

Temperature dependence of the photo-plastic effect in polycarbonate

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The transparent polycarbonate specimens were illuminated with light of suitable wavelength. The magnitude of the photoplastic effect has been detected and found to be strongly temperature dependent in the range 25-100°C. At low temperature, it shows negative photoplastic effect whereas at high temperature it shows positive photoplastic effect. This observation suggests a way to distinguish among several theories of photoplasticity.

[Keywords: Photoplastic effect, Polycarbonate]

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1 Introduction

Now-a-days, researchers are very much interested in the non-linear character of materials. The photoplastic method using transparent polymers is a very reliable method to simulate the elastoplastic behaviour of prototype materials. Hetenyi¹ was first to report such studies on photoplasticity. Later on, the same concept was developed for a wider exploitation in the field of stress analysis^{2,3-5}. The optical and mechanical behaviour of polymer depends basically on the viscous character of these materials. Therefore, the analysis related to the influence of viscosity in the opto-mechanical state of polymeric materials is needed.

At elevated temperature polymer chains exhibit rapid micro-brownian motion, which confers flexibility and fluidity upon macroscopic specimens. Upon cooling, thermoplastic polymers can be hardened by two distinct mechanism: crystallization and veritification. At high temperatures, the bonds are very weak and viscous flow occurs easily at a little or no applied stress. At very high temperature (150°C), the polymer burns or chars. This temperature T_d , the degradation temperature, limits the usefulness of the polymer and represents the upper temperature at which the polymer can be formed into a useful shape. An important feature of viscoelastic materials is the similarity between the strain increments at a given strain rate and the levels of temperature, that is, the behaviour of viscoelastic materials at high tempera-

ture and high strain rates is similar to that at low temperature and low strain rates.

The primary effect of crystallinity on the electrical and optical properties is associated with the changes in dielectric constant and refractive index arising from the difference in density between the crystalline and amorphous regions. In the case of visible light, this difference leads to scattering, which may be large if the regions responsible (crystallites or lamellae, and spherulites) are significant in size compared to the wavelength of light. As the degree of crystallinity decreases with temperature approaching to melting temperature stiffness and yield stress decreases correspondingly. These factors often sets limit on the temperature at which a polymer is useful for mechanical purpose.

The interactions of electromagnetic radiation with polymers involve, at the most, the cooperative movement of small groups of atoms. The crystalline melting point is usually taken to be independent of molecular weight in the polymer range.

Polymers⁶⁻⁹ are sensitive towards temperature and various types of thermal pre-treatment and so also are polycarbonates. Polymers are found to have degraded and also developed several properties after such treatment. The changes in the mechanical properties after the above treatment are of considerable importance. The effect of temperature on the photoplastic effect (PPE) of the polycarbonate has been dealt with in the present study. It is expected that the effect of

temperature on the PPE of the polycarbonate will provide useful information regarding instantaneous changes in polymeric chain flexibility.

2 Experimental Details

A dumb-bell shaped specimens of $6 \times 2.5 \times 30$ mm dimensions were cut from a uniform transparent polycarbonate sheet supplied by M/s Chemical Agencies Bombay. The mechanical measurements were conducted in tension on an Instron testing machine (model 4467) at VRCE, Nagpur, capable of controlled head rate. Load and strain were measured by a load cell and an extensometer respectively. The cross-head speed used was 1 mm/min, providing a strain rate of 10^{-4} s. A temperature chamber with quartz window was used in the experiments that covered a temperature region from 300-500 K. The specimens were stretched uniformly under a constant strain rate and at a constant temperature

To obtain temperature dependence of PPE the sample was first loaded under a constant temperature without illumination until plastic deformation begins. It was then illuminated by a 100W condensed mercury bulb at distance of 75 mm from the specimen and the deformation was allowed to proceed under illumination at a constant machine rate until fracture occurs. The same procedure was adopted for different temperatures of 25, 40, 50, and 70°C at the same strain rate, same intensity and same exposure time. In this experiment the specimens were kept inside the temperature chamber whose temperature was controlled within the range of $\pm 1^\circ\text{C}$, so that the temperature of the specimen is not affected significantly.

3 Results and Discussion

Without illumination—Fig. 1(a) shows the load-elongation curve for polycarbonate at room temperature and Fig. 1(b) shows the load-elongation curve for polycarbonate specimen at 100°C. The temperature of 100°C, reveals that the crystallinity decreases at high temperature and both stiffness and yield stress decreases. Large extension without permanent deformation occurs. The modulus of elasticity also decreases, in the present investigation its value at room temperature (25°C) is $0.8/\text{A}^2$ and at 100°C, its value comes out to be $0.02/\text{A}^2$. At high temperature bonds are weak and viscous flow occurs easily at a small applied load, viscosity of the polycarbonate decreases.

