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Section 2.3. Large deformation of polymers

Structural changes in glassy polycarbonate induced by cyclic stresses

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Glassy polycarbonate was subjected to cyclic stresses and the changes in its structure were studied by DSC, positronium annihilation lifetime spectroscopy (PALS), and SAXS. On increased exposure to cyclic loading, the enthalpy overshoot near T_g increased in a manner similar to increasing physical aging. However, the 'hole' size as revealed by PALS increased, unlike physical aging. SAXS reveals an increase in the short range order and the amplitude of density fluctuation. These results are consistent with both the DSC and the PALS results. We conclude that mechanical loading does cause changes in the glassy structure.

1. Introduction

Non-equilibrium glasses including polymer glasses spontaneously approach the equilibrium state. During this process, known as physical aging, structural and physical property changes occur. Further, the relaxation spectrum shifts to longer times [1]. Since the relaxation behavior of a glass is determined in part by the structure of the glass, it is meaningful to ask whether a thermodynamic variable which changes the structural state will also change the aging behavior. It is already known that higher temperature accelerates the physical aging process [1]. Rejuvenation, i.e., reversal of aging, occurs upon increasing the temperature above T_g. Stress has also been said to affect the structural state [2–5]. Yet, McKenna and co-workers have argued that mechanical stress does not affect the structural state; instead, they attribute the observed effects to viscoelastic memory [6].

The investigations cited [2–6] have two important aspects in common. The first is that mechanical experiments were used as measures of the structural state of the glasses. The second is that no microscopic evidence has been produced by these workers to show whether the structure has indeed been changed or remains constant. The present contribution is also motivated, in addition to the intrinsically interesting question of mechanically induced aging and rejuvenation, by a rather more prosaic concern, namely, the effect of cyclic stress on the failure behavior of glassy polymers, commonly known as fatigue failure. The connection between physical aging and fatigue is based on the observation [7] that low amplitude cyclic loading leads to premature, brittle failure, whereas high amplitude loading leads also to premature, albeit ductile failure. Further, physically aged polymer glasses exhibit shorter failure lifetimes at low stress amplitudes, whereas the ductile failure lifetime at high stress amplitudes remains little changed by physical aging [7]. These observations make it apparent that there is a similarity between aging by cyclic stress and aging by thermal treatment. The objective of this work is to determine if cyclic loading changes the structure of the polymer glasses. In addition to the use of macroscopic techniques such as enthalpy relaxation and viscoelastic measurements, we also employ microscopic

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techniques. These are positronium annihilation lifetime spectroscopy (PALS) and small angle X-ray scattering (SAXS). The former has been used [8,9] to assess changes in the average 'hole' size in polymer glasses upon aging. The latter has been used [10] to investigate changes in density fluctuation in polymer glasses subjected to various cooling and pressure histories. These techniques complement each other in that SAXS detects electron density fluctuation whereas PALS is more sensitive to the absence of electrons. To construct a more complete picture of the changes in the glassy structure, both sets of information are necessary (yet may still be insufficient).

2. Experiments

2.1. Material and thermal treatment

The material used in this research is a bisphenol-A polycarbonate (PC) resin produced by the Dow Chemical Co. M_w is 37200 g/mol and M_n is 14700 g/mol. The material was molded into 3 or 6 mm thick sheets, then cut into smooth dumbbell-shaped specimens. Before the specimens were used or heat-treated, they were carefully polished by hand to avoid surface crazing during the fatigue test. All specimens were appropriately heat-treated prior to cyclic loading to have well-defined thermal as well as mechanical histories. They were first annealed at 165°C, about 15°C above the T_g, for 40 min to erase previous thermal and mechanical histories. They were subsequently cooled to room temperature at a rate of about 20°C/min to obtain a 'fresh' sample; or, in some cases, they were first brought to an aging temperature, T_e ($T_e < T_g$), and maintained at that temperature for a period, t_e, and then quenched to room temperature to obtain an 'aged' sample.

