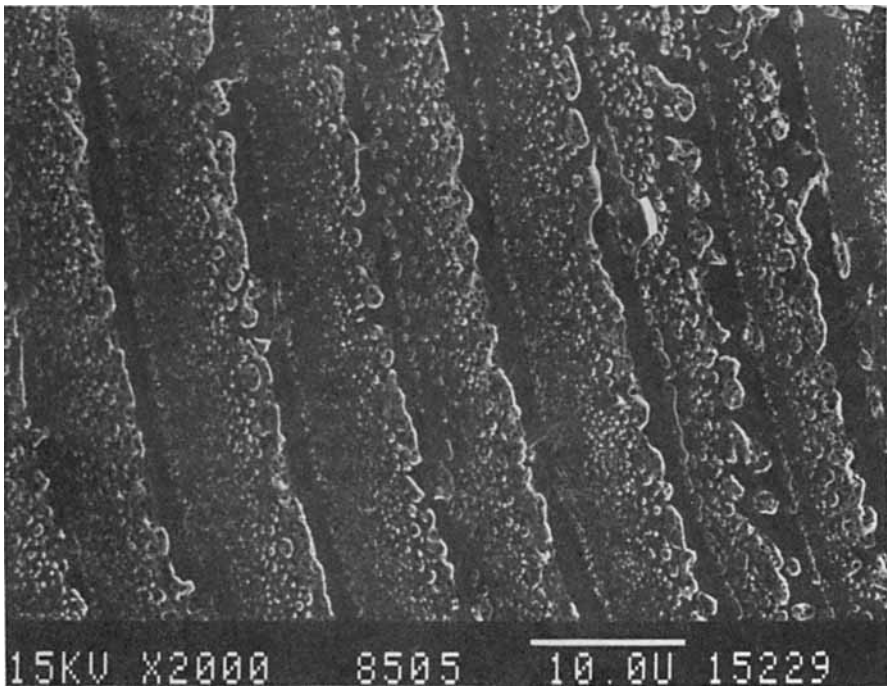


Fig. 13. Closer examination of ring structure of poly(ester-carbonate) I microcavity of Figure 11 (further from nucleation site).

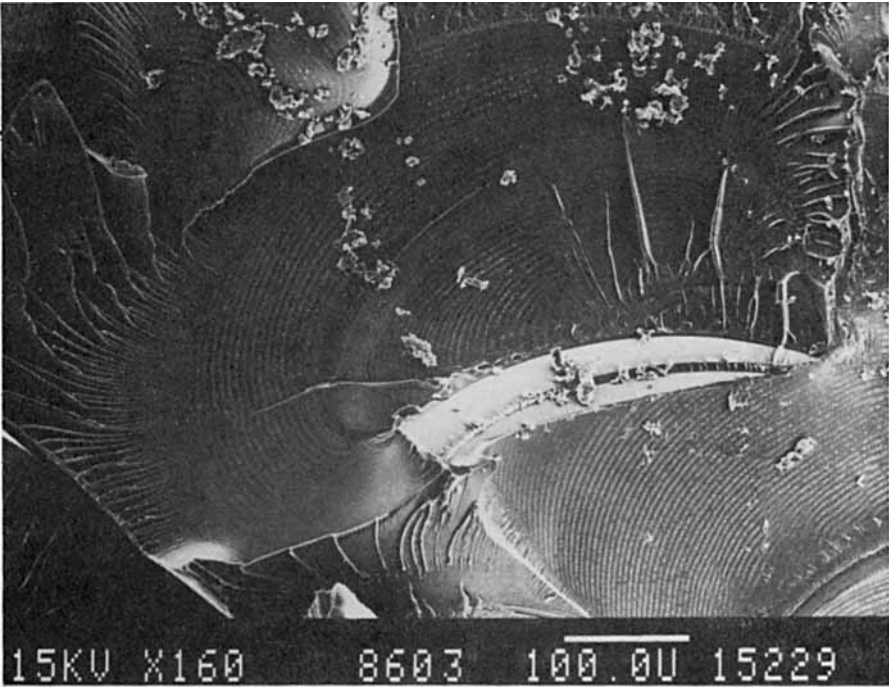


Fig. 14. Microcavity on fracture surface of polycarbonate.

