

An Unusual Visual Microcracking/Healing Phenomenon in Polycarbonate at Room Temperature

M. NARKIS* and J. P. BELL, *Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268*

Synopsis

Polycarbonate samples show no visible changes upon removal from boiling water. However, during a subsequent storage stage at room temperature they begin to develop visible disc-shaped microcracks whose number and size increase with time. At a certain time during the room temperature storage period a healing process begins leading in many cases to a complete visual disappearance of the microcracks. The cracking/healing phenomenon is explained in terms of water-supersaturated systems undergoing water phase-separation creating water filled microcracks. These thin water filled microcracks then lose their water to the environment during drying at room temperature, close, and visually heal.

INTRODUCTION

Polycarbonates are well known to deform in a ductile manner and to fail in a brittle manner after annealing below T_g . The exact conditions for this ductile-brittle transition depend upon many parameters such as molecular weight, thermal history and processing conditions, annealing temperature and time, and the environments employed.¹⁻⁴ Numerous literature publications can be found reporting the effects of thermal history and solvent exposure on the mechanical properties of polycarbonates. Surprisingly, however, only a few researchers have studied humidity or water effects on the mechanical behavior of polycarbonate, in spite of the fact that polycarbonate products are being utilized in a variety of applications where direct contact with water is experienced. Injection-molded polycarbonate irrigation devices are subjected to dynamic loading by the water pressure, and frequently to impact loading, depending on the flow conditions in the piping. In addition, these devices undergo thermal cycling and UV irradiation due to their direct exposure to atmospheric conditions. Polycarbonate embrittlement after exposure to humid atmospheres or to water at elevated temperature has been reported by several authors.^{3,5,6} In one publication the water effect was interpreted in relation to the internal stress distribution.³ In another publication water is assumed to be absorbed in polycarbonate by filling up holes, causing an increase of the T_g .⁵ Water hydrolysis causing gradual molecular weight reductions to a critical molecular weight ($\bar{M}_w = 33,800$, $\bar{M}_n = 14,300$, below which polycarbonate embrittles) was also reported.⁶ The purpose of the present communication is to describe an unusual phenomenon in which polycarbonate samples previously exposed to boiling water develop visible microcracks at room temperature, in the absence of external stress.

* Permanent address: Department of Chemical Engineering, Technion City, Haifa 32000, Israel.

EXPERIMENTAL

ASTM tensile, flexure, and tensile-impact specimens all 3.5 mm thick were injection-molded using a screw injection molding machine (Ankerwerke, Germany). The polycarbonate was an injection molding grade (Lexan 143, General Electric Corp.). Samples were exposed to boiling distilled water for periods from 1 to 8 days and then taken out and stored at room temperature in a desiccator, in air, and in water. The samples were frequently visually inspected, photographed, and tested in tension.

RESULTS AND DISCUSSION

The samples exhibited no visible changes from the starting appearance immediately upon removal from the boiling water. However, after being stored at room temperature they began to develop microcracks, whose number and size increased with time. After a maximum number and size was reached, this was followed by a healing stage leading in many instances to a complete visual disappearance of the microcracks. The storage time at room temperature required for the microcracks to visually appear depended upon the previous water boiling period, and ranged roughly from 6 h (8 days boiling) to 48 h (1 day boiling). The water content in samples taken out from the boiling water was about 0.6% by weight, while the room temperature saturation concentration is about 0.3% by weight. Thus when the bars are removed from the boiling water the equilibrium saturation condition at 100°C is interrupted, the sample suddenly becomes supersaturated and water tends to diffuse out from the polycarbonate specimen. The rate of water removal at room temperature from the supersaturated system depends upon the surrounding environment; the desorption is most rapid in the desiccator and slower in the air and water immersion. This room temperature rate of water removal has a significant effect on the microcracking/healing phenomenon. Small microcracks appeared and healed faster in the desiccator-dried samples, as compared with the room-temperature water-stored samples. Additionally, all samples dried in the desiccator visually healed completely while some (samples boiled for 5 and 8 days) water-stored samples apparently reached a plateau condition of a small number of relatively large microcracks.

The room temperature microcracking phenomenon in water-stored samples (after a 5-day exposure in boiling water) is shown in Figure 1. It is important to note that the microcracks are located within the interior of the specimens and not on their surface. The maximum size shown of a microcrack is about 1.5 mm. The number and size growth of the microcracks are clearly seen in the photographs. The absence of a pronounced healing process in the water-stored specimens is evident in the figure. Figure 2(A) shows a 3-day air-stored sample (after boiling in water for 5 days) containing microcracks and the same sample completely healed after 2 additional storage days in air [Fig. 2(B)]. Figure 2(B) compares also two samples of similar water boiling history (5 days) and the same period of storage at room temperature (5 days) in water and in air. A clear difference is seen in Figure 2(B) between the sample undergoing faster water removal rate into air and the water-stored sample. A "2-dimensional" disc shape (the discs are very thin) is typical to the microcracks as can be better seen in Figure 3. The exact appearance of the microcracks in the photographs depends on the disc plane orientation relative to the observation direction. The very thin

