

# Hydroxyapatite–polyethylene composites: effect of grafting and surface treatment of hydroxyapatite

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The mechanical properties of hydroxyapatite–polyethylene composites have been improved by increasing the interfacial bond between the hydroxyapatite reinforcing particles and the polyethylene. Two types of surface treatment have been investigated: both use silane coupling of the hydroxyapatite, either with or without grafting of the polyethylene. These treatments have led to the presence of a silicon-containing interphase promoting chemical adhesion and penetration of the polymer into cavities in the ceramic particles. The resultant bond has improved the mechanical properties and fracture behaviour of the composites.

## 1. Introduction

Hydroxyapatite (HA) reinforced high density polyethylene (HDPE) composites have been developed as bone analogue materials [1–4] and have been successfully used clinically in low load bearing applications for the last five years [5, 6]. The current composite of hydroxyapatite and polyethylene has solely a mechanical interlock between two phases produced by shrinkage of the polyethylene onto the hydroxyapatite particles during cooling from the compounding temperatures. To improve the properties of the composite, an increase in the interfacial bond strength was tried, using silanation of the hydroxyapatite and grafting of the polymer phase. Polyethylene is non-polar and hydrophobic and to achieve affinity between the polyethylene and the filler, the introduction of a polar group is necessary. Acrylic acid grafted onto polyethylene has been found to improve interfacial adhesion to other fillers [7]. Coupling agents have an important contribution in enhancing the filler–polymer interaction: they promote molecular bonding and thus improve interfacial adhesion [8].

## 2. Materials and methods

The polyethylene used was Rigidex HM4560XP (BP Chemicals) with a density of  $0.945 \text{ Mg m}^{-3}$  and mean particle size of 1 mm. This was grafted using analytical grade acrylic acid without further purification. The hydroxyapatite was P88 grade powder (Plasma Biotol Ltd, Tideswell, UK) with monomodal particle size distribution and median particle size of  $4.14 \mu\text{m}$ . The particles of P88 can be seen to be agglomerates of finer crystallites and the coupling agent used was 3 Trime-thoxysilylpropylmethacrylate (Union Carbide, A174).

Prior to compounding, the polyethylene was grafted. Acrylic acid (5% by weight relative to HDPE) and benzoyl peroxide were dissolved in acetone to form a solution. The polyethylene granules were then added to the solution and left to stand overnight while the acetone evaporated. The hydroxyapatite powder was silanated using A174 as described previously [9].

Two types of HA/HDPE composite, having 20% and 40% by volume of HA were produced. The composites consisted of either silanated HA and non-treated polyethylene or silanated HA and acrylic acid grafted HDPE granules. The HDPE granules were mixed with the HA and manually kneaded to break down any large agglomerates. This mixture was then compounded and grafted using a Betol BTS 40L co-rotating twin screw extruder. The mixture was manually fed into the extruder and, by controlling the feed speed, a stable motor current was maintained. Relatively low temperatures ( $110\text{--}140^\circ\text{C}$ ) were used in the initial barrel zones, to allow grafting to take place, and temperatures between  $160$  and  $190^\circ\text{C}$  were used in the later zones. The composite was extruded as wires which were cooled by passing through room temperature distilled water. These wires were coiled and dried before pelletizing. The pellets were subsequently powderized using a centrifugal mill with liquid nitrogen cooling and compression moulded at around  $200^\circ\text{C}$  into  $140 \times 140 \times 4 \text{ mm}$  plates using a hot press. The percentage of grafting was obtained from the powderized material, before compression moulding, using selective extraction with xylene–methanol and xylene titration [7]. Infrared spectra were obtained using a diffuse reflectance accessory on a Nicolet 800 FTIR spectrometer.

Tensile test specimens were made from the compression moulded plates according to ISO 527. The

dumb-bell specimens were subsequently annealed at 80 °C for 24 h. Tensile tests were conducted on an Instron 6025 at a crosshead speed of 0.5 mm min<sup>-1</sup>. Extension was measured using an Instron extensometer for the determination of Young's modulus, but was removed when the strain reached 1% and thereafter strain was found from the crosshead displacement. The load-extension curves were recorded with an x-y plotter and stress-strain curves were reconstructed from these. A minimum of five specimens were tested at each composition and the results compared, using Student's *t*-test, with data for non-grafted, non-coupled material prepared in an identical manner [10]. To assess the chemical benefit of the grafting at the interface, notched impact specimens were cooled in liquid nitrogen and impacted using a Charpy impact tester. The energy of fracture was not calculated as the aim was to produce fracture surfaces showing the internal structure of the composite. These fracture surfaces were gold coated and viewed using an JOEL-6300 microscope with an X-ray dispersive spectrometer attached.

