Effect of pre-soak and dissolved gas content on craze nucleation and creep of poly(methyl methacrylate) in methanol

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Craze nucleation and growth in stressed poly(methyl methacrylate) exposed to a methanol environment is strongly influenced by any exposure to that environment before application of the stress. It is also significantly influenced by the dissolved gas content of the methanol. It is demonstrated that increased exposure to methanol prior to application of the creep stress results in a decreased craze density and there exists a critical pre-soak time after which no crazes are nucleated. The critical pre-soak time is a function of dissolved gas content and creep stress. The variation in creep response is examined and a qualitative explanation in terms of fluid penetration is proposed.

INTRODUCTION

The creep response of a polymer can be significantly influenced by many of the parameters which describe the condition of the polymer, the environment to which the polymer is exposed and the procedural technique used for the test. For creep studies to have real significance it is important therefore that such parameters be carefully controlled or documented and their degree of influence understood, at least qualitatively. The effect of some of these parameters (e.g. temperature, surface tension and solubility parameter of the environment, and molecular weight and thermal history of the polymer) has received considerable attention from investigators. Others, however, are not well understood, with the result that it is sometimes difficult to make comparative studies between results from different laboratories. This paper describes the results of tests isolating two parameters which have received scant attention to date, namely gas content of the fluid environment and the time for which the polymer is exposed to its environment before application of the creep load.

The importance of the latter was discovered during preliminary work investigating the former and the resulting literature search revealed observations by two investigators[1,2], indicating that the length of time a specimen remained immersed in a fluid, prior to the beginning of a test, affected the subsequent creep response. No explanation for their observations were offered and a more comprehensive study was clearly warranted.

Williams *et al.*[3] measured craze growth rates in poly(methyl methacrylate) (PMMA) in gassed and degassed methanol and noted significantly different growth rates with the crazes propagating faster in the degassed fluid. The measurements were made at the two extremes of gas concentration and no clear insight could be gained on the relative importance of gas content on creep response at the level of concentration normally found when the liquid is in equilibrium with the surrounding atmosphere. As a result, a study was initiated to examine the creep response and the craze patterns resulting from tests conducted in methanol with various gas concentrations.

EXPERIMENTAL

Equipment and technique

The specimens used in the programme were cut from a single 2.5 x 1.25 m cast sheet of nominal thickness 3.2 mm. The PMMA had a density of 1.185 Mg/m^3 and a glass transition temperature, determined by the loss modulus method, of 105° ± 2°C. The methanol used was a reagent grade and was discarded after each test.

The test specimens were manufactured, using a rotary cutter, to the shape shown in *Figure 1.* This shape ensured that craze nucleation occurred at the mid-length and simplified the photographic technique used in subsequent craze growth rate investigations. It has the disadvantage that the stress varies along the specimen length; however, the varia-

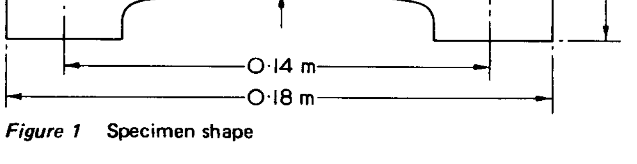

Figure 1 Specimen shape

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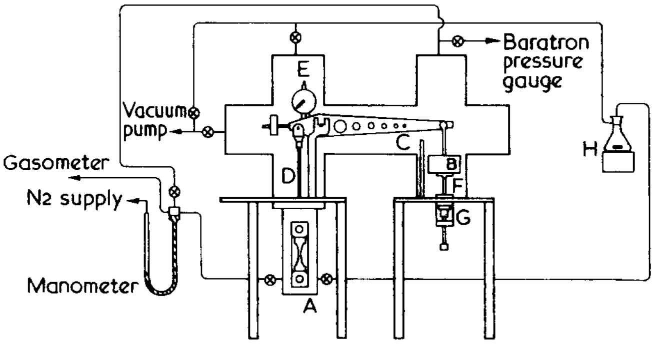

Figure 2 Schematic of the experimental apparatus

tion over the centre 6 mm is only 0.5% and craze growth measurements and observations were restricted to this area.