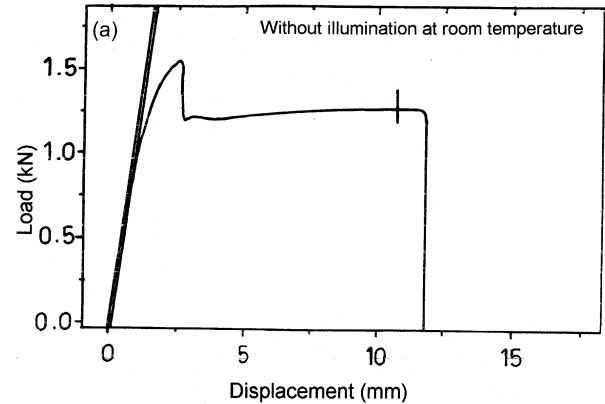


Fig. 1(a)—Load-elongation curve without illumination. At cross-head speed 1 mm/min

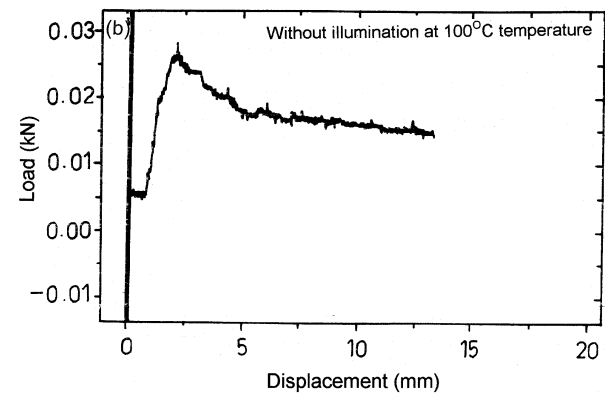


Fig. 1(b)—Load-elongation curve of polycarbonate without illumination at temperature 100°C. At cross-head speed 1 mm/min

With illumination—The present experiments are prompted by the following observation: While a specimen of polycarbonate is being strained plastically, at 25°C and illuminated with light (100 W condensed mercury bulb) then a decrease in the flow stress is observed. If the light was turned OFF, the flow stress returns to its normal level in dark i.e. a Negative Photoplastic Effect is observed. This effect can be observed many times on switching ON and OFF. A typical stress strain curve at room temperature is shown in Fig. 2(a) where the specimen is illuminated repeatedly by ON and OFF.

At 40°C, initially the stress decreases when light was ON for 45 s and reaches its normal value when light was turned OFF for 45 s. When the strain is high the effect on stress when light is ON and OFF have the same effect i.e. when the light is ON or OFF, slight increment and then decrement in stress occurs as shown in Fig. 2(b). This reveals that initially at this temperature a negative photoplastic effect (NPPE) is observed.

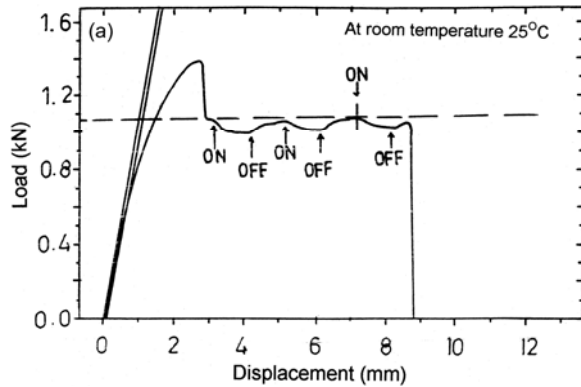


Fig. 2(a)—Load-elongation curve at 25°C room temperature. At intensity 20.4 (Arb) for 60 sec exposure time, at cross-head speed 1 mm/min

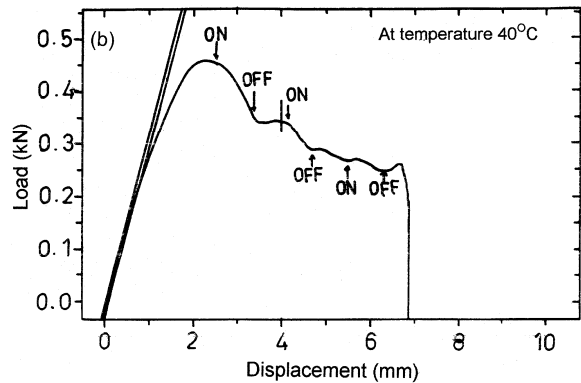


Fig. 2(b)—Load-elongation curve at 40°C temperature for 45 sec exposure time, at intensity 21.5 Arb unit. At cross-head speed 1 mm/min

