Photoplastic Effect in Polycarbonate Using Tensile Deformation

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ABSTRACT: The studies on photoplastic effect of polycarbonate has helped significantly in understanding the elastoplastic behavior of polycarbonate. When a plastically deformed specimen (polcarbonate) is suddenly illuminated with light of proper wavelength, a decrease in flow stress is observed, deformation leads to the softening, of specimen, i.e., to the negative photoplastic effect obtained at room temperature. On switching off, deformation stress reaches its level in the dark. The studies on the negative photoplastic effect mechanism can offer ways to control the properties of photoelectronic devices. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2703–2707, 2003

INTRODUCTION

The photoplastic effect (PPE) is the phenomenon in which the plastic flow stress of a material is altered by the absorption of light. Both positive (hardening) as in most II–VI compounds[1] and negative (softening) as in GaAs[2] photoplastic effects have been reported. The phenomenon of photoplastic effect is also known as a photomechanical effect.

Polycarbonate has been used as a model material in photoplasticity by several researchers.[3,4–8] The resulting studies were limited by the appearance of Luder's bands. Brinson[4] has developed a stress-optic law by simultaneous measurement of thickness changes and birefringence in a region of gross plastic yielding where the polycarbonate specimen is stressed beyond the yield point, defined as the point of Luder's band formation. He has also used the residual birefringence to describe the ductile fracture of a polycarbonate plate in pure bending.[5] Time-dependent viscoelastic and plastic flow domains in polycarbonate has been studied.[6] The time dependence of a delayed fracture in polycarbonate has been investigated.[7] Tougui et al.[8] have shown that in polycarbonate optical-creep behavior obeys the creep power law. They therefore suggested a nonlinear photoviscoelastic theory inspired by the nonlinear viscoelastic theory formulated by Shapery.[9]

The radiation-induced chemical changes that occur in polymeric materials have received considerable attention over recent decades. They can be subdivided into the changes arising from nonionizing radiation (photolysis) and those caused by ionizing radiation. Photolysis can provide useful property changes, and is used in fields such as lithography, but these effects are limited to thin films. The absorption of ultraviolet or visible light by matter is represented by the following relationship

$$M + h\nu \rightarrow M^*$$
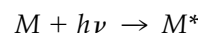
where $h\nu$ equals the energy of photon absorbed, and (*) denotes an excited state. The photolysis process is controlled because the only energy that can be absorbed is that which corresponds to the different possible energy states of the molecule, and these are regulated by quantum mechanical considerations. Furthermore, all the energy of the photon must be transferred to the molecule in the excitation process.

The irradiation of polymers in the solid state produces excited species (primarily free radicals), some of which have very long half-lives. Due to high viscosity of the medium, recombination (which would otherwise rapidly eliminate these radicals) is hindered. This is particularly true if polymer is in a glassy state, below T_g or if radicals are trapped in a crystalline phase.[10]

The object of the present investigation was to continue development of method for elastoplastic stress analysis using the optical effects of transparent polymeric materials.

EXPERIMENTAL

A smooth strip specimen cut out from a uniform transparent commercially polycarbonate plane sheet of thickness 3 mm. The prismatic specimen whose dimension are shown in Figure 1. has a cross section of
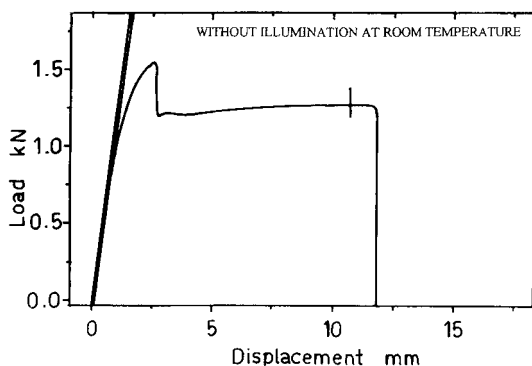
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Figure 1 Load–elongation curve without illumination at a crosshead speed of 1 mm/min.

8×30 mm². The polymer sheet was supplied by M/s Chemical Agencies, Mumbai.

