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Polyacids as bonding agents in hydroxyapatite polyester-ether (Polyactive^{TM} 30/70) composites

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A previously developed method to improve the interface between hydroxyapatite (HA) and a polyester-ether (Polyactive^{TM} 70/30) by using polyacrylic acid or poly(ethylene-co-maleic acid) has been applied to HA/Polyactive^{TM} 30/70 composites noting that polyactive^{TM} 30/70 contains less polyethylene glycol (PEG) segments and a higher concentration of rigid poly(butylene terephthalate) (PBT) segments. The mobility of the PEG segments is significantly affected by the existence of a high concentration of rigid PBT segments. Our experimental results show that this method is indeed suitable for making HA/Polyactive^{TM} 30/70 composites. The hydrogen bond/dipole interaction forming ability of the PEG segment is not affected by the existence of relatively large amounts of PBT segments. By using these coupling agents, the mechanical properties of the composite can be significantly improved both in dry and wet states. A fractographical study of the fracture surfaces revealed that the surface modified HA particles maintain better contact at fracture. It also showed that larger HA particles may initiate cracks and that such particles may be responsible for a decrease in the tensile strength of the composites.

1. Introduction

Several kinds of polymer–hydroxyapatite composites have been developed as bone substitute materials [1–3]. The reasons for using hydroxyapatite (HA) as a filler in composites are to reinforce the polymer, especially to increase the stiffness, and to improve the materials' bone bonding properties which is essential for achieving early bone ingrowth and fixation of implants by bone tissue. It has been found that adding a certain amount of hydroxyapatite to the polymer matrix may turn a non-bioactive polymer into a bone-bonding composite [1–3]. However, a lack of interfacial bonding between the HA and the polymer matrix hinders the synthesis of composites with satisfactory mechanical properties [3, 4].

Polyactive^{TM} is a copolymer of polyethylene glycol (PEG) and poly(butylene terephthalate) (PBT) that has good biocompatibility. By changing the weight ratio of PEG/PBT, a series of copolymers with different structures and properties can be obtained. It has been found that when the weight ratio of PEG/PBT is higher than 55/45, Polyactive^{TM} has bone bonding abilities and is biodegradable [5–8]. However, when the weight ratio of PEG is higher then the polymer has poor mechanical properties and cannot be used as a load bearing biomaterial. When the weight ratio of PEG is lower, e.g., 30%, the material has a much higher stiffness and strength but has no bone-bonding ability. A logical way to get a stronger material with bone bonding ability is thus to use HA as filler to reinforce Polyactive^{TM} with a 30 wt % PEG and 70 wt % PBT composition (Polyactive^{TM} 30/70).

In earlier studies we have developed a new and specific method to introduce interfacial bonding between HA and Polyactive^{TM} 30/70 by using polyelectrolytes such as polyacrylic acid (PAA) and poly(ethylene-co-maleic acid) (EMa) [9]. The principle is that both PAA and EMa can be firmly adsorbed onto the surface of HA [10–13], and can also form hydrogen bond or dipole complexes with PEG [14]. In this way the HA particles will better adhere to the polymer matrix, so that the resulting composite material will possess sufficient strength [9].

Our initial studies on Polyactive^{TM} 30/70 showed promising results, and the extension of this work to PEG/PBT polymers with a weight proportion of 30/70 is now of interest. It is known that the molecular weight of both PEG and PAA plays an important role in the formation of intermolecular complexes [15]. Polyactive^{TM} 30/70 has fewer PEG segments and a higher PBT content in its structure. The variation in the PEG/PBT ratio will affect the domain size and the aggregation structure of the copolymer. Therefore, the hydrogen bond forming ability of PEG will probably be affected by the existence of more and longer rigid PBT segments [16], making it necessary to study the

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suitability of surface modification techniques for HA in HA/Polyactive$^{\text{TM}}$ 30/70 composites.

2. Experimental procedures

2.1. Materials and methods

Polyacrylic acid ($M_w = 5000$, 50% water solution) and poly(ethylene-co-maleic anhydride) were obtained from Aldrich. Poly(ethylene-co-maleic acid) was prepared by dissolving poly(ethylene-co-maleic anhydride) in distilled water (Fig. 1). The hydroxyapatite was synthesized and sintered in our laboratory. It was milled and sieved to a powder with a particle size range from 1–45 μm. Polyactive$^{\text{TM}}$ 30/70 was obtained from HC Implants bv, The Netherlands. The molecular weight is about 1×10^5 Da.

