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Influence of Ringer's solution on creep resistance of hydroxyapatite reinforced polyethylene composites

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In vitro creep studies of polyethylene, both unfilled and filled with hydroxyapatite at 0.20 and 0.40 volume fraction, have been performed. The samples were immersed in Ringer's solution at 37 °C for 1, 7, 30, 90 and 150 days prior to isochronous and creep tests in the same condition. The creep properties of unfilled polyethylene is unaffected by the immersion, but the isochronous modulus and the creep resistance of filled polyethylene were reduced. The effect increased with increasing volume fraction and time of immersion. This reduction is related to the penetration of the solution into the material, softening the interface.

1. Introduction

When polymers encounter fluid environments in service, their response to the environment is an essential design consideration since the structure and mechanical properties can be altered by diffusion of liquids into polymers. The presence of small fluid molecules interspersed in the polymer molecular chains tends to ease the mobility of these chains and increases the susceptibility to deformation. The diffusion of liquid may act both as a plasticizer [1, 2] and a crazing agent [3, 4], leading to a worsening of mechanical properties, including creep resistance; in some cases, the fluids even dissolve the polymers [5]. This effect is frequently referred to as environmental stress cracking or stress corrosion cracking.

Materials for medical applications encounter a hostile environment in the human body due to the combination of physiological fluid and body temperature. This environment adversely affects such mechanical properties of polymeric biomaterials as tensile strength, modulus and creep rupture [6–9]. Hydroxyapatite reinforced polyethylene (HAPEX^{TM}) composites have been developed as bone replacement materials with a modulus closely matched to bone, reducing the risk of stress shielding and consequent bone resorption, while having a reasonably high toughness to prevent catastrophic failure in the body [10]. HAPEX^{TM} has been used successfully for orbital floor reconstruction [11], a low load-bearing application. This study investigates the influence of simulated body environment upon the creep properties of HAPEX^{TM}.

2. Experimental procedures

2.1. Materials and specimen preparation

The matrix material used was a high density polyethylene (Rigidex HM4560EP, B.P. Chemicals Ltd, UK) and the filler was hydroxyapatite (Grade P88, Plasma Biotal Ltd, UK) with a mean particle size of 4.14 μm. These two materials were mechanically premixed by a commercial mixer and then compounded using a twin screw extruder (Betol BTS40L) producing composites at filler volume fractions of 0.20 (20 HA/PE) and 0.40 (40 HA/PE) [12]. Unfilled polyethylene (HDPE) was processed similarly through the Betol twin screw extruder. 4 mm thick sheets of these materials were prepared by compression moulding and tensile specimens, conforming to ISO 527, were then milled from the plaques using a pantograph. The machined surface was smoothed using fine abrasive paper. All the specimens were gamma irradiated at a dose of 2.5 Mrad by Isotron Ltd using ^{60}Co γ-radiation following standard procedures for medical devices.

2.2. Weight change measurements

Specimens were weighed before being immersed in buffered (pH 7.5) Ringer's solution at 37 °C for 1, 7, 30, 90 or 150 days. They were then taken out and the excess solution was carefully wiped from the surface. They were reweighed and the fractional weight change of material was calculated using Equation 1:

$$\%\ \text{fractional weight change} = \frac{(\text{weight after immersion} - \text{initial weight})}{\text{initial weight}} \times 100 \qquad (1)$$

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2.3. Isochronous and creep experiments

The samples were tested at 37 °C in Ringer's solution in a tensile creep machine (Stephenson Engineering plc, UK), which is described in detail elsewhere [13]. The specimen was loaded by applying weight via a lever arm with the help of a non-linear dashpot to ensure fast but non-vibratory loading. The strain was measured at the gauge length by an LVDT system connected to the specimen via extension arms. Isochronous stress–strain experiments were performed by repeatedly loading each specimen at successively higher constant stresses for 100 s, after which the strain was recorded, with intervening periods of zero stress for 400 s during which the specimen recovered. The applied stress and the 100 s strain at each load level were plotted to give the isochronous stress–strain graphs.

