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The effect of the environment on the stress crazing of polycarbonate

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The effect of a number of different liquids on the rate of crazing of polycarbonate was studied. It was found that liquids either had no effect on the mechanical response, caused immediate cracking and fracture or caused a measurable rate of crazing, depending on the solubility parameter of the liquid. The rate of crazing in those liquids that caused crazing was found to vary inversely with the square root of time, indicating that diffusion through the end of the craze controlled the craze growth. Pre-immersion in one of the solvents, ethanol, had a strong effect on the subsequent rate of crazing under a constant load. The pre-immersion of pre-cracked samples initially caused an increase in rate of crazing. After a pre-immersion time of roughly 24 to 72 hours, the subsequent rate of crazing decreased with an increase in pre-immersion time. When the pre-immersion was conducted on an uncracked specimen and the crack was generated after the pre-immersion, the subsequent rate of crazing increased steadily with pre-immersion time. An explanation for the observed results is given.

1. Introduction

In a previous publication [1], the effect of ethanol on the environmental stress crazing of polycarbonate was described. The crazes started from a central hole which acted as a stress concentrator. A review of the existing theories for craze initiation and growth as well as the state of the art in this area was given. It was shown in that publication that the principal strain is the controlling parameter for craze initiation and growth.

In the present paper, the effect of different liquids on the environmental stress crazing of polycarbonate is described.

2. Experimental

Plates of Lexan polycarbonate, 8 in. long, 2 in. wide and $\frac{1}{4}$ in. thick were cut from as received extruded sheets, the length being in the extrusion direction. Stress–strain curves of standard ASTM tensile samples cut from these sheets revealed that the tensile properties of the material in the machine and transverse directions were almost identical and that the plates, for all practical purposes, were isotropic. The sides of the plates were machined and then polished by 600 grit. metallurgical paper and a 90° notch, 0.2 in. in depth, was cut in the middle of one of the sides. A crack, 0.3 in. in length, starting from the notch, was then fatigued in a 1230 model Instron machine at 30 Hz and low load satisfying the requirement of the standard [2].

The samples were clamped inside a special tank with glass windows, to allow observation, and loaded to a desired constant load in an Instron testing machine. The crazing solvent was then poured into the tank. The lengths of the crazes originating from the tip of the crack were measured at different times by a travelling microscope. Some of the samples were first immersed for a predetermined time in ethanol after the notch was prepared, either prior to or after the crack was fatigued. Only then were these samples tested in ethanol at a constant load in the Instron.

3. Results and discussion

The crazes always started from the sharp fatigued crack acting as a stress concentrator.

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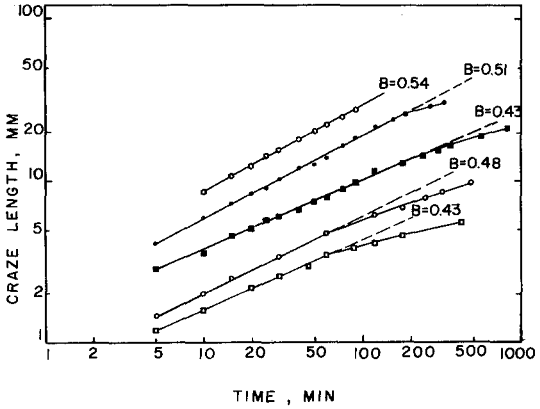

Figure 1 The dependence of craze length on time. ○ Ethanol 1500 p.s.i; ● ethanol 2000 p.s.i; o ethanol 2500 p.s.i; □ butanol 1500 p.s.i; ■ butanol 2000 p.s.i. B is the slope of the curves.

Figs. 1 and 2 show the craze growth in the polycarbonate samples in five different environments. It can be seen that in all the environments and at all the studied stress levels, the initial portion of the curves are straight lines with a slope B, close to 0.5, indicating that diffusion through the end of the craze control the craze growth [1, 3]:

$$l = Kt^{0.5} \tag{1}$$

where l is the craze length, t is the time elapsed and K is a constant (for a specific solvent–polymer system at a constant temperature and stress level).

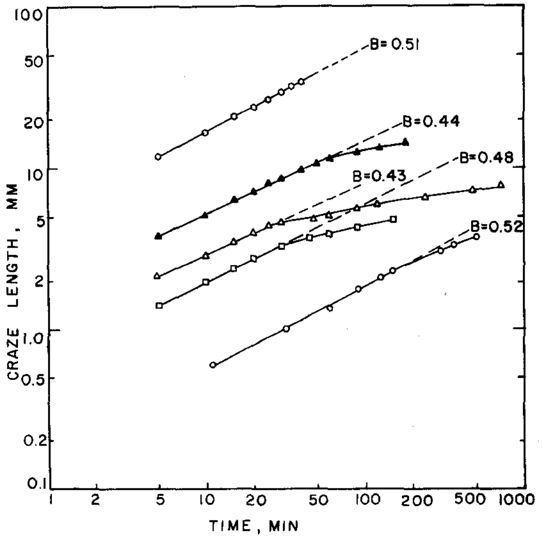

Figure 2 The dependence of craze length on time. ○ cyclohexanol 1500 p.s.i; □ cyclohexane 1500 p.s.i; △ hexane 1500 p.s.i; ▲ hexane 2000 p.s.i; o methyl carbitol 900 p.s.i.