2.2. Coating of the HA particles

Aqueous PAA and EMa solutions were prepared and used to coat the HA powder. The pH of the PAA and EMa solutions were adjusted to pH 7 by using 10 wt % NaOH solution, and the final concentrations of PAA and EMa were 2.5 wt % and 1.5 wt % respectively. The HA was sintered, ground and sieved to a fraction with a particle size of 1–45 μm.

The HA particles (200 g) were suspended in 200 ml of either the PAA or EMa solution. The suspensions were stirred for 20 h at room temperature and then the particles were separated from the solution by centrifugation. The particles were then re-suspended in distilled water and washed three times and were initially dried overnight at 110 °C and then in a vacuum oven at 80 °C for at least 72 h. Control HA particles underwent the same procedure but with NaCl solution instead of either the EMA or PAA solutions.

2.3. Characterization of the HA particles

HA particles were characterized by specific surface area measurement using the Brunauer–Emmett–Teller (BET) method, scanning electron microscopy (SEM) and a Coulter Particle Counter. These measurements were performed both before and after surface modification by the PAA and EMa, as described elsewhere [9].

The amount of surface adsorbed EMa and PAA was quantitatively measured by using a Total Organic Carbon analyser (TOC, D.C.-190, T.O.C. Analyser). An amount of 0.54 g of coated HA particles was first dissolved in 100 ml hydrochloride acid solution of pH 1, then 10 ml of this solution was used for analysing the carbon content in the TOC.

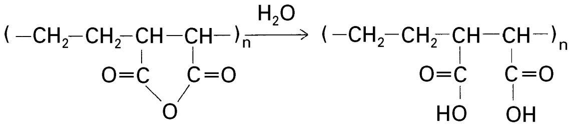

Figure 1 Preparation of EMa.

In order to measure the effect of PAA or EMa modification on the surface properties of the HA particles, a semi-quantitative sedimentation method was used: 0.5 g of HA was transferred to 1.4 cm diameter test tube containing 10 ml of distilled water. After shaking, the time needed for the supernatant to become clear was recorded.

2.4. Preparation of composites

The surface modified and control HA particles were premixed with Polyactive$^{\text{TM}}$ 30/70 granules at 25 wt % and 50 wt % concentrations and then blended twice at 200 °C using a single screw extruder (Codlin, 20×25). The granulated materials were hot pressed into 2 mm thick and 11×30 cm^2 sheets at a temperature of 230 °C and a 2 MPa pressure. Standard dumb-bell specimens were cut from the sheet using an ISO R37 type 1 die, and the specimens were then used for mechanical and other testing. All the specimens were kept at room temperature for 4 days before mechanical testing was performed.

2.5. Mechanical testing

In order to evaluate the effectiveness of the surface treatment, we determined the tensile strength, elongation to break and the elastic modulus of each composite in both the dry and wet states (after swelling in distilled water). The wet state testing was carried out after the specimens had been immersed in distilled water for 48 h. The specimens were taken out of the distilled water and kept wet during the testing process. Tensile tests were performed in a Hounsfield HN200 testing machine. The crosshead speed was 50 mm min^{-1} and the gauge length was 25 mm. In order to determine the elastic modulus, a strain gauge extensometer (Instron) was used to measure the specimen extension. Ten specimens were used for each test. The area under the stress–strain curve (AUC) was also calculated to estimate and compare the fracture energy of the 50 wt % filler composites.

2.6. Degree of swelling of the composites

Rectangular specimens of a size $2 \times 10 \times 20$ mm^3 were used for swelling tests in distilled water at room temperature. For each composition, the swelling test was performed with two specimens.

The specimens were taken out of the distilled water at set time intervals and the water at the surface was quickly removed with tissue paper. The degree of swelling at different time intervals was calculated to the following equation:

$$S_w = \frac{W_t - W_0}{W_0} 100\% \tag{1}$$

where S_w is the degree of swelling and W_t is the weight of the sample at time t and W_0 is the weight of sample in the dry state at the beginning of testing.

2.7. Fracture surface study

The fracture surfaces of mechanically tested specimens were observed by light microscopy and scanning electron microscopy (SEM) using a Philips 525 SEM. All the samples were sputter coated with gold before SEM examination.

3. Results

3.1. The particle characteristics

Table 1 summarizes the characteristics of the HA particles both before and after surface modification by the PAA and EMa.

Fig. 2 is an SEM micrograph of the hydroxyapatite particles used in this study. The SEM study showed that large HA particles had a porous structure and that the HA particle sizes were in the range of 1–50 µm. There was minimal change in the particle size and the surface morphology after surface modification by the EMa and PAA (Fig. 3(a–c)).