Low strain rate tensile test from 2 mm/min to 1 mm/min were performed on a commercial Instron tester—4467-30 KN, with a built-in load cell and chart recorder, capable of controlled head rate. Load and strain were measured by a load cell and an extensometer, respectively. The strip tensile specimens were stretched uniformly up to failure under a constant strain rate and at a constant room temperature. A typical load elongation variation is recorded by extending a specimen in an Instron testing machine with a crosshead rate of 1 mm/min. This shows the load elongation curves without illumination.

To study the photoplastic effect, the influence of illumination on the specimen was observed. The present experiments were carried out as follows.

Specimens of dimension cut out from the same sheet of polycarbonate were deformed in tension at a constant strain rate at room temperature. While the specimen is deforming, a 100 watt mercury bulb is used (at a fixed distance) to illuminate the specimen. The light source is turned "ON" for a short period of time, roughly 1 min to 2 min, and then off.

The same procedure was adopted for different exposure times of 30, 45, and 60 s at different intensities of light.

RESULTS AND DISCUSSION

Stress–strain curve of polycarbonate without hlumination

The deformation from the origin upto the point (A) in Figure 1 has been associated with the bending or stretching of the interatomic bonds between atoms of the polymer molecules. This type of deformation is nearly instantaneous. It is also recoverable, and there is no permanent displacement of the molecules with respect to each other. The deformations that occur between point (A) and (B) of Figure 1 have been associated with the straightening out of a kinked or coiled portion of the molecular chains. This can occur without intermolecular slippage.

The extension of specimens to a level greater than the elastic limit may cause the displacement of molecules with respect to each other. This situation is similar to that of Newtonian flow of a liquid. There is no tendency for these displaced molecules to slip back to their original positions; hence, such deformations are not recoverable. Unlike the behavior of metals, plastic deformation is not a consequence of dislocation movement in polymers. Instead, viscous flow, or sliding of the chains past one another under load, causes permanent deformation in polymers. The drop in the stress beyond the yield point can be explained by the chain morphology. Initially, the chains may be highly tangled and intertwined. When the stress is sufficiently high, the chains begin to entangle and straighten. As the chains straighten, necking also starts, permitting continued sliding of the chains at a lesser stress. However, eventually the chains become almost parallel and close together; stronger Van der Waals bonding between the more closely aligned chains requires higher stresses to continue the deformation process.

Again, the ability of the stress to cause chain slippage is related to time. If the stress is applied slowly, the chains will be able to slide more easily past one another; if the stress is applied rapidly, sliding may be minimized, and the polycarbonate may tend to behave like a brittle material.

With illumination

Influence of light pulse duration

Figure 2(a), (b), and (c), shows the stress–strain curves at room temperature when specimens are illuminated with same intensity of light (i.e., 20.4 Arb. Unit) for different exposure times of 60, 45, and 30 s, respectively. It is evident from the curves that saturation in the stress level occur for 60- and 45-s exposure times when the light was switched "ON" and "OFF." For 30-s exposure time, saturation in the stress level is not observed.

Figure 3 shows the relation between exposure times and magnitude of photoplastic effect ($\Delta \sigma_p$) at two different intensities. It is observed that $\Delta \sigma_p$ increases with increasing exposure times for both the intensities.

