

Chemically coupled hydroxyapatite–polyethylene composites: structure and properties

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Abstract

Silanation of hydroxyapatite and acrylic acid grafting of polyethylene were employed to improve bonding between hydroxyapatite and polyethylene. The structure and properties of chemically coupled hydroxyapatite reinforced high-density polyethylene (HA/HDPE) composites were subsequently investigated using various techniques. It was shown that there existed a silicon-containing interphase between the hydroxyapatite particle and the polyethylene matrix. The silane coupling agent used promoted chemical adhesion between hydroxyapatite particles and the polymer. The use of the silane coupling agent also facilitated the penetration of polymer into cavities in individual ceramic particles, which resulted in enhanced mechanical interlocking at the matrix-reinforcement interface. With a strong bond (both mechanical and chemical) being formed between hydroxyapatite and polyethylene, chemically coupled HA/HDPE composites possessed improved mechanical properties and fracture behaviour. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxyapatite; Silanation; High-density polyethylene; Grafting; Structure; Properties

1. Introduction

Particulate hydroxyapatite (HA) reinforced high-density polyethylene (HDPE) composite has been developed since early 1980s as an analogue material for bone replacement [1–7]. The closer modulus matching of HA/HDPE composite to bone shows promise in solving the problem of bone resorption that has been encountered with the use of implants made up of conventional materials such as metals and ceramics which possess much higher modulus values than human cortical bone [4,8]. One of the most recent clinical applications of this material is for orbital reconstruction and volume augmentation [9,10]. In the simple HA–HDPE system, there exist only two phases: dispersed hydroxyapatite ceramic particles and continuous high-density polyethylene. Therefore, only mechanical coupling which has resulted from the shrinkage of polyethylene around hydroxyapa-

tite particles, during composite processing is achieved between the hydroxyapatite reinforcement and the polyethylene matrix. Consequently, mechanical properties of HA/HDPE composite that is manufactured via an established conventional route approach the lower bound for human cortical bone [7] and load-bearing application of this composite material is limited. Similar materials also suffered from the disadvantage of inadequate mechanical properties and could only be used for low load-bearing applications [11]. For major load-bearing applications, significant increases in modulus and strength are required for the composite.

Major factors affecting thermal, physical and mechanical properties of particulate (i.e., the filler) reinforced polymer composites include the polymer structure and molecular weight, the filler type and volume fraction, and the interfacial state between the filler and the polymer. Other factors such as filler surface treatment and matrix modification also play an important role. In order to increase the interfacial strength between the two component phases and hence to improve mechanical properties of the resultant HA/HDPE composite, both silane coupling and polymer grafting were investigated [12]. The presence of silanation and grafting in new HA/HDPE composites was confirmed by chemical and spectroscopic analyses.

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Various research groups in the past also successfully introduced an interfacial phase between the reinforcement and the matrix for respective polymer–matrix composite [13–17]. In general, such an introduction promotes the adhesion between the reinforcement and the matrix and hence improves mechanical properties of composites. In this paper, results obtained from the detailed study of structure and properties of chemically coupled HA/HDPE composites are reported.

2. Materials and methods

2.1. Materials and composite manufacture

Two series of new HA/HDPE composites were investigated: one with the silane coupled hydroxyapatite, the other with the silane coupled hydroxyapatite and the acrylic acid grafted polyethylene. The HDPE used in this investigation was Rigidex HM4560XP (BP Chemicals Ltd., UK). The hydroxyapatite powders used were of two grades: P81B HA and P88 HA, both commercially available from Plasma Biotol Ltd., UK. The silane coupling agent was 3-trimethoxysilylpropylmethacrylate (A174, from Union Carbide, USA). Analytical grade acrylic-acid was used in the as-received condition. The manufacturing process for HA/HDPE composite containing silane coupled hydroxyapatite consisted of silanation of hydroxyapatite, blending of treated hydroxyapatite with HDPE, compounding through a twin-screw extruder, pelletising, powdering, and compression moulding. The manufacturing process for HA/HDPE composite containing silane coupled hydroxyapatite and acrylic acid grafted polyethylene consisted of silanation of hydroxyapatite, coating of HDPE granules with acrylic acid, blending of treated hydroxyapatite with coated HDPE, compounding and acrylic acid grafting through the twin-screw extruder, pelletising, powdering, and compression moulding. Two batches of new HA/HDPE composites were manufactured. Feasibility studies were conducted on the first batch of material (composite A), with the second batch (composites C–F) being produced in relatively large quantities for detailed structure and property investigations. HA/HDPE composite without silane coupling and polymer grafting was also produced via an established route [7] in order to obtain results for comparison. The structure and properties of all composites were studied at two main stages of the manufacturing processes: extrusion and compression moulding. Table 1 shows composition of these HA/HDPE composites.

2.2. Dispersion and distribution of hydroxyapatite in polyethylene

The dispersion and distribution of hydroxyapatite particles in the polyethylene matrix was investigated for the

Table 1
Composition of HA/HDPE composites

Composite	Filler	Filler volume (%)	Silane coupling	Acrylic acid grafting
A	P81B HA	7	Yes	Yes
C	P88 HA	20	Yes	No
D	P88 HA	40	Yes	No
E	P88 HA	20	Yes	Yes
F	P88 HA	40	Yes	Yes
G	P88 HA	10	No	No
H	P88 HA	20	No	No
K	P88 HA	40	No	No

new HA/HDPE composites after compounding and compression moulding. The specimen preparation procedure included sectioning, mounting, grinding, polishing, ultrasonic bath cleaning and drying by compressed air. Specimens were polished progressively using suspension of alumina of 7, 2 and 0.1 μm particle sizes. The polished surfaces were examined under a JEOL6300 scanning electron microscope (SEM) after being lightly gold coated.

