

THE EFFECTS OF SEA WATER IMMERSION ON THE MECHANICAL PROPERTIES OF LOW DENSITY POLYETHYLENE

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تأثير مياه البحر على الخواص الميكانيكية
لمادة البولي اثيلين منخفض الكثافة

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تمت دراسة تأثير مياه البحر لفترات زمنية تصل إلى السنة على مادة البولي اثيلين المنخفض الكثافة وذلك باستخدام التقنيات الميكانيكية والفوق صوتية في مختبرات كليتي الهندسة والعلوم بجامعة قطر، وقد اظهرت النتائج أثراً لزم التعتيق في المياه المالحة على خواص المادة الميكانيكية، نوقشت نتائج البحث على أساس درجة ثبات المادة في مياه البحر وفرت عن طريق التفاعلات الكيميائية وعمليات الامتصاص الفيزيائية التي تمت في الوسط الأيوني المتوفر في مياه البحر، وقد تم ربط ذلك مع التفاعل الفيزيائي المميز الذي يشتمل على تفكك روابط المادة وفقدان البلمرة والذي يفسر باستخدام الخواص الميكانيكية.

Keywords : Polyethylene - Mechanical Properties - Ultrasonic Sea Water Immersion.

ABSTRACT

The effects of immersion of low-density polyethylene (LDPE) in seawater for times of up to one year were studied using mechanical and ultrasonic techniques. The studies were carried out in the laboratories of the Faculties of Science and Engineering in the University of Qatar.

The results demonstrate an interaction between ageing time and seawater immersion. The experimental results indicated that mechanical properties are sensitive to varying periods of seawater immersion. The results are discussed in terms of the stability of LDPE in seawater and explained in terms of chemical reactions and physical absorption processes taking place in the presence of high ionic concentrations present in seawater. Significant physical interactions are reported and mechanism involving chain scission and depolymerisation are proposed to explain the mechanical test results.

INTRODUCTION

The State of Qatar is characterised by adverse geomorphic and climatic conditions such as contaminated ground water, ambient salinity, high temperatures and humidity. Chloride and sulphate salts extensively contaminate the ground water and the moisture laden environment. Previous work [1] has shown that LDPE is very sensitive to weathering (sunlight, humidity and elevated temperatures). The results obtained showed that the strength of the experimental material (LDPE, QAPCO grade FD 0374) decreased with increasing ageing for times of up to 7 days, after which the strength started to recover, whereas ductility decreased continuously with ageing time. The results are discussed in terms of oxidation which is thought to dominate the degradation process in the first week and crosslinking which starts to be effective after one week of ageing.

There are many applications in which engineering plastics are exposed to water, including seawater. This requires knowledge of the anticipated rate of deterioration of their properties. Furthermore, the sea is sometimes used as a cheap and readily available rubbish dump by boats and by certain municipalities throughout the world. This results in serious litter problems, which are threatening the coastline and beaches in many countries [2]. Such problems led, in the last few years to an increasing awareness of environmental pollution. Synthetic polymeric materials are readily detectable in all kinds of waste. Thus, it is intended in this work to investigate the effects of seawater on the mechanical properties of LDPE, grade FD0374, which is a continuation of the previous work [1]. The results may be used in understanding the material stability or degradability in such an environment.

It should be mentioned that polymeric materials generally absorb moisture to some measurable degree when immersed directly in water or when exposed to atmospheric moisture [3]. A figure of <0.015 wt % for LDPE [4] has been given. Allen and Boner [3] reported that the absorption of water could have both reversible and irreversible effects on the properties and performance of plastics. Absorbed moisture may act as a plasticizer, reducing the strength of the plastic reversibly and may also induce irreversible mechanical damage by means of micro-cracking, crazing or chemical degradation of the polymer structure.

EXPERIMENTAL

Films of LDPE (grade FD0374) with thicknesses of 100 and 300 μm were supplied by Qatar Petrochemical Company (QAPCO). The melt flow index for the material was 3.7 g/10 min with a crystalline melting point of 110-120°C and density of 920 kg m^{-3} . Tensile samples with gauge length of 25 mm and width of 10 mm were cut from these films. In addition, pellets from the same material were compression moulded in the University of Qatar into discs (25 mm diameter x 2 mm thick) at 30 MPa and 165°C for 20 minutes. These discs were used to perform the ultrasonic measurements.