3.2. Degree of swelling of the composites

Fig. 4 shows the degree of swelling as a function of time for the composites. The swelling gradually reached equilibrium after 48 h of immersion in distilled water for all the composites. The swelling degrees of the 25 wt % EMa– and 25 wt % PAA– composites are somewhat lower than that of the HA composites with the same filler content but the three types of 50 wt % composites displayed nearly the same degree of swelling.

TABLE I The particle characteristics

	Size from SEM (µm)	Surface area (m^2 g)	Sedimentation time (mins)	Amount of coating (mgC g^{-1})
HA	1–50	1.75	50	As control
EMa–HA	1–50	n.d.	180	0.57
PAA–HA	1–50	n.d.	1200	2.29

Note: n.d. = not determined

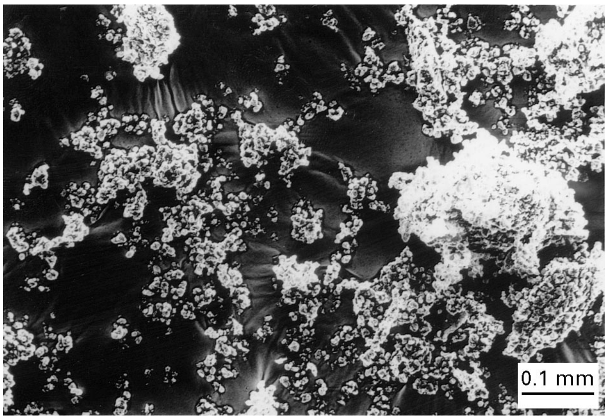

Figure 2 SEM micrograph of the HA particles used in this study. Note the porous structure of the large HA particles. The sizes of the HA particles were measured to be in the range of 1–50 µm.

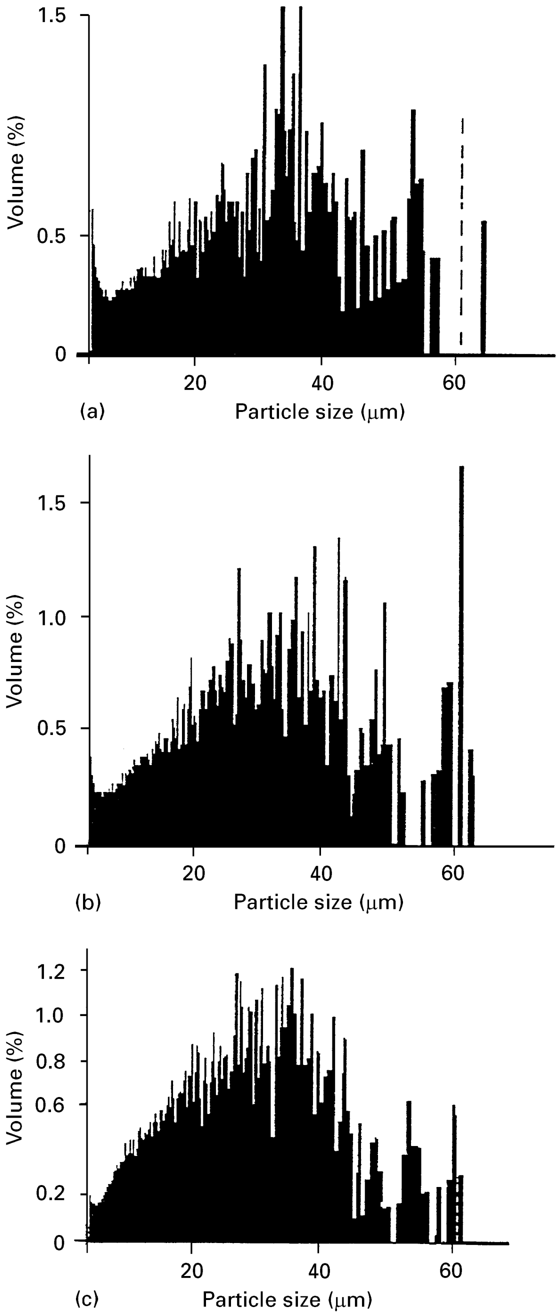

Figure 3 Particle size and size distribution of HA particles before and after surface modification; (a) the particle size distribution pattern of the control HA particles, (b) and (c) are the particle size distribution patterns for EMa–HA and PAA–HA particles respectively.

3.3. Mechanical properties

Fig. 5 is a schematic illustration of a typical stress – strain curve for the 50 wt % composites under dry conditions. The differences in the mechanical properties for the composites can be clearly seen in this figure.

