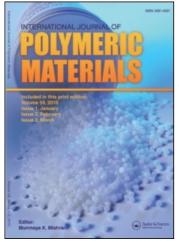
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The Effect of Dead Sea Water on the Mechanical Properties of Polycarbonate

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The work presented in this paper is an attempt to investigate the effect of aging in Dead Sea water on the mechanical properties of polycarbonate under different temperatures and strain rates. The mechanical properties as Young's modulus, yield stress and yield strain have been studied as a function of aging time. Other physical parameters such as the activation energy and the activation volume are estimated from the analysis of the obtained data using the Eyring theory of yielding. It was found that the mechanical behavior of polycarbonate is effected by aging in Dead Sea water where the effect of aging decreases with test temperature and disappears at high temperature.

KEY WORDS Polycarbonate, mechanical properties, aging, sea water.

1. INTRODUCTION

The chemical and physical aging is a very important phenomenon which has several concerns for many research groups to understand for example the effect of water on the physical and mechanical properties of polymers. It has been shown that water sorption can affect the surface and the bulk polymer properties. Many techniques were reported in literature to investigate the aging effects on polymers and their composites.¹⁻⁴ For example, the resistance to plastic deformation is an interesting approach to show the effect of water on the mechanical properties of polymers. Mechanical studies as fracture, fatigue, microhardness, and tensile tests have been largely used to study the influence of distilled, aqueous, and salt solutions on the stability and performance of many polymers and polymer composites. The process of water and aqueous solutions in some polymer adhesives works as plasticizers which cause volume changes in polymer matrix and thus decreasing the observed mechanical properties.⁵⁻⁹

The principal objective of this study is to investigate the effect of the distilled water and the salty Dead Sea water on the elastic and plastic deformation of polycarbonate polymer under different testing conditions of temperature, strain rate, and aging time. Following the yielding behavior as a function of aging time would be useful in detecting the effect of Dead Sea water on the mechanical properties of polycarbonate. Determination of some microscopic parameters as the activation stress volume and the activation energy may shed light on the influence of water on chemically aged polycarbonate. In previous studies we followed the effect of Dead Sea water on the electrical and dielectric properties of polycarbonate.¹⁰ As far as we know there is no any reports in literature deal with aging of polymers in Dead Sea water. The glassy polycarbonate polymer was chosen for the present study because it has good physical and engineering properties; and to reduce the effect of crystal-linity as a factor affects the aging behavior and the yielding process.

2. EXPERIMENTAL WORK

The polymer used in this work is a lexan polycarbonate sheet of 0.26 mm thickness provided by Dr. J. Starr of the General Electrical Company in USA. The polymer has a density of about 1.2 gm/cm³ and observed glass transition temperature of about 148°C.

Tensile specimens were cut from the lexan sheet using a cuttering machine. Part of these specimens was aged (treated) in distilled water and Dead Sea water. The aged specimens were weighted before and after aging for different aging times: 4, 10, 20, 30, 40, and 50 days. The immersed specimens were carefully cleaned, dried, and weighed by using a sensitive balance.

Tensile tests were done by holding the specimens in special grips built for this purpose. The specimens were aligned accurately with the tensile axis. Tensile tests were carried out using Instron machine model 1026 fitted with a heating chamber. A thermometer was used to read the temperature near the specimen of 1 cm gauge length. About a period of 20 minutes was allowed to elapse before the test was performed. The changes in the mass of aged specimen in Dead Sea water were determined by weighing measurements. Polarized microscopy technique was used to investigate the mode of deformation of polycarbonate.

3. RESULTS AND DISCUSSION

The Dead Sea or the "Salt Sea" which is located in the west of Jordan has extremely saline water of chemical contents¹¹ shown in Table I.