Intensity effect

At an intensity of 20.4 Arb. unit, when the light was switched "ON," exponential decay in flow stress occurs and when the light was "OFF," stress linearly increases and acquires its normal level. At this intensity saturation in the stress level occurrs when the light pulse duration is 60 and 45 s. For 30 s, saturation level does not occur. Figure 2(a), (b), and (c) shows the
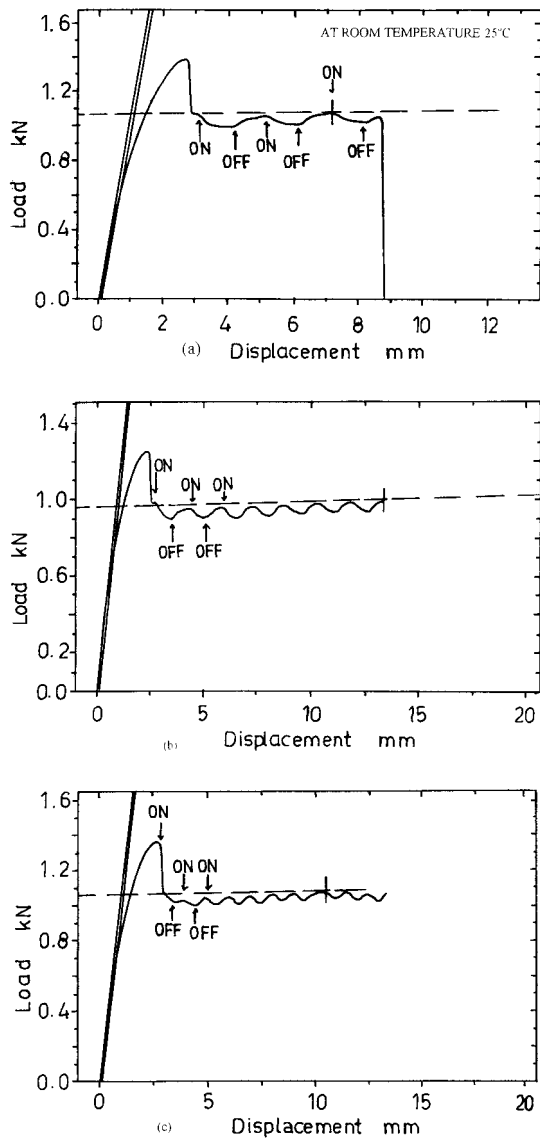
Figure 2 (a) Load–elongation curve at an intensity of 20.4 (Arb). for 60-s exposure time, and At a crosshead speed of 1 mm/min. (b) Load–elongation curve at an intensity of 20.4 (Arb), for 45-s exposure time, and at a crosshead speed of 1 mm/min. (c) Load–elongation curve at an intensity of 20.4 (Arb), for 30-s exposure time, and At a crosshead speed of 1 mm/min.

PPE at this intensity for 60-, 45-, and 30-s pulse duration, respectively.

Figure 4(a) and (b) shows the PPE at an intensity of 6.9 Arb. unit, for 60-s and 45-s pulse durations, respectively. At this intensity when light was switch ON for 60 s. then a decrement in flow stress occurs, and when switched "OFF" for 60 s, stress acquires its normal value shown in Figure 4(a); however, the effect is small compared to the intensity of the 20.4 Arb unit. Figure 4(b) represents the load–elongation curve for a 45-s pulse duration in which initially when the light is switched "ON," flow stress decreases, and when switched "OFF," decrement in flow stress again oc-
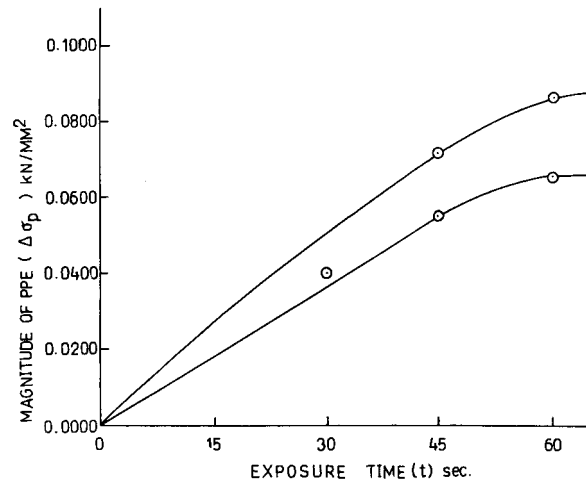

Figure 3 Variation of $\Delta\sigma_p$ with exposure time, at an intensity of 20.4 (Arb), and at an intensity of 6.9 (Arb).

currs. Further, when the light is on for 45 s, a decrement of stress occurs, and thereafter, when the light is off, a flow stress increases and acquires its normal value, and this process continues up to failure.