Samples were immersed in seawater for increasing times. The immersion times were 2 days, 4 days, 1 week, 2 week, 1 month, 2 months, 4 months, 6 months and 1 year.

Tensile testing was carried out using a LLOYD Instruments materials testing machine linked to a remote microcomputer for data acquisition and analysis. The load was measured by a load cell of 5 kN capacity, while the displacement was measured using an internal extensometer. The speed of testing was 100 mm/min. The Lloyd Data Analysis Package (DAP) was used to analyse the tensile properties from the load-extension diagrams. Detailed information about DAP are outlined elsewhere [5]. Four samples were tested for each immersion time and the average values were calculated.

Ultrasonic measurements were performed on the disc samples using a Krautkramer Ultrasonic unit Model USL-32. All the measurements were carried out at a frequency of 4 MHz. The velocity of sound propagation, V_s (mm/s) through the sample can be determined from the equation:

$$V_s = 2D/T \quad (1)$$

Where D is the length of the test sample in the direction of measurement, in mm, and T is the measured transit time, in sec. It should be mentioned that the attenuation of elastic waves at ultrasonic frequencies are utilised in this work for the determination of a sonic modulus (E) which is suitable for determining the mechanical properties of crystalline polymers [5]. It is known also that a sonic pulse in the MHz range causes real displacements of the

molecules from their equilibrium position as it passes through a specimen [6]. Thus, the velocity of the wave in the material will depend on its density and stiffness [7], which may be expressed as

$$C_{ii} = \rho V_{ii}^2 \quad (2)$$

Where C_{ii} is the stiffness constant in a particular direction; ρ is the density of the material; and V_{ii} is the velocity of a particular wave propagating in a particular direction.

For an isotropic sample, the sonic modulus may be given by the following equation (8):

$$E = [C_{11} (C_{11} + C_{12}) - 2C_{12}^2] / (C_{11} + C_{12}) \quad (3)$$

The unknown C_{12} for isotropic bodies may be obtained from the following relation (8):

$$v_{12} = C_{12} (C_{11} - C_{12}) / (C_{11}^2 - C_{12}^2) \quad (4)$$

Where v_{12} is the in-plane Poisson's ration, which for the investigated LDPE was assumed to be 0.315 [9].

RESULTS AND DISCUSSION

Statically stressed samples of LDPE have been found to exhibit similar behaviour to amorphous polymers in that the storage modulus measured by dynamic mechanical analysis showed a sudden decrease followed by a continual rise when an increasing stress was applied [10,11]. These effects are thought to be associated with stress induced changes in free volume in the amorphous phase of LDPE. Any influence which increase the free volume is expected to produce similar results.

When polymers are in contact with liquids two possibilities are present. Chemical reactions may take place induced by the chemical reactivity of the liquid, dissolved substances, such as sodium chloride, and the polymer. Solid polymers may also absorb liquids if the solubility parameter is favourable. This is particularly the case with organic liquids but water may also act as a limited solvent. Absorption results in swelling, shape change and even total dissolution. The stronger the interaction of solvent and polymer the greater is the swelling effect and the greater the resulting internal stresses. In addition chemical reactions may occur. In the present case we must consider possible interactions between seawater and LDPE. LDPE is semi-crystalline in

structure and thus contains amorphous and crystalline phases. It is expected that seawater preferentially attacks the amorphous phase because of its high free volume.

Figures 1 and 2 show stress versus strain curves for both thicknesses of the LDPE films (100 and 300 μ m) after increasing times of seawater immersion. Yield strength is a convenient measure of strength [12] and the yield strengths, ductilities (nominal strain to fracture) and toughness (integrated area under the stress versus strain plots) are shown in Figures 3 and 4. It can be seen that the yield strength is particularly sensitive to seawater immersion within the first two days showing a sharp decrease. Subsequently the yield strength can be seen to rise and stabilise until after approximately six months a gradual decrease in apparent. The total decrease after one year immersion was approximately 1Nmm⁻² for the 100 μ m thick film and 2.5Nmm⁻² for the 300 μ m film.