2.3. Cryogenic impact fracture

In order to investigate the interfacial state of HA/HDPE composites, flat fracture surfaces were obtained by cryogenically impact fracturing composite specimens. Rectangular bars were made from compression moulded HA/HDPE composites. These bars were then notched and side grooved. Specimens were immersed in liquid nitrogen for at least 2 min so that they were cooled uniformly to about -193°C before being mounted onto a bench-top Charpy impact tester. Immediately after the specimen was mounted onto the impact machine, the pendulum was released. All specimens fractured in the plane that was defined by the notch and side grooves during impact. Obtaining fracture surfaces which revealed fracture paths in the composites and the bond condition at the particle–matrix interface was the objective and hence no attempt was made to record and compare impact properties of composites in this investigation. (Comparative studies of the impact resistance of these materials were conducted on an instrumented impact tester and the results will be reported in another publication.)

2.4. Tensile testing

Mechanical properties of new HA/HDPE composites were evaluated by tensile testing. Tensile specimens were made from compression moulded HA/HDPE plaques according to an ISO standard (ISO 527). These specimens were subsequently annealed at 80°C for 24 h and they were tested 48 h after the heat treatment. Normal tensile tests were conducted on an Instron 6025 testing machine at a crosshead speed of 0.5 mm/min. An Instron

extensometer (maximum displacement: 1 mm) was mounted onto the test piece for the accurate measurement of specimen extension in order to determine its Young's modulus. It was removed from the specimen when strain exceeded 1.0% and thereafter the strain was calculated from the crosshead displacement. The test continued to the fracture of the specimen in most cases. Load-extension curves were recorded with an *X-Y* plotter, and data were printed out during and at the end of the tests via an interfaced computer, from which stress-strain curves could be reconstructed. At least five specimens were tested for each composition of the composites.

2.5. Surface examination and EDX analysis

Infrared spectra of hydroxyapatite particles before and after silane surface treatment were obtained using a Nicolet 800 FTIR instrument.

Two scanning electron microscopes (JEOL6300 and JEOL6300F) were used to examine selected tensile and cryogenic impact-fracture surfaces of HA/HDPE composites. The JEOL6300F microscope is a field emission SEM which allows low-voltage operation and high-magnification microscopy with high resolution. The detection and X-ray mapping of elements such as Ca, P and Si were

achieved by using an energy-dispersive X-ray spectrometer (EDX) attached to the JEOL6300 microscope. SEM specimens were cut from fractured composite pieces and mounted onto SEM stubs. They were cleaned with compressed air jet and lightly gold coated before examination.

3. Results and discussion

3.1. Distribution of hydroxyapatite in polyethylene

It has been reported that coupling agents improve the dispersion of ceramic fillers in polymer matrices [18,19]. Some researchers attributed such an effect to the plasticising role of the coupling agent in the composite during manufacture. Others pointed out that this feature came from better wetting and adhesion for a filler after being treated with a coupling agent. However, the dispersion and distribution of hydroxyapatite ceramic particles in the new, extruded HA/HDPE composites was not as satisfactory as was anticipated. At low magnifications, SEM specimens prepared from extruded (i.e. compounded) materials for the structural examination exhibited porosity and ceramic particle agglomeration (Fig. 1).

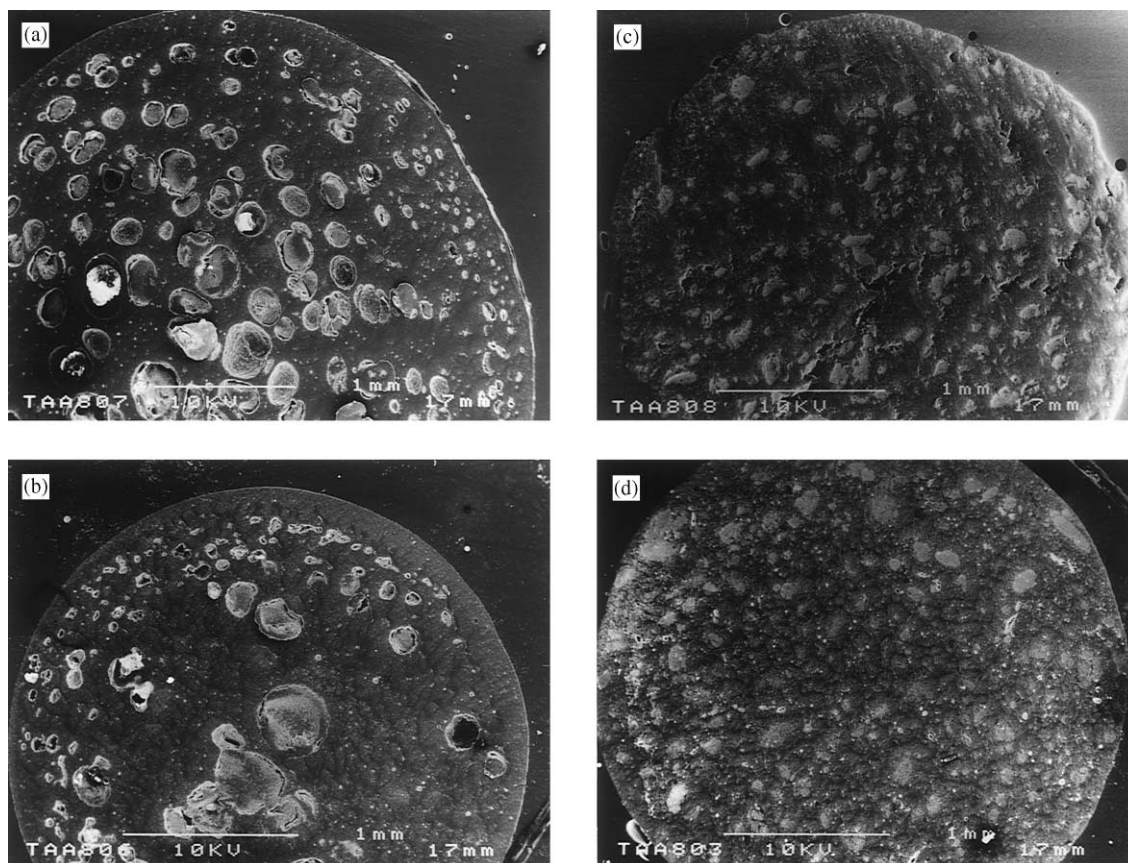


Fig. 1. Cross-sections of new HA/HDPE composites after extrusion exhibiting the presence of pores and ceramic particle agglomeration: (a) composite D, (b) composite D, (c) composite E, (d) composite F.

