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THE EFFECT OF DEAD SEA WATER ON THE MECHANICAL PROPERTIES OF POLYCARBONATE

BY

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TO MY PARENTS

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ABSTRACT

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

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The work presented in this thesis 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 activition 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 affected by aging in Dead Sea water where the effect of aging decreases with increasing the test temperature and it becomes weak or vanishes at high temperatures.

CHAPTER ONE
INTRODUCTION

1.1 Mechanical Properties of Polymers :

The mechanical properties of high polymers are of interest in any application where they are used as structural materials. The use of plastics, rubber and fibers is determined primarily by their mechanical properties rather than by their chemical behavior because virtually all service conditions and the majority of end-use applications involve some degree of mechanical loading. Few straight forward measurements on a material give its elastic constants and plastic properties such as tensile strength, modulus, elongation and impact strength. These elastic constants as Poisson's ratio can be used by design engineers to calculate the deformation of any shape of body under any type of load [1,2,3]. It is found that mechanical properties of polymers are very sensitive to many physical factors like temperature, strain rate, structural morphology, and the surrounding environment. When a polymer is immersed in gases or liquids as vapor or water for different periods of time; this aging mechanism may modify the polymer properties in almost all aspects, especially the mechanical behavior.

1.2 Polymer, Definition :

A polymer consists of large molecules, each is built up by the repetition of small, simple chemical units forming huge molecules. In some cases repetition is linear, where a chain is built up from its links. In other cases the chains are branched or interconnected to form three - dimensional networks. The unique properties of polymers are attributed to their long chain structure, and the key physical properties are directly dependent on the molecular weight and molecular structure [4,5] .

1.3 Amorphous and Crystalline Polymers :

Amorphous or glassy polymers are defined as those polymers which do not crystallize even when cooled from the melt extremely slowly ; and only show a glass transition temperature when a property such as specific volume is plotted against temperature . Crystalline polymers are those

polymers whose molecules are arranged in an ordered manner and show a crystalline melting point as well as a glass transition temperature. It's worth to note that crystalline polymers are properly called semicrystalline because they are seen to be partly crystalline [6,7]. One can make sharp distinction between amorphous and semicrystalline polymers by using X-ray diffraction technique which is capable to distinguish ordered from disordered states. The amorphous materials produce only diffuse patterns that consist principally of few halos as shown in Fig .1a. In contrast, anisotropic semicrystalline substances yield diffraction patterns of few sharp circles as shown in Fig. 1b [8].

1.4 The Polycarbonate Polymer :

Polycarbonate is a tough , transparent, glassy polymer whose large bulky structure contains phenol groups in the main chain with only small groups as shown by Fig.2, so its generally called Bisphenol-A-polycarbonate [9]. The polycarbonate may be fabricated by all conventional thermoplastic processing operations, especially injection and extrusion molding. Extrusion produces films and sheets as those used in the present research work. The mechanical properties of polycarbonate at room temperature are in the same range as those of other thermoplastics at reduced temperatures [10]. Below their Tg, most amorphous polymers are stiff and brittle in tension, but the polycarbonate polymer is an exception . The stress - strain curve in uniaxial tension is typical of ductile material, consisting of an initial Hookean region followed by shear yielding and plastic deformation to a total breaking elongation of 120 % as shown in Fig .3 for the given Lexan samples. Extreme toughness, transparency, resistance to burning and maintenance of useful engineering properties over a temperature range from -200 to + 140 $^{\circ}$C are the outstanding features of

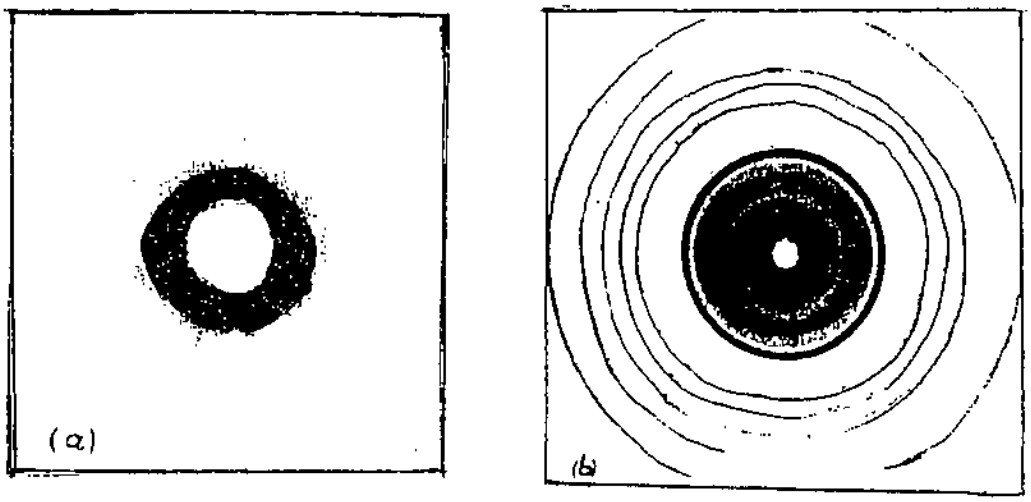


Fig. 1. X-Ray diffraction patterns of

(a) amorphous material (b) semicrystalline material [8]

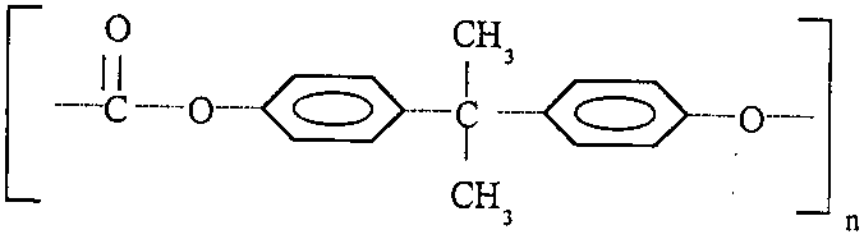


Fig. 2 Bisphenol - A - Polycarbonate [9]

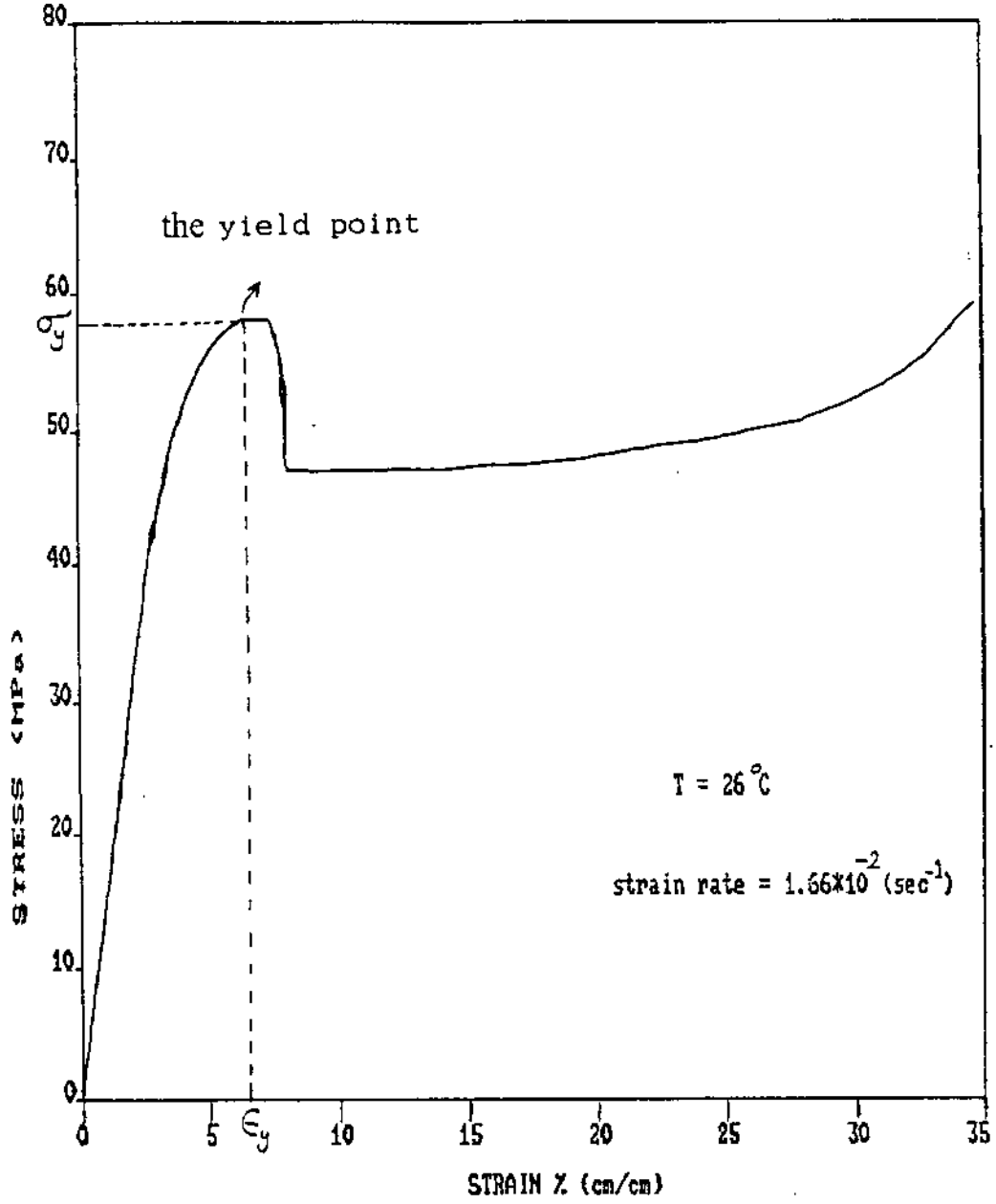


Fig. 3 Typical stress - strain curve of the given Lexan polycarbonate

polycarbonates; these properties qualify polycarbonates for bubble helmets, for astronauts; canopies for supersonic aircrafts; break- resistant windows for buildings, buses and trains. Combination of electrical insulation and mechanical housings for appliances; steam - sterilizable food - processing equipment; computer housing where its good mechanical, electrical, and fire - resistance properties are needed [9,10,11] .

1.5 The Dead Sea :

The Dead Sea or the " SALT SEA" is located in the west of Jordan. Bit by bit, the Dead Sea's water level is decreasing and rendering its water more saline . The Dead Sea location is shown in Fig . 4 on the Jordan map. The contents of the Dead Sea water [12] are shown in table (1).

Table (1) :

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

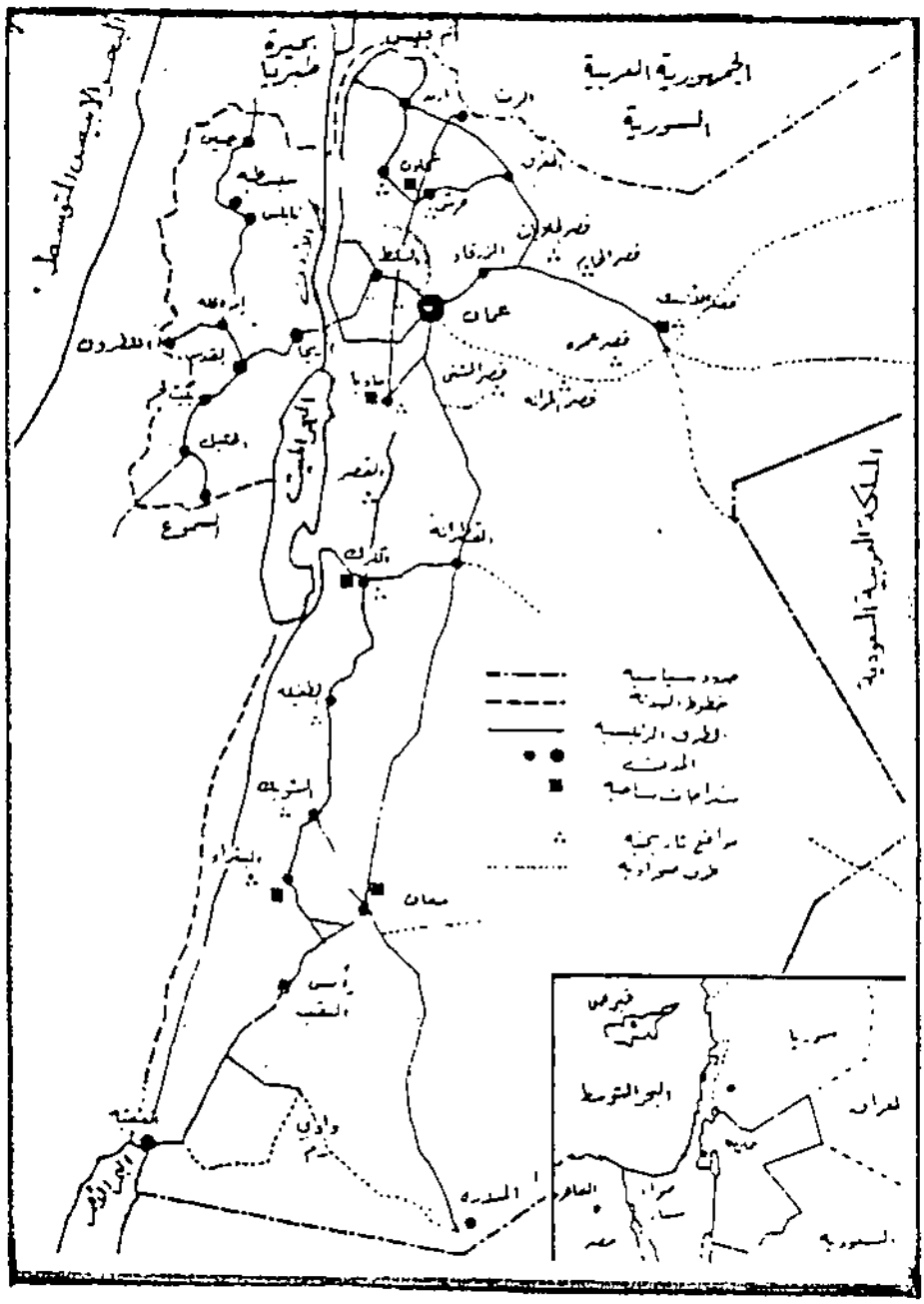


Fig. 4 The Dead Sea location on Jordan map

The estimated total amounts of these salts is over 43 billion tons. The exact origin has been disputed by different scientists throughout the years, but the most logic explanation is that these salts have been leached from surrounding mountains and valleys [12]. High concentration of minerals and complexes had given the Dead Sea water special chemical character which may causes some modifications on the physical and chemical properties of any substance. Therefore, we were convinced to investigate the effect of aging in Dead Sea water on the mechanical properties of plastic materials such as the polycarbonate polymer. The measured PH value for Dead Sea water is 6.58, which indicates that water is mainly alkaline.

1.6 Aging Phenomenon :

Aging is a weakly time - dependent process which causes gradual deterioration of the polymer properties due to chemical, thermal, and mechanical exposure under static conditions. Workers distinguished between three kinds of aging, chemical, physical and thermal aging [13] .

Physical Aging is a gradual continuation of the glass formation that sets in around the glass transition temperature. Therefore, it affects all those temperature - dependent properties which change drastically and abruptly at Tg. During aging , these properties change in the same direction as during cooling through the Tg range; the material becomes stiffer and more brittle [7,13] .

Thermal Aging of the polymer is defined as the gradual variation of the material properties when exposed to heat treatment for a period of time (as annealing of polycarbonate samples for 45 hour at temperature 120 $^{\circ}$C) and studying the thermal and mechanical changes [14] .

Chemical Aging: It is found that when a glassy surface of a polymer is exposed to a humid atmosphere, reactions take place at and below the glass

surface , these reactions result in chemical and structural changes, and are mainly due to the movement of the highly mobile alkali ions within the glass [15] . Thus the chemical aging of materials can be defined as the gradual changes in the properties of solids when exposed to any solvent or at least to humid atmosphere. Many effects are noticed from the chemical aging like degradation, photooxidation, or water sorption [13,14]. Water absorption has been reported to change the mechanical properties; blisters, disc cracks, and delaminations have been observed on several tested materials. Several studies have indicated that the weight gain curves for polymers immersed in water show a decrease after reaching a maximum [13,16,17] .

1.7 Degradation of Polymers :

Polymers are supposed to be comparatively resistant to chemical attack. However, exposure of pure polymers to the influence of climate or other chemical environments leads to deterioration in physical and chemical modifications which are grouped together under the polymer degradation [3]. When polymers are exposed to liquids or vapors, the main forms of degradation are swelling and dissolution. With swelling , the liquid or the solute diffuses into the polymer; the small solute molecules fit into the polymer surface and occupy some position among the polymer molecules. This forces the macromolecules apart such that specimen expands or swell, furthermore, the increase in chain separation causes a reduction of the secondary intermolecular bonding forces. As a consequence, the yield stress is depressed and the material becomes soften and more ductile. Dissolution occurs when the polymer is completely soluble in a solvent. Different polymers show wide variation in their susceptibility to degradation and these differences can be correlated to their chemical structure. However, the mechanism of degradation is complex and there is no complete explanation of it . In commercial products it is usual to incorporate small proportions of

various compounds, termed stabilizers, which are more or less effective in postponing degradation[14, 18,19] .

1.8 Previous Work :

There are many studies which have been carried out on the mechanical properties of polycarbonates. Those studies have concentrated on the effect of temperature, strain rate, and hydrostatic pressure on the yielding behavior of polycarbonates. One of the earliest workers was C.Bauwens [6,9,20]. In his studies on polycarbonates, the polymer had been shown to be a tough , rate dependent polymer in which the modulus and yield stress increase with increasing strain rate. Also, C. Bawens and J.C Bawens [21] have studied the viscoelastic behavior of three polycarbonate samples: original samples, annealed samples for 45 hour at 120 °C , and quenched samples (firstly annealed for 1 hour at 165 °C and then ice quenched). The results obtained show that the Young's modulus calculated seems to be the same for the three samples while the yield stress differs perceptibly. From all studies on mechanical properties of polycarbonate, it was found that a polycarbonate is a rate sensitive material and its data show a good fit to the rate process theory of deformation proposed by Eyring , whereby molecules move over a potential barrier in an activated process . A hardball model is presented as a first approximation to this activated process of deformation [9,21,22]. Zihlif and Goswami [23] studied the low-temperature deformation of polycarbonate samples in the temperature range of 88 to 295 °K. Compressive test results show that the yield stress of polycarbonate is temperature dependent and the yield stress increases sharply at low temperatures. A shear yielding process of glassy polymers was represented by Argon theory which assumes that the basic mechanism of local plastic deformation is performed by disclinations or kinks in the molecules which move under the action of an external stress

field. Vijayan, and Baer [11] have studied a model of shear yielding in edge-notched sheets of polycarbonate under slow tensile loading. Optical microscope techniques were used to characterize the flow lines through the specimen thickness of the plastically deformed regions; three modes were observed namely core yielding, line shear and intersecting shear. Zihlif and Ward [24,25] had studied the effect of hydrostatic pressure in tension and torsion on the mechanical properties of polycarbonate. In torsion tests it is found that the maximum shear stress increases with the applied pressure [25]; the same behavior was observed on other polymers such as polyethylene and polystyrene [24].

1.9 The Present Work :

In this thesis work the mechanical properties of polycarbonate sheets are investigated after being immersed in both distilled and Dead Sea water for different time intervals. Actually the main aim of this study is to know to what degree the mechanical behavior will be influenced by aging in both Dead Sea water and distilled water over ranges of temperatures and strain rates. More specifically , the work covers the following :

(i) The effect of aging process in distilled and Dead Sea water on the tensile properties of polycarbonate as the Young's modulus and yield stress.

(ii) The effect of temperature on the tensile properties of aged samples in distilled and Dead Sea water.

(iii) The effect of strain rate on the tensile properties of aged samples in distilled and Dead Sea water .