3.4. Elastic moduli

Increasing the filler content increases the elastic-modulus of each composite in dry conditions. Water causes a distinct decrease in the elastic modulus values (Fig. 6). However, the EMa–HA and PAA–HA composites maintained higher elastic moduli after

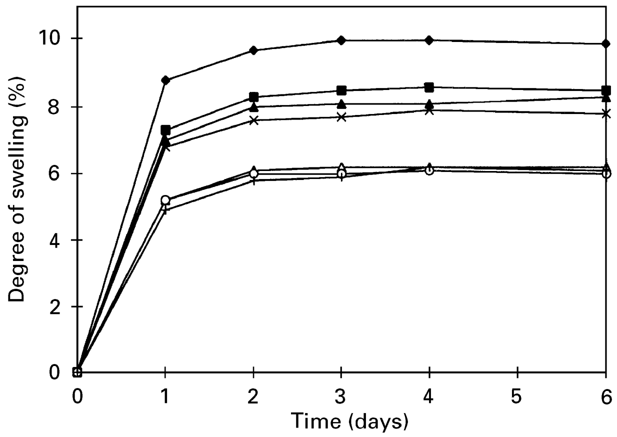

Figure 4 Degree of swelling for the composites as a function of time. Note that the degree of swelling for all the composites nearly reached equilibrium after 48 h immersion in distilled water. Key: (◆) polyactive, (■) 25 wt % HA, (▲) 25 wt % EMa, (×) 25 wt % PAA, (△) 50 wt % HA, (○) 50 wt % EMa and (+) 50 wt % PAA.

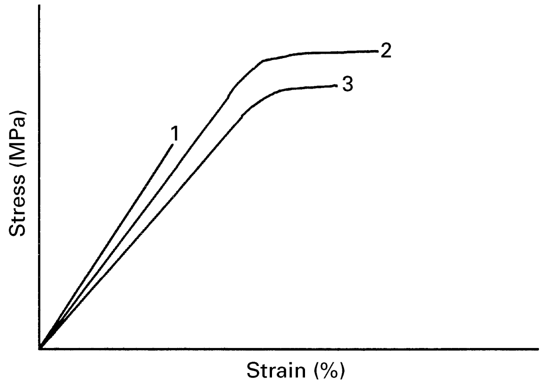

Figure 5 A schematic illustration of a typical stress–strain curve of a 50 wt % filler composites. (1) 50 wt % HA composites in dry state. (2) 50 wt % PAA–HA composites and (3) EMa–HA composites.

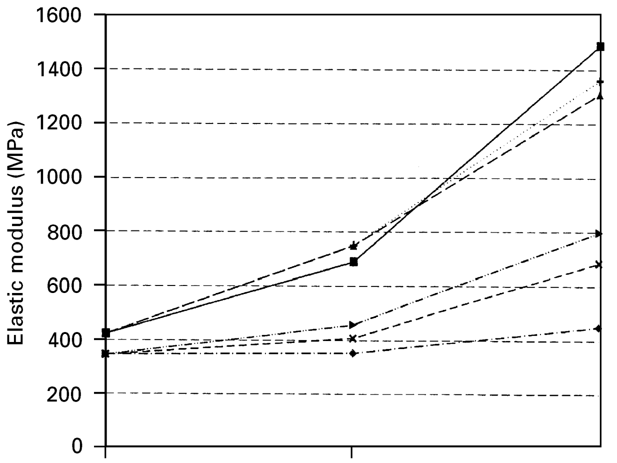

Figure 6 Elastic moduli of composites in both the dry and wet states (distilled water). The effect of the coating can be clearly seen from the E-moduli of the composites in wet state. The studied materials were: (■) HA, (▲) EMa–HA, (+) PAA–HA, (◆) HA (wet), (×) EMa–HA (wet) and (▶) PAA–HA (wet).

being immersed in distilled water. There was no significant difference between the elastic moduli of the EMa– and PAA–HA composites both in the dry and wet states.

3.5. Tensile strength

The tensile strength values of the composites are shown in Fig. 7. It can be seen that the strengths of all the composites in dry conditions are slightly decreased for the 25 wt% filler containing samples. A larger filler amount causes a further decrease in the strength value. Water also has a negative effect on the strength of the composites. However, the wet strengths of composites with surface modified HA particles remained significantly higher than those containing the unmodified filler.