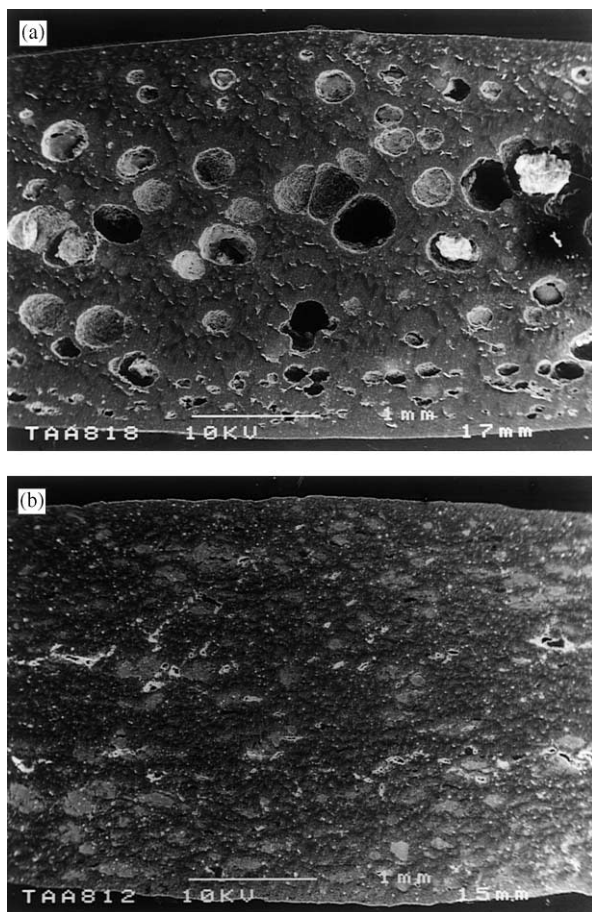


Fig. 2. Longitudinal sections of new HA/HDPE composites after extrusion showing the difference in pore size and distribution: (a) composite D, (b) composite F.

It appeared that the HA/HDPE composite with silane coupled hydroxyapatite and acrylic acid grafted polyethylene possessed less and smaller pores than the HA/HDPE composite with silane coupled hydroxyapatite only. However, the former showed a greater degree of hydroxyapatite particle agglomeration than the latter. Examination of longitudinal sections of the extrudates also revealed such a difference (Fig. 2). These results are different from those obtained from simple HA/HDPE composite, which exhibits a homogeneous distribution of hydroxyapatite particles in polyethylene after extrusion [7]. At high magnifications, away from particle agglomerates, the hydroxyapatite particles were well dispersed and a good distribution of hydroxyapatite in polyethylene was achieved (Fig. 3). The powdering process prior to compression moulding tended to break down some hydroxyapatite particle agglomerates. Hence much less particle agglomerates were encountered during the SEM examination of compression moulded materials. The dispersion and distribution characteristics shown in Fig. 3 were preserved after compression moulding and no macropores were found in the compression moulded plaques.

3.2. Mechanical properties

Tensile testing results for the first batch of materials produced (composites A and G) are tabulated in Table 2. For HDPE, the manufacturer quoted 0.68 GPa and 23.5 MPa for tensile modulus and tensile strength at yield, respectively. Compression moulded unfilled polyethylene plaques gave 0.65 GPa and 17.9 MPa as Young's modulus and yield strength correspondingly. Fig. 4 exhibits initial parts of stress-strain curves of composites A and G (up to respective yield point), showing the effect of silanation of hydroxyapatite and acrylic acid grafting on the behaviour and properties of the HA/HDPE composite. Although the mean particle size of hydroxyapatite in composite A was nearly twice that in composite G, which should lead to lower mechanical properties of composite A than those of composite G, as finer ceramic particles would enhance the performance of the composite [20], yield strength and fracture strain of the composite with silane coupled hydroxyapatite and acrylic acid grafted polyethylene (i.e., composite A) were significantly improved. This indicated that chemical treatments of both the filler and polymer could result in an HA/HDPE composite with enhanced performance. The exceptional deformation capability of composite A was evident when tested and untested tensile specimens were put alongside each other.

For the second batch of materials produced, Table 2 also summarises their tensile properties. Typical stress-strain curves of silane coupled only, and silane coupled and acrylic acid grafted HA/HDPE composites exhibited improved ductility and fracture behaviour as compared to simple HA/HDPE composite. Fig. 5 compares the initial stress-strain curves (up to respective peak stress) of the two series of composites produced in the second batch, which shows the effect of the coupling agent and acrylic acid grafting on the improvement of tensile strength of the composites. It also indicates the strength and modulus enhancement with the increasing amount of hydroxyapatite in composites. Unlike composite A, no necking was observed for the second batch of chemically coupled HA/HDPE composites during tensile testing except for composite C.