(iv) Analysis of the mechanical results and determination of the activation volume and the activation energy for the yielding process for both unaged and aged samples.

The present study is included in this thesis as :

- Chapter One: Introduction
- Chapter Two: Theoretical aspects
- Chapter Three: Experimental work
- Chapter Four: Results and discussion .
- Chapter Five: Conclusion and future work .

CHAPTER TWO
THEORETICAL ASPECTS

2.1 Yield Behavior of Isotropic Polymers :

Topic of yield goes in general under the mechanical property called "Plasticity". Yielding of solids is a physical phenomenon which follows the elastic deformations when they are subjected to external stress field. The yield point of a material is defined as the highest stress it can endure without manifesting a permanent stress upon unloading [24,26] .

2.2 Stress- Strain Curves :

Many of the mechanical characteristics of a material can be deduced from the tensile tests. In a tensile test we measure the extension of a polymer under increasing loads. It is more convenient to compare materials in terms of stresses and strains rather than loads and extensions of a particular specimen of a material [27]. The stress- strain curve of a certain polymer shows normally a drop in the applied load over a range of strain rates and temperatures. This observed stress drop is called the "Yield point". Tensile tests of polymers usually show a relatively sharp yield drop as shown in Fig. 2.1 a. But when the stress drop does not occur the yield point can then be defined as the point of intersection of two tangent lines of the stress-strain curve [24] as shown in Fig. 2.1b .

2.3 Definition of the Mechanical Parameters :

The most important parameters of the stress-strain curves are : the Young's modulus (E), the yield stress(σ_y) and the yield strain (ε_y). These parameters can be determined after the testing is performed [1,28]. Fig. 2.2 illustrates stretching of a polymer specimen under a tensile load. The original specimen has a length L_o and a cross - sectional area A_o. A tensile force F extends the length of the specimen by an amount ΔL to give a stretched length of L. The Young's modulus (E) of a material which obeys

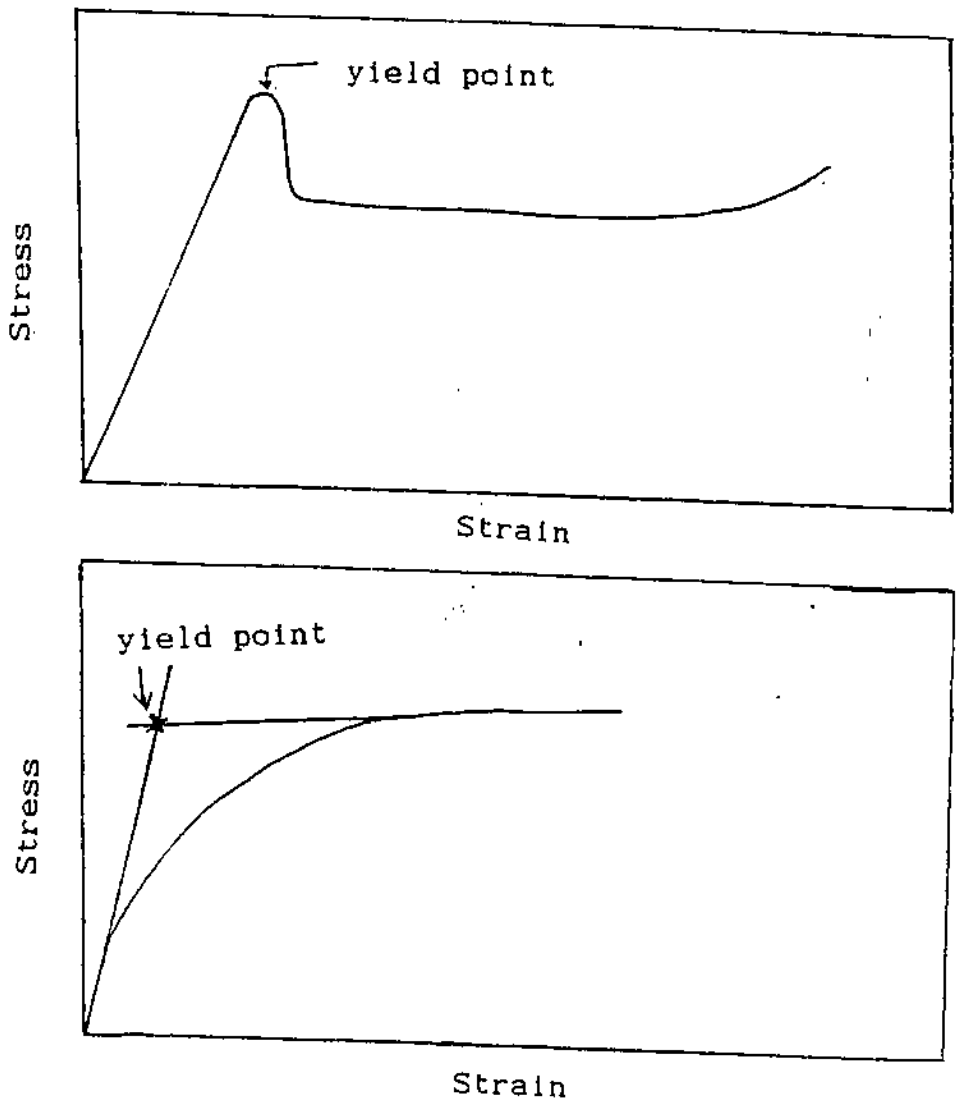


Fig. 2.1 Stress - strain curves of deformed polymers
The yield points are indicated by arrows.

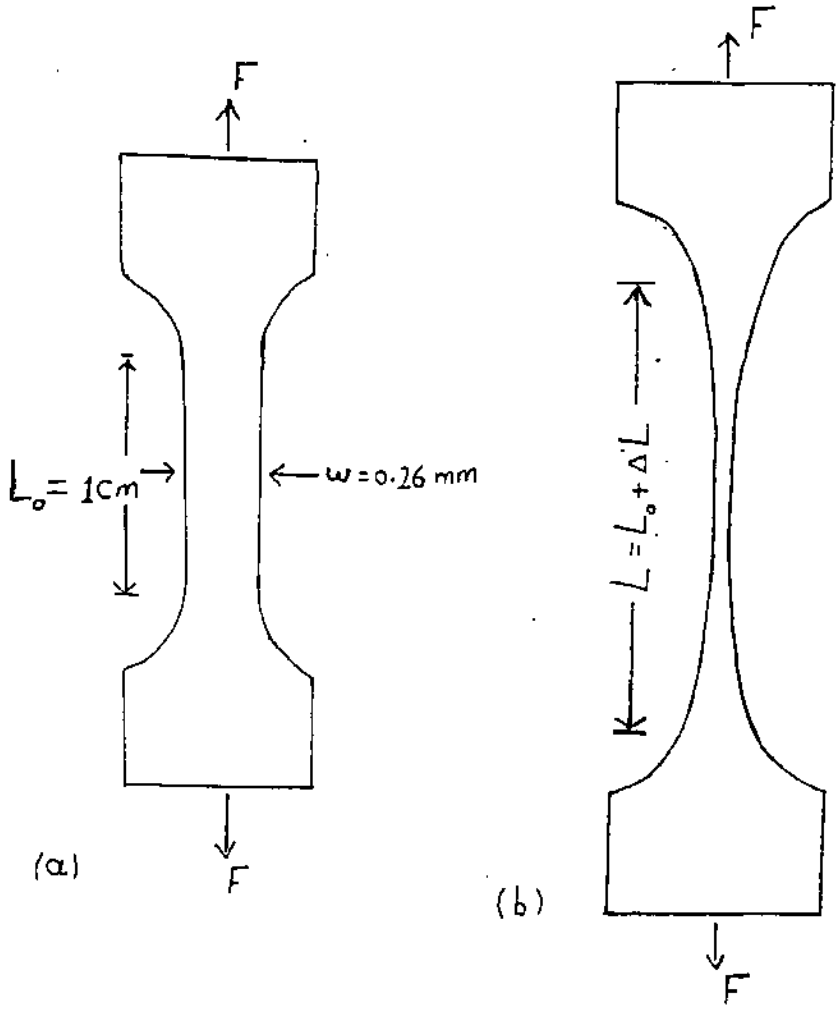


Fig. 2.2 (a) specimen design
(b) specimen after tensile deformation

Hook's law is defined as the ratio of the tensile stress to the tensile strain, or

$$E = \frac{\text{Tensile stress } \sigma}{\text{Tenisle Strain } \varepsilon} \quad \text{.....(2.1)}$$

where, the stress is define as the force per unit area.

Or

$$\sigma = \frac{F}{A} \quad \text{.....(2.2)}$$

and the strain is defined as :

$$\varepsilon = \frac{\Delta L}{L_o} \quad \text{.....(2.3)}$$

So equation 2.1 can be written as :

$$E = \frac{F/A}{\Delta L/L_o} = \frac{\sigma}{\varepsilon} \quad \text{.....(2.4)}$$

The stress at the yield point is the "yield stress" and the strain at the yield point is the "yield strain". The yield stress and yield strain can be determined from the stress drop as shown in Fig. 1.3 which illustrates a typical stress-strain curve of isotropic polycarbonate specimen at room temperature. The yield stress and the yield strain are denoted by σ_y and ε_y.

2.4 The Eyring Rate Theory

Many workers tried to understand the nature of yield behavior of polymers through the Eyring rate theory [6,9,22] which provides a basic for the present analysis. Its aim is to correlate the effects of temperature and strain rate on flow stress, and it seeks to do this from a molecular model of the flow mechanism [6]. The basic idea is a segment of polymer macromolecule must pass over an energy barrier in moving from one equilibrium position to another under load. Consider an atom oscillating in a potential barrier defined by the neighboring atoms along the line KK' as in Fig. 2.3a. If its frequency is ν, then the atom will approach the barrier

(between atoms (X and Y) ν times per second. The situation in (b) has a very small probability to occur. Once the atom reaches this barrier, it is soon rejected back except for the case when is supplied with a sufficient amount of energy (E_a) as shown in Fig. 2.4a. If , the atom will jump to position β as shown in Fig. 2.3c. The point introduced by Eyring [6,20] is that the application of stress τ modifies the barrier height as shown in Fig. 2.4b, so the energy required to facilitate the jump now is not (E_a) but ($E_a - \tau V^*$) and the mean time t of a forward jumping is

$$\bar{t} = \frac{1}{\nu}\exp\left[\frac{Ea - \tau\, v^*}{RT}\right] \qquad \text{.....(2.5)}$$

where, E_a is the activation energy of the rate process, τ is the applied 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. According to the Eyring assumption ($1/\bar{t}$) is proportional to the strain rate and the final form of Eyring equation becomes:

$$\dot{\varepsilon}_y = \dot{\varepsilon}_\circ \exp\left[-\left(\frac{Ea}{RT}\right)\right]\exp\left(\frac{\sigma y\, V^*}{2RT}\right) \qquad \text{.....(2.6)}$$

where σ_y is the axial yield stress in tensile test and related to the shear yield stress as $\tau = \sigma_y/2$. Equation (2.6) can be finally arranged as

$$\frac{\sigma_y}{T} = \frac{2}{V^*}\left[\left(\frac{E_a}{T}\right) + 2.303R\log\left(\frac{\dot{\varepsilon}_y}{\dot{\varepsilon}_\circ}\right)\right] \qquad \text{.....(2.7)}$$

This equation implies that a plot of (σ_y/T) against log $\dot{\varepsilon}_y$ for a series of temperatures will give a linear relationship [6,20,29,30] as shown in Fig.2.5 from which both V^* and E_a can be determined. From the equation (2.7), the slope is given by:

$$\frac{d(\sigma_y/T)}{d(\log\dot{\varepsilon}_y)} = \frac{2\times 2.303\times R}{V^*} \quad \text{.....(2.8)}$$

This equation gives the activation volume V*. E_a can be determined from relation (2.7) which implies that:

$$\left[\frac{\sigma_y}{T_1}\right]_a = \left[\frac{\sigma_y}{T_2}\right]_b \quad \text{.....(2.9)}$$

Where a and b are two points shown in Fig. 2.5. The relation (2.7) can be written as:

$$\frac{E_a}{T_1} + 2.303\ R\ \log(\dot{\varepsilon}_{y}^{T_1}) = \frac{E_a}{T_2} + 2.303\ R\ \log(\dot{\varepsilon}_{y}^{T_2}) \quad \text{.....(2.10)}$$

or

$$E_a = \frac{2.303R(\log\dot{\varepsilon}_{y}^{T_2} - \dot{\varepsilon}_{y}^{T_1})}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \quad \text{.....(2.11)}$$

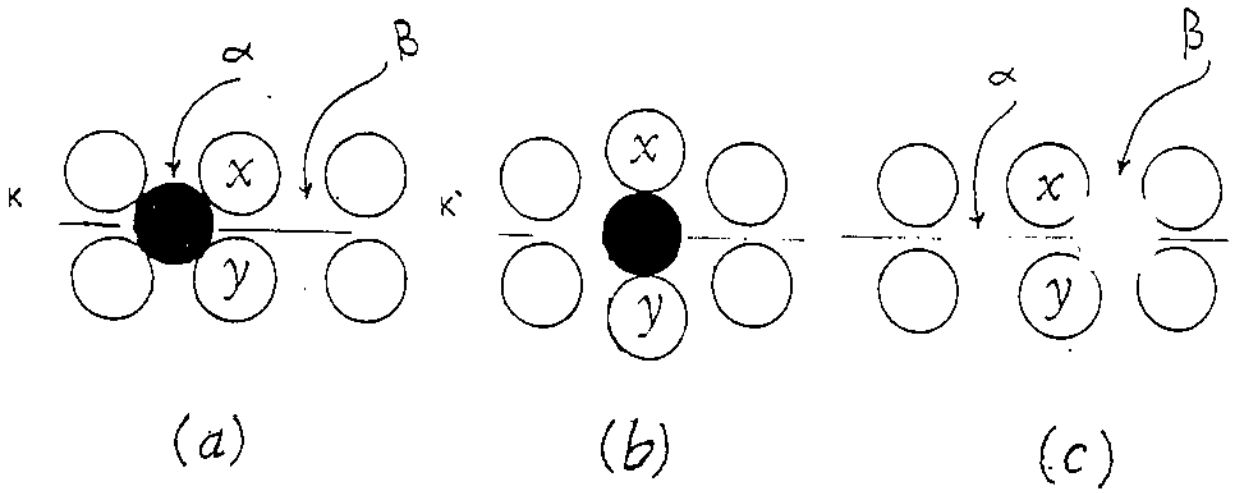


Fig. 2.3 The probability jumping [6]

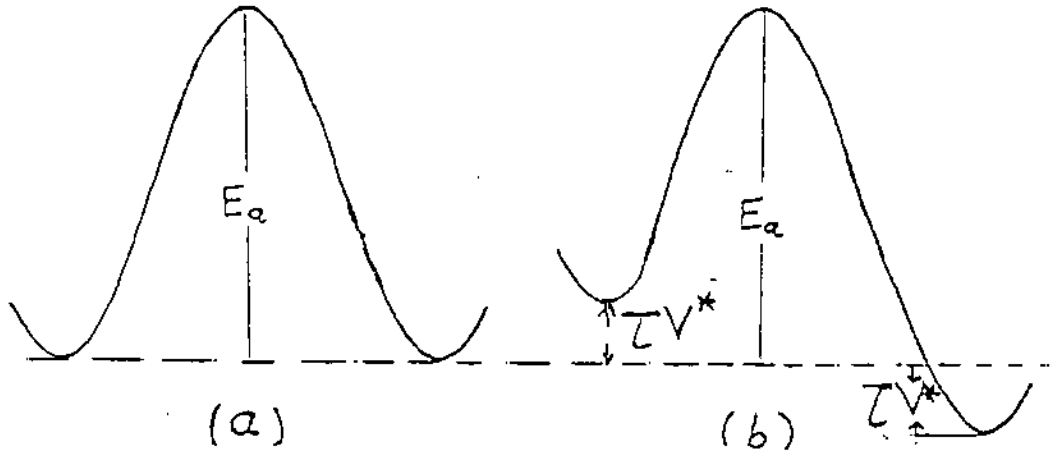


Fig. 2.4 The Eyring model of solid flow

(a) In absence of stress

(b) In presence of stress

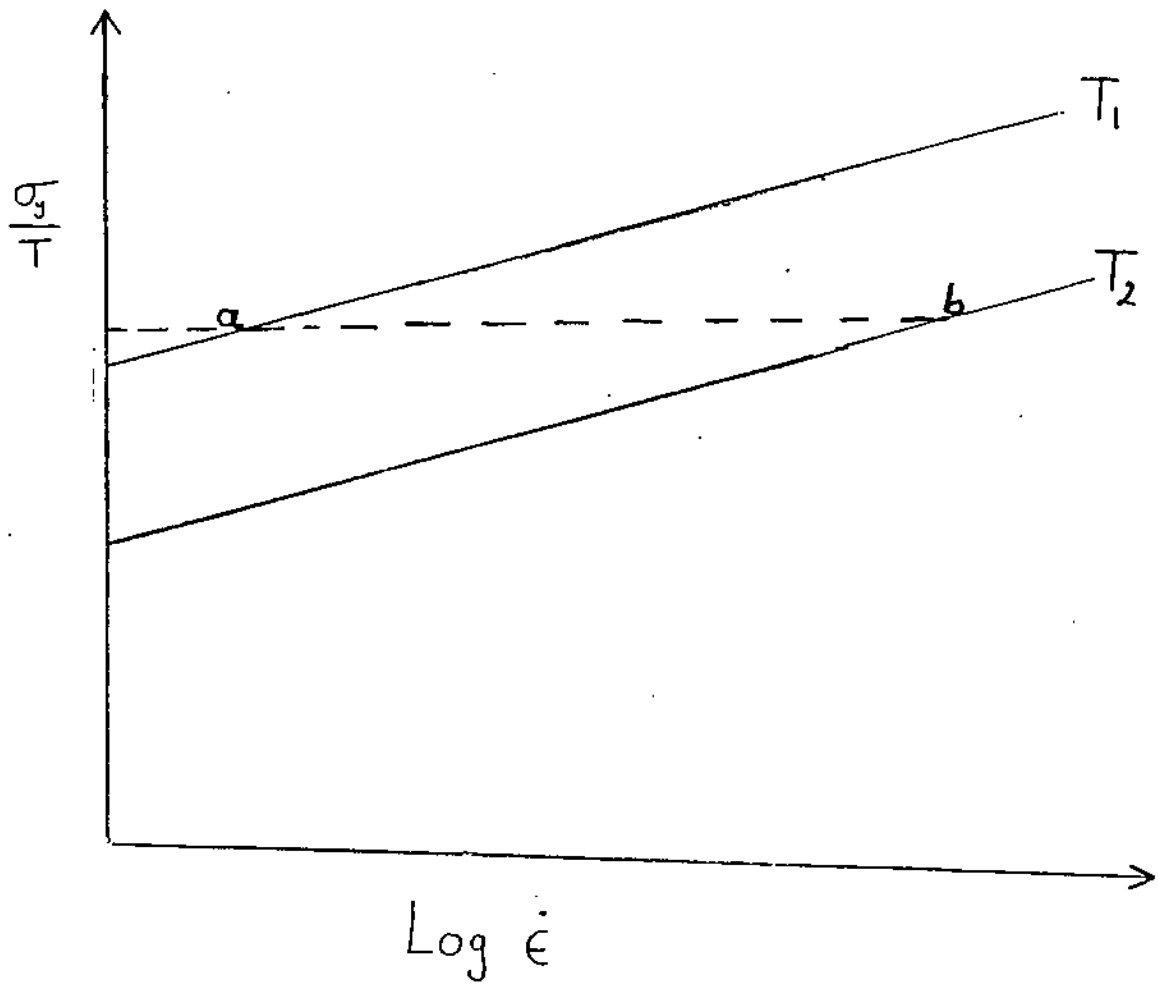


Fig. 2.5 Determination of the activation energy and the activation voluome [6]

CHAPTER THREE
EXPERIMENTAL WORK

3.1 Material

The material used in this work is a lexan polycarbonate sheet of 0.26 mm thickness manufactured in the General Electrical Company in USA and provided by Dr. J. Starr. The polycarbonate has a density of about 1.2 gm/cm^3 and glass transition temperature of about 148 $^{\circ}$C [14,31]. Tensile specimens were cut from the sheet using a cuttering machine illustrated in Fig. 3.1. The geometry of samples is illustrated in Fig. 3.2, and the dimensions of test specimen are approximatly $10 \times 0.26 \times 2.2$ mm.