2.2. Cyclic loading

A servo-hydraulic testing machine was used to apply various constant load amplitudes (zero to tension sinusoidal) at 5 Hz at 55°C. The frequency of 5 Hz was chosen for producing relatively little self-heating yet allowing rapid completion of loading history. The fatigued specimens were usually kept at a low temperature (about 0°C) immediately after the test for subsequent structural characterization. The time interval between the end of the fatigue test and the subsequent measurements was minimized to prevent the sample from any structural recovery or aging at the storage temperature.

2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were carried out with a Perkin–Elmer DSC-7. The scanning rate was 10°C/min. The samples used for DSC were sliced into thin discs with parallel faces from a specimen along the cross-section by using a low-speed diamond saw cooled by a water bath. The saw speed was adjusted to minimize damage caused by either heat or stress. The specimens were subsequently punched out into disks that fit the aluminum DSC pans perfectly to ensure maximum contact. The enthalpy overshoot is taken to be the area of the first scan above the extended upper baseline (equilibrium line) subtracted from that of a subsequent scan.

2.4. Positron annihilation lifetime spectroscopy (PALS)

A 30 μCi ^{22}Na positron source was deposited on the surface of a copper disk and covered with a 3 μm nickel foil. This source assembly was then placed on the surface of the polymer sample to form a sandwich. The PALS measurements were performed with a conventional fast-timing coincidence method and the lifetime spectra were resolved into three exponential components using the computer program NEWPOSIFIT. About 17.5 $\times 10^6$ counts were collected for each lifetime spectrum in approximately 80 min. All the measurements were conducted at room temperature. Both the lifetime and the intensity values obtained for PC are consistent with literature results [8,9].

2.5. Small angle X-ray scattering (SAXS)

SAXS data were obtained using a Rigaku SC-20 small angle scattering goniometer. Samples 1 mm

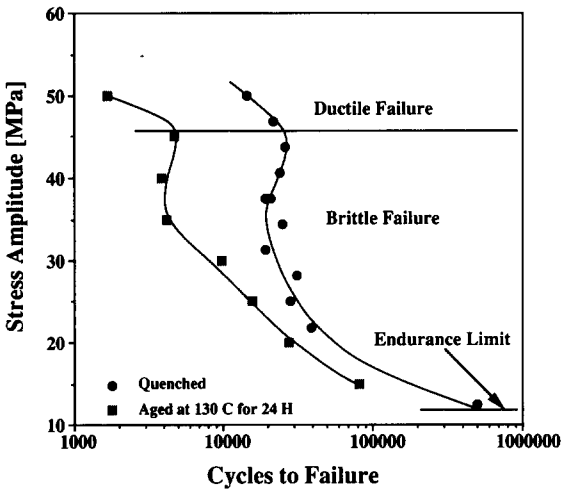

Fig. 1. The relationship between the stress amplitude and the number of stress cycles to failure. Visible crazing occurs just before failure.

thick were used and were cut from the fatigued specimen as described in section 2.3. The Rigaku X-ray system employs a movable detector, the parameters of which were set as follows: scanning rate = 1.0°/min, scanning interval = 0.1° and scanning range = 0.5–19.0° (2θ). For clarity of presentation, the data in fig. 4 have been smoothed. It should be noted that the peak at $2\theta = 5°$ is due to background.

3. Results

Figure 1 shows a S–N diagram, in which the number of cycles to failure is plotted against the corresponding stress amplitude for fresh and previously aged specimens. The aged material exhibits a significantly reduced lifetime with a craz-