For composites C and D where silane treated hydroxyapatite was used as the filler at two volume percentages (20 and 40 vol%, respectively), it was observed that the material was more ductile than either simple HA/HDPE composite or composites E and F. The filler when surface treated with a silane coupling agent should be able to disperse more favourably in the polymer matrix and to have better adhesion to the matrix. The fracture strain of the composite increased with the presence of the coupling agent as the compatibility between the matrix and the filler was improved, resulting from the plasticizing effect. However, increasing the hydroxyapatite content from 20 to 40 vol% led to the formation of

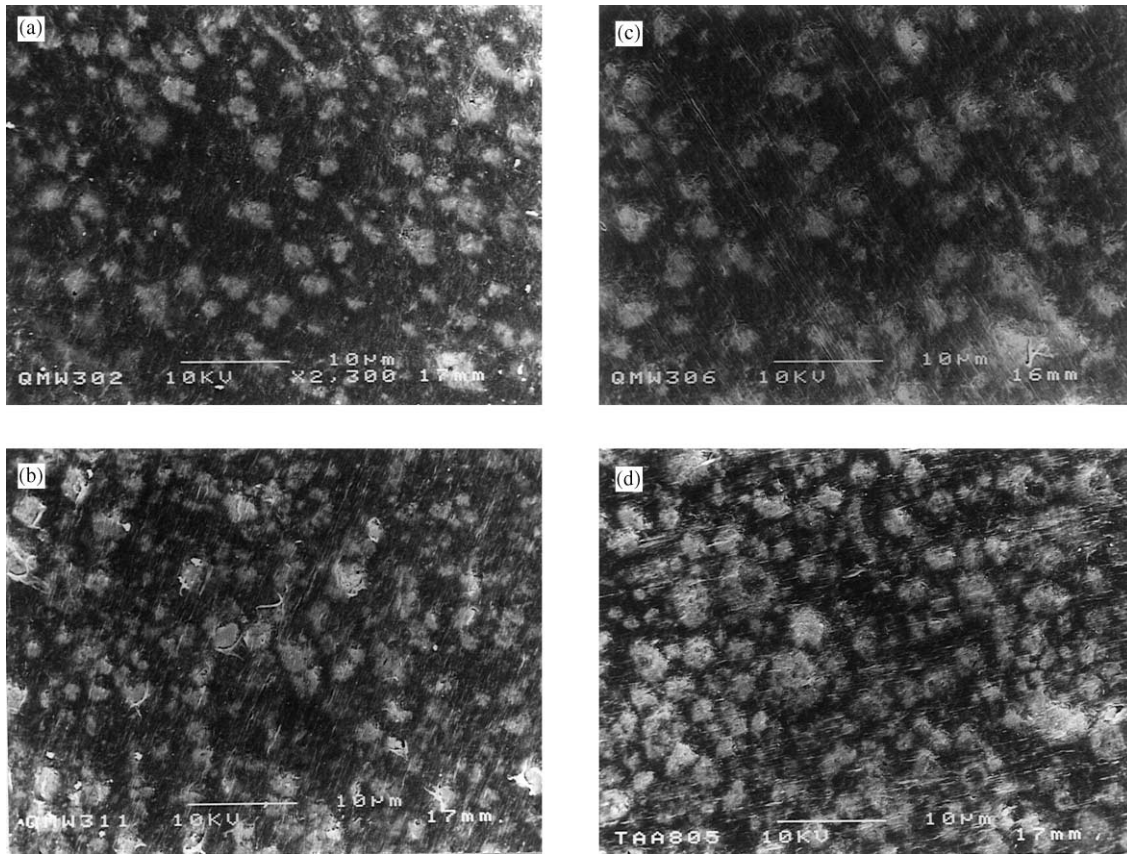


Fig. 3. Distribution of hydroxyapatite particles in new HA/HDPE composites: (a) composite D, (b) composite D, (c) composite E, (d) composite F.

Table 2
Tensile properties of HA/HDPE composites

Composite	Filler volume (%)	Tensile strength (MPa)	Young's modulus (GPa)	Fracture strain (%)
A	7	18.34 ± 0.42	0.88 ± 0.04	> 500
C	20	17.01 ± 0.19	1.54 ± 0.02	> 100
D	40	22.08 ± 0.05	3.66 ± 0.20	7.8 ± 0.6
E	20	19.97 ± 0.07	1.81 ± 0.05	39.7 ± 1.5
F	40	23.16 ± 0.40	3.87 ± 0.21	6.8 ± 0.6
G	10	17.30 ± 0.27	0.98 ± 0.02	> 200
H	20	17.77 ± 0.09	1.60 ± 0.02	34.0 ± 9.5
K	40	20.67 ± 1.56	4.29 ± 0.17	2.6 ± 0.4

more stress-concentration points in the composite, which can cause the rapid fracture of a material when stressed. Hence composite with 40 vol% of hydroxyapatite showed much reduced fracture strain as compared with composite with 20 vol% of hydroxyapatite. Because of the plasticising effect of the silane coupling agent, it appeared that both composites C and D exhibited slightly lower Young's modulus and tensile strength than the simple HA/HDPE composite with corresponding hy-

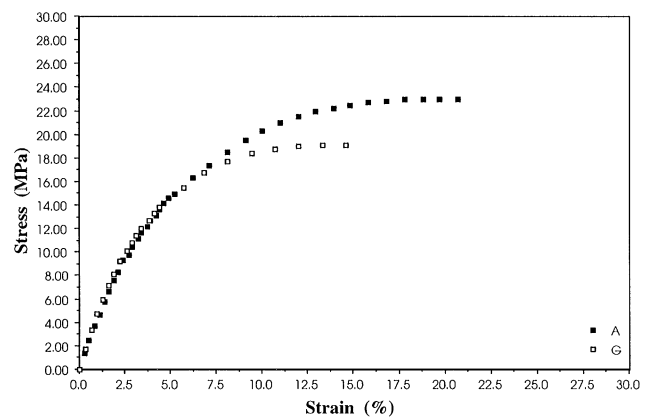


Fig. 4. Initial parts of stress-strain curves for composites A and G showing the effect of chemical coupling.

droxyapatite volume percentages. For composites E and F, acrylic acid grafting introduced polar groups ($-\text{COOH}$), which can produce hydrogen bonding in the polyethylene matrix which in turn can form ionic bonds with hydroxyapatite. By acrylic acid grafting of polyethylene and silanation of hydroxyapatite, a synergistic effect was obtained as a result of improved adhesion and