Any reaction are expected to be initially restricted to the surface of the specimens. Over a longer period absorption of water would be expected to play a part.

The degree of crystallinity, chain conformation and microstructure are expected to have significant roles in the progress of these reactions and absorption processes, ions present in seawater are expected to play a significant role in the degradation of the polymer. Two sequential steps have been identified i.e. main chain scission followed by degradation. The activation energy for main chain scission is reported to be less than that of depolymerisation [13] during prolonged seawater immersion. Chemical attack is not restricted to the bulk amorphous phase but also seems to occur at chain fold sites in the crystalline lamellae [14, 15]. And thus the crystalline phase is also affected.

The decrease in ductility of the LDPE specimens can be seen in Figure 3 for both film thicknesses. This suggests that chemical degradation both at the surface and within intermolecular voids is taking place. The resulting reduction in molecular mass would be expected to produce a decrease in ductility.

Sonic measurements of velocity and elastic modulus were

carried out on compression moulded samples in the form of discs after immersion in seawater for various times Fig 5. The microstructure of these samples is certainly different from the film samples and the samples are considerably thicker. Differences in degree of crystallinity, spherulite size and general microstructure will be present. However, the samples show a drop in sonic modulus after short immersion times in line with the reduction of mechanical properties evident in the film samples. This indicates that surface effects are important at short immersion times and are responsible for the drop in properties during the first two days of immersion. It is extremely unlikely that significant penetration of the disc samples would occur in this timescale.

CONCLUSION

1. Immersion of the LDPE in seawater caused deterioration in the mechanical properties of the material, probably by chemical attack.
2. The chemical degradation of the material was not restricted to the surface of the specimens but extended to the intermolecular voids inside the material. However, surface effects dominate at short immersion times.
3. Ultrasonic measurement showed a similar trend. The samples show a drop in sonic modulus which is in accord with the reduction of the mechanical properties obtained with the tensile samples.

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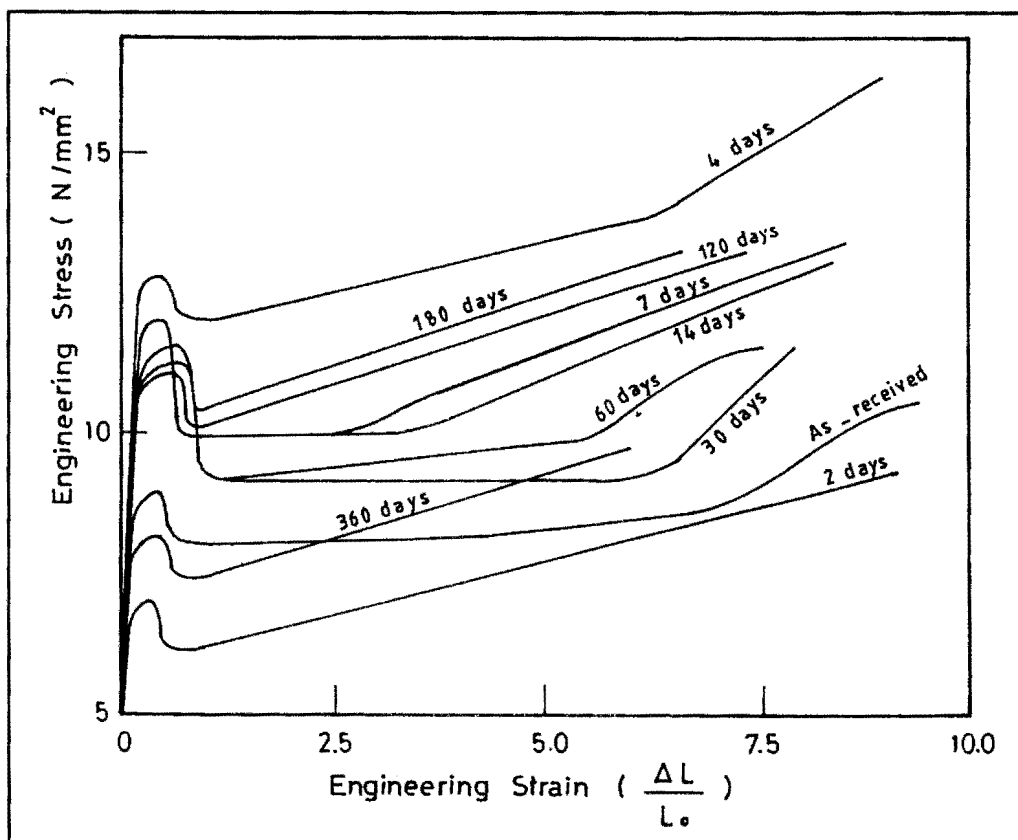