Sodium Chloride	7.8%
Potassium Chloride	1.21%
Magnesium Chloride	14.48%
Magnesium Bromide	0.48%
Calcium Chloride	3.75%
Water	72.28%

The chemical aging in polymeric materials can be defined as the gradual changes in their properties when exposed to solvents or humid atmospheres. Many effects were noticed due to chemical aging like degradation and oxidation result in some structural changes take place during specific chemical reactions. However, the structural developments are mainly due to movement of highly mobile alkali ions within the polymer surface.^{1,2,10}

Upon removal from Dead Sea water, the polycarbonate specimens did not show any visible changes especially after washing and drying. But when the samples were weighed before and after aging, some mass changes are observed. The weight percent change during water absorption was determined from the relation:

$$Wt\% = \frac{W(t) - W(0)}{W(0)} \times 100$$

where, Wt% is the weight percent change at time t, W(t) is the weight of the polymer sample after immersion in water for time t, and W(0) is the weight of dry polymer sample at zero time.

Figure 1 shows the weight gain as a function of aging time for both distilled and Dead Sea water. Experimental results show that weight gain is increased with increasing the aging time, and the specimen seems to be saturated after 40 days. Also, it was found that the amount of mass absorbed by sample aged in Dead Sea water is larger than that aged in distilled water. Values of the weight gain are very small and this fits the known fact that polycarbonate has low water absorption.¹² The fast initial gain may reflect the water diffusion into the sample surface and saturation in the polycarbonate by water.⁹ The increasing in the gain when the polymer is aged in Dead Sea water indicates that the amount of water sorption becomes larger in highly salted water. The rate gain (W%/t) was estimated and the results were plotted as a function of aging time as shown in Figure 2. The rate mass gain (W%/t) decreases sharply with time. This behavior fits the saturation condition and proves again the case of low water absorption during aging of polycarbonate.

Figure 3 shows the variation of Young's modulus with temperature at strain rate equals 1.6×10^{-2} sec⁻¹ using five types of polycarbonate samples (untreated, aged for 30 days and aged for 50 days) in both distilled water and Dead Sea water. Results show that at relatively low temperature, the values of the elastic modulus for aged samples are less than those of unaged ones, and these values decrease gradually with aging time. It is also shown that the amount of decreasing in the elastic modulus in case of aging in Dead Sea water is larger than that in case of aging in distilled water. For increasing temperature, the curves become closer and closer until they meet at high temperatures. This behavior gives an indication that the effect of aging becomes weaker with increasing temperature and nearly disappears at high temperatures. The temperature was fixed at room temperature and the variation of the Young's modulus is studied as a function of aging time as shown in Figure 4. It is clear from the two curves obtained for distilled and Dead Sea water that with increasing the aging time Young's modulus decreases gradually and saturates after 40 days of aging. It can be seen that the Dead Sea water may act as a plasticizer agent by lowering the elastic modulus.

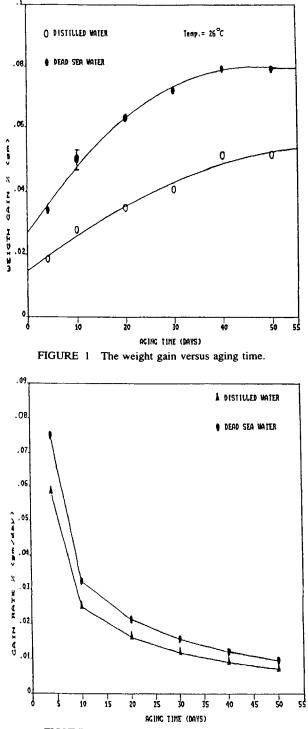


FIGURE 2 The gain rate versus aging time.

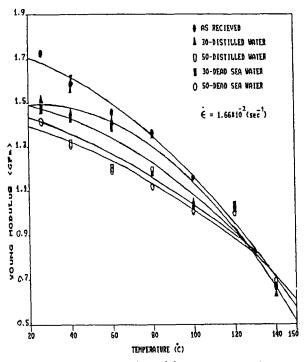


FIGURE 3 The Young's modulus versus temperature.