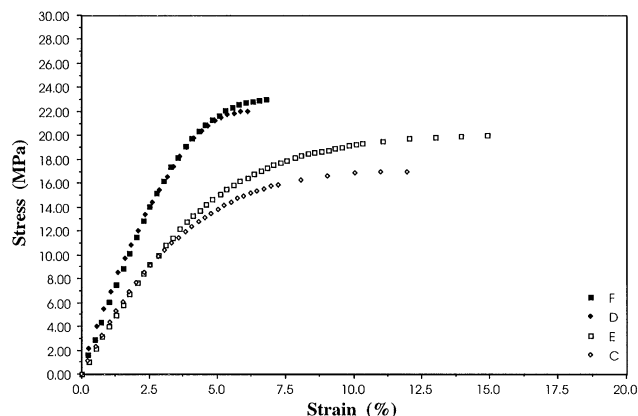


Fig. 5. Initial parts of stress-strain curves for the second batch of new HA/HDPE composites showing effects of ceramic volume percentage and chemical treatments.

interaction between the filler and the matrix. Therefore, the highest strength was achieved for HA/HDPE composites through both silanation of hydroxyapatite and acrylic acid grafting of polyethylene. As for composite E, it exhibited similar fracture strain as compared with simple HA/HDPE composite but still possessed higher tensile strength and Young's modulus. Composite F showed higher strength and fracture strain but lower modulus than the simple HA/HDPE composite. It is evident that acrylic acid grafting embrittled high-density polyethylene (compare fracture strain: composite E vs C, composite F vs D). However, it is also obvious that, by comparing overall mechanical properties of all HA/HDPE composites, improved performance has been achieved through both acrylic acid grafting and silanation rather than by silanation of hydroxyapatite only.

3.3. Surface examination and EDX analysis

Fig. 6 shows infrared spectra of hydroxyapatite particles before and after being treated with the silane coupling agent. The presence of bands for the carboxyl group ($\sim 1720\text{ cm}^{-1}$) and SiO group ($\sim 1300\text{--}1200\text{ cm}^{-1}$) indicated the availability of the coupling agent on the surface of hydroxyapatite.

Cryogenic impact-fracture surfaces of chemically coupled and non-coupled HA/HDPE composites were carefully examined under the field emission SEM. It was revealed that polyethylene penetrated into some hydroxyapatite particles during composite thermal processing and formed polymer networks in the particles for the chemically coupled composites. Consequently, the polymer network remained in the hydroxyapatite particle after cryogenic fracturing (Fig. 7).

With the EDX attachment to the JEOL6300 SEM, detection of elements whose nuclear number is greater than 11 was possible at the particle-matrix interface on

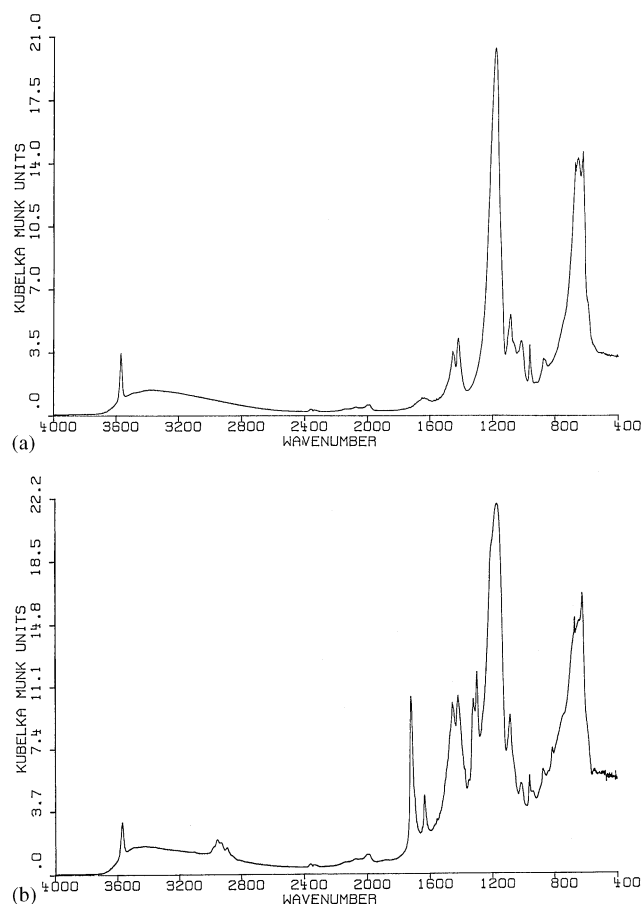


Fig. 6. Infrared spectra of hydroxyapatite particles (a) before silane treatment, (b) after silane treatment.

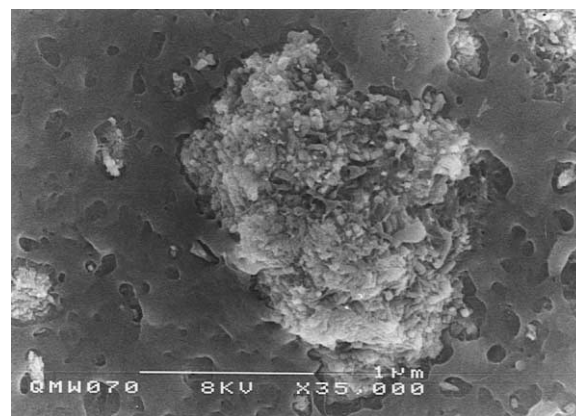


Fig. 7. Cryogenic impact-fracture surface of chemically coupled HA/HDPE composite showing polymer fibril network formation in a hydroxyapatite particle.

fracture surfaces. Fig. 8 shows areas on the cryogenic impact-fracture surfaces of composite A where EDX analyses were performed. Using X-ray spot analysis, both the hydroxyapatite particle surface (Fig. 8a) and the polymer