It has been noted that the use of conventional extensometry in crazing environments produces 'premature' craze nucleation and growth at the extensometer attachment points. In view of this, and also the choice of non-constant specimen cross-section, it was decided to monitor overall specimen extension, rather than strain, during the creep test. Since the investigation of creep response was to be comparative in nature (for different soak times and gas concentrations) and the specimen geometry did not vary, this sacrifice was considered worthwhile in view of the 'more natural' craze nucleation pattern which resulted.

The machined edges of the specimens were prepared by carefully sanding in a longitudinal direction with 600 grit paper, since previous work[4] has shown that craze nucleation stress is dependent on specimen surface finish. The specimens were finally annealed, at a temperature of 120°C for 4 h followed by slow cooling, and stored in the temperature-controlled laboratory (21° ± 1°C).

The tests were performed on a dead-weight lever loading creep machine which is completely enclosed in a pressure vessel and connected to a mechanical vacuum pump capable of drawing vacuums of less than 100 μmHg (13.3 N/m^2). A schematic diagram of the apparatus is shown in *Figure 2*. The specimen is contained in the environmental chamber A with the load being applied by the weight B via lever C and rod D. The movement of the lever arm and, therefore, with a suitable calibration constant, the extension of the specimen was measured by the dial gauge E. Strains of the order of 5×10^{-5}, i.e. the thermal expansion due to a 1°C temperature fluctuation, could be detected. The pressure vessel surrounding the lever consisted of two 150 mm diameter Corning glass X^s and the load was applied by lowering the support F using the through-wall, linear movement, vacuum fitting G.

The pressure in the chamber was measured using either a mercury manometer (10–760 mmHg) or a model 210 Baratron pressure gauge (10^{-5}–10^2 mmHg). Fluid could be degassed at station H and transferred to the environmental chamber when required without exposure to the outside environment. The gas content of the fluid was measured by a motorized Natelson Microgasometer, model 650 with a specially designed manometer which connected directly to the environmental chamber. The craze pattern was examined visually and photographically through 2 glass windows in the environmental chamber.

The following procedure was adopted as standard for the tests. A specimen was mounted in the environmental chamber C, and the required load supported at F. A vacuum of approximately 200 μmHg was applied for 500 sec. Methanol was degassed at station H until the required gas concentration was obtained and held until the temperature returned to the test temperature. The pressure in the degassing flask and environmental chamber was allowed to equalize for 100 secs, then the methanol was transferred to the chamber. The specimen remained unstressed in the methanol for a specified period of time (pre-soak time), then the load was applied to the specimen. The elongation was monitored with time and visual or photographic observations of the centre region of the specimen were made.

DISCUSSION OF RESULTS

The first set of tests examined the effect of varying the pre-soak time on the creep response of PMMA in methanol which had a saturation concentration (for atmospheric pressure) of gas. The test procedure was similar to that described above except that the fluid was stirred gently in the degassing station while the flask was exposed to the laboratory atmosphere. Creep tests were performed at stresses of 13.8, 20.7, 27.6 and 34.5 N/m^2 with pre-soak times varying upwards from 10 sec. The resulting elongation/time plots for two stress levels are displayed as *Figures 3* and *4*.

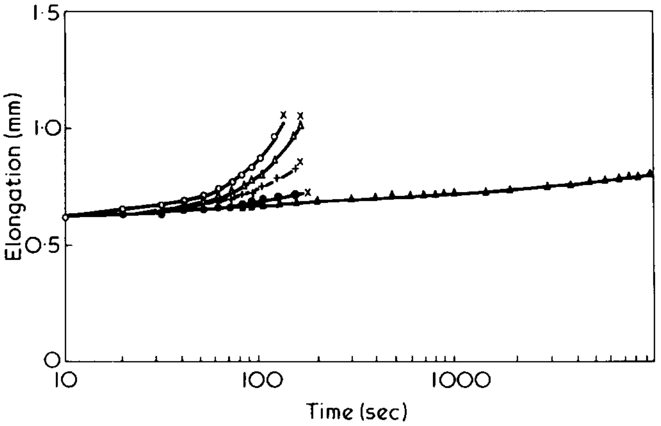

Figure 3 Specimen elongation *versus* time for various soaking times, at a creep stress of 20.7 MN/m^2. Pre-soak times: ▲, 5000 sec; ●, 1000 sec; +, 500 sec; △, 100 sec; ○, 10 sec; x, fracture