This result is in agreement with the previously reported results for ethanol induced crazes in polycarbonate growing from a hole [1]. Similar results were also obtained by Marshall *et al.* [3] for methanol-induced crazing in PMMA. It can be seen from these figures that after a time, depending on the environment and stress level, the craze growth slows down indicating a tendency toward craze arrest. A probable cause for this slow-down in the rate of crazing is a decreased "effective tensile stress" on the uncrazed part of the sample due to a bending moment acting on it. Craze arrest can be caused in this case when the craze tip is brought below the critical strain for craze growth for a given solvent and stress level. A similar result as in Figs. 1 and 2 was also obtained with a 50% ethyl carbitol (diethylene glocol monoethyl ether) and butyl carbitol (diethylene glocol monobutyl ether) mixture.

Sternstein and Sims [4], working with poly (methyl methacrylate) and a 50% ethanol–water mixture as the crazing environment, found that the change in craze length with time could be described by two straight lines. The second line, corresponding to longer times, was found to be of a higher slope. No explanation for this behaviour was given. Kitagawa and Motomura [5] measured the rate of craze growth in polycarbonate sheet samples. The crazes were initiated from a crack made by a fretsaw or razor blade and kerosene was used as the crazing and cracking medium. They obtained nonlinear plots of craze length versus time on a log–log diagram, requiring a viscoelastic model to relate craze length to the applied stress and time. At the stress levels and time scale investigated in the present study, creep could be scarcely detected, if at all, and the polycarbonate could be assumed to behave as an elastic material. The results in the present study are phenomenologically different than those reported in the two above mentioned papers, but are in general agreement with the results of Marshall *et al.*

Table I summarizes the liquids investigated together with their solubility parameters and remarks about the effect on polycarbonate. Only the first six solvents produced measurable craze growth.

Fig. 3 shows the change of craze length with time after the fatigue cracked samples were immersed for a predetermined time in ethanol

TABLE I Solubility parameters of studied liquids

Liquid	Solubility parameter, δ (cal. cm^{-3}) $^{1/2}$		Remarks
Ethanol	12.92*	12.7†	Crazing agent
Butanol	11.30	11.4	Crazing agent
Cyclohexanol	10.95	11.4	Crazing agent
Methyl carbitol	10.72	–	Crazing agent, polymer attacked
Hexane	7.24	7.4	Crazing agent
Cyclohexane	8.18	8.2	Crazing agent
Butyl acetate	8.46	8.5	Cracking agent, polymer severely attacked
Dibutyl phthalate	–	9.3	Cracking agent, polymer severely attacked
Water	23.5	23.4	Polymer not effected

*Brandrup and Immergut [6], p. 348. Applies to whole column.
†Brandrup and Immergut, p. 341. Applies to whole column.

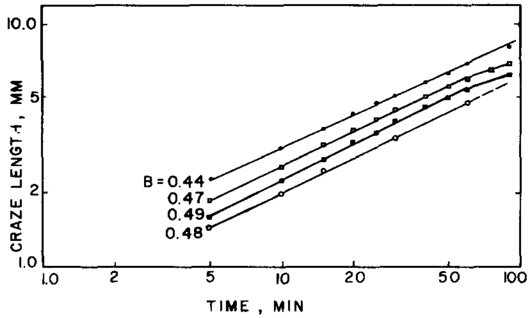

Figure 3 The dependence of craze length on time (1500 p.s.i.) for precracked samples, exposed to ethanol. ○ Unimmersed sample; ● after one day exposure; □ after seven days exposure; ■ after 21 days exposure.

prior to testing in this liquid (pre-cracked samples). It can be seen that Equation 1 also describes the behaviour of the pre-immersed samples. Immersion, however, does affect the rates of craze growth. The slowest rate of crazing occurs in samples that are not pre-immersed. The rate of crazing at first increases with pre-immersion time, then reaches a maximum and starts to decrease with pre-immersion time. The maximum increase in the rate of crazing occurs at some point point less than 72 h of pre-immersion.

The rate of crazing, dl/dt, can be calculated from:

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \frac{l}{t}\,\frac{\mathrm{d}(\ln l)}{\mathrm{d}(\ln t)} \tag{2}$$

As d(ln l)/d(ln t), the slope of the curves, is almost constant, it is clear that at a constant time the rate of crazing is proportional to the craze length. This observed behaviour can be explained as follows. As the sample is immersed in the liquid, diffusion into the polymer starts causing a compressive stress on any exposed surface of the sample. On the other hand, the polymer is softened by the liquid. In short-term exposure, the compressive stress built up at the crack tip is small. The plastic zone at the tip is softened, however, enabling the crazes to grow with a faster rate. As the exposure time increases, higher compressive stresses at the crack tip are built up. It is known that compressive stresses suppress craze growth [7]. The "relative compressive zone" formed at the crack tip will tend, therefore, to inhibit craze propagation.