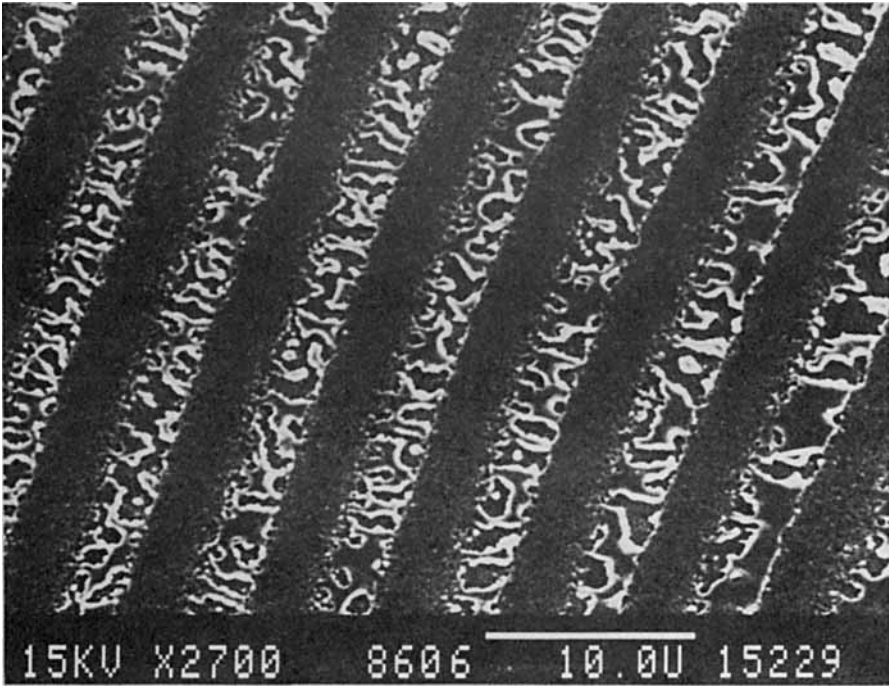


Fig. 15. Closer examination of ring structure of the polycarbonate microcavity of Figure 14.

DISCUSSION OF RESULTS

The hydrolytic stability of polycarbonate has been studied by many investigators.^{1,2,14-18,20,21} All have shown a significant loss in molecular weight accompanied by a loss in mechanical properties when exposed to hot, humid environments. Recently, a unique failure mechanism (microcavity formation) for polycarbonate has been reported for these environments.¹⁻⁴ Microcavity formation has also been observed with epoxy,⁵ silicone rubber,⁶ and polyester²² subjected to hot water exposure.

The morphology of polycarbonate microcavities was previously shown¹ to be a series of uniform concentric rings (ridges and valleys) around a central nucleation site. This was also shown for a poly(ester-carbonate) microcavity² as well as demonstrated in this paper. Several types of similar failure morphologies are noted in the literature. Fatigue striations corresponding to advancing crack front due to individual loading cycles are common with metals and have been reported for various polymers.^{8,11} Another type of crack growth with morphology similar to the microcavities noted here is termed discontinuous crack growth. The fracture bands progress across the material in a discontinuous fashion relative to the loading cycles. The morphology noted for this type of fracture appears more similar to the microcavity morphology observed in this study. One distinction of interest noted between fatigue striations and discontinuous crack growth bands is the location relative to the crack initiation site. Discontinuous crack growth bands are observed closer to the crack initiation site. This feature, in addition to the qualitatively observed morphology similarities, leads to the conclusion that the typical microcavity morphology can be considered similar to discontinuous crack growth bands.

The morphology of the extruded poly(ester-carbonate) II microcavities is somewhat different in that large striations with less uniform surface structure exist. This region may represent a transition from discontinuous crack growth to a fatigue striation behavior. These types of roughened bands have not been observed with polycarbonate but have been observed in some poly(ester-carbonate) microcavities in injection-molded specimens.

Scanning electron microscopy of the fracture surfaces of both poly(ester-carbonate) and polycarbonate reveals details not previously observed. The concentric bands consist of alternating rings (e.g., ridges and valleys) of material, in which microvoids are evenly dispersed, and rings of dense material. With the present information, the origin of the microvoids can only be hypothesized. Phase separation of water occurs within the rings creating voids (or water-filled volumes when wet). The phase separation around the microcavity nucleus creates internal pressure. Around the edge of the microcavity, the polymer is under a dilatant stress, thus yielding a region where phase separation can more easily occur. In order to assure that the microvoids were not an artifact of the microscopy technique, optical microscopy of the microcavities ($\sim 500\times$) also revealed rings of microvoids.