Creep tests were conducted at stress levels of 4, 6 and 8 MPa for HDPE, 20 HA/PE and 40 HA/PE. All measurements were carried out in Ringer's solution at 37 °C. The first 10 s of data were discarded.

3. Results

3.1. Weight change

Fig. 1 shows percentage weight change after immersion in Ringer's solution at 37 °C. It can be seen that the weight of polyethylene remains relatively constant while 20 HA/PE and 40 HA/PE composites gained weight. For both 20 HA/PE and 40 HA/PE the initial change in weight is high, but levels off after time. The amount of weight gain increased with increasing time of immersion and volume fraction of the composites. HDPE and 40 HA/PE samples stored in air at room temperature and at 37 °C for 7 days were also weighed. No changes of weight could be detected for either materials at either temperature.

3.2. Isochronous stress–strain relationship

The stress–strain curves of composites after immersion are depicted in Figs 2–4. Immersion decreased the modulus of the composites, but had no effect on unfilled polyethylene. The curves for unfilled polyethylene appear to be comparable at all immersion periods. Fig. 5 shows the decrease in modulus due to immersion. The curves for the composites show an initial sharp decrease in modulus which stabilizes after time.

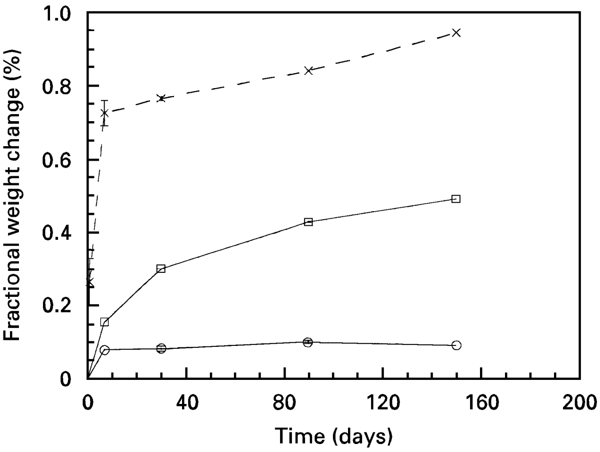

Figure 1 Influence of immersion in Ringer's solution at 37 °C on the weight of 2.5 Mrad γ-irradiated materials: × 40 HA/PE; □ 20 HA/PE; ○ HDPE.

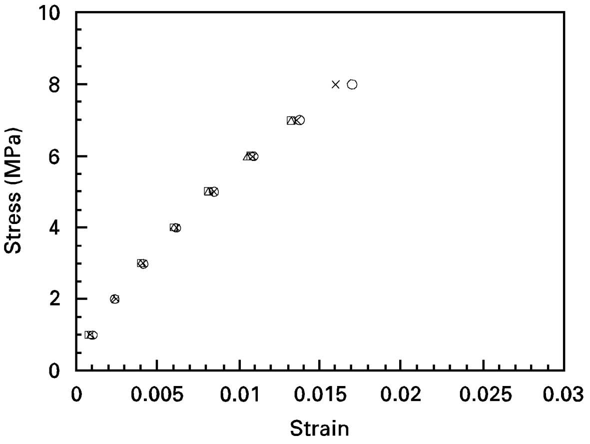

Figure 2 Influence of immersion on 100 s isochronous stress–strain relationship of 2.5 Mrad γ-irradiated HDPE at 37 °C in Ringer's solution: ○ non-immersed; □ 30 days; × 90 days; △ 150 days.