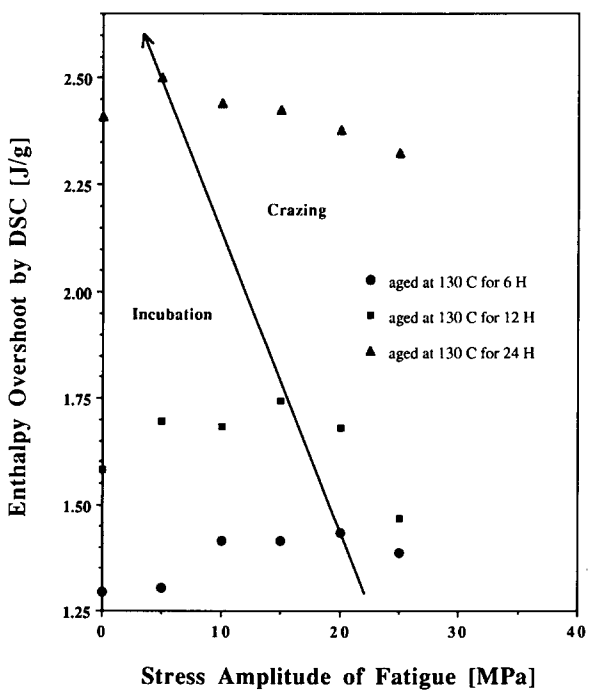

Fig. 2. The enthalpy overshoot as measured by DSC at 10°/min as a function of stress amplitude and aging time. The solid line marks the onset of visible crazing.

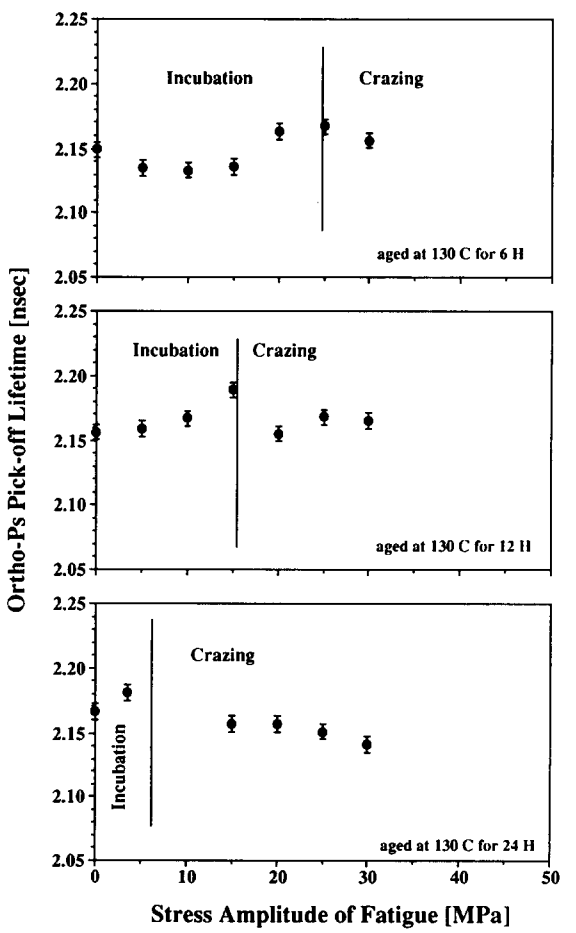

Fig. 3. The o-PS pick-off lifetime, τ_3, as a function of the stress amplitude at various aging times. The solid lines mark the onset of visible crazing.

ing region that extends to higher stress amplitudes. Figure 2 shows the enthalpy overshoot for samples subjected to various t_e and subsequent fatigue stress amplitudes for a constant 8000 cycles. A solid line is used to demarcate regime I (incubation) where no visible changes are occurring in the glass and regime II where crazing appears. In regime I a statistically significant stress dependence is exhibited although microscopy has revealed no visible heterogeneities. Such increases in the enthalpy overshoot is usually associated with physical aging. By comparison, aging without mechanical loading for the same period of time produces no detectable increase in the enthalpy overshoot. This implies that the glass structure is more significantly changed by cyclic stresses even at relatively low levels. In the crazing regime (II), the enthalpy overshoot decreases with stress. Another interesting observation revealed by fig. 2 is that previously aged specimens craze much more readily. This is consistent with the S–N data in fig. 1 and with Takemori's results [7]. We do not currently have an explanation for the decrease in enthalpy in regime II. Figure 3 shows the orthopositronium pick-off lifetime as a function of stress amplitude. By contrast with pure physical aging, where the lifetime decreases with aging, the lifetime in regime I actually increases. This can be literally interpreted to mean an increase in 'hole' size with fatigue. This perplexing behavior can be reconciled with the DSC results if we analyze the SAXS results in fig. 4, which show that the amorphous peak at $2\theta = 18°$ (0.49 nm) increases in intensity with fatigue up to the demarcation line (in stress) between regimes I and II, while the broad angular range from $2\theta = 0°$ to the amorphous peak also increases in intensity. These results indicate that there is increased short-range order as well as increased density fluctuation over a wide spatial scale. The former is consistent with the DSC results and the latter with the PALS results. The decrease in the SAXS peak ($2\theta = 18°$) intensity at higher stresses is due to the presence of crazes in the specimens.

