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Some Observations on Fatigue and Crazing of Polycarbonate (Bisphenol A)

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Abstract

Amorphous, unoriented polycarbonate (bisphenol A) films are cyclically fatigued at several tensile stress levels below their yield stress. The fatigued films have been investigated by X-ray scattering, density measurements, and dynamic mechanical tests (Rheovibron). The X-ray data suggest a decrease of the interchain distances in the fatigued films by about 1 %. In spite of this improved packing the overall density shows a decrease (of 0.08 %). The dynamic mechanical testing reveals shifts of both the α and β relaxation peaks towards lower temperatures. In addition, many of the fatigued film samples fracture at the cryogenic temperatures during the tests on the Rheovibron. These results lead to the conclusion that microvoids are formed in the fatigued polymer. The microvoids are distributed throughout the fatigued polymer and weaken the material.

Introduction

Knowledge of the fatigue behavior of a polymeric material is of utmost importance to the design engineer. Fatigue studies in bulk polymers have been carried out but the mechanisms at work during the fatigue process are not yet fully understood. So far most of the study has progressed along the line of fatigue studies in metals, viz., in the area of crack initiation, crack propagation and ultimate failure. However, even the simultaneous investigation of such macroscopic phenomena along with the microscopic phenomena of crazing, shear banding, and plastic flow are insufficient to give a complete picture of the fatigue processes in polymers. Therefore, the objective of the present study has been to investigate "homogeneous fatigue", i.e. that period of the fatigue process where the above mentioned discontinuities become not yet apparent.

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In the present study, load controlled low-cycle, cyclic tensile fatigue of polycarbonate films was carried out. The number N_a of fatigue cycles applied to a sample was taken to be smaller than the number N_f of cycles for final breakdown. The upper stress level σ_{max} was chosen in such a way that the polymer remained within its anelastic limit. Thus, the tensile stress always remained below the yield stress σ_y. The fatigued polymer films were characterized through X-ray scattering, density measurements, and dynamic mechanical tests (Rheovibron).

Experimental

Material

Unoriented amorphous polycarbonate (bisphenol A) films of 3 mil (0.075 mm) thickness were obtained from General Electric Company, Mt. Vernon, Indiana. The film material had a yield stress σ_y of 57 MPa and a density of 1.1976 kg/m^3.

Tensile fatigue

Polycarbonate films were cyclically fatigued* between 4.3 and 52.1 MPa at a frequency of 5 cycles/min. The elongations of the films were recorded in the first five cycles and also at the end of the desired number of fatigue cycles. A maximum strain rate of 50 %/min was employed. Minute birefringence is noticeable in PC films immediately after their fatiguing. But it disappears in about 12 hours during which time the sample has relaxed. All tests were conducted after the above time period. The fatigue conditions of different samples and some of the resulting property changes are indicated in Table I.

X-ray scattering studies

X-ray scattering was used to determine changes in the interchain distance due to fatigue. The data were obtained from flat PC samples on photographic films using a Statton box camera. Fine ZnO powder was smeared on these polymer film specimens for calibration purposes. The diffused halo patterns were scanned**. The Bragg distance (d_{Bragg}) was calculated using Bragg's law. In the present study, X-rays were produced from a copper target by applying a voltage of 50 kV and a current of 20 mA. Cu K_α radiation was obtained by using a nickel filter.

Density measurements

Densities of unfatigued and fatigued PC films were measured in a density column filled with aqueous NaBr solution. The column covered the density range between 1.121 and 1.232 g/ml and was calibrated by five balls of densities known with a precision of ± 0.0001 g/ml.

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* Instron, model TMS

** Joyce-Loeble automatic recording densitometer, model MD 111 CS

Table I

FATIGUE OF POLYCARBONATE FILMS

Specimen	lower	upper	Fatigue cycles	Density	Temperature of		Comments
	cyclic fatigue stress			10^3 kg m^{-3}	α-peak	β-peak	
No	[MPa]		No		°C	°C	
0	0	0	0	1.1976	+ 145	- 78	reference sample
1	4.3	42	1338	-	+ 134	- 83	
2	4.3	32	2000	1.1968	+ 122	- 93	
3	6.2	47	2000	1.1966	-	- 93	sample breaks at - 87 °C
4	8.6	52	5000	1.1968	-	- 106	sample breaks at - 88 °C
5	8.6	47	5800	1.1968	-	- 88	sample breaks at - 73 °C
6	8.6	47	6000	1.1966	-	-	crazing occurs

Dynamic mechanical measurements

A dynamic viscoelastometer* was employed to plot the tan δ vs. temperature data at a frequency of 35 Hz. The data was recorded between the temperature limits of - 150 °C and + 150 °C at a heating rate of 2 °C/min.