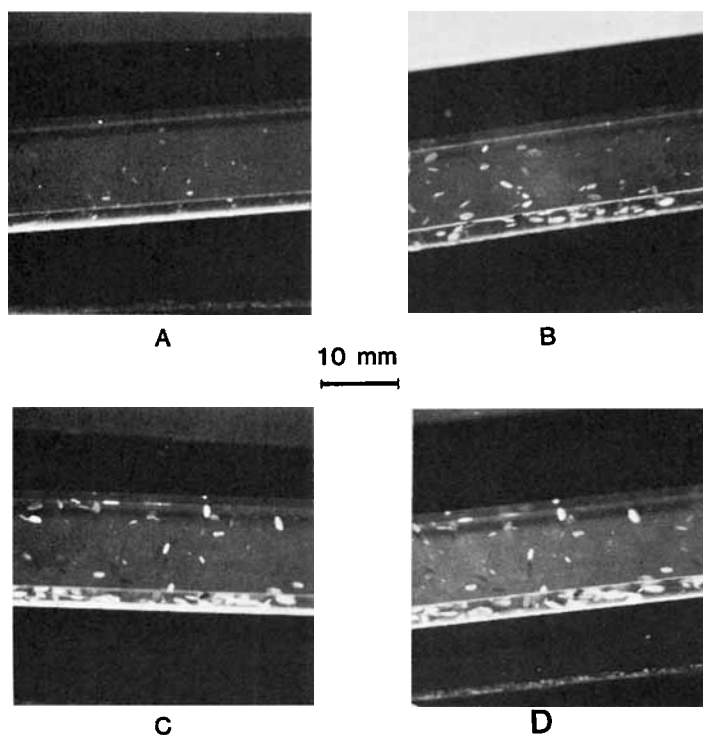


Fig. 1. Appearance of disc-shaped microcracks in injection-molded flexure bars after boiling in water for 5 days and storing in water at room temperature for (A) 22 hrs, (B) 3 days, (C) 6 days, (D) 8 days.

needlelike shapes shown in Figure 3 are actually 2-dimensional discs whose plane coincides with the observation direction. The disc-shaped microcracks have light-reflecting properties, and some of them will appear and others disappear by tilting the specimen. Polycarbonate samples cut from commercial extruded sheets (exact polycarbonate grade unknown) have not shown any visual microcracking following water boiling and storage at the various room temperature conditions. In addition, an injection-molded sample did not show any visible microcracking following water boiling (8 days), heating in an air oven at 100°C (1 day), and storage at the various room temperature conditions. This sample, however, lost clarity; it developed a "milky or hazy" appearance.

Preliminary tensile property studies have shown that some samples having no visual microcracks have become embrittled because of the boiling water treatment. Some other samples deformed in a ductile manner just after boiling in water, but became brittle upon subsequent storage at room temperature.

Preliminary electron microscopy studies of fracture surfaces have shown complicated structures having microcracks containing some internal fibrils, surrounded by developed texture and regions showing mixed brittle and ductile failures. The detailed structures were found to be highly dependent upon the boiling/room temperature storage procedures.

It is thus shown that very important processes affecting the mechanical response of polycarbonate are taking place during the water removal process at room temperature from samples previously boiled in water. This result is

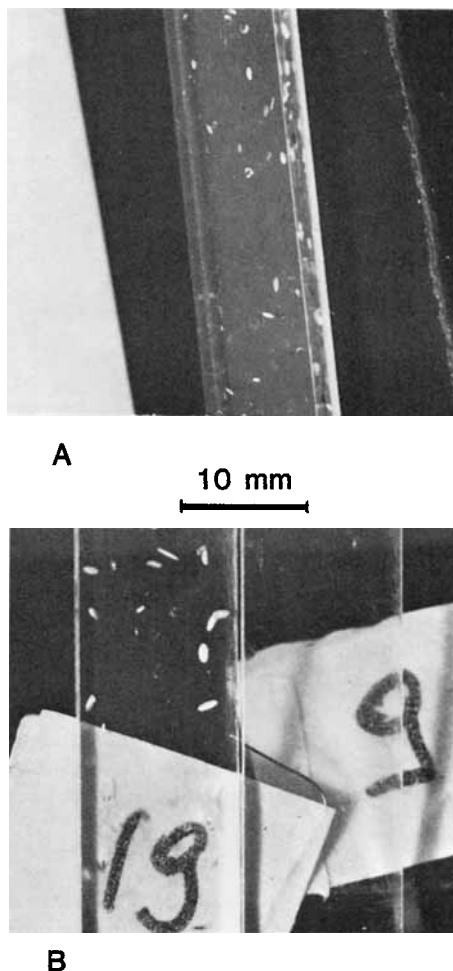


Fig. 2. Appearance of microcracks in the flexure bars after boiling in water for 5 days and storing at room temperature in (A) air, 3 days, (B) water, 5 days, left; air, 5 days, right.