Figure 5(a) and (b) shows the PPE at the intensity 2.5 Arb. unit for 60- and 45-s, pulse duration, respectively. It is evident from the curves that PPE effect is small compared to intensity at (a) and (b). In this case,
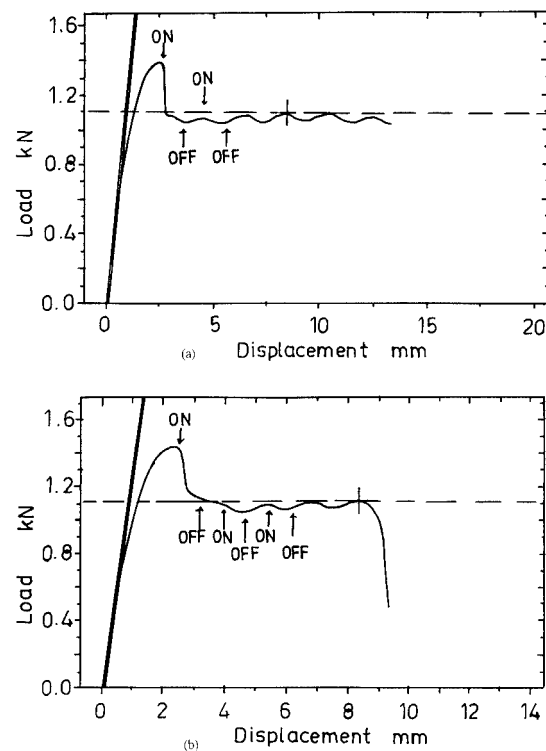

Figure 4 (a) Load–elongation curve at an intensity of 6.9 (Arb), for 60-s exposure time, and at a crosshead speed of 1 mm/min. (b) Load–elongation curve at an intensity of 6.9 (Arb), for 45-s exposure time, and at a crosshead speed of 1 mm/min.
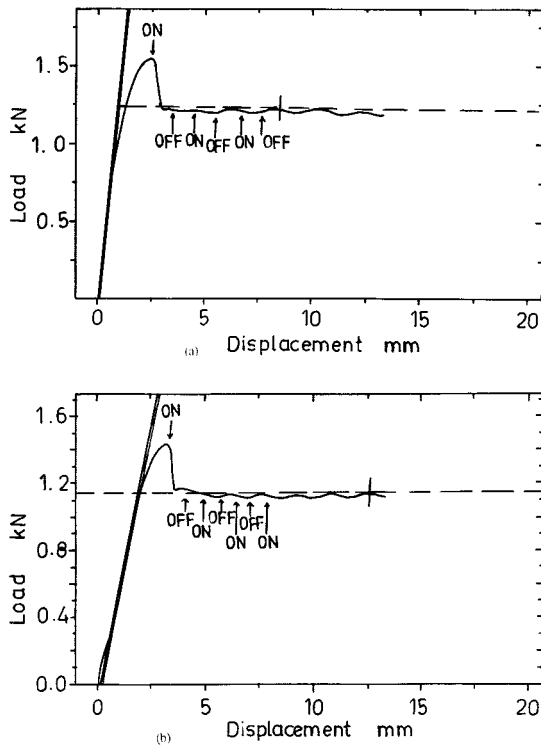
Figure 5 (a) Load–elongation curve at an intensity of 2.5 (Arb), for 60-s exposure time, at a crosshead speed of 1 mm/min. (b) Load–elongation curve at an intensity of 2.5 (Arb), for 45-s exposure time, at a crosshead speed of 1 mm/min.

initially, for both pulse durations of 60 and 45 s, when the light is switched ON and OFF, a decrement of flow stress occurs. Next, when the light is switched ON, a decrement of flow stress takes place, and thereafter, when the light is OFF, an increment of flow stress occurs and acquires its normal value. This process continues up to failure.