### 3. Results

The percentage of grafting was found to be 50% with an efficiency of 0.7%. Fig. 1 shows the infrared spectra for coupled and grafted composites with 20 and 40 vol % HA. The peak intensity increases in the carbonyl region (1650–1730 cm<sup>-1</sup>) for the higher HA content composite. The P–O absorption region shows

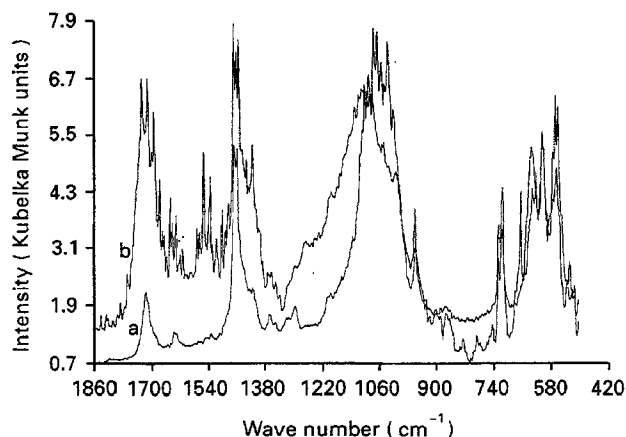


Figure 1 FTIR spectra of (a) 20% by volume of HA with silane coupling agent; (b) 40% by volume of HA with silane coupling agent and grafted polyethylene.

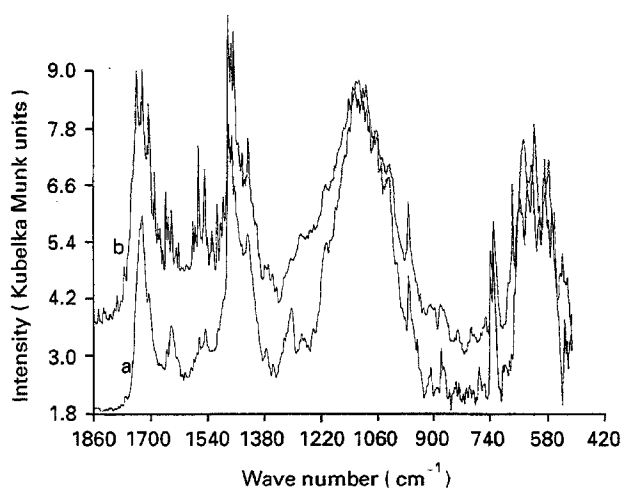


Figure 2 FTIR spectra of 40 vol % HA composites (a) with silane coupling but no grafting of the polyethylene and (b) with silane coupling and grafting of the polyethylene.

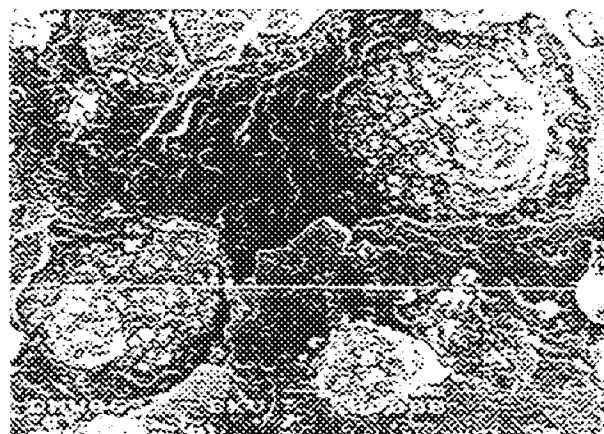


Figure 3 Individual HA particle held by the polymer fibril network on the tensile surface.

broadening arising from the phosphate in the HA. Spectra (Fig. 2) of 40 vol % composites with and without acrylic acid grafting show a multiplet with distinct peaks at 1716 and 1728 cm<sup>-1</sup>, indicating the presence of two different types of carbonyl functionalities. The peak intensity increases with increasing amounts of silanated hydroxyapatite. These FTIR results, with the efficiency of grafting data, confirm the grafting of the acrylic acid onto the polyethylene.