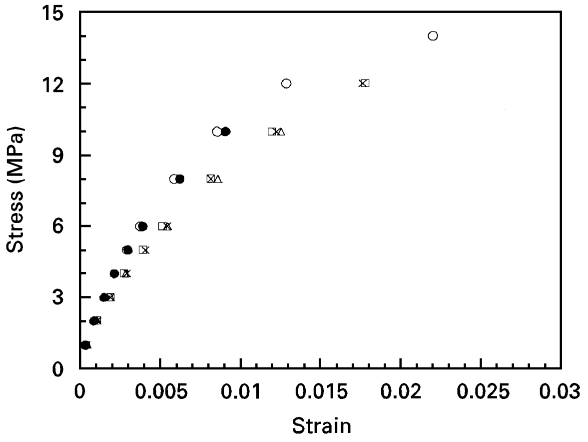

Figure 3 Influence of immersion on 100 s isochronous stress–strain relationship of 2.5 Mrad γ-irradiated 20 HA/PE at 37 °C in Ringer's solution: ○ non-immersed; ● 7 days; □ 30 days; × 90 days; △ 150 days.

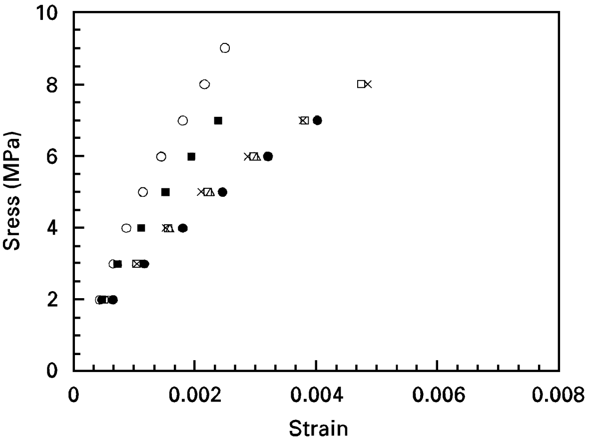

Figure 4 Influence of immersion on 100 s isochronous stress–strain relationship of 2.5 Mrad γ-irradiated 40 HA/PE at 37 °C in Ringer's solution: ○ non-immersed; ■ 1 day; ● 7 days; □ 30 days; × 90 days; △ 150 days.

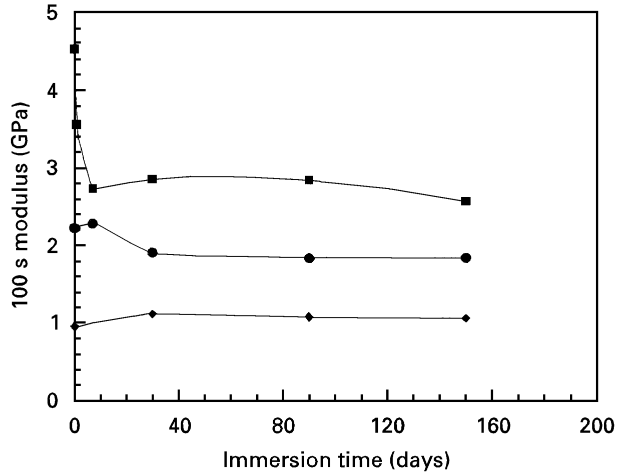

Figure 5 Influence of immersion on 100 s creep modulus, measured at 0.001 strain: ■ 40 HA/PE; ● 20 HA/PE; ◆ HDPE.

TABLE I Effect of immersion in Ringer's solution at 37 °C on 100 s creep modulus of materials

Material	Modulus change (%)				
	1 day	7 days	30 days	90 days	150 days
2.5 Mrad HDPE	–	–	+ 3	+ 2	+ 4
2.5 Mrad 20 HA/PE	–	– 3	– 21	– 26	– 27
2.5 Mrad 40 HA/PE	– 23	– 47	– 42	– 40	– 43

In the case of 20 HA/PE, an immersion period of 7 days had no effect on the modulus, but by 30 days the drop in modulus had stabilized. For the 40 HA/PE a drop was seen after immersion for 1 day and stabilized after 7 days. Table I shows the average values of percentage modulus change with immersion time. The samples of HDPE and 40 HA/PE stored in air at room temperature and at 37 °C for 7 days were also tested. No significant modulus changes after storage in air were observed.