At 50°C, initially, when light is ON for 60 s, the flow stress decreases and occupies its normal level when light is turned OFF i.e. NPPE is observed. In the middle of the curve when light is OFF, stress increases and suddenly decreases to its normal level. When light is ON decrement in stress does not occur but remains almost constant. As soon as plastic strain increases, reverse effect occurs on illumination. When light is ON an increase in flow stress occurs and when light is OFF stress slightly increases and suddenly reaches to its normal value. i.e. a positive photoplastic effect is observed as shown in Fig. 2(c). This is the critical temperature at which a transition from negative photoplastic effect to positive photoplastic effect is observed.

At 70°C, the stress increases when light is switched ON for 45 s and decreases to its normal level when light is OFF for 45 s i.e. at this temperature positive PPE is observed as shown in Fig. 2(d). It is observed that increase in the flow stress occurs when light is

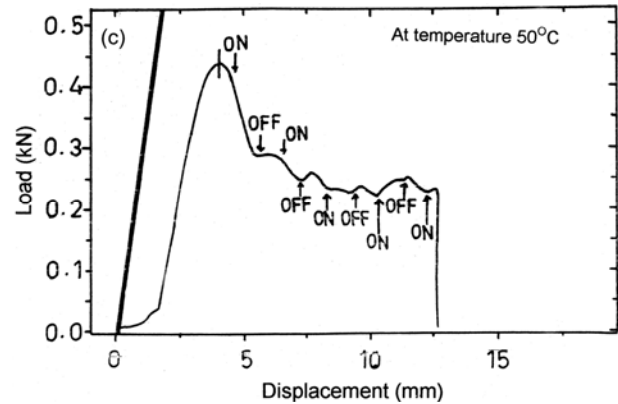


Fig. 2(c)—Load-elongation curve at 50°C temperature for 60 sec exposure time, at intensity 21.5 Arb unit. At cross-head speed 1 mm/min

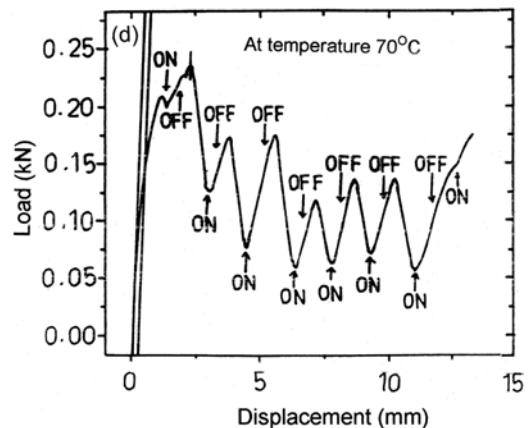


Fig. 2(d)—Load-elongation curve at 70°C temperature for 45 sec exposure time, at intensity 21.5 Arb unit. At cross-head speed 1 mm/min

ON, this increase in flow stress continues in the dark (when light is turned off) during a time (duration of after effect), reaching a certain value (corresponding to the positive PPE $\Delta\sigma_p$) and then decreases rapidly. This effect is called after effect, and its value increases on increasing plastic strain.

At 100°C, a steep rise in flow stress occurs when light is switched ON for 45 s and decrement of stress to its normal level occurs when light is turned OFF for 45 s. At this temperature also a positive PPE is observed as shown in Fig. 2(e). At this temperature an 'after effect' is also observed. The stress continues to increase in the dark during the time reaching a certain value (corresponding to positive PPE) and then decreases rapidly to its normal level. The amount of 'after effect' initially increases and at the middle of

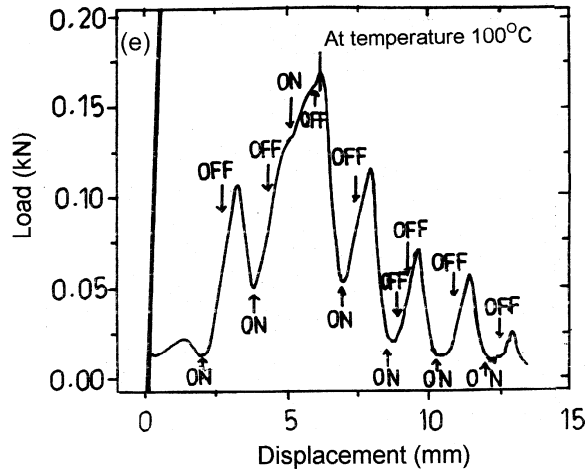


Fig. 2(e)—Load-elongation curve at 100°C temperature for 45 s exposure time, at intensity 21.5 Arb unit; at cross-head speed 1 mm/min

the curve it becomes maximum and again its value gradually decreases.