Solvant-crazing

PC films were solvant-crazed by first immersing them in an ethanol solution for 30 min and then manually flexing them for a few times.

Results

Density data

In cyclic tensile fatigue a decrease of the density was observed. PC film samples, fatigued 2000 cycles between stress levels of 4.3 and 50 MPa, showed a density of $1.1967 \cdot 10^3$ kg/m^3; the same density was obtained for samples fatigued 5000 to 6000 cycles between 8.6 and 50 MPa.

X-ray scattering and birefringence results

A mean Bragg distance (d_{Bragg}) of 0.544 nm was determined from the unfatigued PC film; it is ascribed to the interchain distances by Wignall et al. (1). This distance decreases by about $0.6 \cdot 10^{-2}$ nm in a sample, fatigued 5800 cycles between 8.6 and 48 MPa.

Dynamic mechanical test results

Figures 1 and 2 show the plots of tan δ values as a function of temperature as obtained from unfatigued and fatigued polycarbonate samples. The data show two well recognized relaxation peaks appearing at 145 and - 78 °C, respectively, and a weaker peak appearing at 110 °C. The main peaks have been designated in the literature as α (145 °C) and β (- 78 °C) peaks. The 110 °C peak has been referred to as "β" peak by Boyer (2,3). It is associated with molecular motions similar to those at the glass transition temperature (T_g), but from fewer consecutive units. In the present discussion, the term β peak refers to the relaxation peak at - 78 °C. The weaker peak at 110 °C is referred to as "intermediate" peak.

Comparing the data in figures 1 and 2, the following interesting observations have been made:

- the PC samples fatigued to larger number of cycles and/or fatigued at higher stresses, invariably fracture between - 88 and - 78 °C during the rheovibron test. These tests have been repeated several times to ensure their reproducibility,

- the α and β relaxation peaks obtained from fatigued samples appear at lower temperatures in comparison to the peaks from the unfatigued samples. The α peaks of curves 1 and 2 are shifted

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* Rheovibron, model DDV-II

by - 11 and - 23 K, respectively, the β peaks by between - 5 (curve 1) and - 27 K (curve 4).

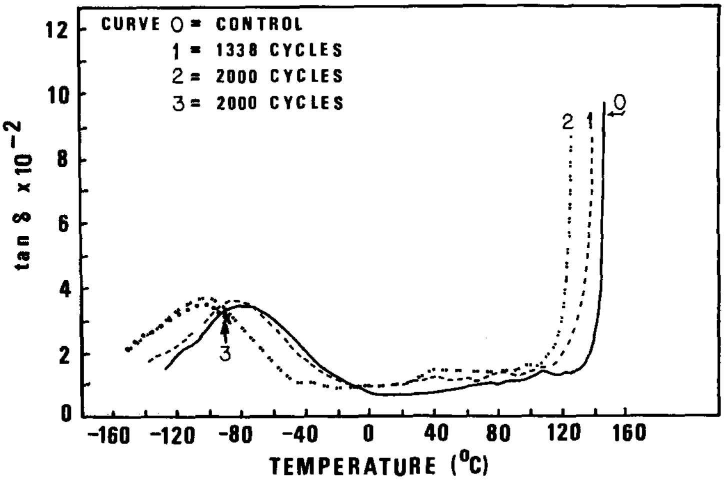

Fig. 1: tan δ vs. temperature plot for unfatigued and fatigued PC. Frequency of test = 35 Hz; Curve 0: control sample, Curves 1-3 belong to films 1-3 (Table I).

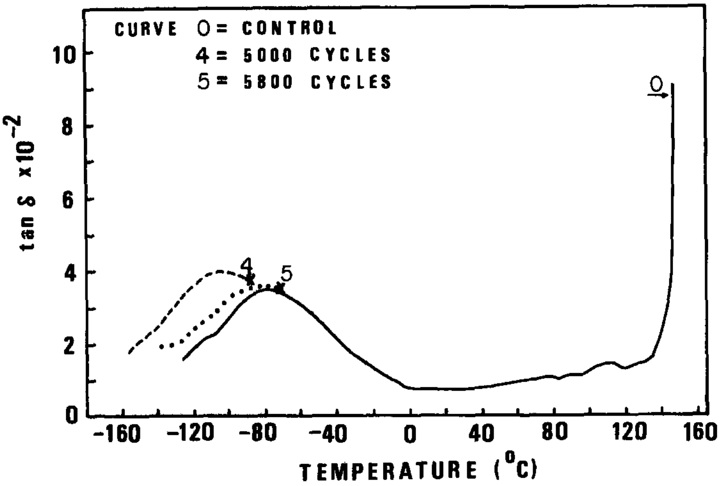

Fig. 2: tan δ vs. temperature plot for PC films. Frequency of test = 35 Hz; Curve 0: control sample, Curves 4 and 5 belong to films 4 and 5 (Table I).