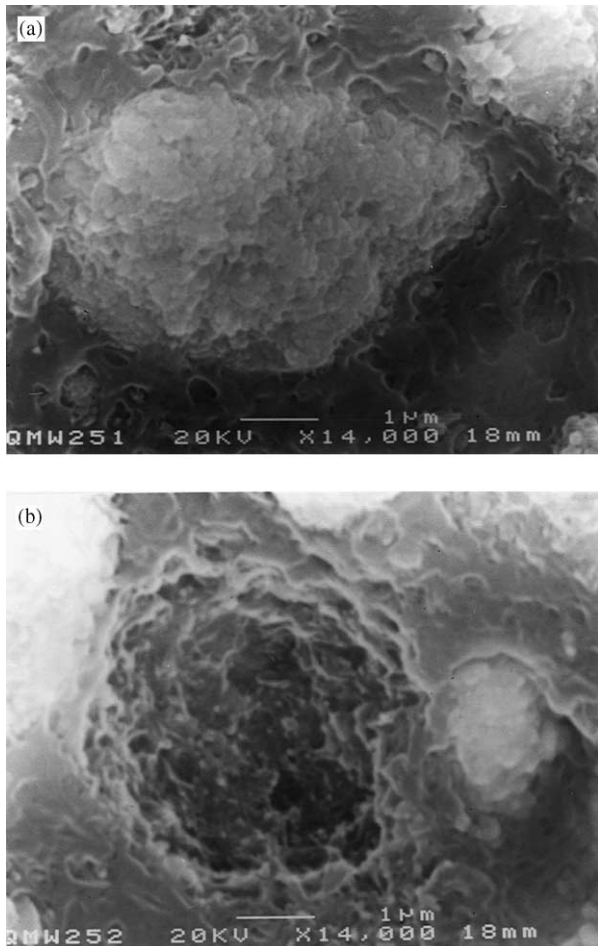


Fig. 8. Areas on the cryogenic impact-fracture surface of chemically coupled composite for EDX analysis: (a) the hydroxyapatite surface, (b) the polyethylene concave surface.

concave surface where a hydroxyapatite particle had been detached (Fig. 8b) showed existence of silicon (Fig. 9). Elemental X-ray mapping was consequently conducted on the cryogenic impact-fracture surface and Fig. 10 displays distributions of elements Si, P and Ca in an area corresponding to Fig. 8a. It appeared that there existed an interphase which contained silicon between the filler and the matrix. Under the cryogenic impact-fracture condition, the fracture path was within this silicon-containing interphase, leading to the detection of silicon from both the particle surface and the polymer concave surface.

SEM micrographs of tensile fracture surfaces for composites C–F are shown in Fig. 11, which reveal the effect of hydroxyapatite particles on the local deformation of polyethylene that surrounds these particles. For both series of new HA/HDPE composites, the polymer matrix underwent extensive deformation in composites with 20 vol% of hydroxyapatite and hence long polymer ligaments were observed on tensile fracture surfaces (Fig. 11a and c). Although most of the hydroxyapatite particles

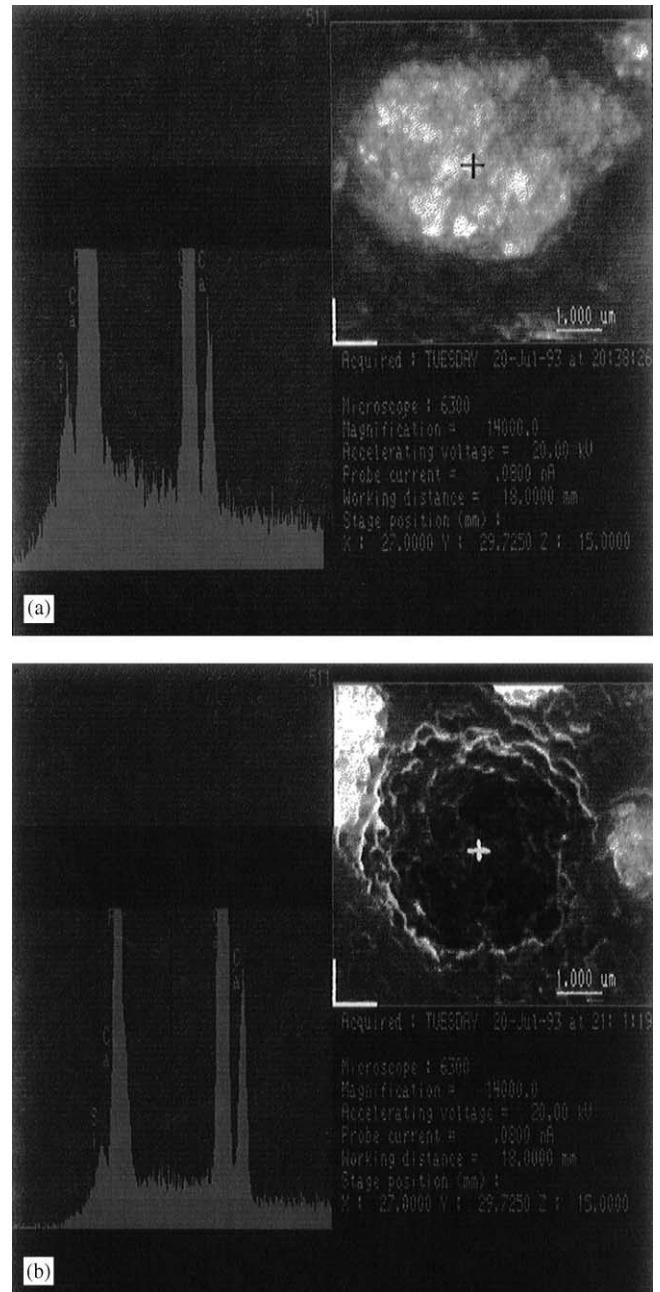


Fig. 9. EDX spectra from spot analysis showing the existence of silicon: (a) the hydroxyapatite surface, (b) the polyethylene concave surface.

were held at the bottom of cavities on these fracture surfaces, there were still quite a few medium to large size particles attaching to the drawn polymer ligaments, which suggests a strong bond between the filler and the matrix. As the hydroxyapatite volume percentage was increased to 40% (i.e. approximately 69% by weight), the polyethylene matrix existed in the form of connected segments surrounding the particles. The polymer also experienced a relatively large local deformation when the composite was under tension (Fig. 11b and d) and