3.2 Specimen Aging in Water:

This work includes two parts, the first part deals with unaged (untreated or as received) samples, and the second part deals with aged (treated) samples in distilled and Dead Sea water. The specimen were weighed before and after aging for different aging times 4, 10, 20, 30, 40, and 50 days. The specimens were weighed by using a sensitive balance. The tensile test specimens were immersed in glasses containing distilled and Dead Sea water. The glasses were cleaned carefully before the use.

3.3 The Tensile Tests

Tensile tests were done by holding the specimens in special grips built for this purpose as shown in Fig. 3.2. The grips were supplied with sand papers to avoid specimen slipping . The specimens were aligned accurately with the tensile axis. Tensile tests were carried out using the Instron machine model 1026 fitted with a heating chamber as shown in Fig. 3.3. The tests were performed at different temperatures and strain rates using unaged and aged samples. A thermocouple and a thermometer were used to read the temperature in the oven. About 20 minutes were allowed to elapse before the test was performed . The strain rate was changed by changing the cross- head speed using a suitable gear box. In this work,

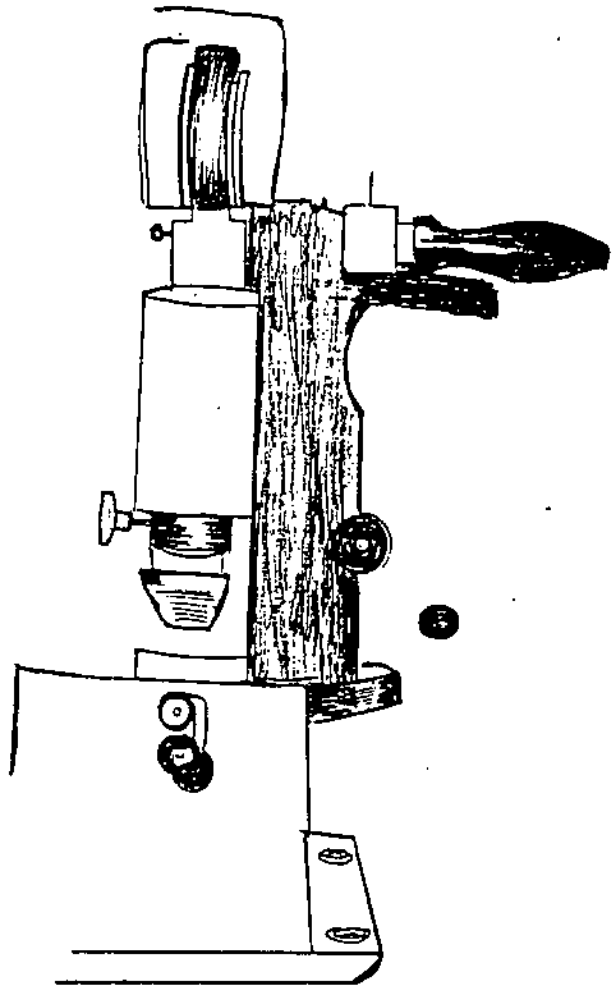


Fig. 3.1 The cuttering machine

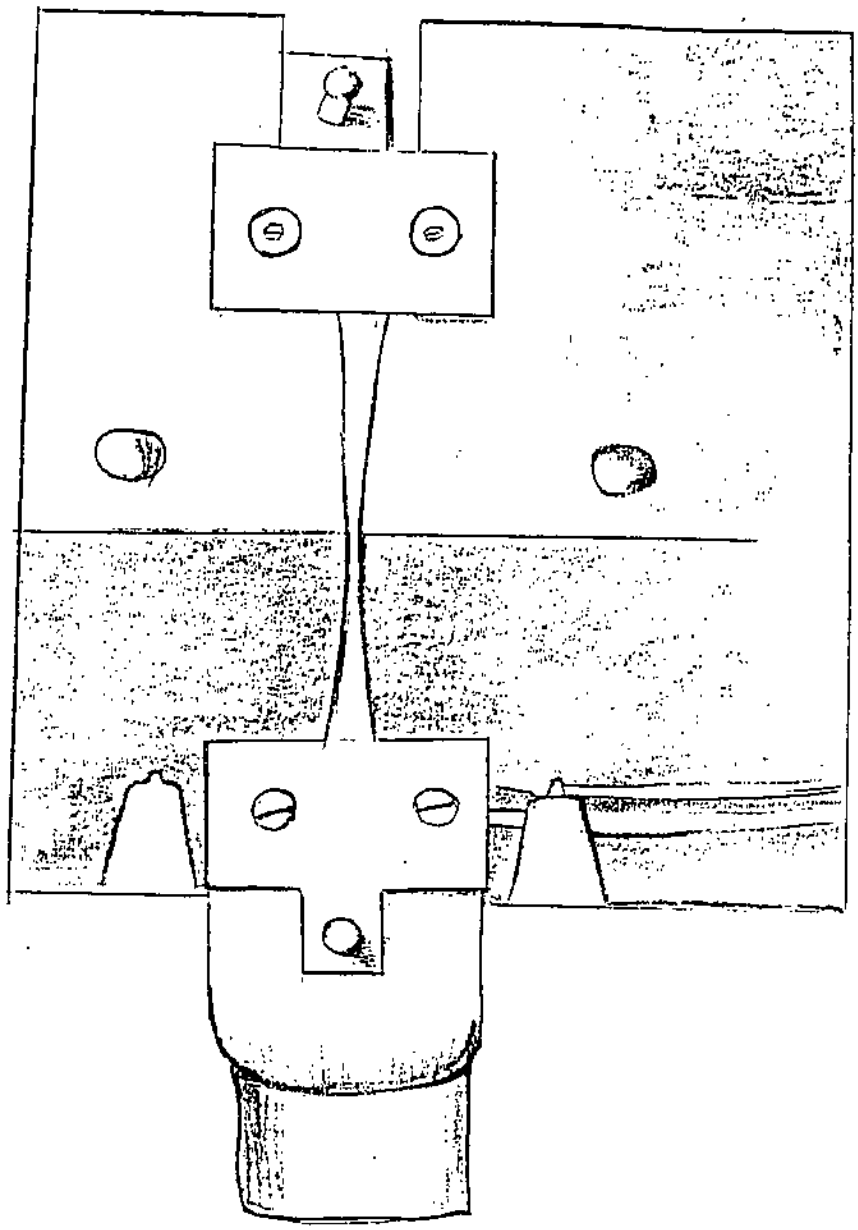


Fig. 3.2 . Specimen is held in grips

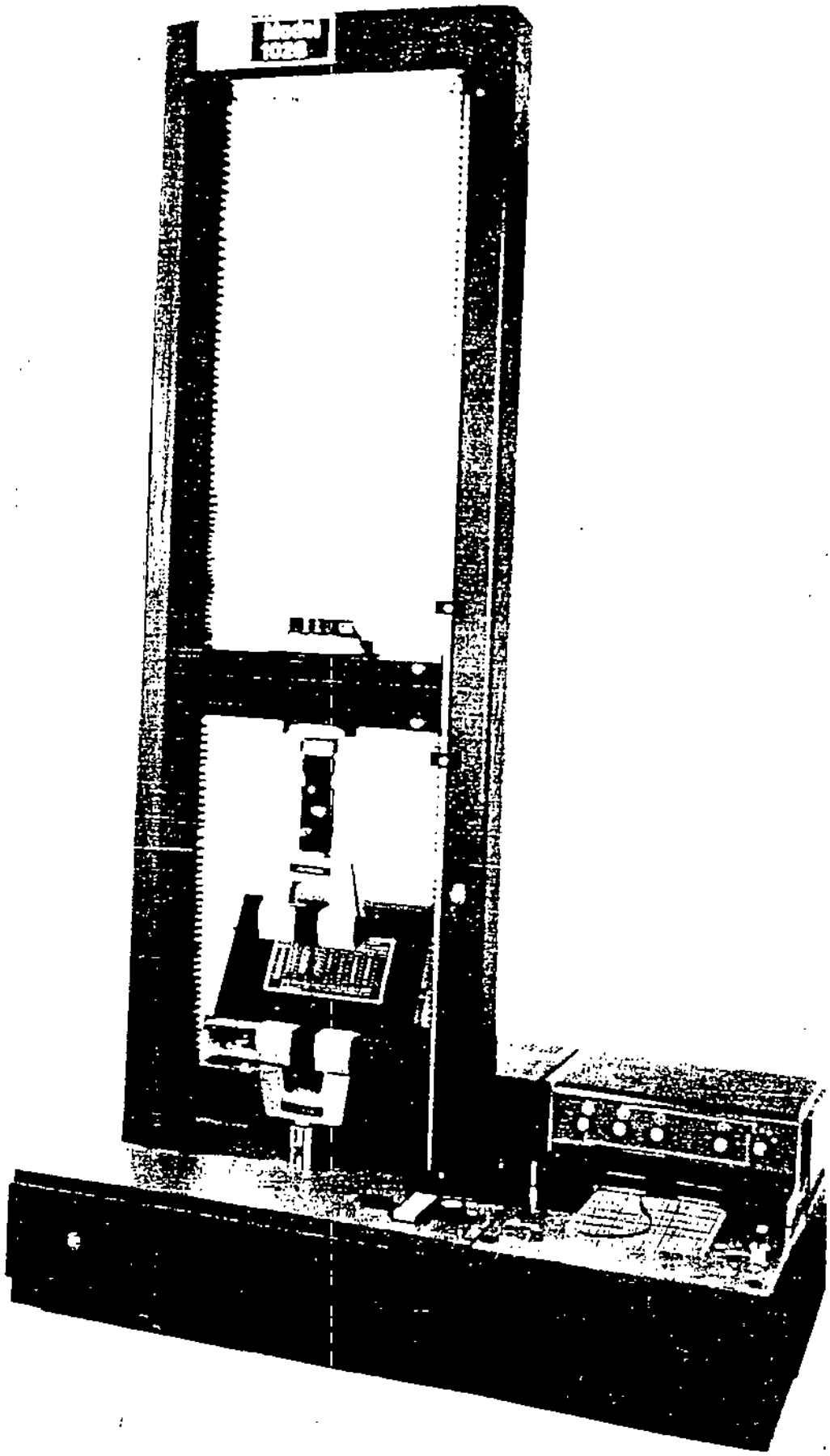


Fig. 3.3. The Instron testing machine model 1026

the cross-head speeds used were 0.1, 0.5, 1, 2 and 5(cm/min) and the corresponding strain rates were 1.66, 8.33, 16.6, 33.3 and 83.3×10^{-2} sec^{-1}. The strain is defined as:

$$\text{Strain Rate } (\dot{\varepsilon}) = \frac{\text{cross - head speed}}{\text{gauge length}} \quad \text{.....(3.1)}$$

The used gauge length was 1 cm. The direct output obtained from the Instron chart recorder is the load-time curve which represents the applied load on the sample as a function of time. The load-time curves were converted to stress-strain curves by using cross sectional area, crosshead speed and chart speed according to the equations:

$$\text{Stress } (\sigma) = \frac{\text{force exerted}}{\text{cross - sectional area}} \quad \text{.....(3.2)}$$

$$\text{Strain } (\varepsilon) = \frac{\text{elongation}}{\text{original length}} \quad \text{..... (3.3)}$$

But,

$$\text{Elongation} = \text{cross - head speed} \times \text{time} \quad \text{.....(3.4)}$$

and

$$\text{Time} = \frac{\text{distance travelled on chart}}{\text{chart speed}} \quad \text{.....(3.5)}$$

Then,

$$\text{Strain} = \frac{\text{cross - head speed} \times \text{distance on chart}}{\text{gauge length} \times \text{chart speed}} \quad \text{....(3.6)}$$

Thus the stress-strain relations can be plotted from the load-elongation curves. The chart speed can also be changed by using a suitable gear box. We use a chart full scale of load 50 newtons which was suitable for polycarbonate. The load was increased until the specimen yielding. The parameters detected from the load-elongation curves are the yield stress, the yield strain, and the Young's modulus. This work was detected for both aged and unaged samples. Aged samples were cleaned by distilled water

and were dried by a drier before the tests were performed. The yield point was determined easily by taking the maximum point on the load-elongation curve from which the yield stress and the yield strain are estimated. The Young's modulus was calculated from the initial slope of the stress-strain plots.

3.4 Weight Change Measurements :

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 sorption was determined from the relation:

$$Wt\% = \frac{W(t) - W(0)}{W(0)} \times 100 \quad \text{.....(3.7)}$$

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(o) is the weight of dry polymer sample at zero time.

CHAPTER FOUR
RESULTS AND DISCUSSION

Many investigations were applied on polycarbonate and mainly concern the effect of temperature, strain rate and hydrostatic pressure on the mechanical behavior of polycarbonate as pointed out in the introduction [25,32, 33, 34] .

In this thesis work we deal with the effect of aging in Dead Sea water and distilled water on the mechanical properties of polycarbonate sheets. This work is done under different variables like temperature, strain rate, and aging time.

4.1 Weight Change Results:

Fig. (4.1) 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 [10]. The fast initial gain may reflect the water diffusion into the sample surface and saturation in the polycarbonate by water [17]. 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 (Wt% / t) was estimated and the results were plotted as a function of aging time as shown in Fig. 4.2. The rate mass gain (Wt% / t) decreases sharply with time. This behavior fits the saturation condition and proves again the case of low water absorption during aging.

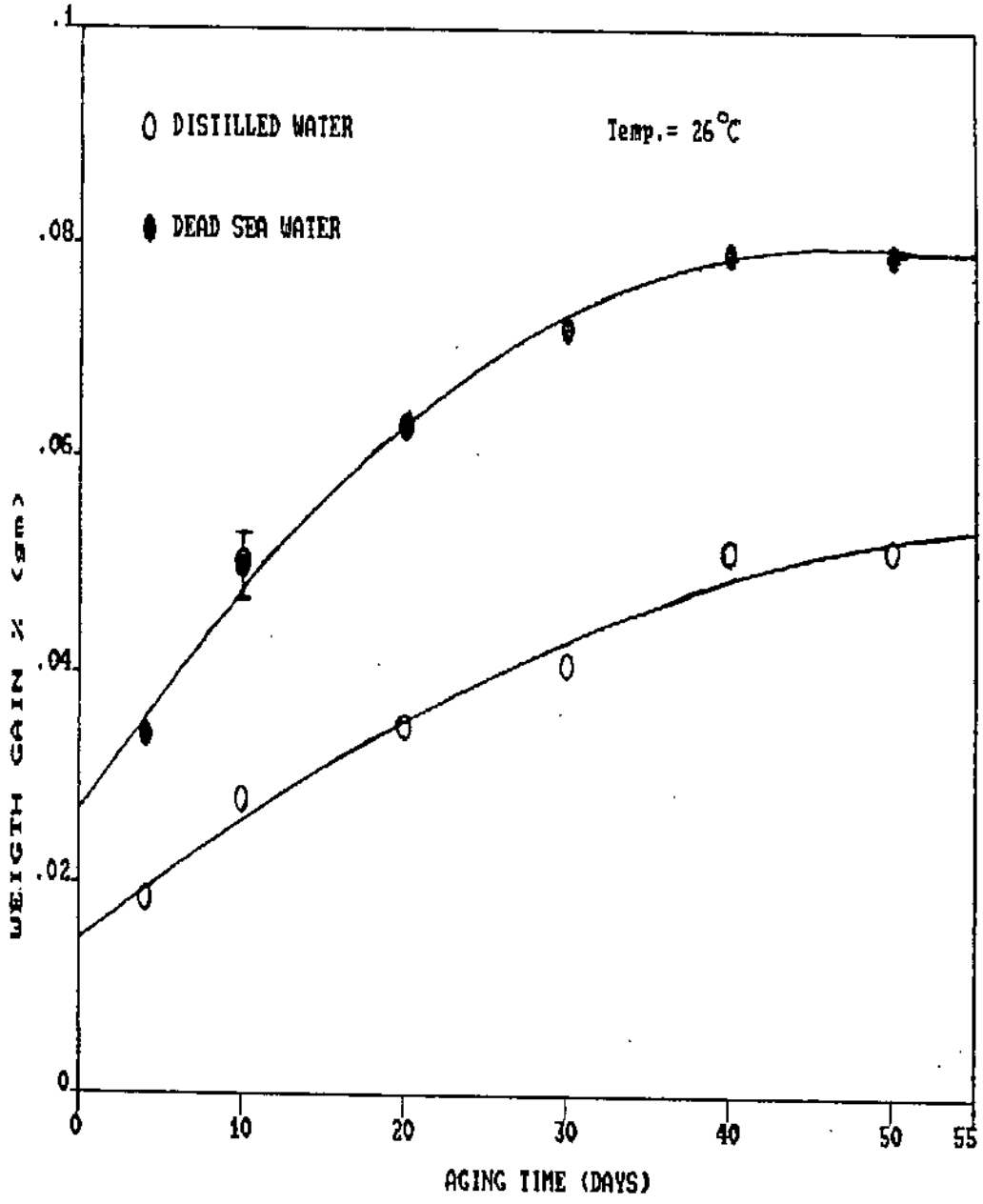


Fig. 4.1 The weight gain versus aging time.

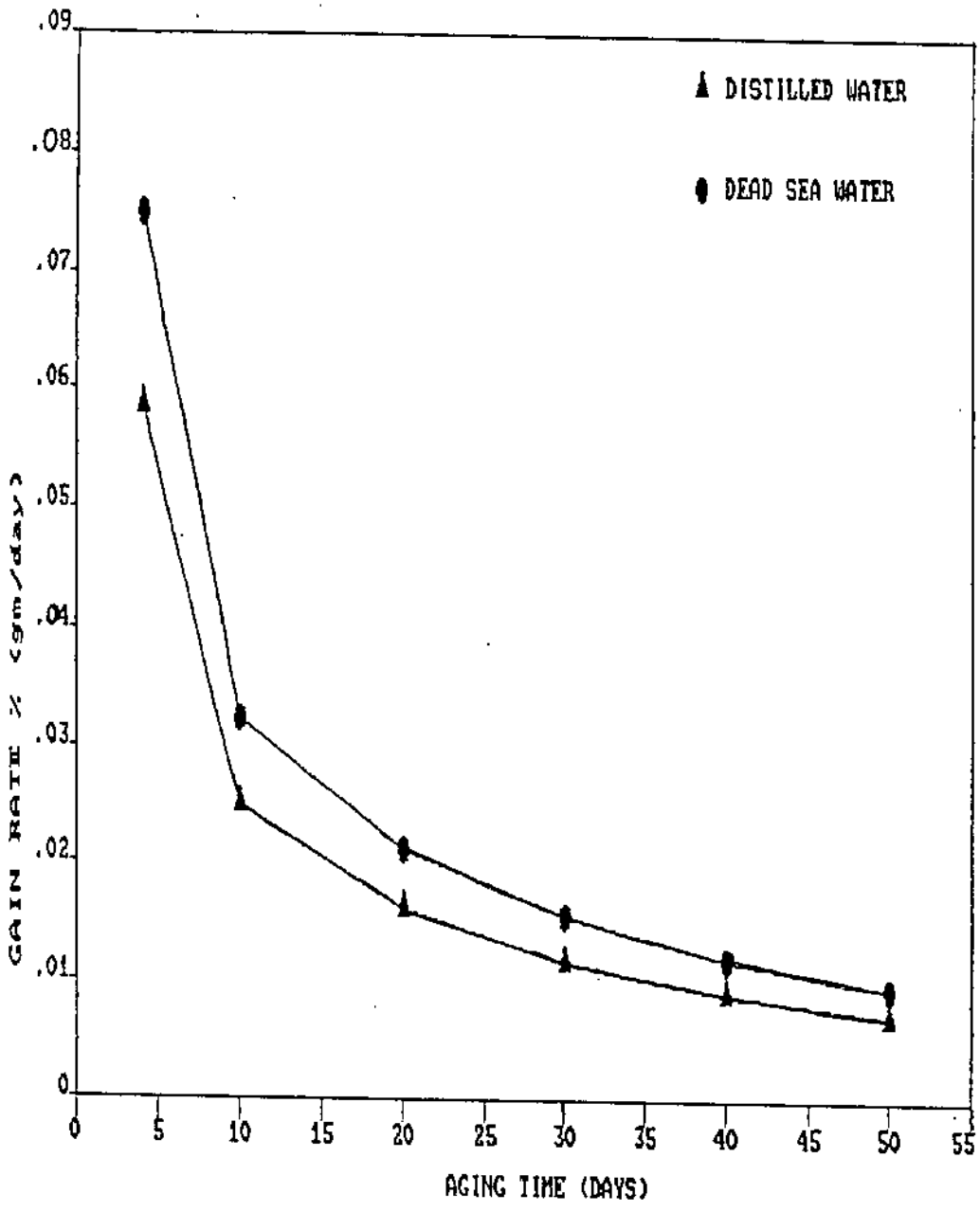


Fig. 4.2 The weight gain rate versus aging time.