Fig (1) Stress-strain curves of LDPE films (100 mm thick) grade FD0374 after different immersion times in seawater.

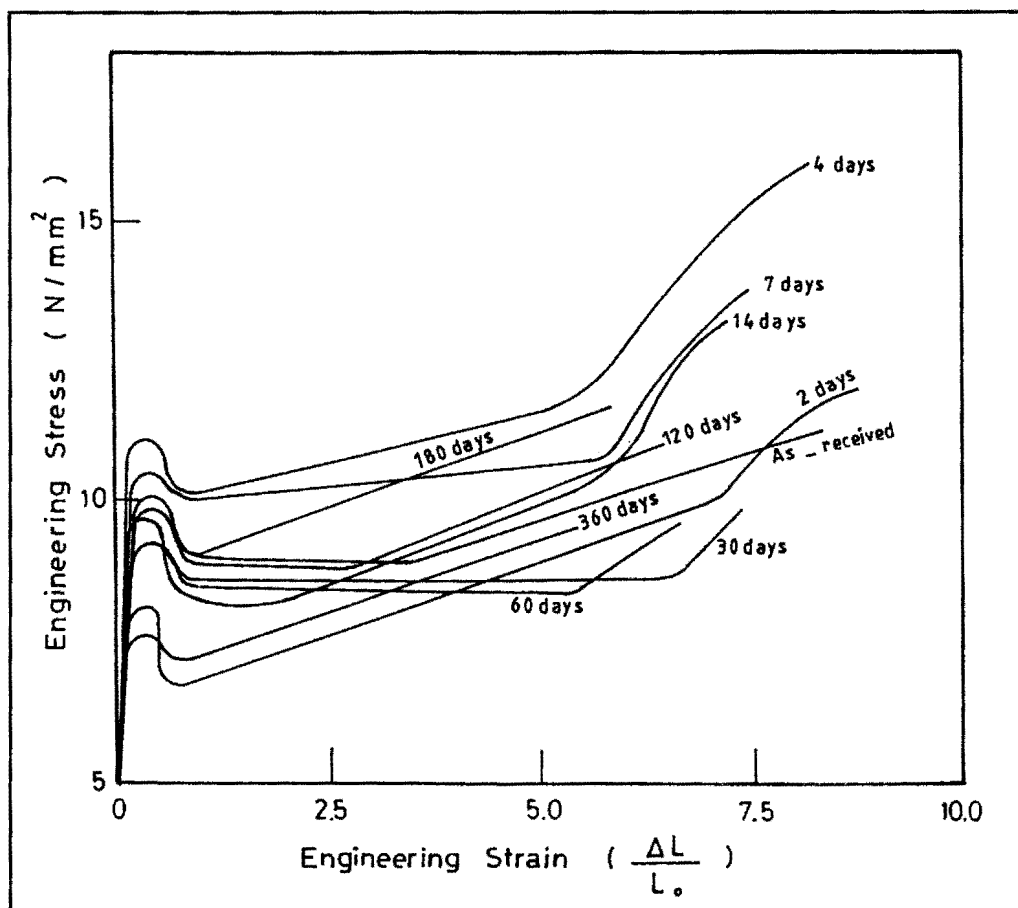


Fig (2) Stress-strain curves of LDPE films (300 m thick) grade FD0374 after different immersion times in seawater.