3.3. Creep properties

Fig. 6 shows the creep behaviour of 40 HA/PE composites at 6 MPa applied stress. All samples exhibit similar-shaped curves; initially a linear region, or secondary creep, and then a region where the creep accelerates, stress whitening occurs and, at higher stress levels, the specimen can fail or at lower stress levels a second linear region starts. The immersed samples show higher creep strain and a shorter time to the onset of rapid strain increase. After immersion for 1 day the creep strain increased and the time to onset of rapid increase in strain decreased. After 7 days immersion the creep strain is further increased, but up to 150 days immersion no further increase in creep strain is seen and the time to onset of rapid increase in strain stabilizes at the 7-day level (Fig. 8). Creep tests of HDPE and 20 HA/PE immersed for 7 days were also carried out at stress levels of 4 and 8 MPa, respectively. No changes were observed for unfilled polyethylene and no tertiary creep was seen within the times for which the tests were performed (Fig. 7), but the creep strain of 20 HA/PE increased in a manner consistent with the isochronous results.

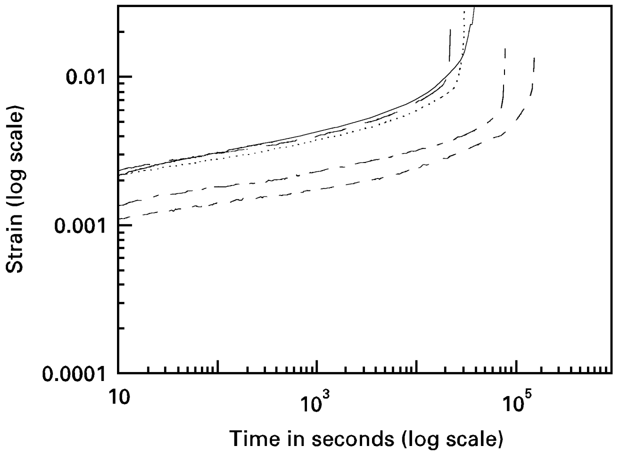

Figure 6 Influence of immersion upon the creep behaviour of 2.5 Mrad γ-irradiated 40 HA/PE at 6 MPa applied stress at 37 °C in Ringer's solution: --- non-immersed; – – – 1 day; —— 7 days; ······ 90 days; — — 150 days.

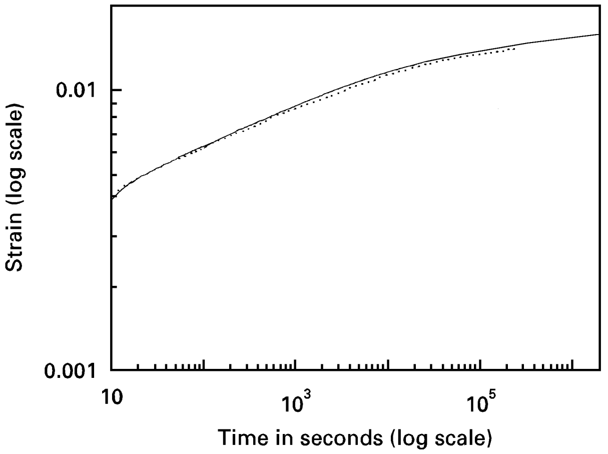

Figure 7 Influence of 7 days immersion upon the creep behaviour of 2.5 Mrad γ-irradiated HDPE at 6 MPa applied stress at 37 °C in Ringer's solution: —— non-immersed; ······ 7 days immersion.

4. Discussion

Immersion of hydroxyapatite reinforced polyethylene composite in Ringer's solution prior to the tests resulted in fluid absorption by the materials. In composite materials, the liquid penetration is conducted by a diffusion mechanism in which the fluid molecules diffuse into the matrix and reinforcing phase. In this case, the majority of the diffusion occurs through the hydroxyapatite since the polyethylene matrix absorbs relatively low amounts of liquid due to its hydrophobic and non-polar nature. The degree of absorption is found to depend on both filler content and the length of immersion. The higher the filler content, the greater the amount of liquid which can diffuse into the composite, confirming the hypothesis that the diffusion of