3.6. Elongation to break

It can be seen that the elongation to break of the composites decreases with an increase in filler content (Fig. 8). Water causes an increase in the elongation to break. Both composites containing surface modified HA particles have a higher elongation to break than the unmodified HA composites. PAA modified composites have the highest value.

3.7. Relative fracture energy of the composites

The difference in the AUC values of the composites is obvious (Fig. 9). The composites containing PAA surface modified HA particles have a much higher fracture energy than composites with unmodified HA particles in both the dry and wet states.

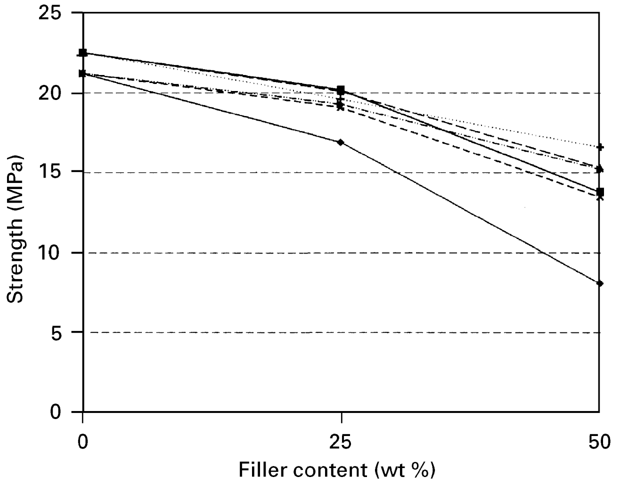

Figure 7 Tensile strength of composites in both the dry and wet states (in distilled water). The tensile strength of HA composites was significantly decreased by immersion in water, while the composites with coating maintained higher strength. The studied materials were: (■) HA, (▲) EMa–HA, (+) PAA–HA, (◆) HA (wet), (×) EMa–HA (wet) and (▶) PAA–HA (wet).

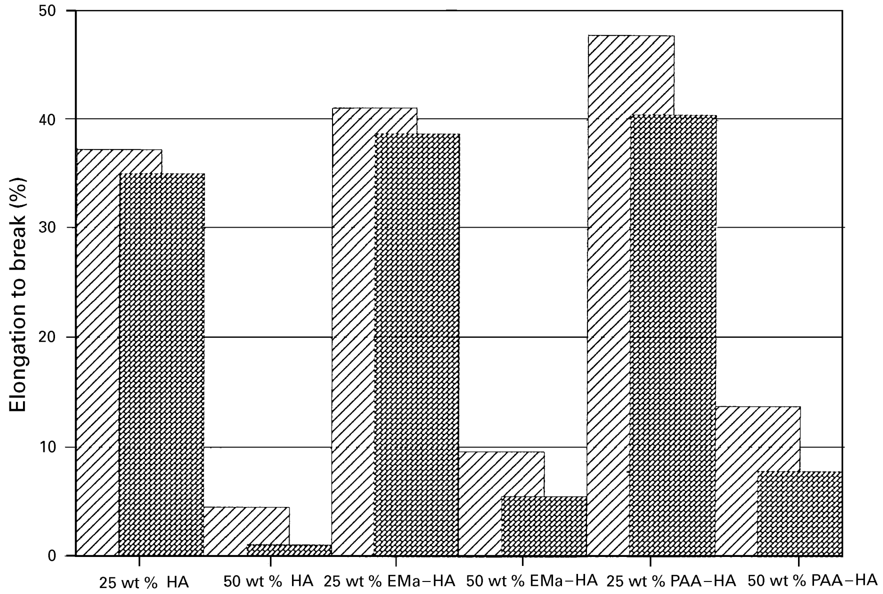

Figure 8 Elongation to break of the composite in both the (▩) dry and (▨) wet states (distilled water). The elongations to break for unfilled Polyactive™ 30/70 are 390% ± 85% (dry) and 187% ± 91% (wet) respectively.