4. Discussion

The results described are still preliminary in that we do not have complete sets of data covering

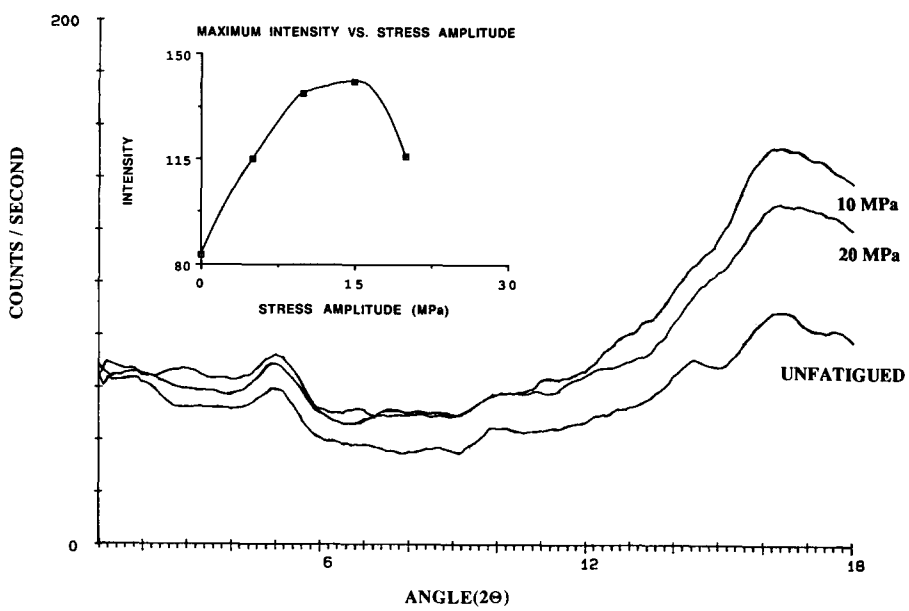

Fig. 4. SAXS of PC aged at 130 °C for 12 h at various fatigue stress levels. The peak at $2\theta = 18°$ is due to short-range order. The scattering at smaller angles is due to density fluctuation.

a wider range of conditions. Space limitation here does not allow us to report the full range of results we obtained using the various techniques and their interpretation. These can be found in forthcoming publications [11–13]. Also, we are not able to explain the observed changes upon crazing. However, within the incubation period, the observations made with different techniques correlate with each other extremely well. They demonstrate clearly that mechanical stress can cause structural changes. We also found that at low stress amplitudes, the short-range order and the hole size both increase. This would lead to a retardation in the mobility of the chains in the glass, making shear deformation more difficult. At the same time, the increased hole size could be a precursor to crazing, which must occur in regions of lower chain density. These inferences must be treated with some caution until corroborated by more data; for now, we have suggested a plausible explanation to the initiation of brittle fatigue failure at low stress amplitudes. It is tempting to characterize the results we found in terms of stress-induced aging and rejuvenation. However, the current results demonstrate that such characterization would be simplistic.

5. Conclusions

We have performed cyclic loading experiments on glassy PC with well-defined thermal histories. The failure lifetime behavior is consistent with that reported in the literature [7]. The behavior can be divided into two regimes: an incubation period in which no visible changes in the structure are observable, and a second period in which crazes are formed and eventually grow into cracks. Our emphasis is on the incubation period. In this periods, DSC measurements reveal enthalpy relaxation behavior similar to glasses that had been subjected to physical aging. However, unlike physical aging, PALS reveals an increase in hole size, and SAXS reveals an increase in density fluctuations as well as short-range order. We conclude that stress does cause structural changes in this polymer glass, though these changes cannot be simply described in terms of physical aging or rejuvenation.

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