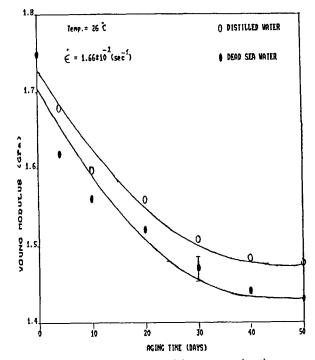


FIGURE 4 The Young's modulus versus aging time.

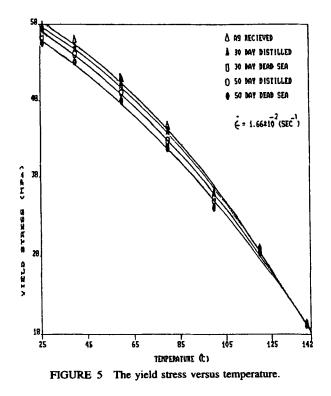


Figure 5 shows the variation of yield stress with temperature for five types of polycarbonate samples (untreated, aged for 30 days and aged for 50 days in both distilled and Dead Sea water). The obtained curves show the effect of chemical aging on the yield stress observed at relatively low temperatures, i.e., at room temperature. The values of the yield stress decreases from about 58.5 MPa for untreated samples to about 55 MPa for samples aged in Dead Sea water for 50 days. The dependence of yield stress on aging time is illustrated in Figure 6. These yield stress values are taken at room temperature and at strain rate equals $1.6 \times 10^{-2} \text{ sec}^{-1}$. The figure shows that the yield stress decreases gradually when aging time increases and reaches a saturation condition after 40 days of aging. Also, from the two obtained curves, we observe that the amount of decrease in the yield stress in case of distilled water is less than that in case of Dead Sea water.

The variation of the quantity (σ_y/T) as a function of log $\dot{\varepsilon}_y$ is shown in Figure 7 for aged samples. The results presented in this graph show that the ratio (σ_y/T) increases linearly with log $\dot{\varepsilon}_y$. Also, the above graph yields two important parameters, the activation energy (E_a) and the activation volume (V^*) . These parameters are calculated using the Eyring equation^{13,14}

$$\frac{\sigma_{y}}{T} = \frac{2}{V^{*}} \left[\left(\frac{E_{a}}{T} \right) + 2.303R \log \left(\frac{\dot{\varepsilon}_{y}}{\dot{\varepsilon}_{y}} \right) \right]$$

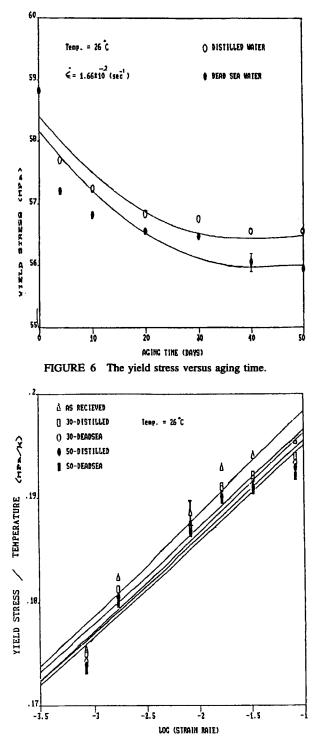


FIGURE 7 The (yield stress/temperature) versus logarithmic strain rate.

where E_a is the activation energy of the rate-process, σ_y is the yield stress, V^* is the activation volume which represents the volume of the polymer segment which has to move as a whole in order the plastic deformation takes place, R is the gas constant, and T is the absolute temperature. The derivative of the Eyring equation is

$$\frac{d(\sigma_y/T)}{d(\log \dot{\epsilon})} = \frac{2 \times 2.303 \times R}{V^*}$$

These equations give the values ov V^* and E_a . Figure 8 shows that the activation energy decreases with increasing the aging time. Figure 9 shows that the activation volume increases with the increase in the aging time. To explain these results, one must consider the molecular model of the flow mechanism suggested by Eyring¹³⁻¹⁵ which says that deformation takes place when molecules move from one stable position to another and his movement needs them to overcome a potential barrier under the yield stress. Now for aged samples, some water holes will diffuse into the surface of the polymer and increase the segmental motion which results in decreasing the potential barrier of at least the surface layers, and thus causes the activation energy to decrease also. The increase in the activation volume with aging time may be related to the increase in the number of the activated structural blocks which had to move as a whole under the plastic deformation during the yielding process.