It is of interest to note that the population of microcavities in poly(ester-carbonate) I injection-molded specimens exist in two types (see Fig. 4). At the region of highest molded-in stress, large microcavities with an apparently higher concentration (particularly for continuous exposure) occur

parallel with the direction of injection mold flow. The other type of microcavities appears randomly distributed throughout the specimen. This has been previously noted for polyetherimides and poly(ester-carbonate)s^{1,2} but not for polycarbonate. The molded-in stress for polycarbonate has been shown to be dissipated during 96°C water immersion (due to proximity of the T_g). As poly(ester-carbonate)s exhibit a higher glass transition temperature than polycarbonate, molded-in stresses cannot be dissipated as rapidly and thus contribute to the formation of microcavities.

Overall, the characteristics of poly(ester-carbonate) are quite similar to polycarbonate relative to hydrolytic stability. The rate of loss in molecular weight and deterioration of mechanical properties are in the same range as polycarbonate reported previously.^{1,2}

Cyclic exposure yields a significantly higher level of microcavity formation for poly(ester-carbonate) than continuous exposure. The increased concentration of microcavities yields a more rapid deterioration of tensile strength and toughness as would be logically expected. The microcavities represent a flaw from which failure can be initiated. This is illustrated in Figure 11 for a fracture sample of poly(ester-carbonate) I and in Figure 14 for polycarbonate.

The equilibrium water sorption for poly(ester-carbonate) is higher than for polycarbonate at both room temperature and 96°C but lower than polysulfone. The differential between 23 and 96°C which denotes the potential of internal stress due to water phase separation during cycling is larger for poly(ester-carbonate) than either polysulfone or polycarbonate. The diffusion coefficient of water for poly(ester-carbonate) is intermediate between polycarbonate and polysulfone. The method of microcavity formation for poly(ester-carbonate) is therefore believed to be equivalent to that of polycarbonate. When the sample is cooled, a level of supersaturation of water occurs leading to phase separation at nucleation sites. This creates internal stress which can lead to failure. The difference between polysulfone (which exhibits no microcavity formation under the experimental condition of this study) and poly(ester-carbonate) is hypothesized to be due to the stress-induced hydrolysis possible with poly(ester-carbonate) but not polysulfone. Hydrolysis creates hydroxyl and carboxylic acid moieties in poly(ester-carbonate)s, thus leading to further water sorption at the nucleation sites of microcavity formation. This leads to a cascading effect as is evident from the multiplicity of microcavities formed during cyclic exposure (Figs. 4 and 7). Several references have noted a healing of the microcavities after removal from boiling water for polycarbonate.^{3,4} This has not been observed for the microcavities formed in cyclic experiments for polycarbonate^{1,2} or for the poly(ester-carbonate)s studied here. Samples removed from boiling water for over a year's duration appear to have the same qualitative level of microcavities.

The deterioration of mechanical properties of poly(ester-carbonate)s in hot, humid environments is hypothesized to consist of three basic causes: (1) The initial loss in toughness is believed due to an annealing effect. This is also observed for polycarbonate under dry thermal exposure. As the tensile strength increases in the initial stages of hot, humid exposure, the annealing effect is further substantiated. (2) A loss in molecular weight leading to material embrittlement. (3) Formation of microcavities, which represents serious flaws

in the sample. This is the major reason for differences in mechanical properties of cyclic vs. continuous exposure.

The steam sterilization results indicate poly(ester-carbonate) I can tolerate only a limited number of cycles before deterioration in the mechanical properties occur. Polysulfone, which has proven performance in steam sterilization and hot water utility, exhibits a drop in toughness believed due to an annealing phenomenon. After an initial drop in toughness, the toughness in both 96°C water and steam plateaus to reasonably constant value as is also observed with dry annealing.²³ The initial loss for poly(ester-carbonate) is also probably more related to an annealing effect prior to the onset of severe embrittlement due to molecular weight reduction. This behavior is similar to that observed for polycarbonate where modest annealing times near the glass transition temperatures yields a remarkable loss in notched toughness.²⁴

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