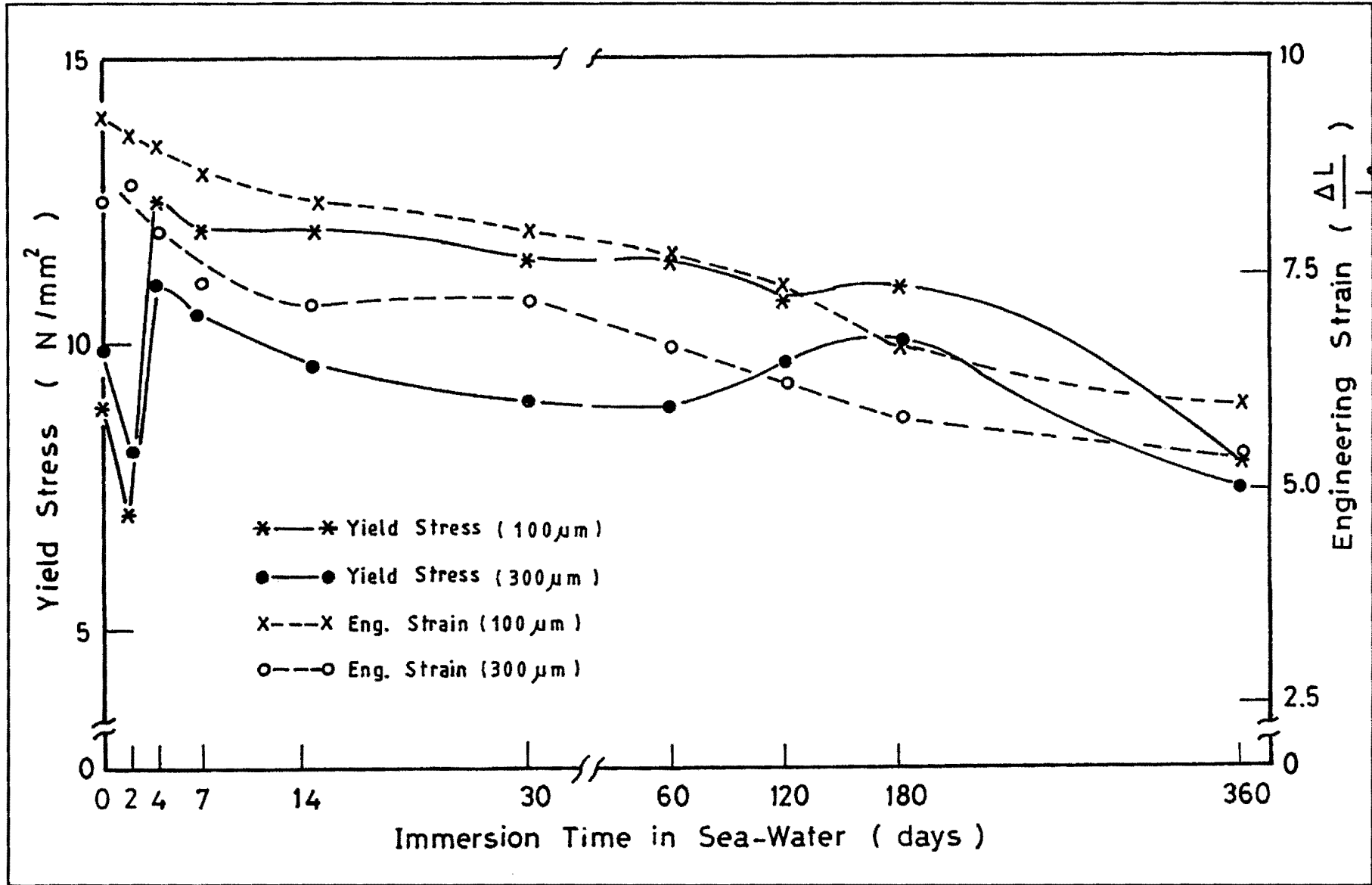


Fig (3) Yield stress and ductility versus the immersion time in seawater for the examined material (100 and 300 m thick).