Discussion

The X-ray results suggest an average decrease of about 1 % in the intermolecular distances in the fatigued samples. This indicates that the PC chains move closer to one another. Nevertheless, the overall densities of fatigued PC decrease slightly in comparison to the unfatigued PC. These results suggest an increase in the free volume due to microvoid formation, preferentially during the first 2000 cycles.

The dynamic mechanical loss data (Figs. 1 and 2) clearly demonstrate a fatigue effect on molecular mobility. The β relaxation peak occurring at about - 100 °C at a test frequency of 1 Hz is associated with the motion of carbonate (-O-CO-O-) groups in the main polycarbonate chain (4). However, it is also suggested (5) that this loss peak consists of three overlapping curves possessing nearly the same activation energies. The loss peak on the low temperature side, i.e., at about - 145 °C, is related to methyl ($-CH_3$) group mobility and another one at about - 50 °C, is related to the phenylene group motions while the maximum of the peak at - 100 °C is due to the mobility of carbonate groups. It can be seen that increasing the number of fatigue cycles from 1338 to 2000 causes α and β peaks to shift more toward lower temperatures. The curves 2 and 3 refer to films fatigued up to the same number of cycles (2000) but to different stress levels. The rheovibron samples taken from film No. 3 always fractured past the β peak.

A comparison between the tensile loss measurement of crazed samples is made in Fig. 3. The β relaxation peak (at - 80 °C) of the fati-

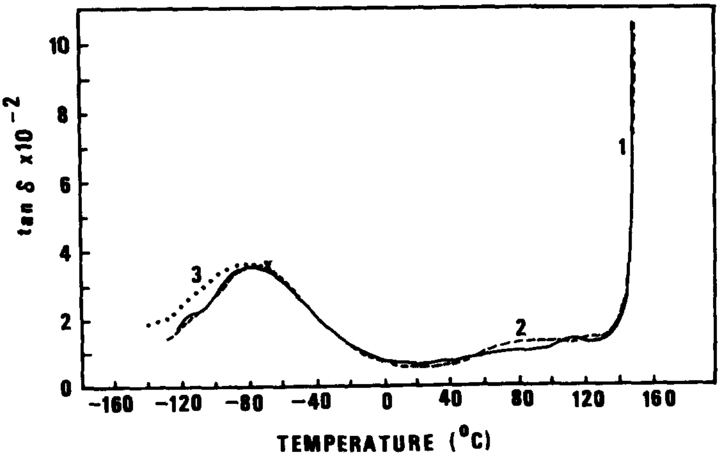

Fig. 3: tan δ vs. temperature plot for untreated PC (Curve 1), solvent-crazed PC (Curve 2) and fatigue-crazed PC (Curve 3, specimen 6 of Table I). Frequency of test = 35 Hz.

gue-crazed sample, Curve 3, becomes somewhat broader and shifts to a lower temperature. Curve 2 shows the α and β relaxation peaks of the solvent-crazed PC sample superimposed upon reference Curve 1 of an untreated PC sample.

It will be noted that the weak intensity intermediate peak originally appearing at about 110 °C is rather obscure and disperses over a much wider and lower temperature range in case of the solvent-crazed PC sample. This is an interesting phenomenon because Watts and Perry (5) associate this weak intermediate peak with the stresses induced in the PC specimens during moulding or drawing. The peak disappears on annealing the specimen. The authors (6) conclude that this intermediate temperature relaxation peak is a precursor to the α-process, probably originating from regions of the unannealed polymer, such as surface zones, subject to frozen-in stresses. The solvent treatment and, to a lesser extent, the surface crazing may have contributed to stress relieves and to the disappearance of a distinct intermediate temperature peak of the solvent-crazed sample.

An optical comparison of the fatigue-crazed and solvent-crazed PC film samples shows that the craze concentration of the latter is considerably larger. Nevertheless, the fatigue-crazed samples break in the dynamic experiments. This indicates that the molecular mechanisms leading to crazing in both cases must be different.

Conclusions

The cyclic fatigue of polycarbonate films leads to macroscopic and molecular changes. On the basis of the reported observations it can be said that in an initial phase of the fatigue process (up to 2000 cycles) well dispersed voids are formed which lead to a decrease in density (by 0.08 %). The molecular packing is locally improved during the whole period as evidenced by the decrease of the interphenyl distances (by up to 1 %). The structural rearrangements increase the molecular mobility (shift of α and β relaxation peaks by up to - 28 K) but constitute a damage (rupture of samples in the rheovibron test, craze formation whithin the total sample volume). Elucidation of the molecular nature of the structural rearrangements will need further study.

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