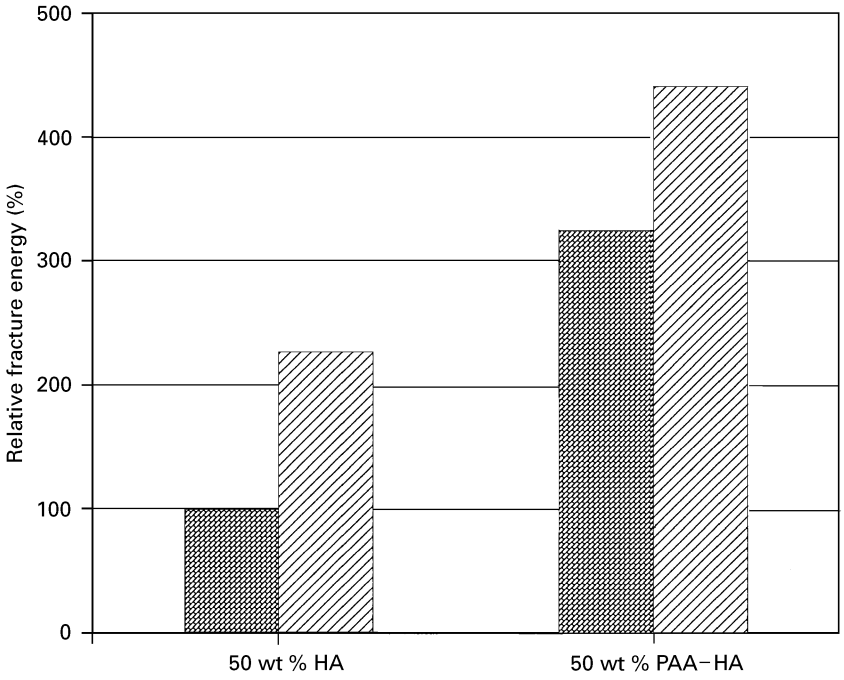

Figure 9 The relative fracture energy of the 50 wt % filler composites in both the (▩) dry and (▨) wet states. The fracture energy of the 50% HA composites in dry state was considered as 100%.

3.8. Fractography study by SEM

The study of the fracture surface of the composites shows that the fracture surface can be roughly classified into two zones. They are referred to as the rough zone (with high deformation) (Fig. 10 (a–c)) and the smooth zone (Fig. 10 (d–f)). Based on the observation that air bubbles could always be found in the rough zone of the fracture surface in the imperfect specimens (Fig. 11), it was concluded that the fracture was initiated in the rough zone and that the crack propagated through the smooth zone. Within the high deformation zone, polymer threads are observed. The HA particles which can be seen in this zone all have large sizes. Within the smooth zone, there are no polymer threads present and all sizes of the HA particles can be observed. The composites with surface modified HA particles and with unmodified HA particles show differences in the appearance of the high deformation zone. Larger areas of these rough zones can be observed in the fracture surfaces of the EMa–HA and PAA–HA composites. In the smooth lower deformation zone, the surface modified HA particles show a more intimate contact with the polymer matrix than in the case of unmodified filler particles (Fig. 10 (d–f)).