Fig. 4 shows results for a second series of ethanol immersed samples. These samples, however, were not fatigued prior to pre-immersion, as in the first series, and contained only the 90° notch. The crack was then fatigued at the end of the predetermined immersion period (post-cracked samples). Again, the rate data are described by Equation 1. The effect of pre-immersion on the rate of crazing of the post-cracked samples is quite different from the effect on the pre-cracked samples. Whereas with the pre-cracked samples

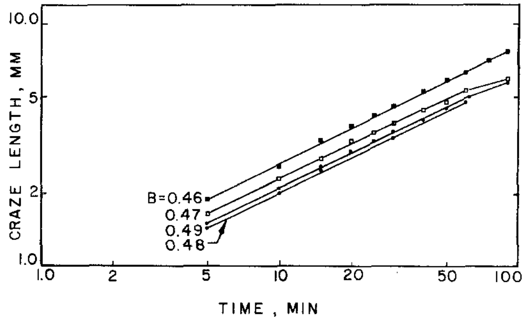

Figure 4 The dependence of craze length on time (1500 p.s.i) for samples exposed to ethanol and post-cracked. ○ Unimmersed sample; ● after one day of exposure; □ after six days of exposure; ■ after 22 days of exposure.

there is a maximum in the rate of crazing occurring after an exposure time of less than 72 h, the rate of crazing in the post-cracked samples increases steadily with an increase of exposure time. This is explained as follows. The compressive stress built up at the surfaces is compensated by a tensile stress which has to be formed in the centre of the sample as the net external force acting on it is zero. Post-cracking cuts through the compressive zone into a tensile region thereby relieving the surface compression at the crack tip. The compression stress on the surface plays therefore no primary role in controlling the rate of crazing. The longer the exposure time, the higher the solvent concentration at the post-cracked tip, the softer the plastic zone is and the higher the rate of craze growth. Also, the deeper the penetration of the solvent through the sides of the sample, the greater the internal tensile stress and the higher the rate of crazing will be.

The practical consequence of this difference is clear. If a polycarbonate part is exposed to a hostile environment, the rate of crazing of the part will be a function of the time at which a stress-concentrating flaw is formed. If the flaw exists prior to the solvent immersion, solvent exposure will tend to make the flaw more resistant to growth after a period of time. On the other hand, a new flaw will tend to cut through surface compressive zones and create regions of high craze growth.

It is worthwhile to mention that whereas an average of 170 000 cycles were required in order to fatigue the crack on the non-immersed samples, only 83 000, 29 000 and 19 000 cycles were required in order to fatigue the crack in the 1-day immersed, 6-day immersed and 22-day immersed samples, respectively. The reduction in the number of cycles required with immersion time is clear in the view of the weakening effect the liquid has on the polymer.

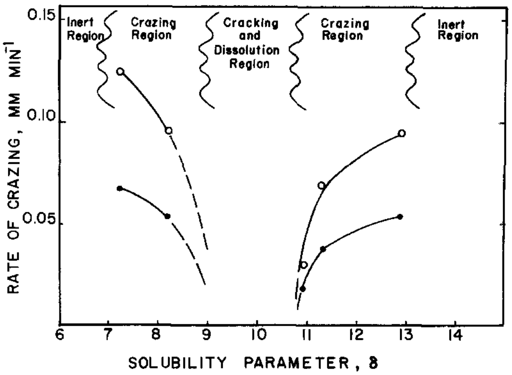

Figure 5 The dependence of rate of crazing on the solubility parameter of the crazing liquid. ○ Crazing rate after 10 sec; ● crazing rate after 30 sec.

In Fig. 5 the effect on the solubility parameter, δ, on the rate of crazing, computed from Equation 2 at constant times of 10 and 30 sec, is shown. The solubility parameter of polycarbonate is reported [5] to fall in the range of 9.3 to 10.6 $(\text{cal.cm}^{-3})^{1/2}$. It can be seen that as the solubility parameter of the crazing liquid approaches the above mentioned range (from below or above), the rate of crazing decreases. A possible explanation of this behaviour could be that the closer the solubility parameter of the liquid to the solubility parameter of the polymer, the more powerful it is in blunting the tip of the crack, thus reducing the effective stress acting on the polymer at this point. Fig. 5 is divided into five regions. When the solubility parameter of the liquid is well below or well above that of the polymer, this liquid falls into the inert regions where there is no effect on the polymer as far as crazing and fracture are concerned (as is the case with water). When the solubility parameter of the liquid falls in the ranges of 7 to 9 and 11 to 13 $(\text{cal.cm}^{-3})^{1/2}$ approximately, it is a crazing liquid for polycarbonate. When the solubility parameter of the liquid is in the range of 9 to 10.7 $(\text{cal.cm}^{-3})^{1/2}$ approximately, it is a cracking liquid for polycarbonate causing dissolution and fracture (as is the case with butyl acetate and dibutyl phthalate).

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