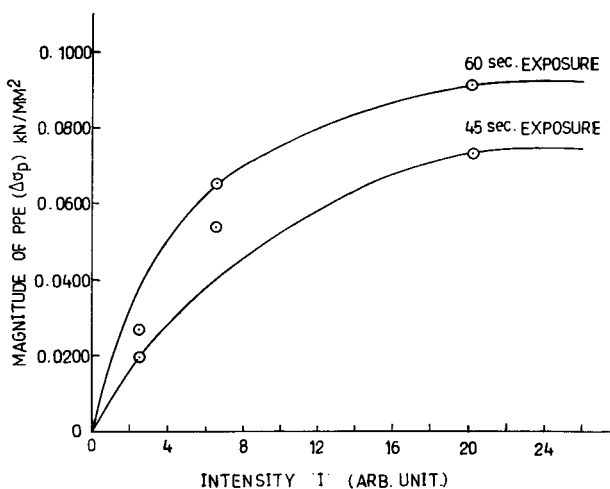Figure 6 shows the relation between magnitude of

Figure 6 Variation of $\Delta\sigma_p$ with intensity of time.
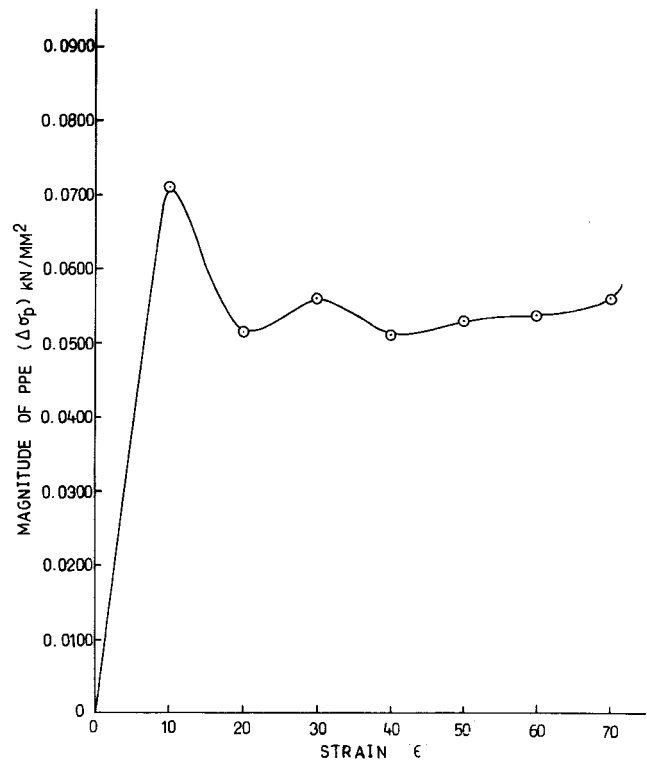

Figure 7 Variation of $\Delta\sigma_p$ with strain level.

photoplastic effect $\Delta\sigma_p$ and intensity of light for two fixed exposure times—60 and 45 s. It is evident from the curves that $\Delta\sigma_p$ increases with increasing the intensity of light, and has a maximum for a long exposure time.

Figure 7 shows the relation between $\Delta\sigma_p$ and strain ε. It reveals that the maximum value of $\Delta\sigma_p$ occurs at a small strain level, i.e., near the yield point. As the strain increases, it becomes small, and near the fracture region its value again increases.

Strain rate effect

Figure 8(a) represents the load–elongation curve of polycarbonate at a crosshead speed of 0.2 mm/min without illumination, and Figure 8(b) and (c) represents the curves on illuminating the specimen at the crosshead speed of 0.2 mm/min. Figure 8(d) shows the illumination curve at a crosshead speed of 0.8 mm/min. On comparing these curves we observe that at low strain rate the photoplastic phenomena is more pronounced.