complementary to the views of other researchers,^{3,5,6} who have attributed all the changes in mechanical properties to the hot humid environment or hot water exposure step. These earlier authors have apparently tested their specimens shortly after taking them out from the treating vessel, thus missing the following property changes at room temperature. The present authors hypothesize that, by imposing sudden nonequilibrium conditions (water supersaturation), water in vicinity of the specimen surface diffuses relatively easily to the environment. However, the supersaturation conditions in the bulk of the specimen remain, causing internal stress buildup, leading to initiation and propagation of crazes, and ultimately to the formation of the very thin discs that actually become water-filled pockets. Thus the supersaturation condition of the observed water is eliminated by slow water removal to the surrounding environment (the rate depends upon the prevailing driving force) and “temporarily” to the narrow disc pockets. These water pockets will start to lose water by diffusion through the continuous matrix to the environment when the water concentration in the polymer will drop below the equilibrium saturation conditions. These temporary

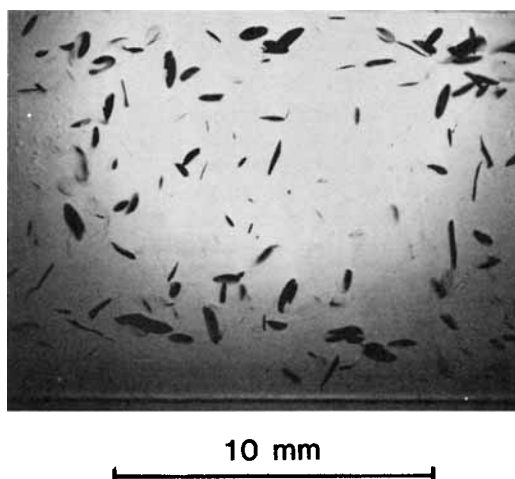


Fig. 3. Disc-shaped microcracks as seen in a transmission light microscope. Sample boiled in water for 8 days and subsequently stored in water at room temperature for 4 days.

pockets will close and heal due to their 2-dimensional character namely due to the closeness of the parallel disc planes. It is also likely that these water-filled pockets are under pressure and that this internal pressure is released by water diffusion out of the pockets. Thus the pocket closure can be partially accomplished by elastic recovery of the pocket "walls" and of the internal highly deformed fibrils connecting the walls. The incomplete healing of microcracks in samples stored in water at room temperature is due to the establishment of an equilibrium saturation condition of polycarbonate in contact with water at room temperature. The only driving force for water to diffuse from the pockets to the surrounding water is the excess internal pressure in the pockets. When this pressure equilibrates by some diffusion and relaxation processes, the pockets remain intact.

The visible disc-shaped pockets are formed in injection-molded specimens containing a certain degree of molecular orientation. Water-filled discs have been also recently observed in an isotropic compression-molded sample (Lexan 143), though to a lesser extent than in their injection molded counterparts.

Water absorption studies in polycarbonate exposed to boiling water have shown that the saturation absorption value is reached in less than 24 h, whereas the mechanical properties continue to change with the boiling time over a much longer period of time. It is thus concluded that molecular weight reduction and morphological changes are responsible for the mechanical property changes during the water boiling process.⁶ The room-temperature phase-separation process depends on the state of internal stresses, molecular weight, and morphology, all of which are affected by the length of the water boiling process. The water removal step at room temperature under supersaturation conditions thus depends upon the length of the preceding boiling step and its accompanying changes.

A detailed report of the time-dependent mechanical properties, structure, and fracture surface morphology will be given in a future paper.

The authors express their thanks to Prof. L. Nicolais for helpful discussions and to Dr. M. Puterman, Mr. A. Priori and Mr. M. Jaworowski, for participation in the experimental work.

References

1. D. G. Legrand, *J. Appl. Polym. Sci.*, **13**, 2129 (1969).
2. P. So and L. J. Broutman, *Polym. Eng. Sci.*, **16**, 785 (1976).
3. S. P. Petrie, A. T. DiBenedetto, and J. Miltz, *Polym. Eng. Sci.*, **18**, 1200 (1978).
4. M. Yokouchi and Y. Kobayashi, *J. Appl. Polym. Sci.*, **26**, 431 (1981).
5. E. Ho and Y. Kobayashi, *J. Appl. Polym. Sci.*, **22**, 1143 (1978).
6. R. J. Gardner and J. R. Martin, *J. Appl. Polym. Sci.*, **24**, 1269 (1979).

Received October 20, 1981

Accepted January 18, 1982