4.2 Stress-Strain Curves:

Polycarbonates are well known to deform in ductile shearing manner as reported by many workers [35]. In this work, the deformation behavior is studied in case of aged samples in distilled and Dead Sea water. The obtained stress-strain curves are shown in Figs. 4.3 and 4.4 at temperatures 26 and 120 °C, respectively. Fig. 4.3 distinguishes between five curves belong to (untreated samples, aged for 30 days and aged for 50 days in distilled and Dead Sea water). These stress-strain curves have the same shape; the deformation of aged samples still in a ductile manner, but the observed differences lie in the slope of the first Hookean part of each curve and in the yield point beyond the Hookean region. At temperature 120 °C, Fig. 4.4 shows five stress-strain curves, with very small differences in the elastic regions and yield points.

4.3 The Young's Modulus Results :

Fig. 4.5 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 and Dead Sea water. Results show that at relatively low temperatures, 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 decrease 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 five curves become closer and closer until they intersect at high temperatures. This behavior gives an indication that the effect of aging becomes weaker with increasing temperature and 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

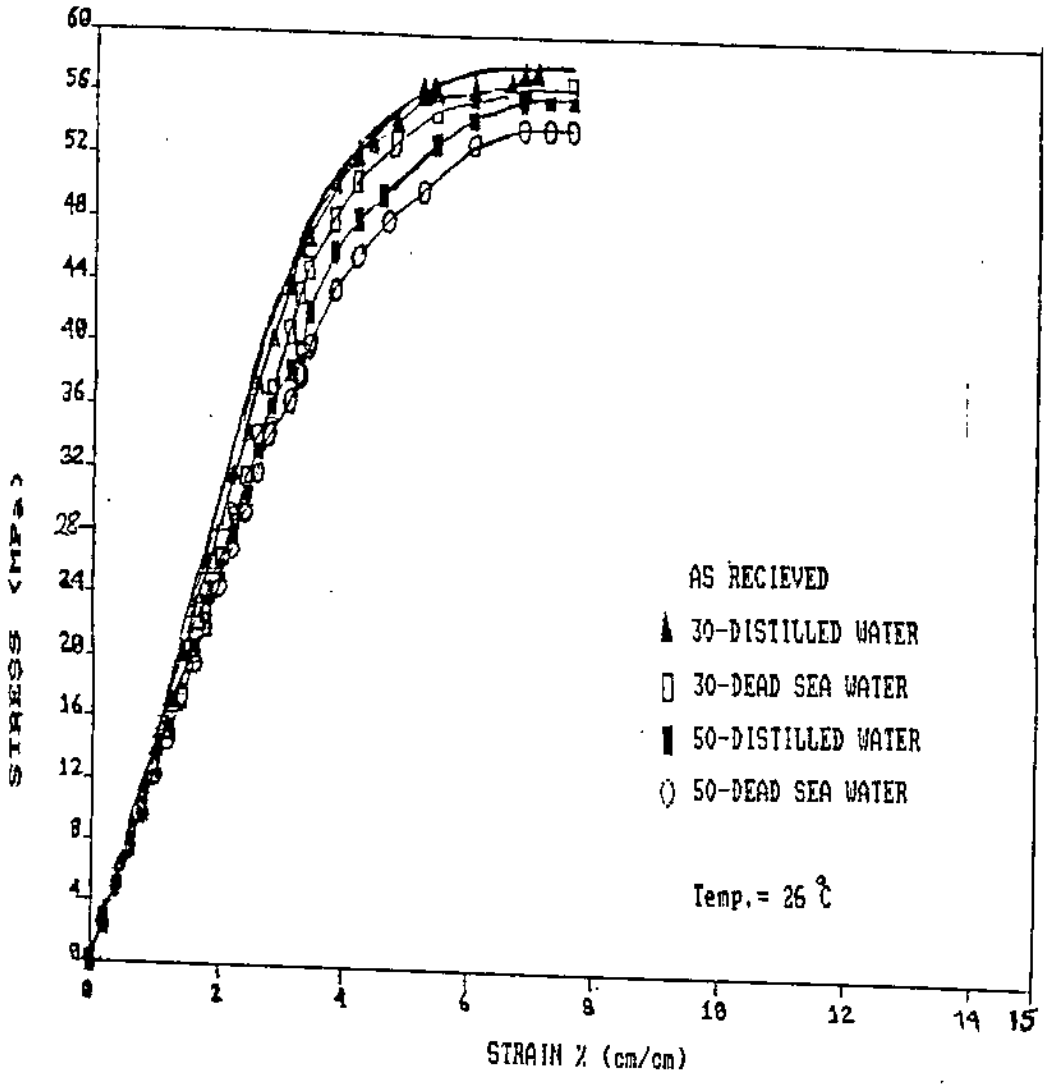


Fig. 4.3 Stress - strain curves of aged polycarbonate samples

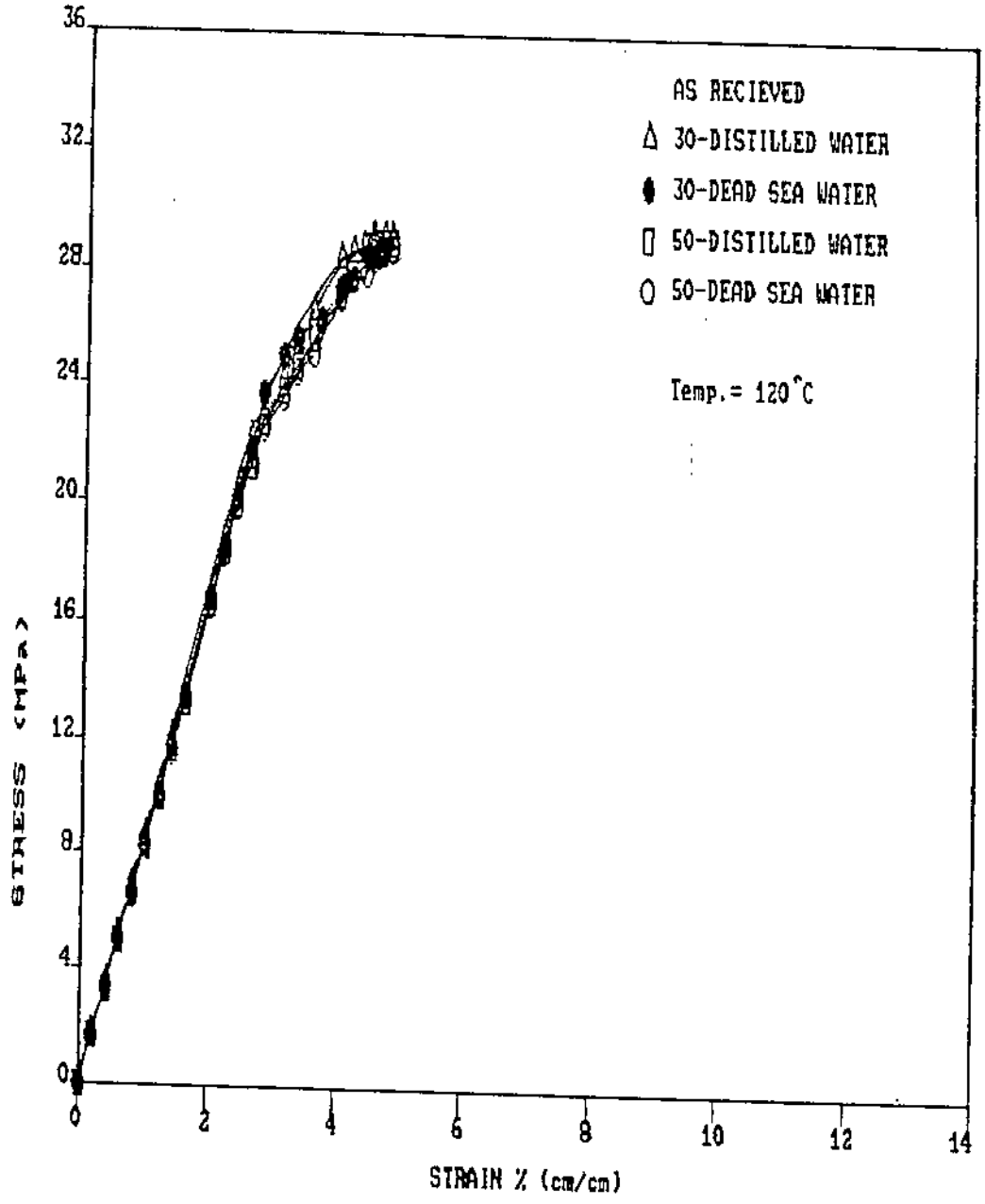


Fig. 4.4 Stress - strain curves of aged polycarbonate samples

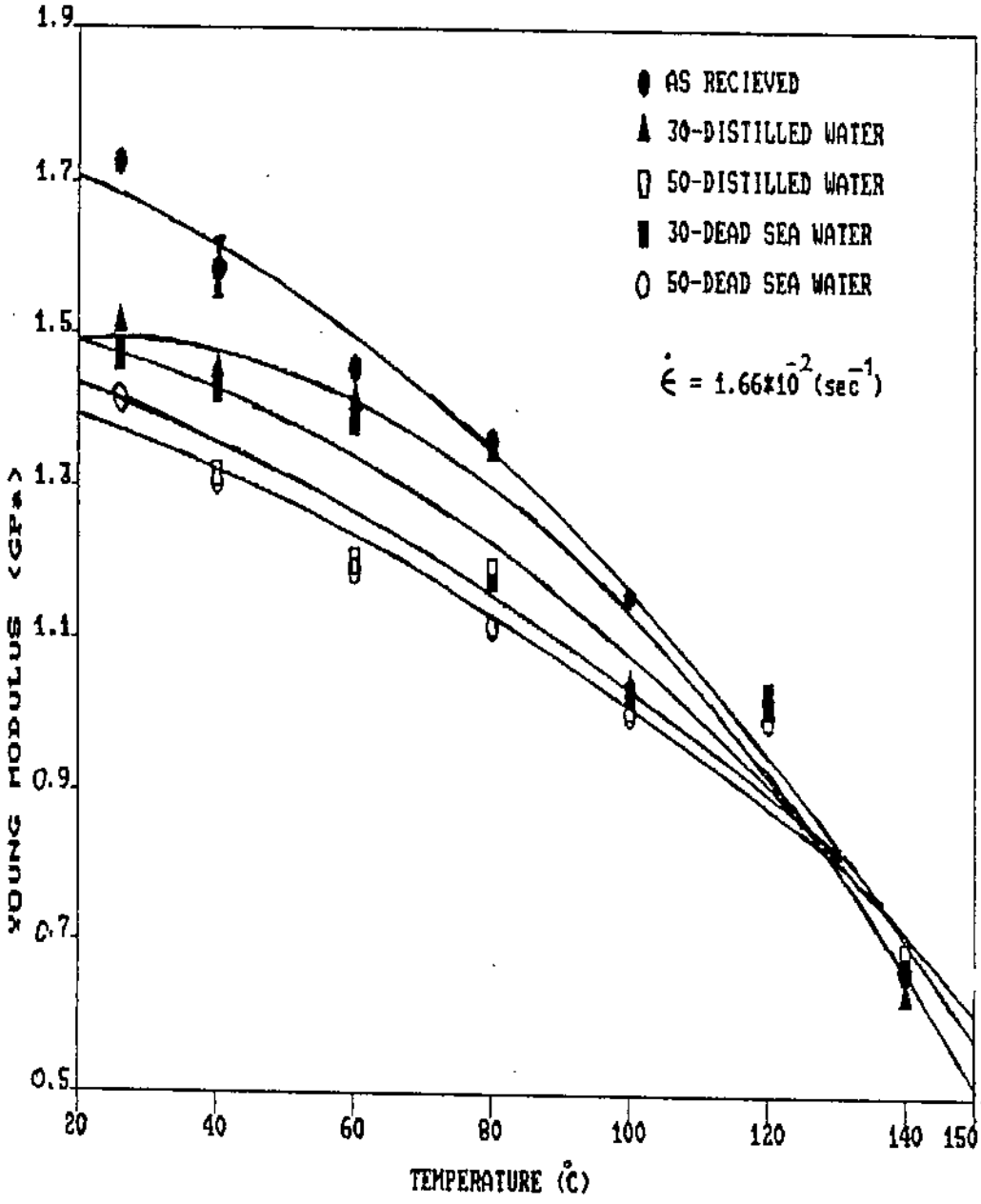


Fig. 4.5 The Young's modulus versus temperature

shown in Fig. 4.6. 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 amount of decreasing in E is larger in the case of aging in Dead Sea water. The dependence of the Young's modulus on the strain rate is shown in Fig. 4.7 and 4.8 for different aging times at 26 and 120 °C, respectively. The effect of aging is clear with a gradual decrease in modulus with aging time especially at low temperatures as shown in Fig. 4.7. This behavior becomes very weak at high temperatures as shown in Fig. 4.8. The observed results may be understood when recognizing that at low temperatures, the motion of chain segments of the polymer is small or even frozen [29]. The aging process gives this motion additional force which increases the segmental motion and as a result decreases the force needed for deformation and hence the modulus values decrease also. On the other hand, at high temperatures the effect of aging is not noticed since the values of the elastic modulus are small.

4.4 The Yield Stress Results :

Fig. 4.9 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 Fig. 4.10. These yield stress values are taken at room temperature and at strain rate equals 1.6×10^{-2} 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,