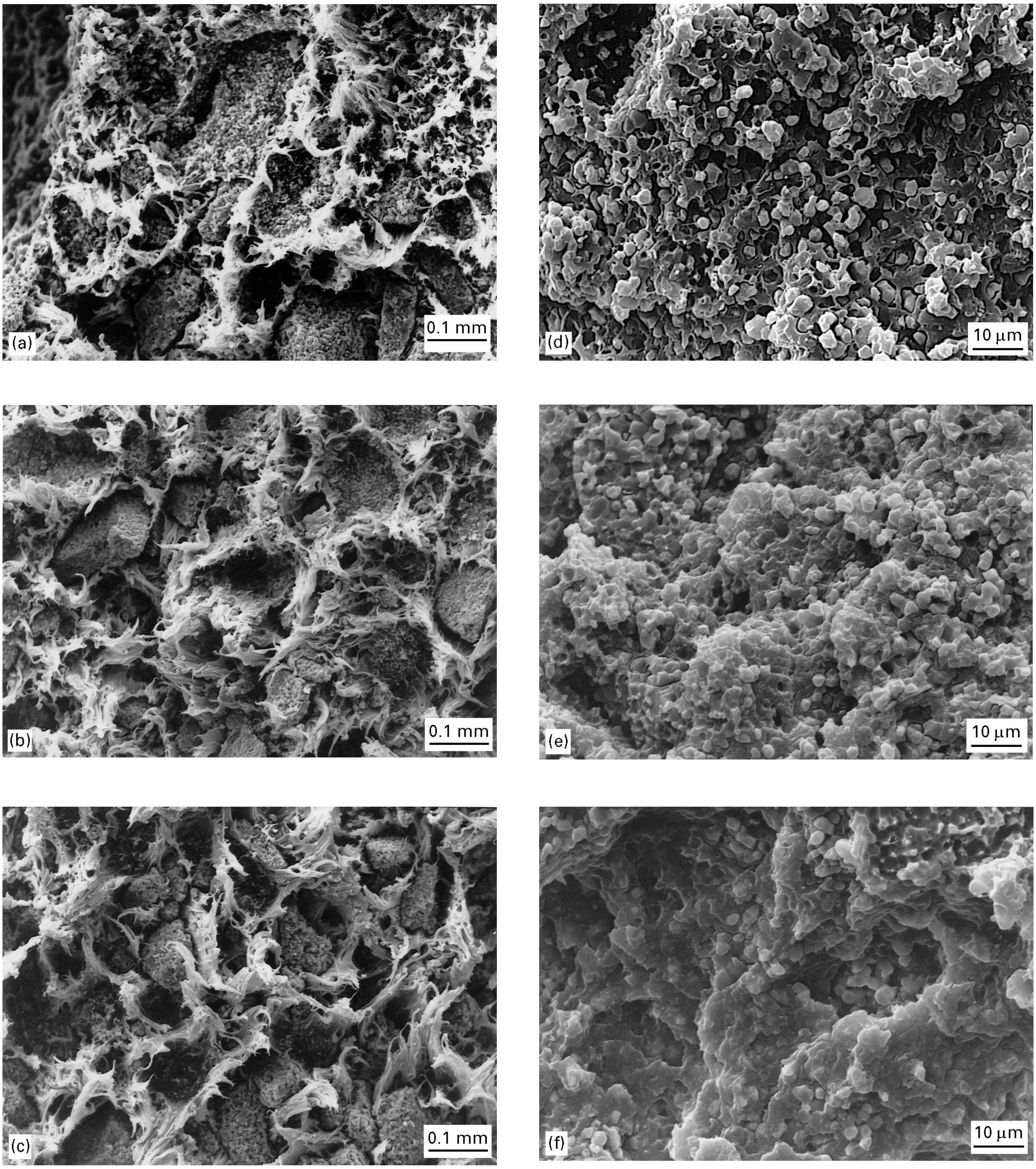

Figure 10 SEM pictures of the fracture surface of the composites, (a) rough zone of the 50 wt % HA composite, (b) rough zone of the 50 wt % EMa–HA composite, (c) rough zone of the PAA–HA composite, (d) smooth zone of the 50 wt % HA composite, (e) smooth zone of the 50 wt % EMa–HA composite and (f) the smooth zone of the PAA–HA composite. Note the obvious differences in smooth areas. Loosely embedded HA particles can be observed in (d) while in (e) and (f) particles still maintain more intimate contact with the polymer matrix. In rough zones, relatively long polymer threads can be observed in (b) and (c).

4. Discussion

Using a filler can be an effective way to improve the stiffness of the composites. In this study, it has been shown that the elastic moduli of the composites were increased in both the dry and wet states. The composites containing unmodified HA particles, however, became brittle when the filler amount was 50 wt %, and the strength of the composite drastically decreased at this high filler content. This can be attributed to the lack of interaction between the HA particles and the Polyactive^{TM} matrix, indicating the necessity of introducing some kind of interaction between the inorganic filler and the organic matrix.

Polycarboxylic acids have been reported to be readily absorbed on to HA surfaces [10, 12–14]. PAA and EMa can form a hydrogen bond complex with PEG not only in aqueous mixtures, but also in heat blended systems [15]. We have previously shown that the PAA and EMa form complexes with PEG segments in the Polyactive^{TM} 70/30 sample [9]. For Polyactive^{TM} 70/30, the concentration of PEG segments is high and therefore these PEG segments have more opportunities

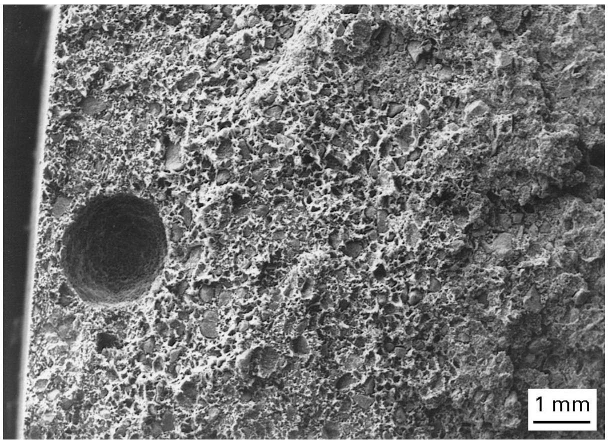

Figure 11 SEM micrograph showing that the crack was initiated by an air bubble that was present in the polymer matrix. A rough zone is observed around the bubble.