The PPE can be explained on the basis of the following mechanism. When stress exceeds the yield strength, the polycarbonate specimen experiences plastic deformation as a consequence of viscous flow or sliding of the chain past one another under load, causing permanent deformation. When the stress is sufficiently high, the chains begin to untangle and straighten. As the chain straightens, necking also occurs, permitting continued sliding of
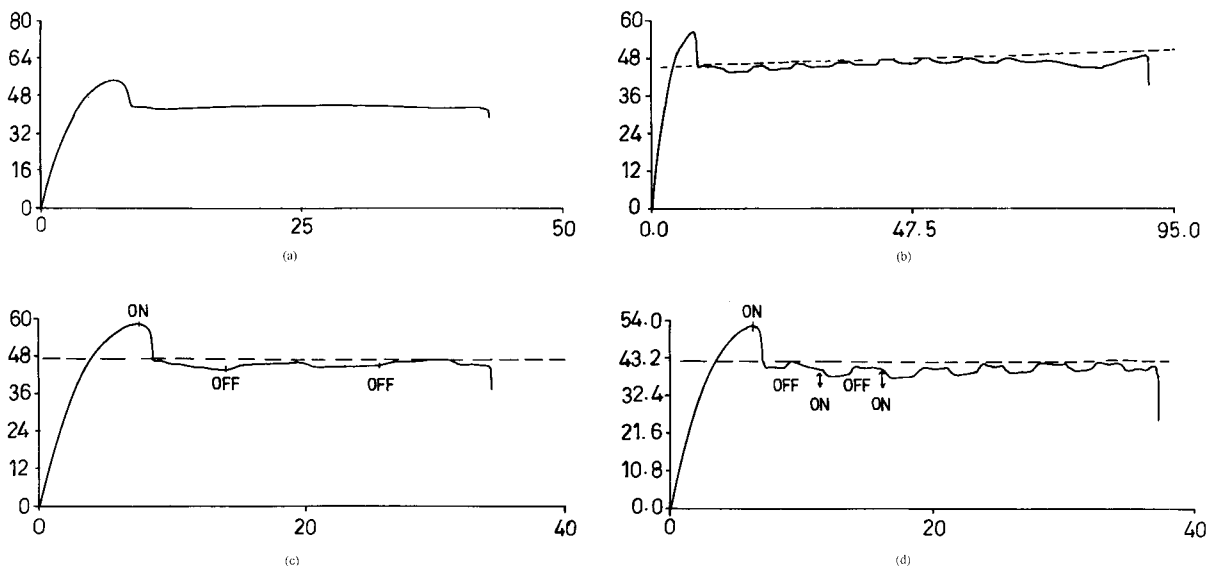
Figure 8 (a) Stress–strain curve of polycarbonate without illumination at a crosshead speed 0.2 mm/min. (b) Stress–strain curve at an intensity of 15.6 Arb Unit, for 10-min exposure time, at a crosshead speed of 0.2 mm/min. (c) Stress–strain curve at an intensity 62.5 Arb Unit, for 10-min exposure time, at a crosshead speed of 0.2 mm/min. (d) Stress–strain curve at an intensity 40 Arb Unit, for 10-min exposure time, at a crosshead speed of 0.08 mm/min.

chains at a lesser stress. This is the favorable situation for absorption of light.

When the polycarbonate specimen is illuminated then during the absorption of light, free electrons and holes are generated. The nonradiative recombination between electron and hole due to high viscosity at room temperature may cause local heating, and subsequently, the viscosity of polycarbonate decreases and the stress causing adjacent chains to slide is decreased, and the hardness of the polymer may decrease. This gives rise to negative photoplastic effect.

Apart from this slow deformation of polymer between the melting, glass transition temperature may promote crystallization by straightening the chains and bringing them into a parallel structure. Specimen is illuminated at this stage of crystallization at which the ratio of crystalline region increases compared to the amorphous region. Because irradiation affects the amorphous part by crosslinking and the crystalline part by scissoning, in this case, due to an increase in the crystalline part, scissoning supresses the crosslinking, and the resultant effect will be the decrease in the stress level of the specimen.

CONCLUSION

During the absorption of light, electrons and holes are generated. The nonradiative recombination between electrons and holes may cause local heating, and subsequently, the hardness of the polycarbonate decreases. This gives rise to a negative photoplastic effect. When the polycarbonate is deformed at a slow rate, an isothermal process may take place, and thus the appearance of a positive and negative photoplastic effect will depend on the temperature of the sample. At room temperature, a negative photoplastic effect is observed.

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