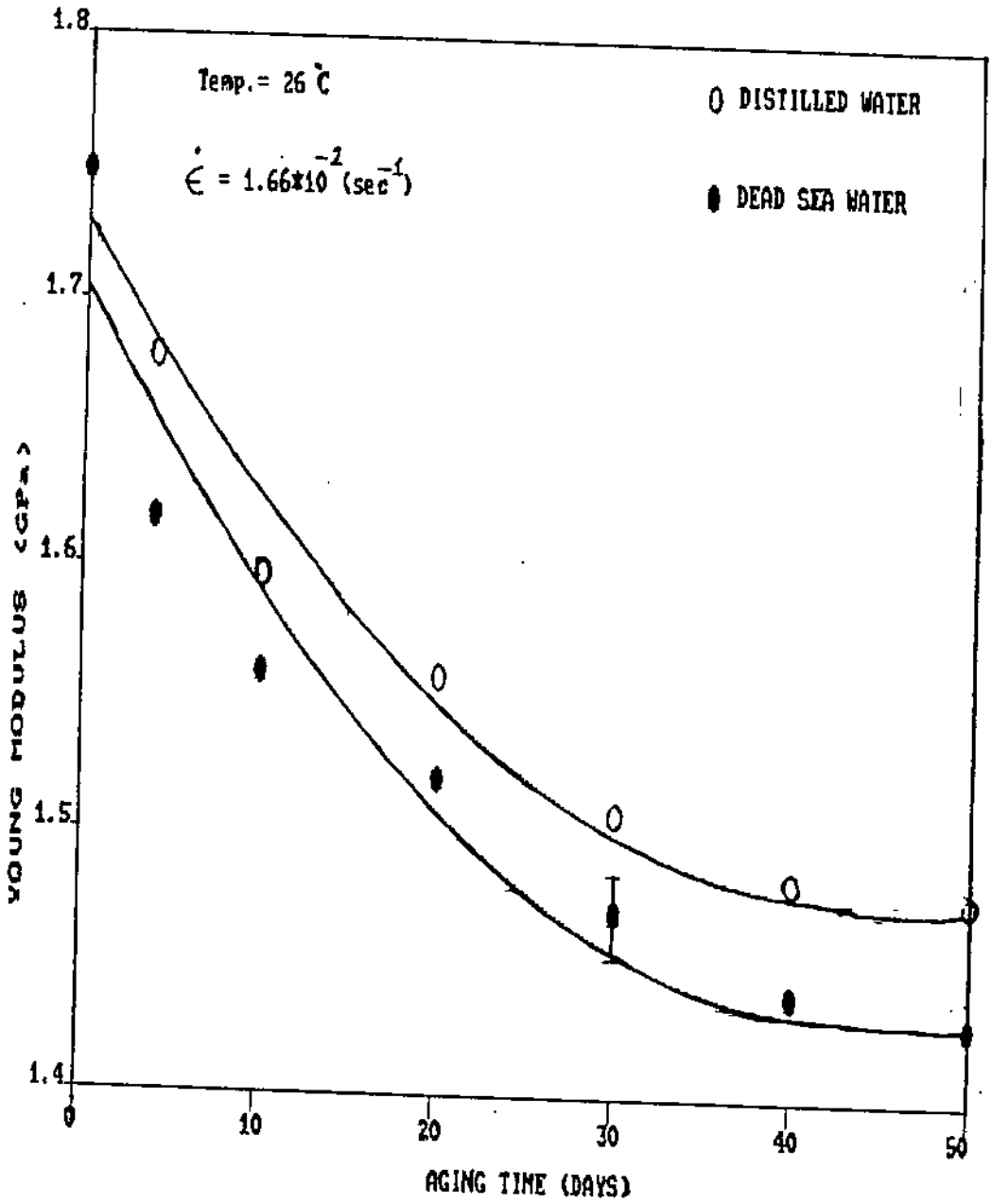


Fig. 4.6 Young's modulus versus aging time

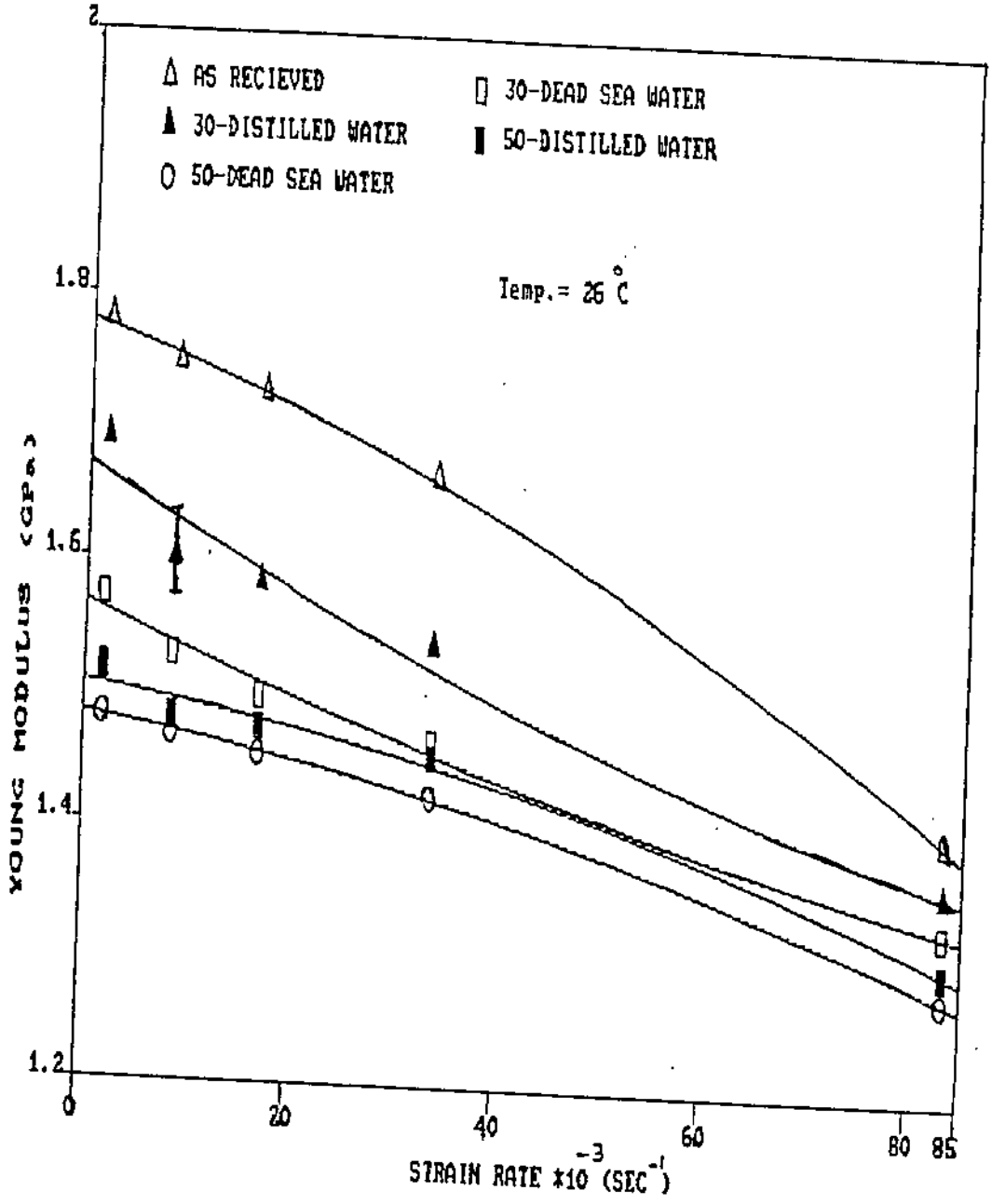


Fig. 4.7 Young's modulus versus the strain rate

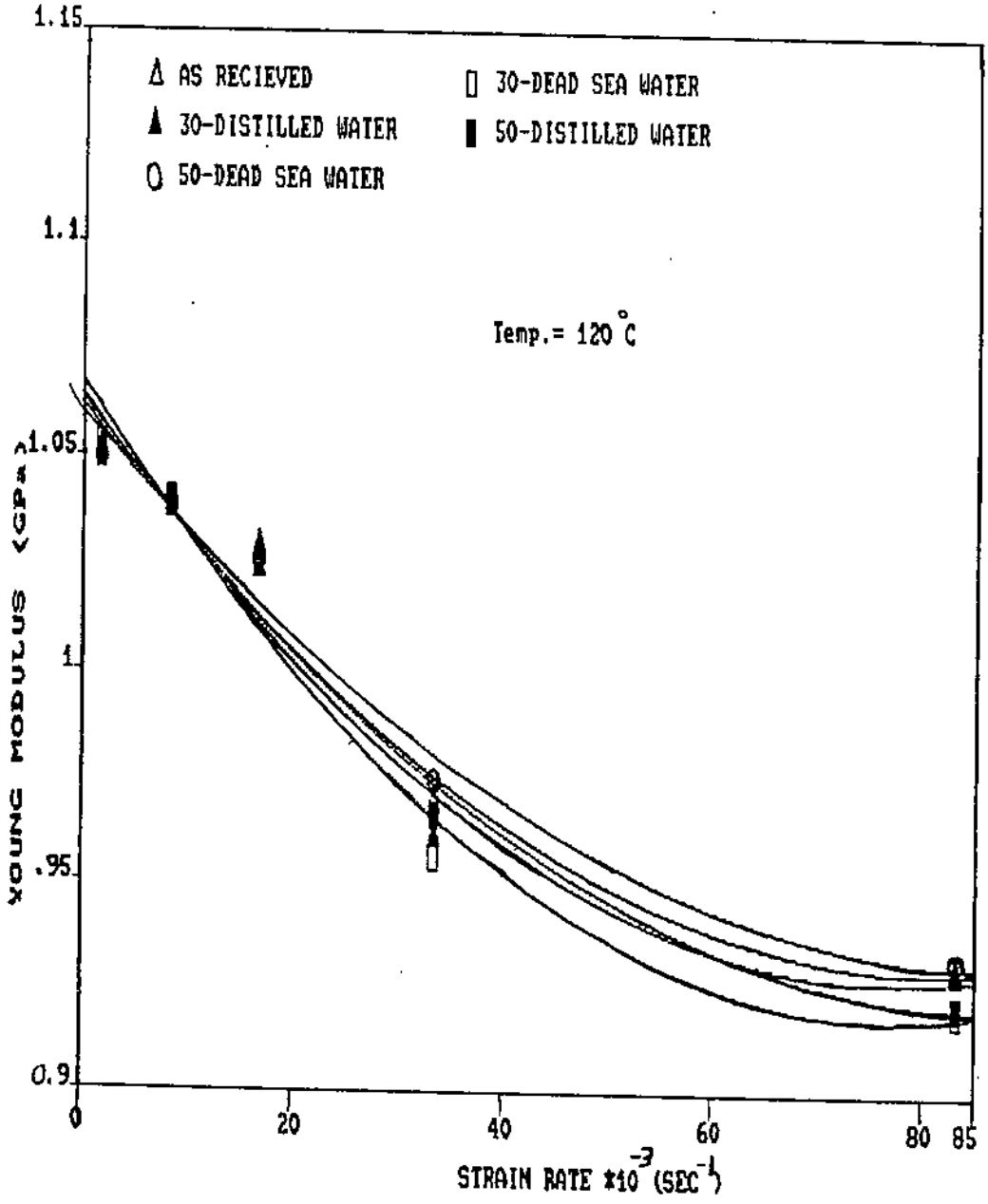


Fig. 4.8 Young's modulus versus the strain rate.

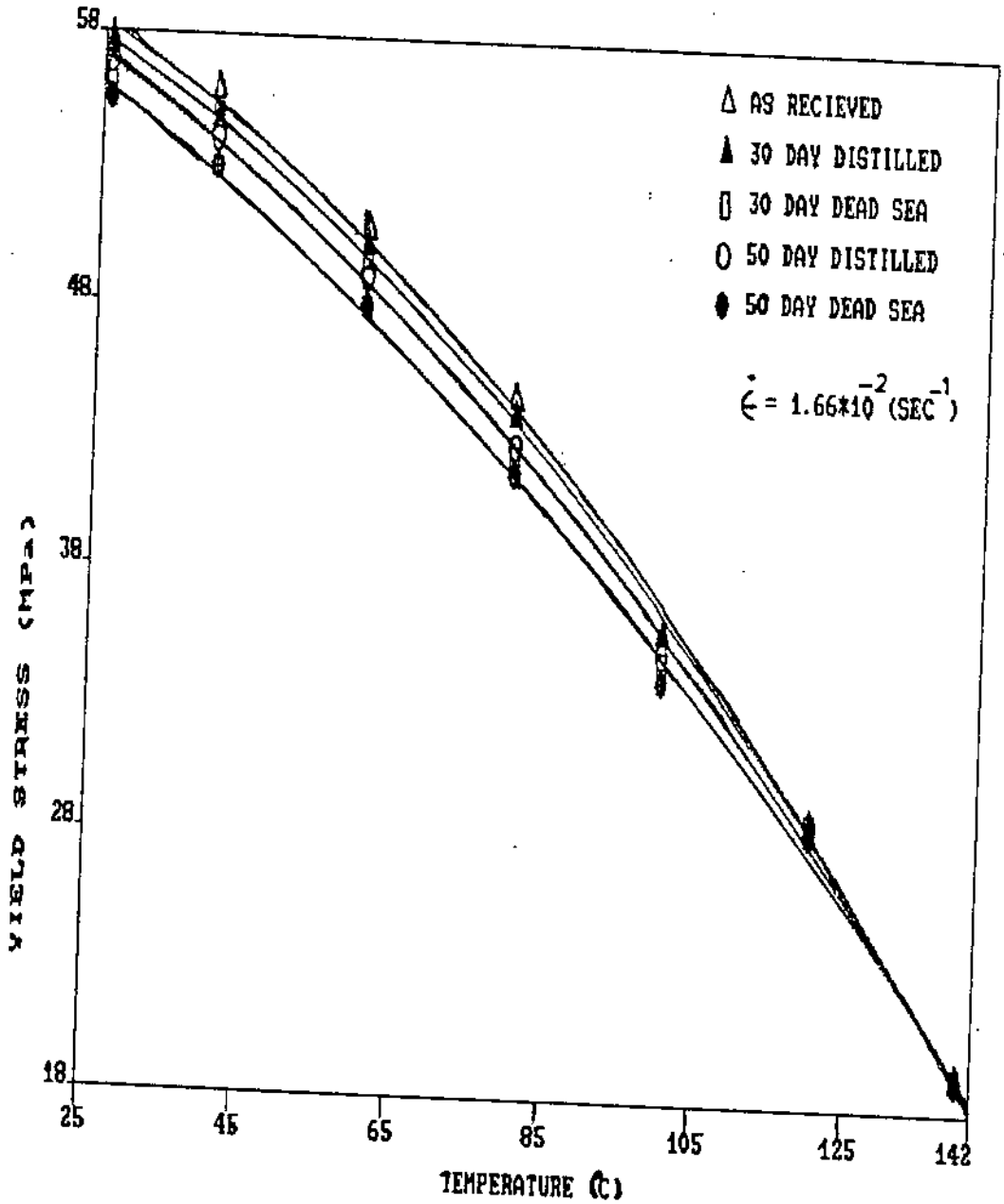


Fig. 4.9 The yield stress versus temperature.

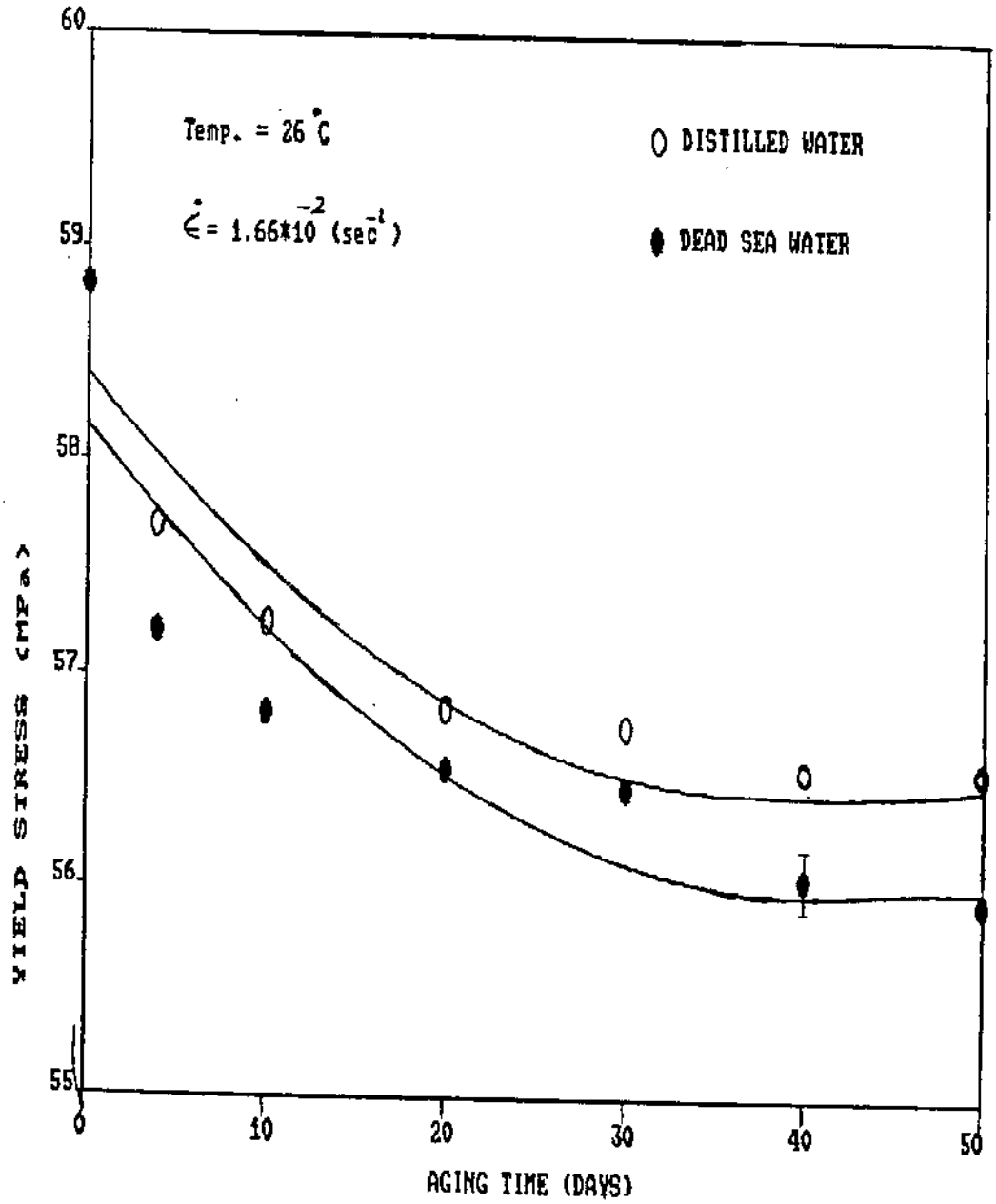


Fig. 4.10 The yield stress versus aging time

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 Fig. 4.11. The results presented in this graph may be summarized in two points: first the ratio (σ_y/T) increases linearly with log $\dot{\varepsilon}_y$, and secondly, at constant log $\dot{\varepsilon}_y$, this ratio increases with decreasing temperature. These results are reported for untreated polycarbonate samples [6]. For aged samples, the same results were observed as shown in Figs. 4.12 and 4.13 at temperatures 26 and 120 °C, respectively. Fig. 4.12 shows that the values of (σ_y/T) decreases with increasing aging time which fits again the obtained results in Fig. 4.10 at room temperature. At high temperature (120 °C), Fig. 4.13 shows five overlapping lines where the values of (σ_y/T) are very close to each other for treated and untreated samples. The above graphs yield two important parameters, the activation energy (E_a) and the activation volume (V^*). These parameters are calculated using Eyring equation [19, 30] mentioned in the theoretical aspects section. The obtained results of aged and unaged samples are plotted as a function of aging time as shown in Figs. 4.14 and 4.15. Fig. 4.14 shows that the activation energy decreases with increasing the aging time. Fig. 4.15 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 Eyring [6, 9, 20] which says that deformation takes place when molecules move from one stable position to another and this movement needs them to overcome a potential barrier as shown in Fig. 2.4. Now, for aged samples, some water holes will diffuse into the surface of the polymer and increases 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

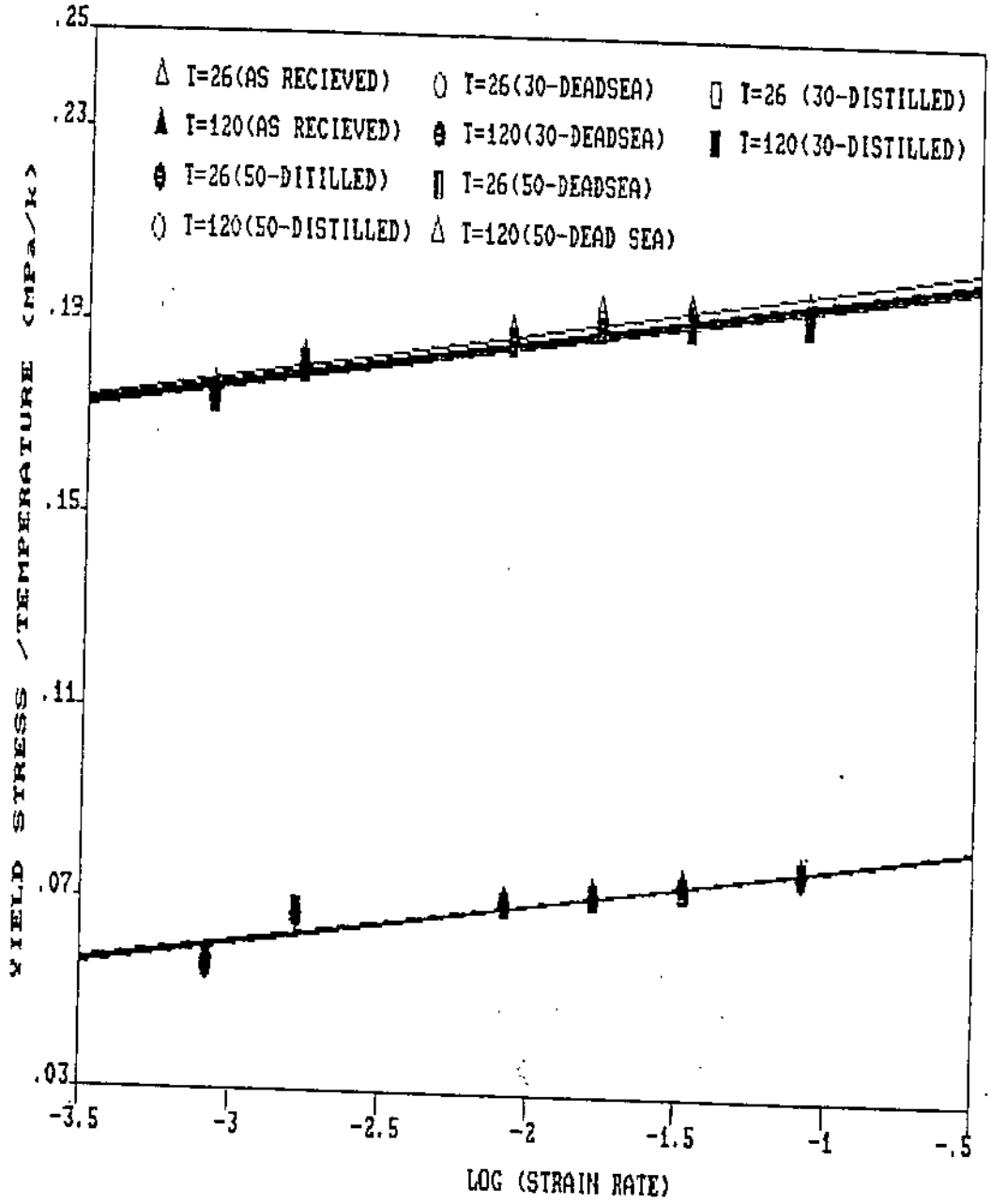


Fig. 4.11 The yield stress versus log (strain rate)