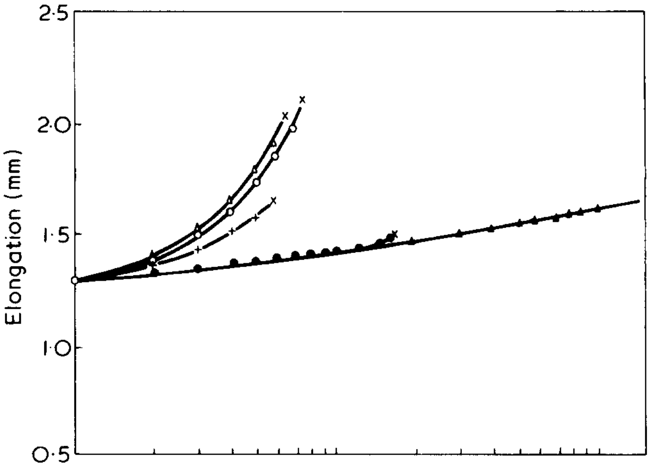

Figure 4 Specimen elongation *versus* time for various soaking times, at a creep stress of 34.5 MN/m^2. Pre-soak times: ▲, 50 000 sec; ●, 10 000 sec; +, 1000 sec; ○, 100 sec; △, 10 sec; x, fracture

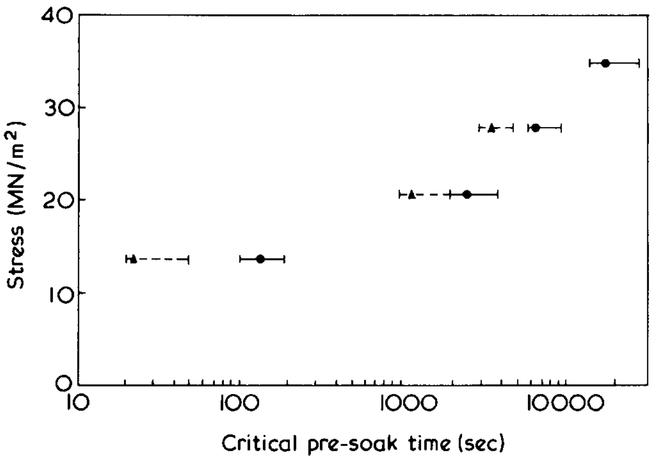

Figure 5 Critical pre-soak time *versus* stress. ●, Gassed methanol; ▲, degassed methanol

It can be seen that as the pre-soak time increases, the elongation at failure decreases. Visual observations indicated that the craze density also decreased as pre-soak time increased. Weidmann *et al.*[5] related the increase in creep strain observed during tensile tests on PMMA in methanol to the growth of crazes, which suggests that the increase in elongation at failure which results in short pre-soak times is due to the accumulation of the local extensions occurring at each craze site. With increased pre-soak times, there came a point beyond which no crazes formed during the subsequent creep test at that stress and the creep response closely resembled that obtained in air at the same stess level. Such a critical soak time was evident for each stress level and the variation with stress is shown in *Figure 5* where the scatter bands define the limits of pre-soak time above which crazes *never* nucleated and below which crazes *always* nucleated in the creep tests conducted at that stress level.