A linear relation between the yield stress (σ_y) and the Young's modulus of some

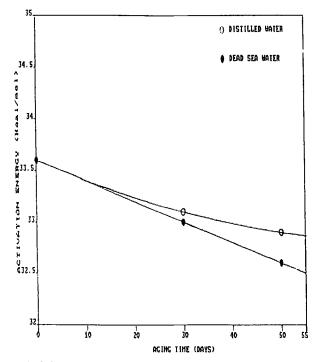


FIGURE 8 The activation energy versus the aging time.

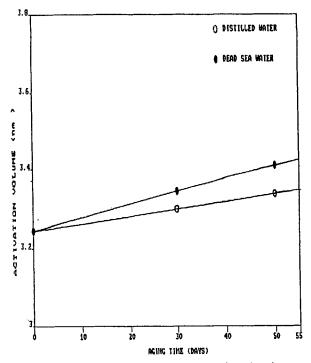


FIGURE 9 The activation volume versus the aging time.

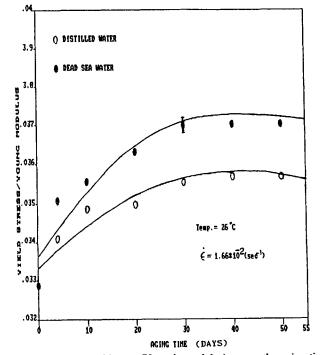


FIGURE 10 The (yield stress/Young's modulus) versus the aging time.

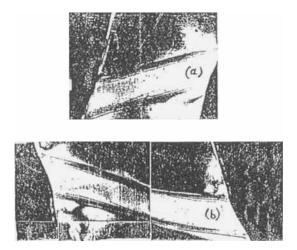


FIGURE 11 Optical photographs of shear bands observed under polarized light for deformed polycarbonate samples: (a) as received, (b) aged for 30 days in Dead Sea water.

glassy polymers reported by a number of workers^{18,19} gives a value for the ratio $(\sigma_y/E) \approx 0.02$ which is near to the value we obtained for the untreated PC samples. The ratio (σ_y/E) was calculated for treated samples and a nonlinear relation is presented between (σ_y/E) and aging time for both distilled and Dead Sea water tests as shown in Figure 10. This result can be discussed by the help of the two Figures 4 and 6 shown previously where the behavior of the elastic modulus and the yield stress with aging time were presented. One can observe that the rate of decreasing in the elastic modulus with aging time is greater than the rate of decreasing in the yield stress with aging time.

Figure 11 shows optical photographs taken under polarized light for deformed polycarbonate samples. The photographs show shear bands in the regions of plastic deformation observed for both aged and unaged polycarbonate samples. However, these photographs exhibit the mode of deformation during yielding which takes place by shear banding or slip-shearing process.^{13,16,17} Examination of the aged samples by the SEM did not show surface crazes or degradation.

4. CONCLUSION

The work presented in this communication covers some of the mechanical properties of unaged and aged polycarbonate samples in Dead Sea water. The yield behavior was studied at different temperatures and strain rates. Other parameters as the activation energy and the activation volume were estimated from the analysis of the mechanical data. From the obtained results the following conclusions can be drawn:

1. The polycarbonate samples show small increase in mass when immersed in Dead Sea water for different aging times and this mass gain saturates after 40 days.

2. The aging effect detected from the observed variation in the Young's modulus and yield stress is pronounced at room temperature, and it becomes much weaker at higher temperatures. 3. The activation parameters of the yielding process were determined using the Eyring theory. The activation energy showed slight decrease, and the activation volume showed slight increase with aging time.

4. The polarizing microscope study showed that the yielding mechanism of both unaged and aged polycarbonate samples is a slip-shearing process.

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