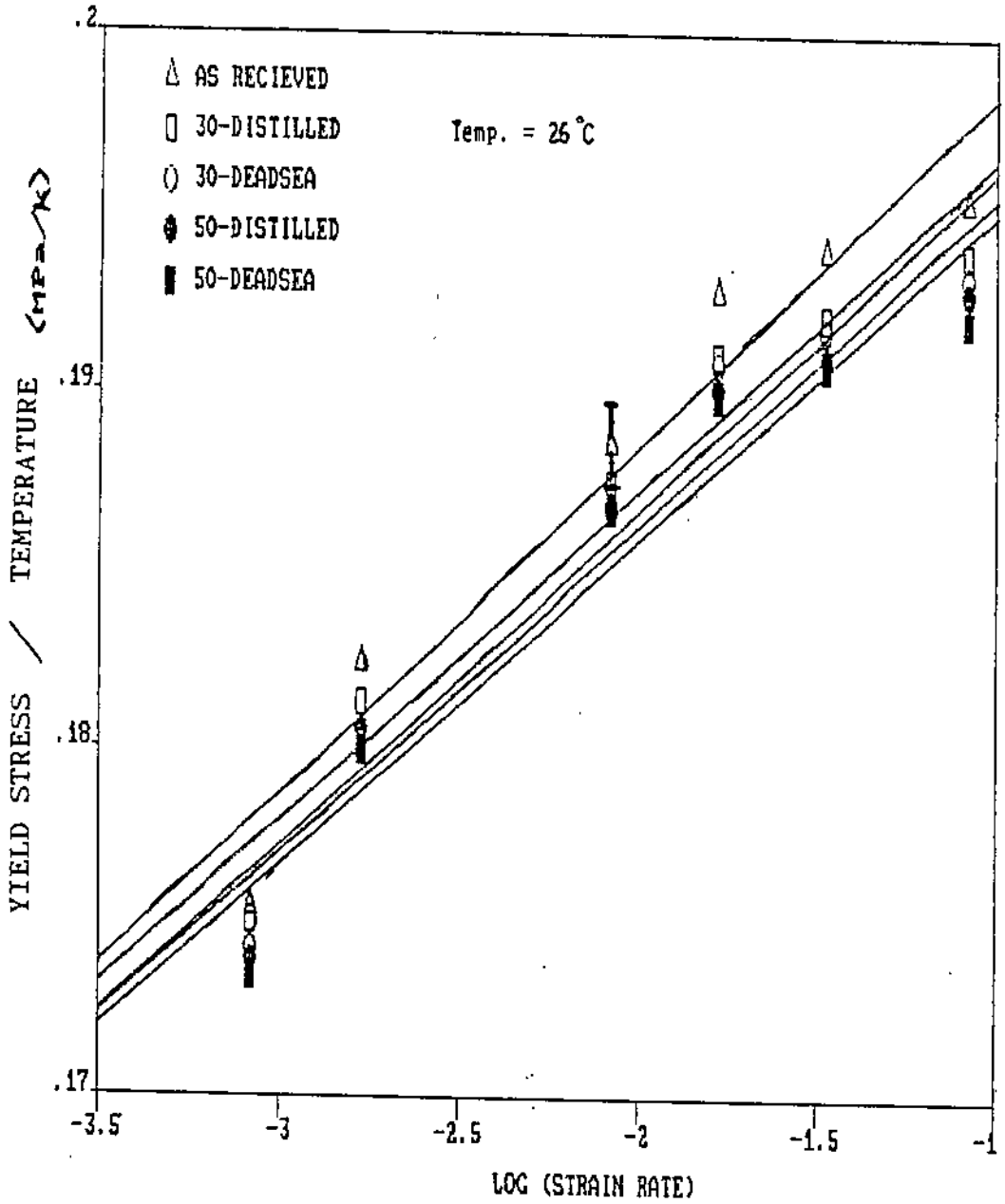


Fig. 4.12 The yield stress versus log (strain rate)

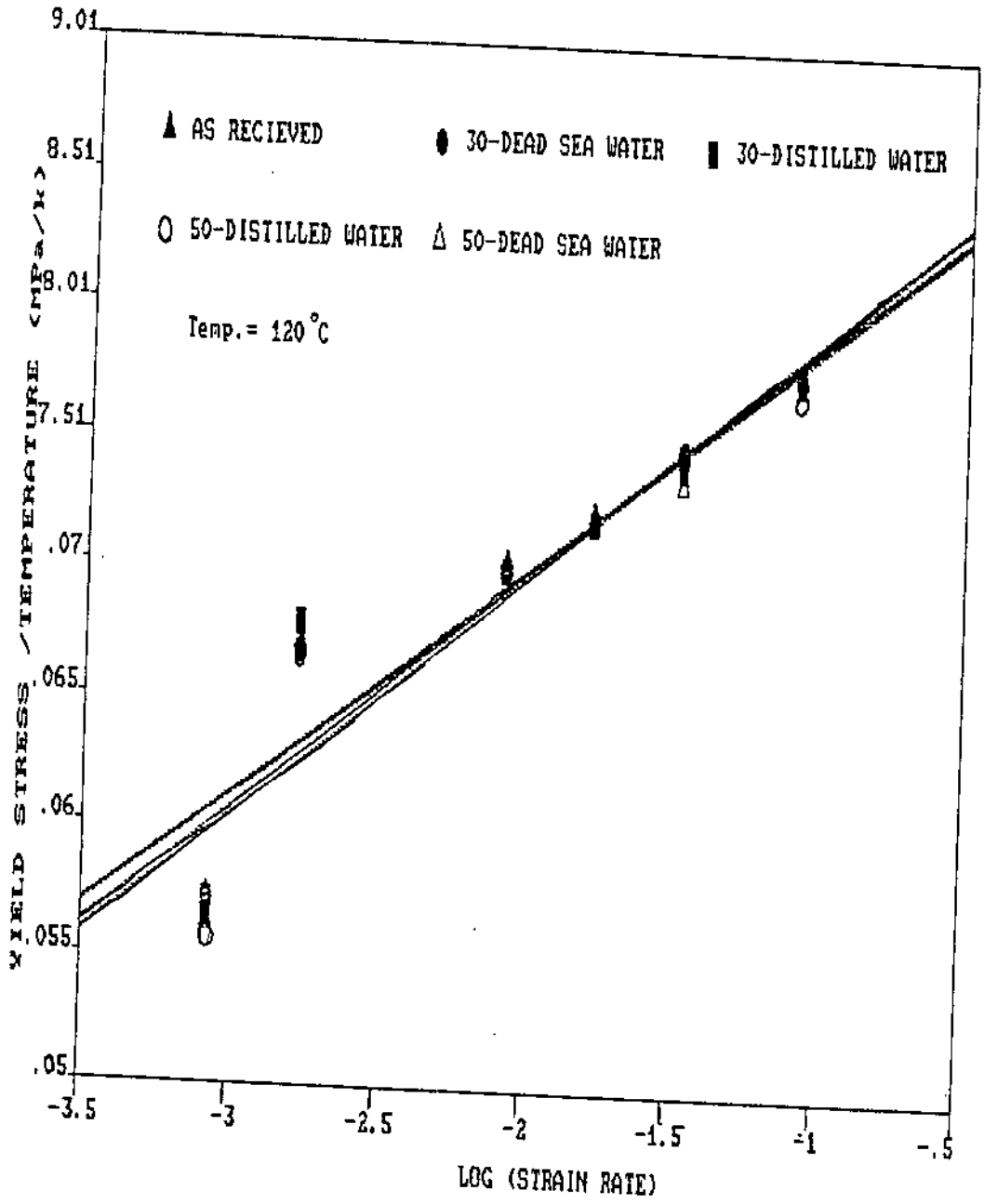


Fig. 4.13 The yield stress versus log (strain rate)

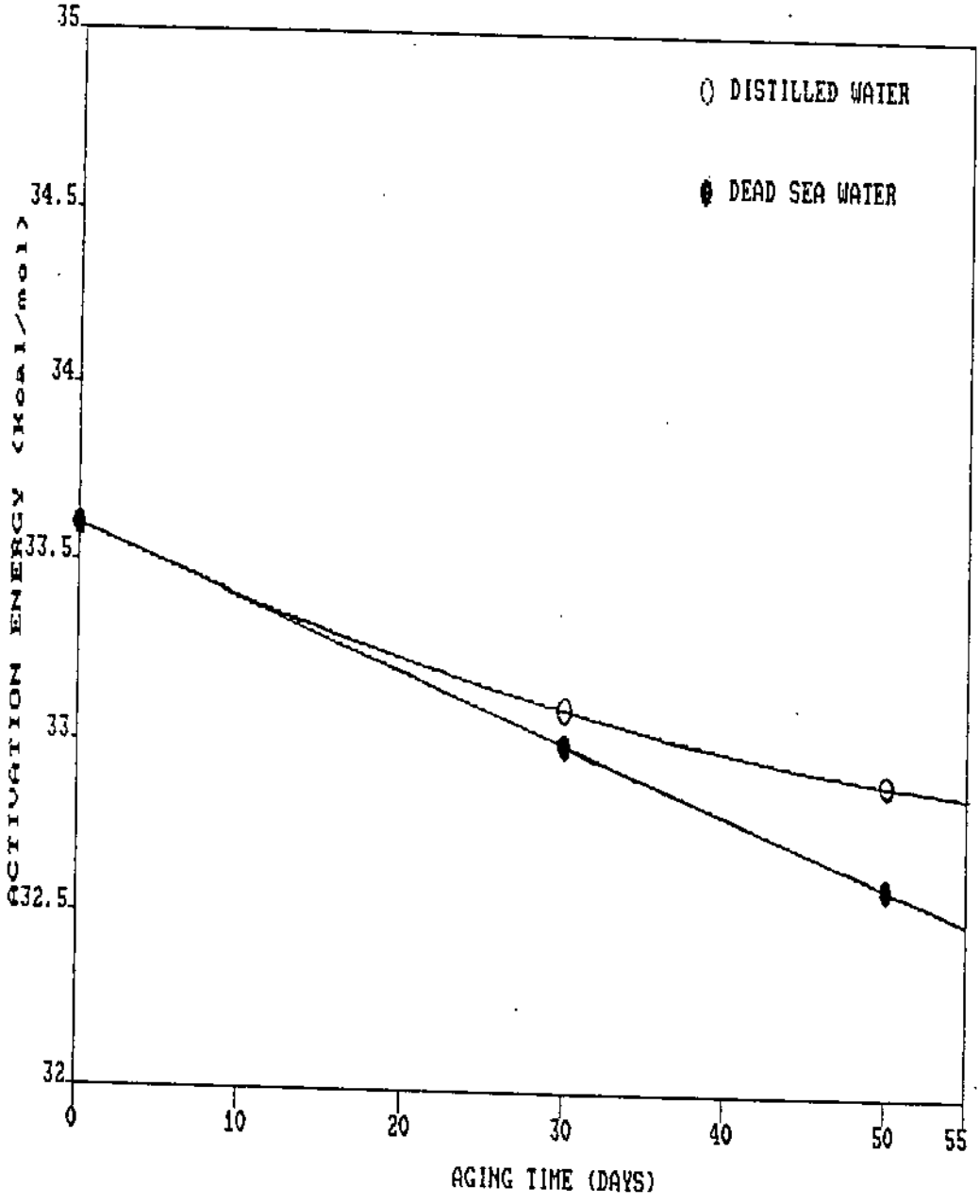


Fig. 4.14 The activation energy versus aging time.

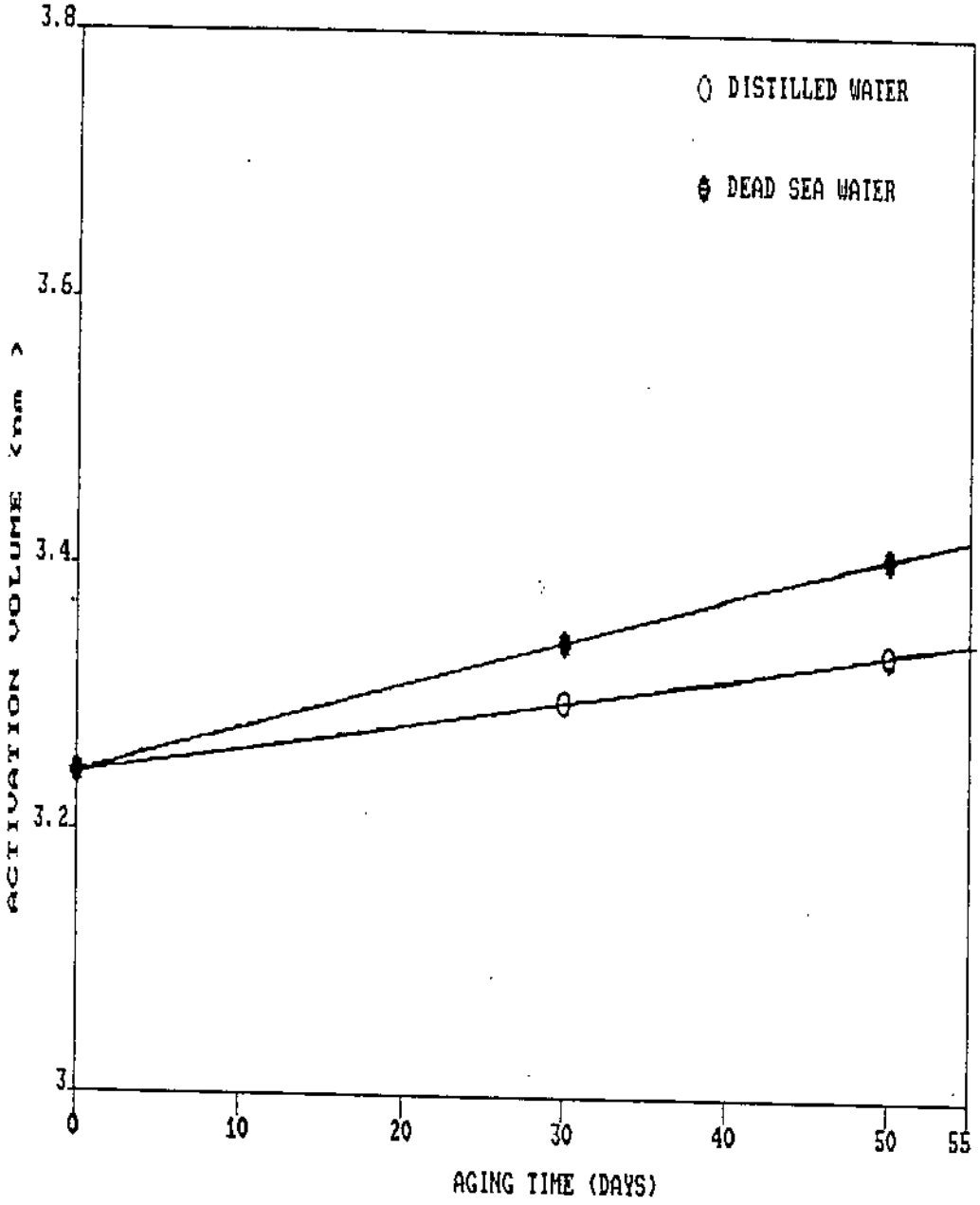


Fig. 4.15 The activation volume versus aging time

structural blocks which had to move as a whole under the plastic deformation during the yielding process.

4.5 The Yield Strain Results :

Fig. 4.16 shows the variation of yield strain with temperature for different treated and untreated polycarbonate samples at constant strain rate. Results show the dependence of the yield strain on aging time especially at low temperatures. More details are obtained from Fig. 4.17 which shows the variation of the yield strain with aging time at room temperature. Results show that with increasing aging time, the yield strain was increasing and the amount of increase in the yield strain values are very small in case of aging in distilled water. The variations of yield strain with strain rate are shown in Figs. 4.18 and 4.19 at temperatures 26 and 120 °C, respectively, for treated and untreated samples. Fig. 4.18 shows again the dependence of the yield strain on the aging time, thus its values vary from about 6.4% for unaged samples to about 7.1% when samples were aged in Dead sea water for 50 days. On the other hand, the dependence of the yield strain on aging time becomes very small at high temperatures, (120 °C) as shown in Fig. 4.19. These results of aging can be related to swelling [13] of the polymer molecules, resulting from diffusion of water into the surface of polycarbonate specimens, which increases the chain separation and thus the material becomes more ductile with larger yield strain.

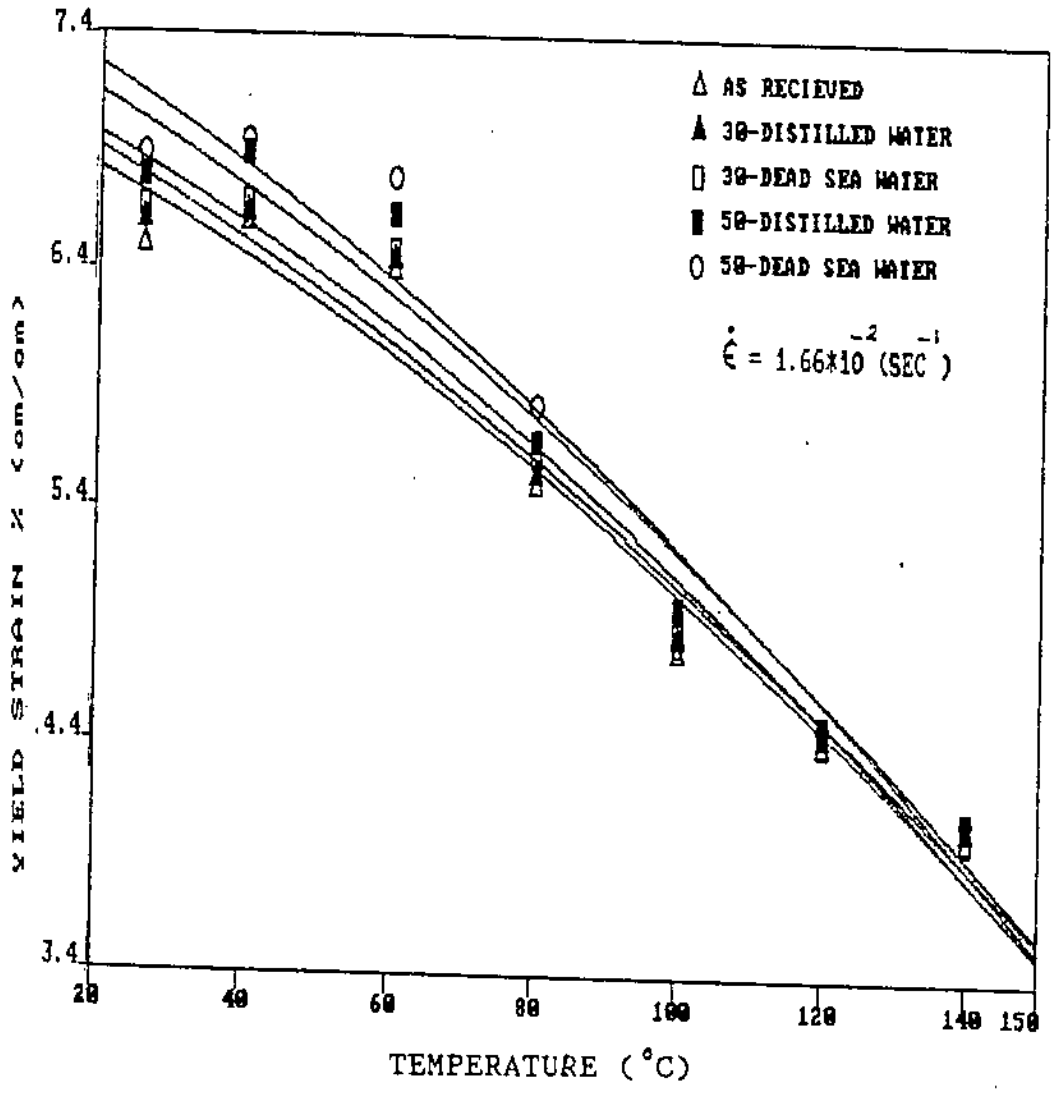


Fig. 4.16 The yield strain versus temperature.