The explanation proposed for the creep dependence on pre-soak time is based on the extent of absorption of the fluid into the polymer matrix. Weight up-take tests had shown (*Figure 6*) that a measurable amount of methanol was absorbed by the PMMA and that the quantity increased with time. Other investigations[6] have suggested that the concentration profile for methanol penetrating PMMA can be approximated by a step function and therefore the depth of penetration (for depths much less than the specimen dimensions) will vary with time in a manner similar to *Figure 6*. Micro-hardness tests on specimens that had been immersed in methanol showed that the absorbed layer was substantially softer than the virgin polymer and so after the pre-soak time, i.e. when the creep test begins, the specimen consists of a virgin core and a thin, soft surface layer, the thickness of which increases with increasing pre-soak time.

Crazes which nucleate at or near a surface are strongly influenced by the stress concentrating effect of surface flaws. The existence of a soft surface layer will have the effect of neutralizing the influence of those surface flaws which it has enveloped. Initially, the number of nucleation sites eliminated will increase with increasing thickness of the soft layer until the softened layer is eventually of a thickness at which all sites, active at that particular stress level, have been eliminated. The time for the fluid to diffuse to such a depth would be the critical pre-soak time for that stress. As the creep stress increases the number of potential craze sites increases and the fluid must penetrate to a greater depth before complete neutralization is effected, hence the increase in critical pre-soak time with increasing creep stress, evident in *Figure 5*.

A second series of tests at similar stress levels and with a similar range of pre-soak times was conducted using degassed methanol (methanol where the gas concentration, C, is less than 1% of the saturation concentration, C_*, i.e. $C/C_* < 0.01$) as the environmental fluid. In addition tests were carried out at a stress level of 20.7 MN/m^2 with a pre-soak time of 100 sec in partly degassed methanol. Absorption measurements using degassed fluid (*Figure 6*) has suggested that degassed methanol was absorbed more quickly than gassed methanol. For the previous explanation to be valid a specimen exposed to degassed fluid for a specific pre-soak time would, compared with its counterpart exposed to gassed fluid, begin the creep test with a thicker, soft, surface layer, i.e. with a greater number of potential craze sites neutralized. It should therefore have a lower craze density and elongation at failure. In addition the time required for the fluid to penetrate to a depth sufficient to neutralize all the craze sites would be shorter; therefore, the critical pre-soak time should be less. Experimental data and observations show that these requirements were fulfilled. The plot of critical pre-soak times vs. stress in *Figure 5* clearly shows that the degassed fluid requires shorter pre-soak times to eliminate all potential craze sites, at each stress level, than gassed fluid. The creep response of 3 specimens subjected to creep stresses of 20.7 MN/m^2 after pre-soak times of 100 sec in methanol with different gas concentrations are displayed in *Figure 7* and show a decreasing elongation at failure and a slower creep rate with decreasing gas concentration. *Figure 8* shows a plot of craze density, defined as the total number of crazes in the central 5 cm of the specimen, against gas concentration and indicates a decrease in craze density with decreasing gas concentration.

CONCLUSIONS

The results of this study emphasize the importance of exercising strong control over the experimental technique used in crazing studies by demonstrating the sensitivity of the resulting craze pattern to pre-soak time. The craze density at any creep stress level decreased markedly with increasing pre-soak time and there exists a critical pre-soak time for each stress level above which no crazes nucleated. This critical pre-soak time increased with increasing creep stress, varying from 150 sec at 13.8 MN/m^2 to 20 000 sec at 34.5 MN/m^2 for

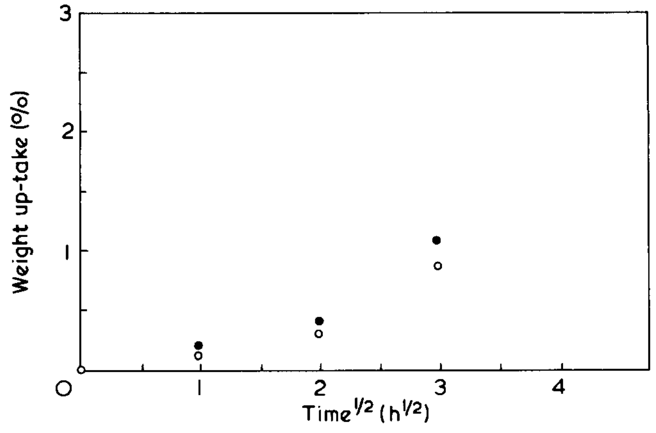

Figure 6 Liquid uptake in PMMA *versus* time for degassed and gassed Methanol. ●, Degassed methanol; ○, gassed methanol;