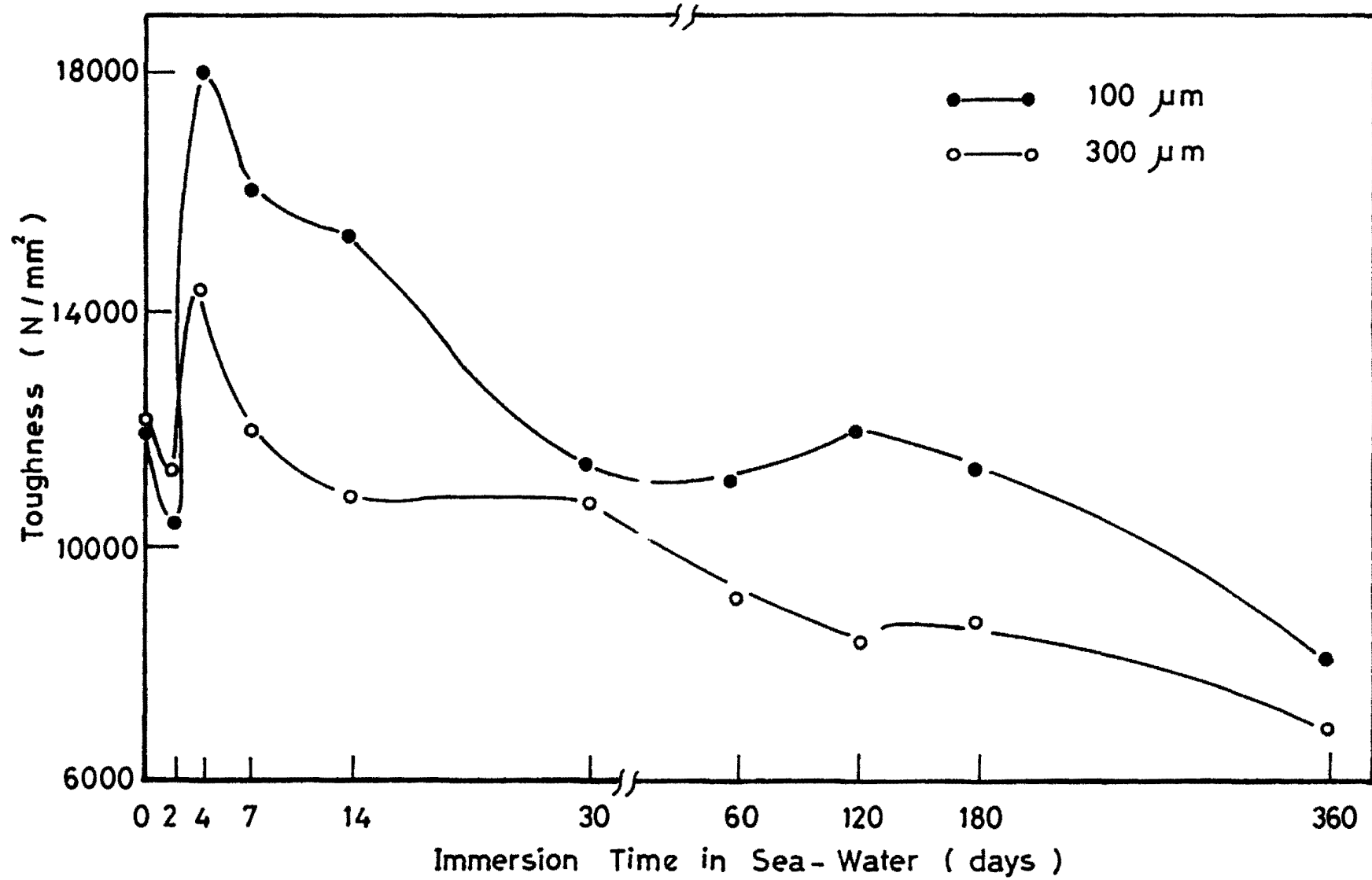


Fig (4) Toughness (areas under the stress/stain curves) versus the immersion time in seawater for the examined material (100 and 300 m thick).