The cryogenic impact fracture surfaces showed that, with both silane coupling and grafting, the polyethy-

TABLE I Tensile test results for HA/HDPE composites showing the use of silane coupling and acrylic acid grafting

Filler volume (%)	Silane coupling	Acrylic acid grafting	Tensile strength (MPa)	Young's modulus (GPa)	Fracture strain (%)
20	No	No	17.77 ± 0.09	1.60 ± 0.02	34.0 ± 9.5
20	Yes	No	17.01 ± 0.19**	1.54 ± 0.02*	> 100
20	Yes	Yes	19.97 ± 0.07**	1.81 ± 0.05**	39.7 ± 1.5
40	No	No	22.67 ± 1.56	4.29 ± 0.17	2.6 ± 0.4
40	Yes	No	22.08 ± 0.05	3.66 ± 0.20**	7.8 ± 0.6**
40	Yes	Yes	23.16 ± 0.40*	3.87 ± 0.21*	6.8 ± 0.6**

(\* Significantly different at  $p < 0.05$  and \*\*at  $p < 0.01$  when compared with the non-coupled, non-grafted material of the same volume fraction filler)

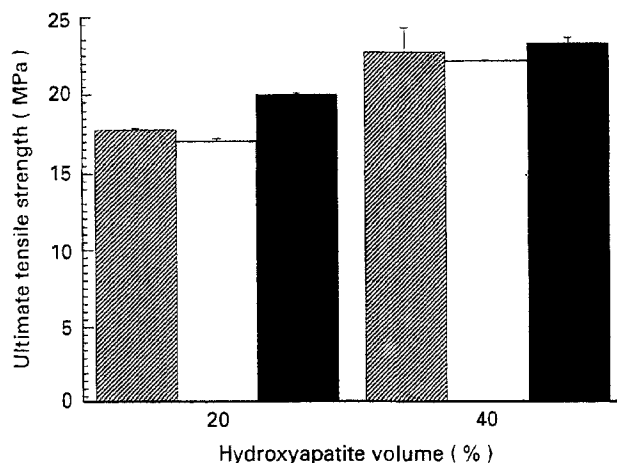


Figure 4 The ultimate tensile strength for hydroxyapatite-polyethylene composites with volume fraction of HA. HA-HDPE: hydroxyapatite and high density polyethylene (▨); HASCA: silane treated HA and HDPE (■) and HASCAA: silane treated HA acrylic acid grafted to HDPE (■).

lene penetrated into the individual hydroxyapatite particles during processing and formed polymer networks within the particles (Fig. 3). Thus after fracture, the polymer network remained in the hydroxyapatite particles. X-ray analysis showed silicon, from the coupling agent, on the exposed surfaces of HA.

The tensile test data are tabulated in Table I and the ultimate tensile strengths are shown in Fig. 4. Non-filled polyethylene had a Young's modulus of 0.65 GPa and yield strength of 17.9 MPa [10]. It can be seen that adding hydroxyapatite increased the Young's modulus. The major benefit of the silane coupling, both with and without acrylic acid grafting, is improving the ductility and fracture behaviour. The silane coupling and acrylic acid grafting increased the tensile strength and, at the lower volume fractions, increased the Young's modulus, but this did not occur at 40 vol %. The silane coupling without acrylic acid grafting decreased the Young's modulus for both compositions. This is possibly due to the plasticizing effect of the silane coupling agent.

#### 4. Discussion

Coupling the HA and grafting the polyethylene prior to compounding has produced a silane interlayer coupling the two phases. The cryogenic fracture surfaces show that the coupling and grafting produces interdigitation of the polyethylene into the hydroxyapatite particles. It would be expected that this interdigitation would increase all the mechanical properties of the composite, but the major effects are actually seen in the fracture strain giving a more ductile material. The work of Guild and Bonfield [11], modelling HA/HDPE composites with the HA being

spherical particles, has shown that the areas of maximum stresses are above the pole and at the interface. When the von Mises' stresses are considered, the stress above the pole increases with increasing amounts of HA, but the stress concentration at the interface drops to a minimum just below 40 vol % HA. This may be part of the explanation as to why coupling and grafting has an effect at 20 vol %, but not at 40 vol % HA. Increasing the amount of hydroxyapatite leads to more stress concentrations and thus reduces the fracture strain, but this effect is offset by the improved plasticity. The reasons why the Young's modulus is not increased at 40 vol % by both silane coupling and acrylic acid grafting need to be further investigated.

#### 5. Conclusions

Major benefits are seen with both silane coupling and acrylic acid grafting which can increase the strength and modulus, particularly at 20 vol % HA, although the fracture strain is most increased by silane coupling alone.

#### Acknowledgements

Support for the IRC programme from the UK EPSRC is gratefully acknowledged.

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Received 29 June  
and accepted 4 July 1995