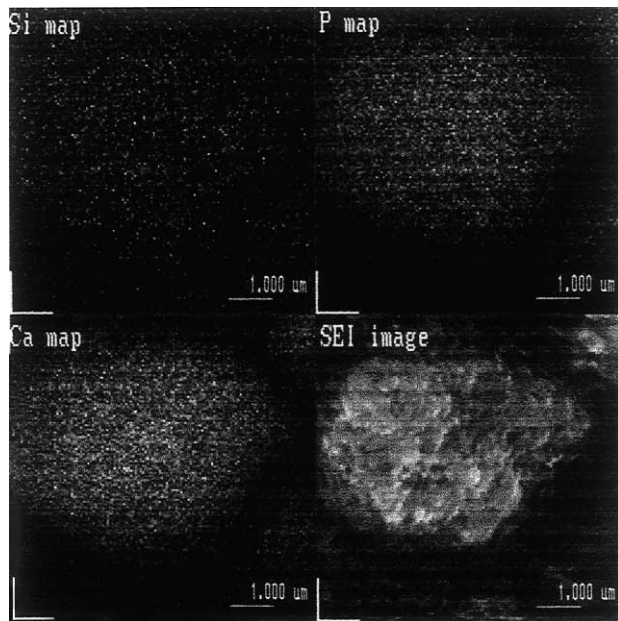


Fig. 10. Distributions of elements (silicon, phosphorus and calcium) in an area corresponding to Fig. 8a.

particles were held at the bottom of dimples on fracture surfaces. Because acrylic acid grafting and silanation of hydroxyapatite induced a stronger bond than pure

silanation of hydroxyapatite, it seems that small particle agglomerates in composite F were less likely to break down into individual particles during composite processing than in composite D. Hence Fig. 11d shows some particle agglomerates, while Fig. 11b exhibits good individual particle separation by the polymer network. It is evident that an increase in hydroxyapatite volume percentage in the composite reduced the matrix deformation (compare Fig. 11b with a and Fig. 11d with c). High-magnification SEM examinations revealed polymer fibrils on the hydroxyapatite-particle surface (Fig. 12) which were not observed on tensile fracture surfaces of HA/HDPE composite without silane coupling or acrylic acid grafting. This indicates that mechanical interlocking was improved between the hydroxyapatite particles and the polymer matrix. The partial, top exposure of hydroxyapatite particles and the gaps between the filler and the matrix shown in Fig. 12 suggest that during tensile testing the tensile stress produced a type of stress concentration that results in dewetting and cavitation at the poles of a near-spherical hydroxyapatite particle. Further stressing caused the cavities to grow in the tensile stress direction, forming dimple-like holes around the particles (Fig. 13). Subsequent matrix deformation under the shear stress condition led to the coalescence of holes and eventually the failure of composites, which should

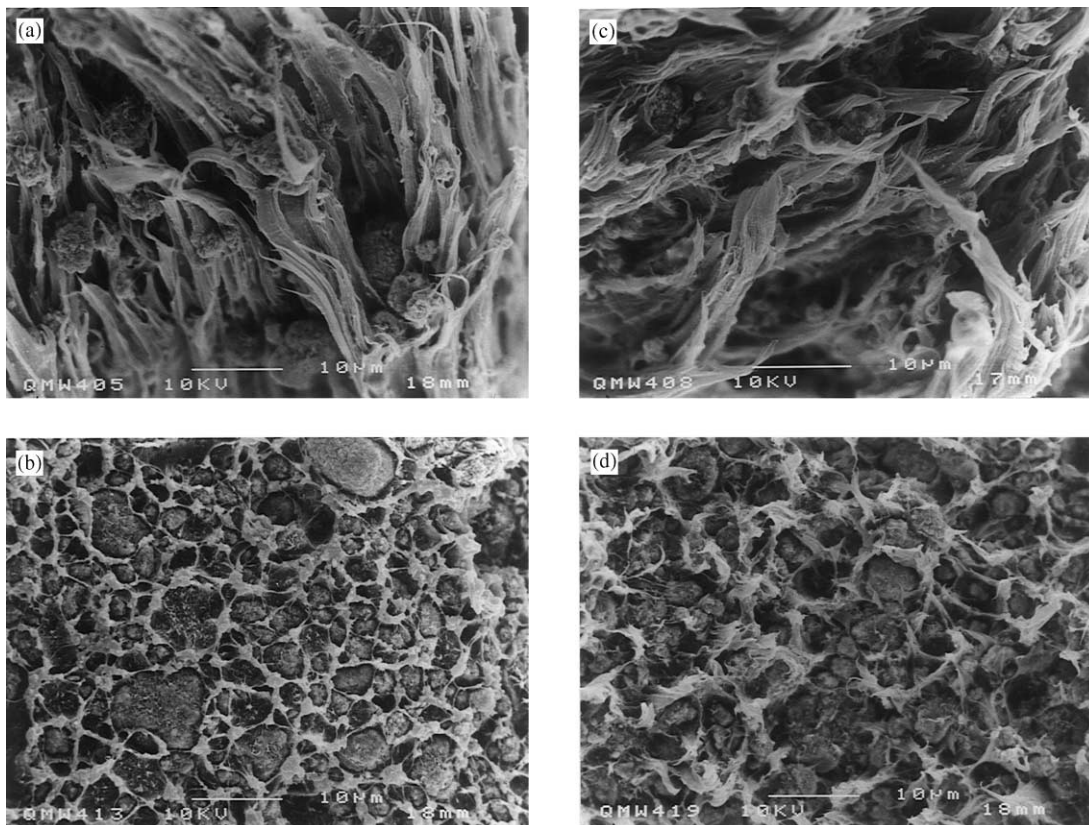


Fig. 11. Tensile fracture surfaces of new HA/HDPE composites showing different fracture characteristics: (a) composite C, (b) composite D, (c) composite E, (d) composite F.