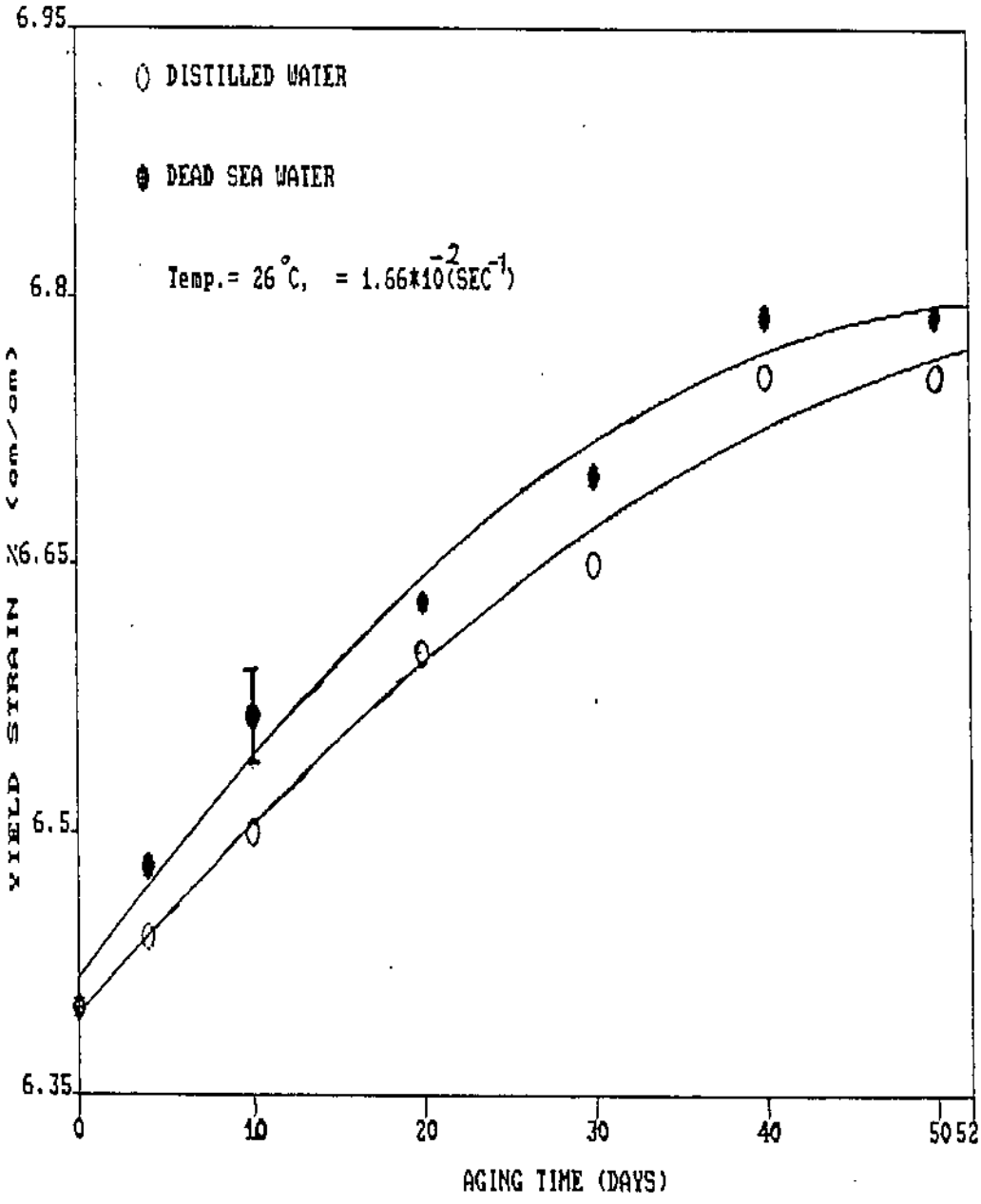


Fig. 4.17 The Yield strain versus aging time.

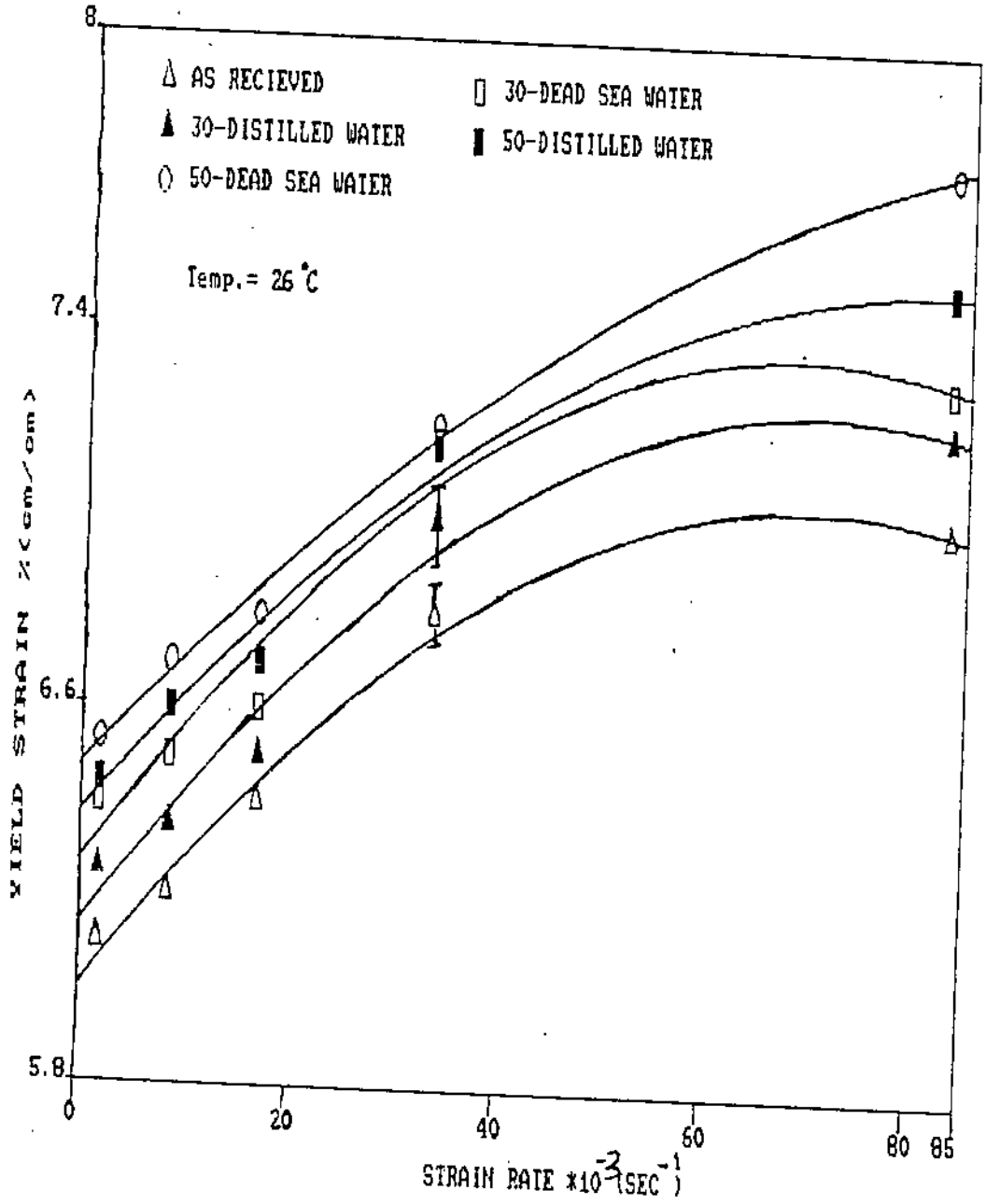


Fig. 4.18 The yield strain versus strain rate

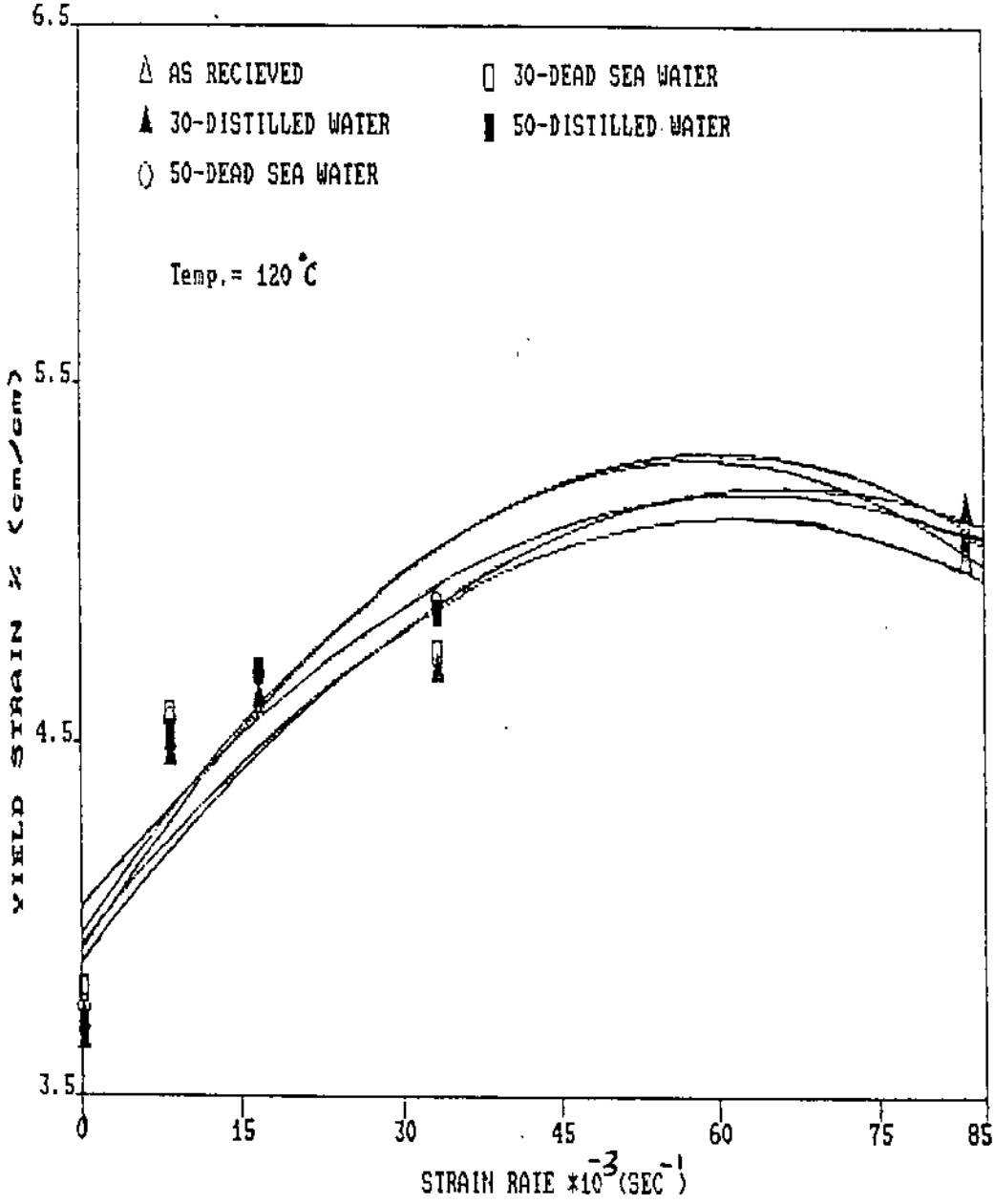


Fig. 4.19 The Yield strain versus strain rate

4.6 Some Correlation Relations :

A linear relation between the yield stress (σ_y) and the Young's modulus (E) is shown in Fig. 4.20. The slope of the line gives the ratio (σ_y/E) which is found to be about 0.033 for untreated samples. The ratio (σ_y/E) is calculated for treated samples and a relation is presented between (σ_y/E) and aging time for both distilled and Dead Sea water tests. A little increase is found in the value of (σ_y/E) with aging time as shown in Fig. 4.21. This result can be discussed by the help of the two Figs. 4.6 and 4.10 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 decrease in the yield stress with aging time. The same result is obtained when the Young's modulus is plotted versus the weight gain as shown in Fig. 4.22 and then this behavior is compared with the behavior of the yield stress versus the weight gain as shown in Fig. 4.23.

4.7 Optical Microscopy Study :

Fig. 4.24 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 [11,23,24,36].

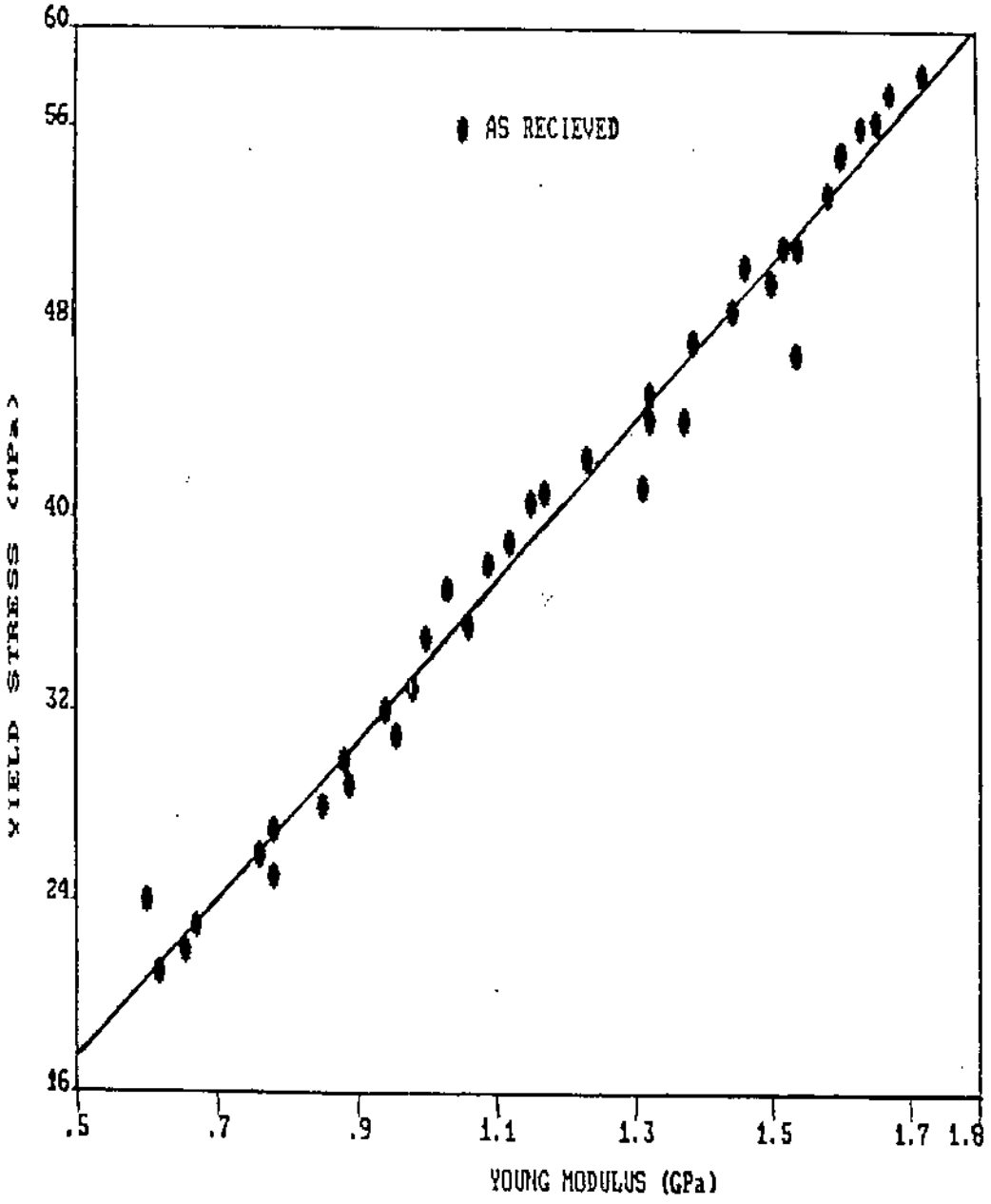


Fig. 4.20 The yield stress versus Young's modulus
(as spun samples)

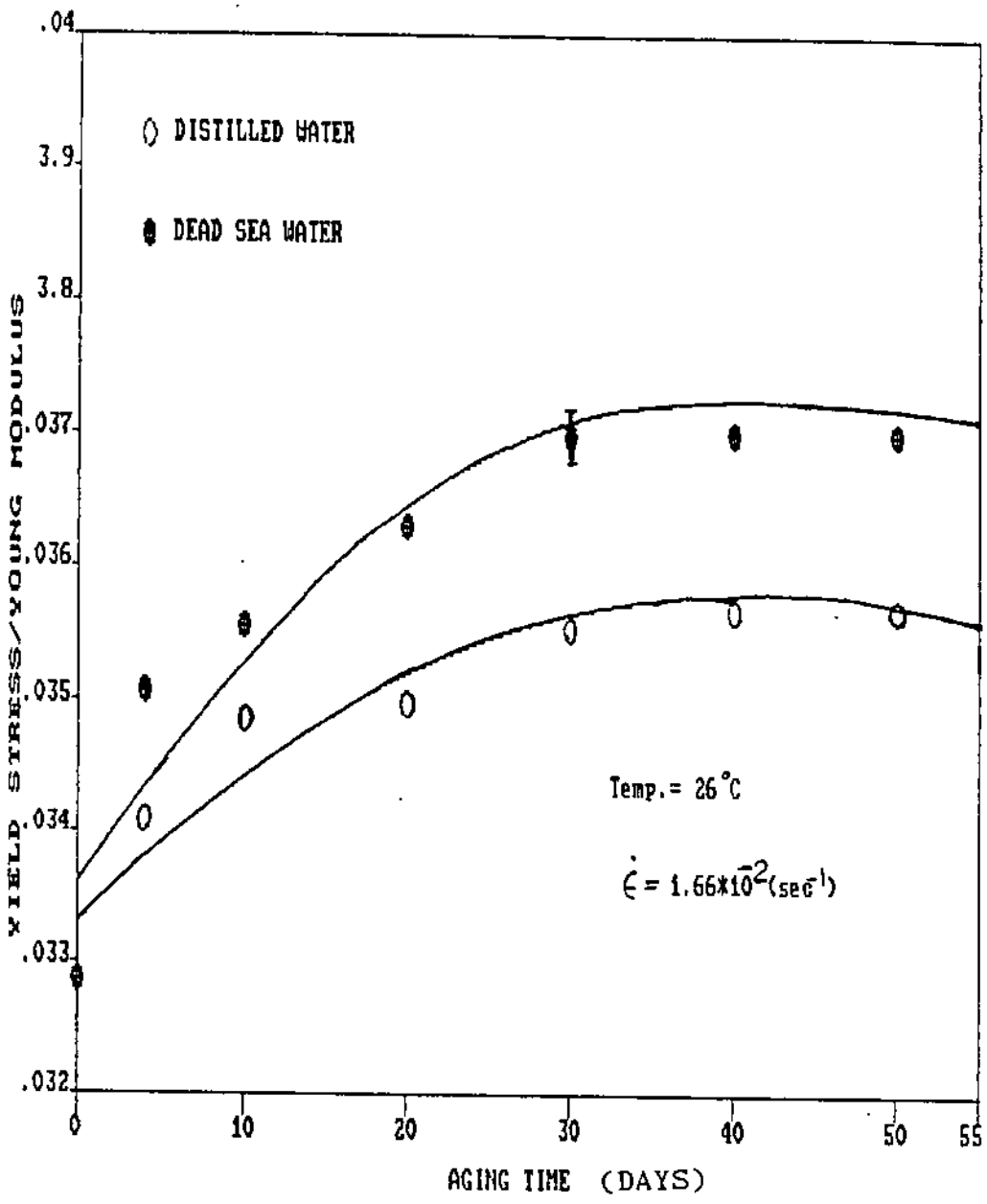


Fig. 4.21. The (yield stress / Young's modulus) versus aging time.