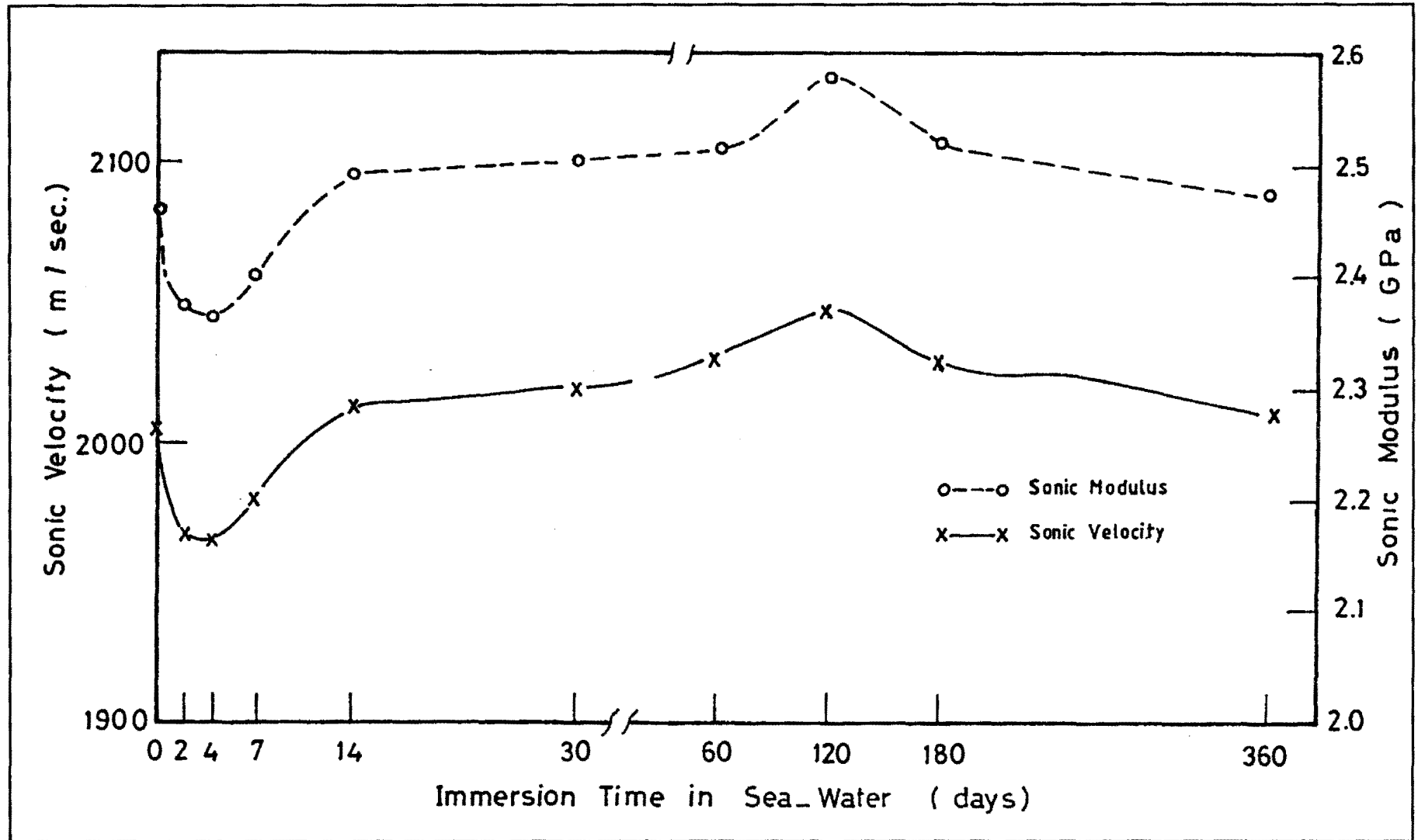


Fig (5) Sound velocity and sonic modulus versus the immersion time in sea water for the examined material.