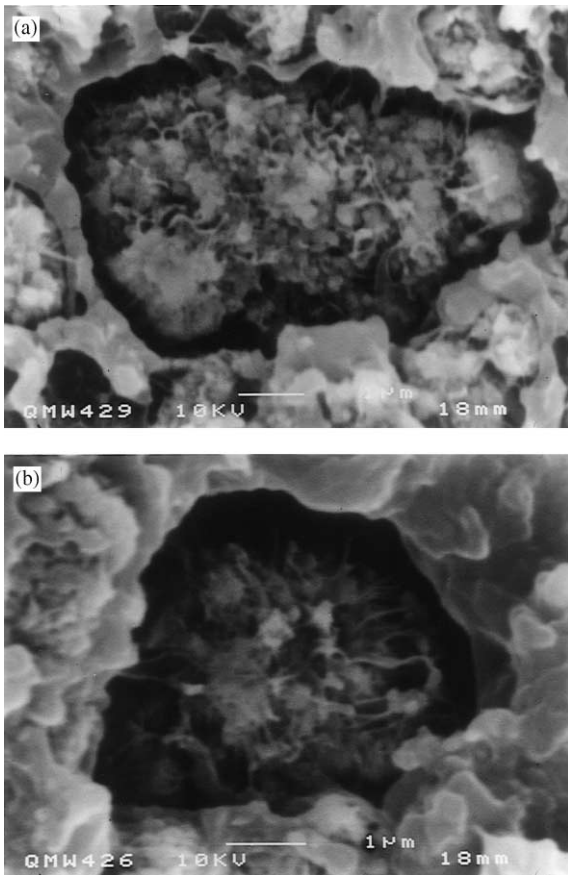


Fig. 12. Tensile fracture surfaces showing polymer network in the hydroxyapatite particles: (a) composite D, (b) composite F.

exhibit the fracture appearance as shown in Fig. 11. Strains needed for the growth and coalescence of holes decreased rapidly as the filler volume percentage increased, which caused the transition of the composite from a ductile mode of failure (such as composites C and E) to a macroscopically brittle fracture behaviour (such as composites D and F). Such a fracture mechanism is not fundamentally different from that for composites with weak bonds between the filler and the matrix as proposed by other researchers [21]. However, with the introduction of silane coupled hydroxyapatite and acrylic acid grafting, a strong bond (both chemical and mechanical) formed between the filler and the matrix, which must have delayed the initial dewetting and cavitation process, thus effectively increasing mechanical properties of the composite (Fig. 13). Even after extensive matrix deformation under tension, the infiltrated polymer network could still hold the hydroxyapatite particles in the fracture surface as is revealed in Fig. 14, which is very different from a simple HA/HDPE composite where detached particles simply remained at the bottom of dimples on the fracture surface.

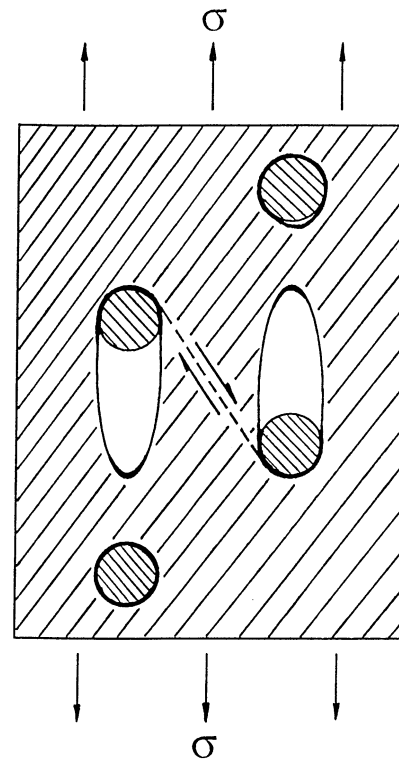


Fig. 13. Schematic diagram showing the fracture process of chemically coupled HA/HDPE composites.

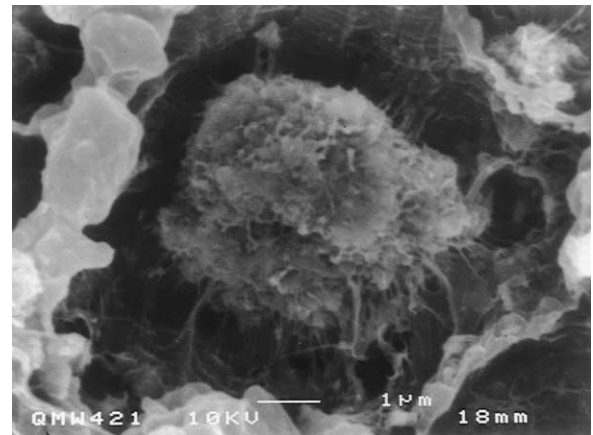


Fig. 14. An individual hydroxyapatite particle held by the polymer fibril network on the tensile fracture surface of composite F.

4. Conclusions

- (1) The introduction of silane coupled hydroxyapatite and acrylic acid grafted polyethylene has resulted in new HA/HDPE composites with improved ductility and tensile strength, even though their Young's modulus is decreased slightly when hydroxyapatite volume percentage is 40%. For both series of new composites, an increase in the hydroxyapatite volume percentage leads to increases in both Young's

modulus and tensile strength with a corresponding decrease in fracture strain.

- (2) Extruded (i.e., compounded) materials possess macropores and particle agglomerates of hydroxyapatite. However, the subsequent powdering process breaks down most of these agglomerates. Consequently, compression moulded composites exhibit fairly good distribution of hydroxyapatite particles in the polymer matrix and no macropores are present in the compression moulded plaques.
- (3) Silicon is detected at the particle–matrix interface of new HA/HDPE composites. The interfacial layer provides chemical adhesion for the particles to the matrix. The silane coupling agent also facilitates polymer penetration into the cavities of hydroxyapatite surface during composite processing, which enhances mechanical interlocking between the hydroxyapatite and the matrix for the resultant composites.
- (4) Improved bonding between the ceramic particle and the polymer which is achieved by both chemical adhesion and tight mechanical coupling leads to improved mechanical properties of new HA/HDPE composites.

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