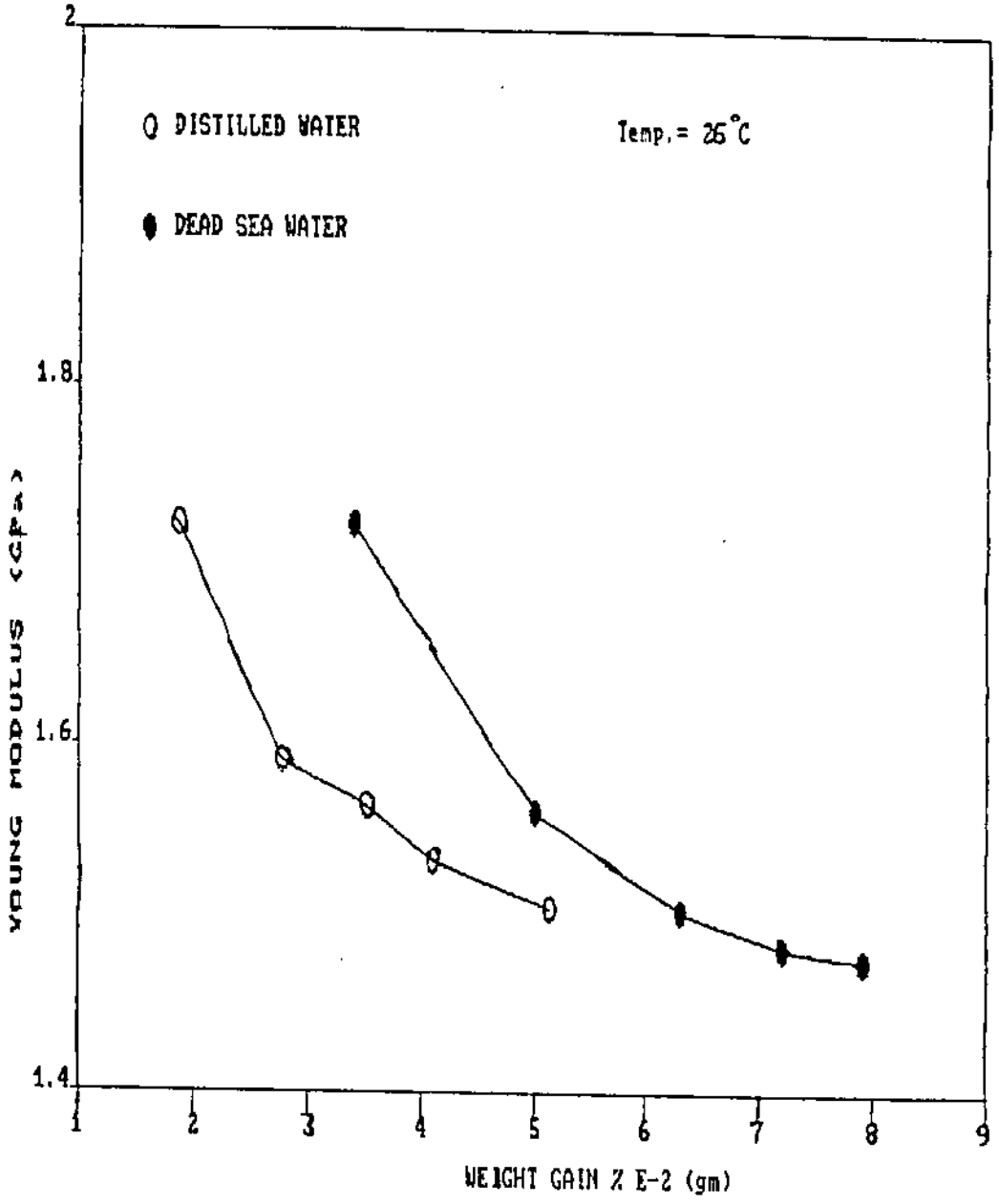


Fig. 4.22. Young's modulus versus weight gain

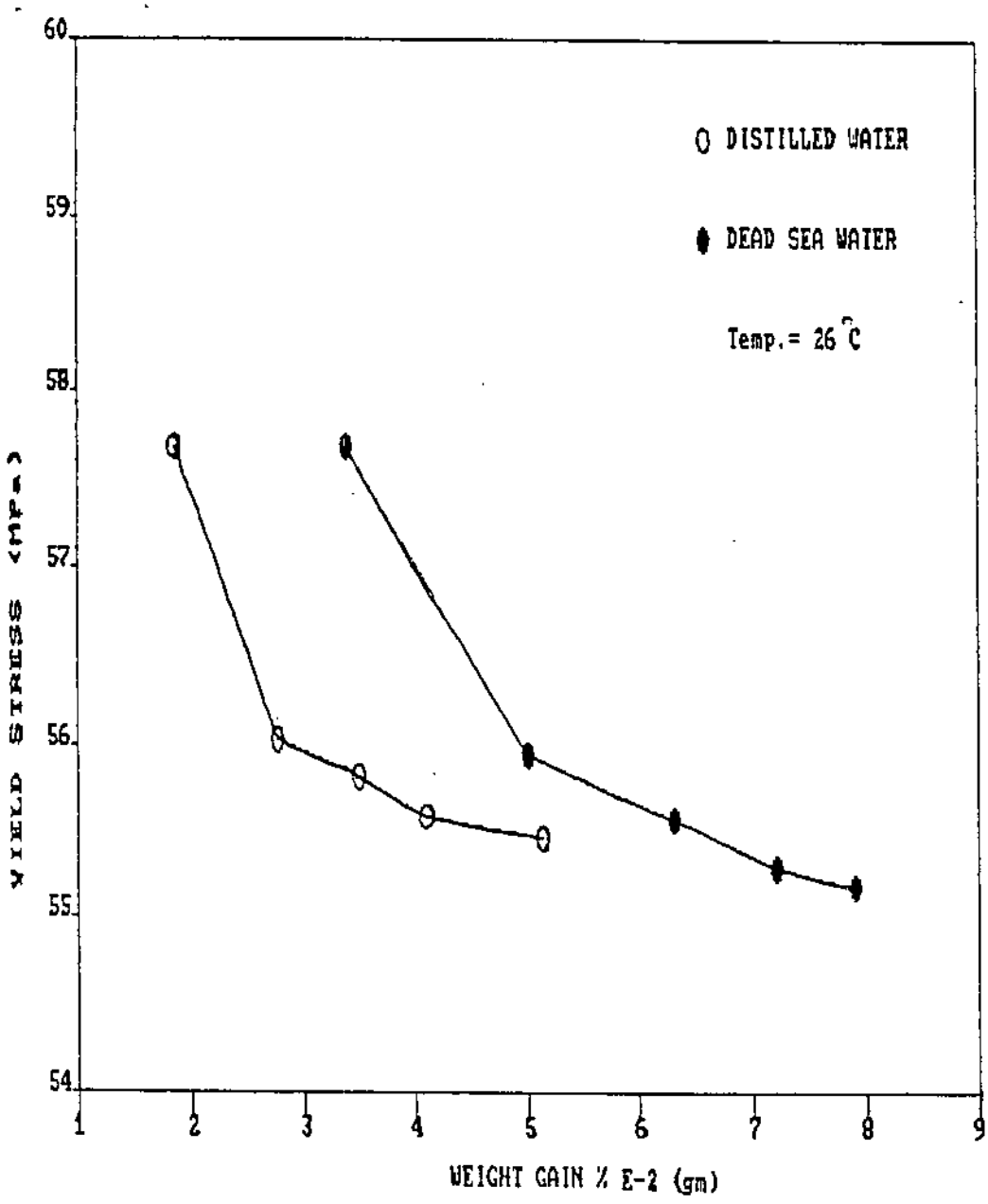
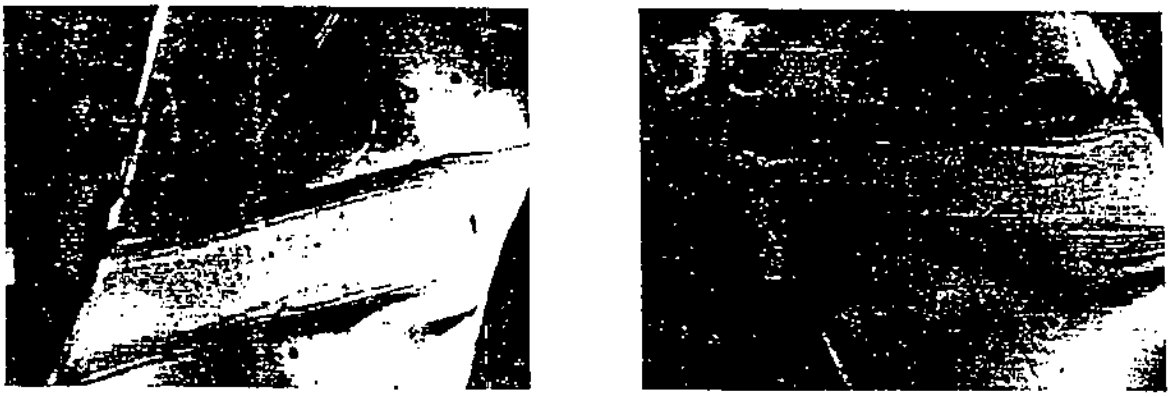
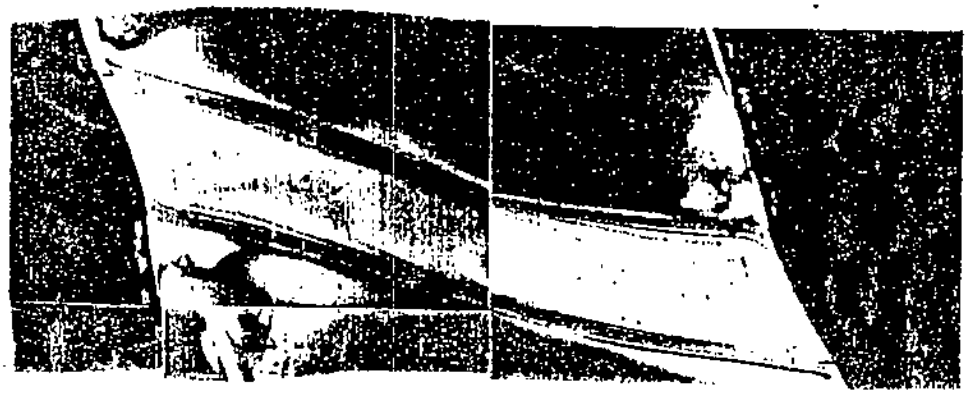


Fig. 4.23. The Yield stress versus weight gain



(a) (b)



(c)

Fig. 4. 24 Optical photographs of shear bands observed under polarized light for deformed polycarbonate samples

(a) as recieved
(b) aged for 30 days in distilled water.
(c) aged for 30 days in Dead Sea water.

CHAPTER FIVE
CONCLUSION AND FUTURE WORK

5.1 Conclusion :

The work presented in this thesis 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 conclusion 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. At relatively low temperatures, the untreated polycarbonate samples have higher elastic modulus and yield stress than the treated (aged) samples.
3. At high temperatures, the mechanical properties as the elastic modulus, the yield stress and the yield strain show no changes in their values when samples were aged in Dead Sea water; which means that the effect of aging becomes weak at high temperatures.
4. The obtained stress-strain curves of aged and unaged polycarbonate samples show that through aging the material becomes more ductile. This can be related to the swelling of polymer molecules resulting from the diffusion of water into the surface of polycarbonate specimens.
5. The activation energy shows slight decrease with aging time, and the activation volume shows slight increase with aging time.
6. The polarizing microscope photographs of the deformed polycarbonate samples showed shear bands for both unaged and aged samples.
7. The mechanism of yielding of polycarbonate is a slip-shearing process.

5.2 Future Work:

1- Studying the effect of radiation like U.V. and ionized radiation on the mechanical properties of polycarbonate.

2- The study of elastic deformation of different samples aged in Dead Sea water by using torsional pendulum.

3- Correlation of the electrical properties and the mechanical properties of polycarbonate may give useful information.

4- Studying the effect of the ionized radiation on the electrical resistivity of polycarbonate.

5- Studying the suitability of the aged polycarbonate samples in Dead Sea water as ion - selective electrodes.

6- Studying the creep behavior of the aged polycarbonate samples in Dead Sea water.

References:

1- L.E. Nielsen, "Mechanical Properties of Polymers", 1st edition, Reinhold Publishing Corporation, New York, 1962, ch. 1, pp. 1-10.

2- V.Shah, "Handbook of Plastics Testing Technology", John Wiley and Sons, New York, 1984, ch.2, pp. 7-23.

3- P.D. Ritchie, "Physics of Plastics", D.Van Nostrand Company, London, 1965, ch.2, pp. 24-26, ch.1, pp. 21-23.

4- F.W. Billmeyer, "Text Book of Polymer Science", 2nd edition, John Wiely and Sons, New York, 1970, ch.1, pp. 3-4.

5- H. Ulrick, "Introduction to Industrial Polymers", Hanser Publishers, New York, 1982, ch.1, pp. 17-20.

6- N.G. McCrum, C.P. Buckley and C.B. Bucknall, "Principles of Polymer Engineering", 1st edition, Oxford University Press, New York, 1988, ch.2, pp. 47-50, ch.4, pp. 142-166, ch.5, pp.172-180.

7- I.M. Ward and Holiland, "Structure and Properties of Oriented Polymers", 1st edition , Applied Science Publishers Ltd., London, 1975, ch.1, pp. 8-17.

8- L.E. Alexander, "X-Ray Diffraction Methods in Polymer Science", John Wiley and sons, New York, 1969, ch.1, pp. 1-43.

9- T.K. Mattioli and D.J. Quesnal, "Rate Process Analysis Applied to the Mechanical Behavior of Glassy Bisphenol-A-Polycarbonate", Polymer Engineering and Science, vol. 27, No. 11, 1987, pp. 848-856.

10- K.Othmer, "Encyclopedia of Chemical Technology", 3rd edition, Growth Substances, New York, 1982, vol. 18, pp. 480-493.

11- M.Ma, K.Vijayan, A. Hilther and E. Baer, "Shear Yielding Modes of Polycarbonate", Journal of Materials Science, vol. 24, 1989, pp. 2687-2696.

12- The Chemical Contents of Dead Sea Water, "Potassium Company Reports", 1990.

13- L.C.E. Struik, "Physical Aging in Amorphous Polymers and Other Materials", Elsevier Scientific Publishing Company, Amsterdam, 1978, ch.1, pp. 1-4.

14- K.S. Jaradat, "The Effect of Dead Sea Water on the Physical Properties of Polycarbonate", M.Sc. Thesis, University of Jordan, Amman, 1993.

15- P.Rogers, D. McPhail and J.Ryan, "Crizzling : A Method to Slow the Aging Process Affecting Glass Collections", Spectrum, vol. 3, 1993, pp. 8-11.

16- S.B. Lee and T.J. Rockett, "Interaction of Water with Unsaturated Polyester, Vinyl ester and acrylic resins", Polymer, Vol. 33, No. 17, 1992, pp. 3691-3697.

17- M.Narkis, L.Nicolais and A. Apicella, "Hot Water Aging of Polycarbonate", Polymer Engineering and Since, Vol. 24, No. 3, 1984, pp. 211-217.

18- A. Peterlin, "Mechinical Properties of Polymeric Solids", Reprinted from Annual Review of Material Science, Vol. 2, 1972, pp. 349-378.

19- V. Diliello, E. Martuscelli, G. Ragosta and A.Zihlif, "Mechanical Properties of Nylon 66/Nickel-Coated-Carbon Fibers Composite", Internal Journal Polymeric Material, Vol. 17, 1991, pp. 93-102.

20- I.M. Ward, "Mechanical Properties of Solid Polymers", 2nd edition, John Wiley and Sons, New York, 1983, ch.11, pp. 270-380.

21- C. Bauwens and J.C. Bauwens, "The Relationship between the effect of Thermal Pre-treatment and the Viscoelastic Behavior of Polycarbonate in the Glassy state", Journal of Material Science, Vol. 14, 1979, pp. 1817-1826.

22- R.E. Robertson, "Theory for the Plasticity of Glassy Polymers", The Journal of Chemical Physics, Vol. 44, No. 10, 1966, pp. 3950-3955.

23- A.M. Zihlif and B. Goswami, "Low-Temperature Plastic Deformation of Polymers", Dirasat, Vol.3, No.1, 1978, pp. 141-154.

24- A.M. Zihlif, "Review Lecture: The Physics of Yield Behavior of Polymers", Proc. 1st. Mediterranean School, Vol.1, Naples, Italy, 11 Sep., 1989, pp. 213-246.

25- R.A. Duckett, B.C. Goswami, L. Stewart, A. Smith, I.M. Ward and A.M. Zihlif, "The Yielding and Crazing Behavior of Polycarbonate in Torsion Under Superposed Hydrostatic Pressure", The British Polymer Journal, Vol.10, 1978, pp. 11-16.

26- W.Brostow and R. Corneliussen, "Failure of Plastics", 1st. edition, Hanser Publishers, Germany, 1986, ch.6, pp. 98-112.

27- J. Case and A.H. Chilver, "Strength of Materials and Structures", 2nd edition, Edward Arnold Publishers, London, 1979, ch.1, pp. 6-9.

28- M. Abu-Samra, "Effect of Metallic Additives on Physical Properties of Polymers, M.Sc. Thesis, University of Jordan, Amman, Jordan, 1983.

29- M.M. El-Abadla, "The Mechanical Properties of Rafia Oriented Polypropylene", M.Sc. Thesis, University of Jordan, Amman, Jordan, 1992.

30- C. G'Sell, and A.J. Gopez, "Plastic Banding in Glassy Polycarbonate Under Plane Simple Shear", Journal of Materials Science, Vol. 20, 1985, pp. 3462-3478.

31- C.W.Macoska and G.J. Vrand, "Tensile Yield Energy in Glassy Polymers", Polymer Engineering and Science, vol. 12, No.6, 1972, pp. 444-449.

32- R. Raghava, R.M. Caddell and G.S.yeh, "The Macroscopic Yield Behavior of Polymers", Journal of Materials Science, vol.8, 1973, pp. 225-232.

33- I.M. Ward, "The Rate of Molecular Networks and Thermally Activated Processes in the Deformation Behavior of Polymers", Polymer Engineering and Science, Vol. 24, 1984, pp. 724-736.

34- R.N. Haward, "The Physics of Glassy Polymers", Applied Science Publishers LTD, London, 1973, ch.5, pp. 295-298.

35- M.Narkis and J.P. Bell, "An Unusual Visual Microcraking/Healing Phenomenon in Polycarbonate at Room Temperature", Journal of Applied Polymer Science, Vol. 27, 1982, pp. 2809-2814.

36- A. Apicella, L. Egiziano, L. Nicolais, and V. Tecci, "Environmental Degradation of the Electrical and Thermal Properties of Organic Insulating Materials, Journal of Materials science, Vol. 23, 1988, pp. 729-735.

ملخص

تأثير مياه البحر الميت على الخواص الميكانيكية للبوليكربونيت

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تتضمن هذه الأطروحة محاولة لدراسة تأثير مياه البحر الميت على الخواص الميكانيكية لشرائح من مبلمر البوليكربونيت. وتشمل هذه الدراسة خصائص المرونة والإذعان وحساب حجم وطاقة التنشيط لعملية الإذعان وذلك بعد معالجة عينات من هذه المادة لفترات مختلفة في مياه البحر الميت. لقد أوضحت الدراسة بوجه عام أن الخواص الميكانيكية لمادة البوليكربونيت قد تأثرت بعملية المعالجة في مياه البحر الميت وذلك من خلال دراسة العلاقات بين الإجهاد والإنفعال خلال فترات معالجة مختلفة. وكان التغير في الخواص الميكانيكية للبوليكربونيت ملحوظا على درجات الحرارة المعتدلة ؛ أما على درجات الحرارة المرتفعة نسبيا فإن هذه الخواص لم تبد أي تغير ملحوظ عند معالجتها بمياه البحر الميت.