Fig. 3 shows the change in the magnitude of the photoplastic effect of polycarbonate with temperature. In this curve it is observed that the photoplastic effect varies from negative to positive as the temperature increases. At room temperature and upto 50°C, it shows negative photoplastic effect and above 50°C, it shows positive photoplastic effect. It can, therefore, be concluded that photoplastic phenomena in polycarbonate is temperature-dependent.

At high temperatures the bonds are weak, and viscous flow occurs easily at little or no applied stress i.e. viscosity of polycarbonate decreases. The light irradiation may enhance the production of ions and free charge carriers in the polycarbonate; due to low viscosity, the Coulomb interaction between ions and free charge carriers dominates the electron-hole recombination¹⁰ and increases the viscosity of the polycarbonate; the stress causing adjacent chains to slide is increased, the hardness of the polycarbonate increases. This gives rise to positive photoplastic effect.

At lower temperature, viscoelastic behaviour becomes pronounced as the stronger bonds make chain sliding more difficult and complex. During the illumination at low temperature, electron-hole recombination dominates the Coulomb charge interaction and decreases the viscosity of polycarbonate at room temperature, the resultant effect will be the negative photoplastic effect.

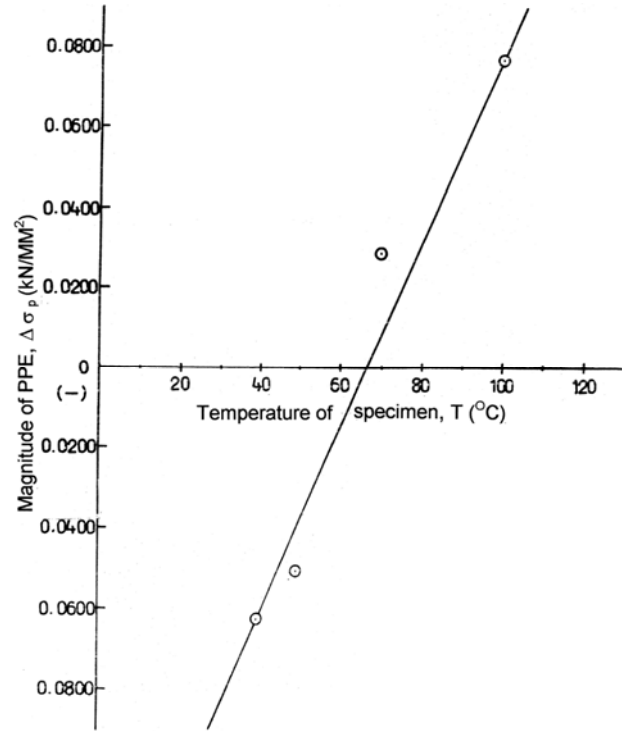


Fig. 3—Variation of $\Delta\sigma_p$ with temperature

This phenomena can also be explained in the manner, that the degree of crystallinity decreases with increasing temperature. The irradiation produces various degree of cross-linking and scissioning in the polycarbonate and thus exhibiting both the increase and decrease in the deformation level. Moreover, the cross-linking and scissioning occurs simultaneously, hence the relative ratio of them decides the deformation characteristic. At high temperature, the crystallinity decreases and the ratio of amorphous region increases as compared to the crystalline region. The irradiation affects the amorphous part by cross-linking and crystalline part by scissioning. Due to increase of amorphous region at high temperature, cross-linking dominates the scissioning and as a result the stress level of the specimen is increased.

4 Conclusions

The studies on photoplastic effect of polycarbonate has become interesting and it has helped significantly in understanding the elastoplastic behaviour of polycarbonate. During the absorption of light, the electrons and holes are generated. The non-radiative recombination between electrons and holes may cause local heating and subsequently the hardness of polycarbonate decreases. This gives rise to negative

photoplastic effect. On the other hand, the light irradiation may enhance the production of ions and free charge carriers in the polycarbonate, subsequently the coulomb interaction between ions and free charge carriers may increase hardness. This gives rise to positive photoplastic effect in polycarbonate.

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