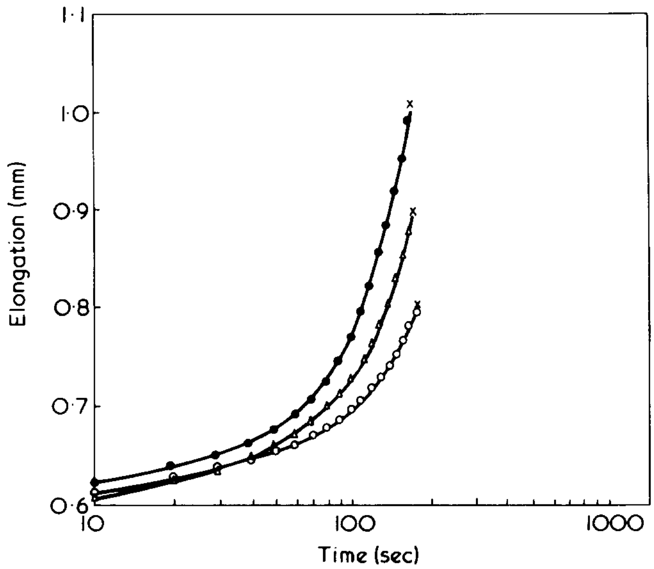

Figure 7 Specimen elongation *versus* time for specimens pre-soaked for 100 sec in methanol with different gas concentrations. Creep stress = 20.7 MN/m^2. ●, C/C_* = 1.00; △, C/C_* = 0.47; ○, C/C_* $\leq$ 0.01; x, fracture

regular methanol. The use of degassed methanol as the environmental fluid produced comparatively fewer crazes, lower elongations at failure and shorter critical pre-soak times, with the degree of effect increasing with decreasing gas content.

The explanation proposed is that fluid being absorbed into the polymer during the pre-soak period produces a softened surface layer which eliminates some of the potential craze sites. After the critical pre-soak time, the depth of penetration is sufficient to eliminate all the craze sites that would be active at that stress. The degassed methanol is absorbed more quickly than regular methanol therefore eliminating more sites for the same pre-soak time and requiring less time to eliminate all active sites resulting in a reduction in the critical pre-soak time relative to the gassed fluid.

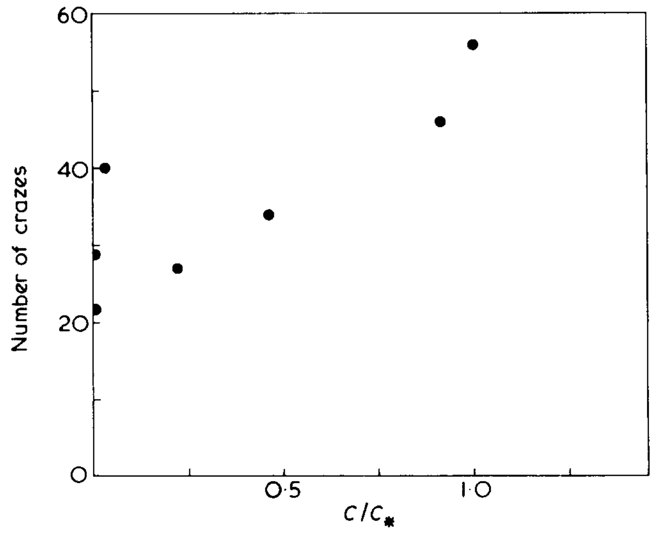

Figure 8 Variation in craze density with gas content. Measurements made after 60 sec with a creep stress of 20.7 MN/m^2

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