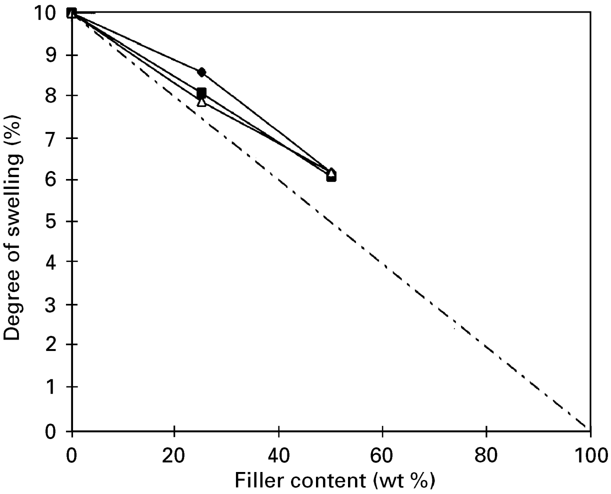

Figure 12 The equilibrium degree of swelling of the composites. Note the difference between the measured values and the expected values based on the assumption that the filler did not take up water. (- - -) expected, (◆) HA, (■) EMa and (△) PAA.

and also the mobility to form complexes with PAA or EMa. However, when the amount of PBT is increased whilst the PEG segment length is kept constant the glass transition temperature of the PEG segment increases and the melting enthalpy of PEG decreases until no PEG crystals can be detected as has been reported by Fakirov and Gogeva [16]. This can be explained by the influence of a higher concentration and longer hard segments of PBT [16]. The increase in the glass transition temperature and the decrease of crystallinity of the PEG phase means that the mobility of the PEG segments is restricted by the high concentration of longer PBT blocks.

Inspite of the restricted mobility for the PEG segments, we can still observe the effect of the surface modification of the HA particles. For the 25 wt % filler composites, such an effect is evident from the higher elongation to break of the EMa–HA and PAA–HA composites in both dry and wet states (Figs 5 and 8). For the 50 wt % filler composites, the effect of the surface modification can be deduced from the higher tensile strengths, elongation to break, elastic moduli and relative fracture energies as compared to the unmodified HA composites in both the dry and wet states. These results suggest that the surface modification of HA with PAA and EMa improves the interface between HA and Polyactive^{TM} 30/70 inspite of the low amount of PEG present. This interfacial improvement leads to a better load transfer throughout the material, and results in better mechanical properties and a higher fracture energy.

Swelling in water caused a significant decrease in the mechanical properties of the composites. Two factors are considered to cause this effect, namely the absorption of water by the polymer matrix and also by the HA filler. As can be seen from Fig. 12, the equilibrium degree of swelling of the composites was higher than the expected values if it is considered that the filler did not absorb water. However it is clear that the filler does contribute to the water absorption of the composites. The water absorbed by the filler was most likely present on the surface of the filler or in the pores of the filler particles. The presence of water on the surface of the filler will certainly affect the adhesion of the filler to the polymer matrix.

From the fracture surface study of the composites we conclude that the crack initiates in the rough zones and propagates through the smooth zones (Fig. 9). In the rough zone, only large particles can be seen. This suggests that these large particles may have initiated cracks at their interface with the polymer matrix, probably because they had a porous structure. Air trapped within the pores resulted in incomplete filling of the pores of the particles by the polymer and in the formation of a less intact interface. In the smooth zone through which the crack propagates the surface modified HA particles maintain a better contact with the polymer matrix (Fig. 9 (e and f)) showing the existence of bonding between them. The occurrence of voids between unmodified HA and the polymer matrix after the sample had been broken shows the lack of interaction between the particles and polymer matrix.

The fractographical study also reveals that the weak point of the composite is still the interface between the HA and the polymer matrix. The observation of relatively large amounts of HA particles on the fracture surface of the composite indicates that the fracture frequently occurred at the interface between the HA and polymer. Further optimization of the surface modification process, such as modifying the surface of the filler in order to render it more hydrophobic or producing chemical linkage between the filler and polymer matrix is thus necessary.

5. Conclusions

The surface modification of HA particles using polyacrylic acid and poly(ethylene-co-maleic acid) was demonstrated to be an effective way to improve the interface between HA and Polyactive^{TM} 30/70 as was the case with Polyactive^{TM} 30/70. It has been shown that the hydrogen bond forming ability of PEG is not affected by the existence of relatively large amounts of PBT segments. Composites with surface modified HA particles maintain better mechanical properties when they are in an aqueous environment and at high filler contents (50 wt %). Our results also suggest that smaller HA particles with a relatively smooth surface will be a better filler for the synthesis of HA/Polyactive^{TM} composites.

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