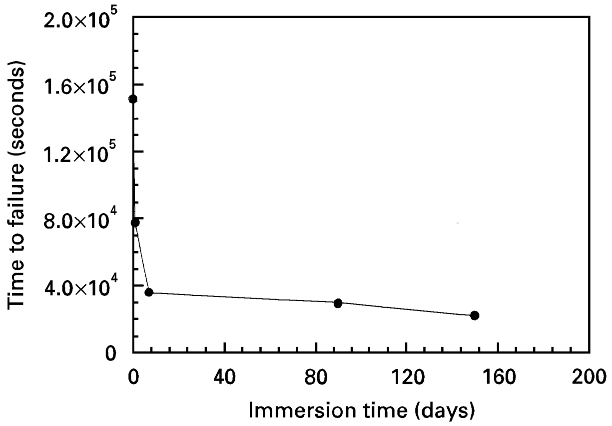

Figure 8 Influence of immersion time on time to failure of 2.5 Mrad γ-irradiated 40 HA/PE at 37 °C in Ringer's solution loaded at 6 MPa.

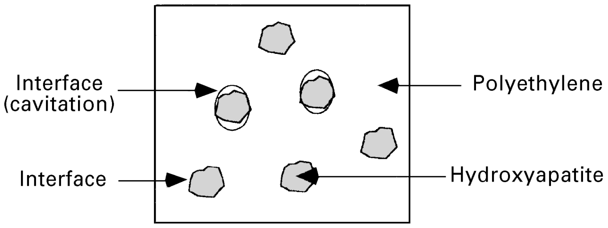

Figure 9 Locations of liquid penetration in the composite.

solution is mainly into hydroxyapatite particles. In addition, the fluid can also diffuse through the interface between the two constituents by capillarity and microcrack transport mechanisms [14]. The equilibrium solution absorbed by 40 HA/PE is around twice that of 20 HA/PE composite. Electron microscopy has shown that even at 0.4 volume fraction there is no particle-to-particle contact in this composite. The absorption curve of 40 HA/PE started to level off sooner than 20 HA/PE. This is due to the greater numbers of penetration sites (both particles themselves and interfacial area) for accelerating liquid penetration (Fig. 9). The length of time of immersion is obviously another factor since it controls the time available for diffusion. The longer the exposure time, the higher the amount of fluid absorbed until saturation occurred. The isochronous data for both composites showed a decrease in modulus after immersion in Ringer's solution. This result is attributed to the plasticization effect brought about by the liquid penetration, since materials stored in air at 37 °C for the same times showed no signs of modulus decrease. The fluid disrupts the interface between the hydroxyapatite particles and polyethylene matrix easing deformation of the materials. In addition, unfilled polyethylene also showed no signs of modulus or weight change up to 150 days of immersion. 20 HA/PE, however, showed a decrease in modulus after 30 days, whereas 40 HA/PE deteriorated at shorter times and its modulus decreased after immersion for 1 day in Ringer's solution prior to testing. 40 HA/PE showed a greater reduction in modulus than 20 HA/PE for the same immersion time.

Creep data exhibited similar trends to the isochronous data. The creep strains of the immersed samples of 40 HA/PE (1, 7, 90 and 150 days) were higher than non-immersed samples at the same applied stress, whereas HDPE (7 days) and 20 HA/PE (7 days) showed similar properties to the non-immersed materials. The divergence in the creep strain of immersed samples in a long strain–log time plot (Fig. 6) occurred at a much shorter time than for the non-immersed 40 HA/PE. This result is again attributed to the effect of the liquid on interface adhesion in the composite. Immersion times after 7 days appeared to have no effect on the creep behaviour of immersed 40 HA/PE. This is due to the amount of liquid absorbed reaching equilibrium after 7 days, as shown by the weight change measurements; so times of immersion greater than 7 days should have no further significant effects on the properties.

5. Conclusions

The creep resistance of hydroxyapatite-reinforced polyethylene composites was reduced by immersion in Ringer's solution. This effect is due to the penetration of fluid into the materials. The decrease in creep resistance and the increase in the amount of fluid penetration was found to be a function of filler volume fraction and immersion times.

Acknowledgements

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