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Effect of filler surface morphology on the impact behaviour of hydroxyapatite reinforced high density polyethylene composites

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Abstract Instrumented falling weight impact tests have been carried out to characterize the impact behaviour of hydroxyapatite reinforced high-density polyethylene composite (HA-HDPE) in order to use this biomaterial in skull implants. The effects of HA filler surface morphology and volume fraction on the fracture toughness were studied, and fracture mechanism investigated. Impact resistance was found to be markedly improved by using a sintered grade HA filler with smooth particle surface instead of spray dried grade HA with rough surface. SEM examination of impacted fracture surfaces revealed that the improvement of impact resistance was due to the stronger interfacial bonding between smooth HA particles and HDPE polymer matrix compared with that between rough HA and HDPE, which results in more energy absorption during impact and hence better fracture resistance.

Introduction

Many artificial materials have been used as skull reconstruction implant, including metals (such as titanium), polymers (such as PMMA), and ceramics (such as hydroxyapatite) [1]. However, each of them have their own drawbacks, for example, polymers have low elastic modulus and low strength; ceramics are brittle; metals are heavy, difficult to shape, and not particularly MRI compatible. Titanium is relatively radiolucent and biocompatible, however, its high heat and electrical conductivity, high cost and poor malleability are the major disadvantages. Therefore, the search for a biocompatible, readily available and readily shape-able material has lead to research that continues today.

To respond to these problems, hydroxyapatite reinforced polyethylene (HA-HDPE) composite was investigated as a skull reconstruction implant to repair skull defects. HA-HDPE composite is a proven biomaterial as a bone substitute, which has been used clinically as middle ear prostheses and orbital floor implants since 1980's [2–5]. For skull reconstruction implants, it is very important to understand the impact behaviour of the biomaterials because head injury is a major cause of death and disability and head injury and skull fracture are mostly attributed by impact force. The impact behaviour of HA-HDPE composite has been investigated previously with consideration of the HA filler volume fraction and HDPE matrix types [6]. The results showed that the impact property increased with decreasing HA filler content and higher HDPE matrix molecular weight. As discussed in the previous paper, the interfacial bonding between ceramic particulate filler and polymer matrix plays an important role for the impact resistance of composites. Therefore many studies have been carried out to modify the material surfaces and enhance adhesion between filler and matrix, such as using a coupling agent, hence improve the impact toughness of the composites [7–12]. However, at high filler fraction, coupling agents have limited effect on the impact properties of the composites because the reduced amount of matrix will not be sufficient to sustain plastic deformation [13,14]. The impact behaviour of the composites is also found to be associated directly with the filler particle size, shape and uniformity of distribution [7,9,15].

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In this paper, two grades of HA filler with different surface morphologies have been used to compound HA-HDPE composites without a coupling agent. The impact behaviour of these two HA filled composite have been investigated.

Materials and methods

Materials

Hydroxyapatite reinforced polyethylene composites were produced by compounding synthetic hydroxyapatite (HA) filler into high-density polyethylene (HDPE) matrix.

A grade of high density polyethylene (HDPE, Rigidex HM4560XP) was used in this study (supplied by BP Chemical Ltd.), with molecular weight $M_w = 249{,}233$ and density = 945 kg m^{-3}.

Two types of synthetic hydroxyapatite powders were used in this study. One was spray dried HA powder, HA1 (P218R); the other was sintered HA powder, HA2 (P220S). Both HA powders were supplied by Plasma Biotal Ltd., UK. X-ray Diffraction (XRD) analysis was carried out to examine the crystalline structures of the two grades of HA powders, using D-5000^{TM} X-ray diffractometer with 2θ values from 25 to 40°, step size of 0.02°, and a step time of 2.5 s. Power was set at 40 kV and 40 mA. It can be seen that the XRD patterns (Fig. 1) of the two HAs, HA1 and HA2, appear to be identical. All the main peaks matched well with ASTM standard crystalline pattern (JCPDS 9-432) of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). These results indicate that both HAs used in this study had same crystalline structures and were relatively pure synthetic hydroxyapatite.

HA particle surface morphology was examined using JEOL 6300 scanning electron microscope. Fig. 2 shows the particle morphology of HA1 and HA2 powders. It can be seen that HA1 is relatively spherical in shape and has extremely rough surfaces, which consist of clusters. HA2 is more irregular in shape, but has smooth and well-defined surfaces.

The particle size distribution and specific surface area of both HA powders were measured using a Malvern Masteriser and the BET analysis method (Micromeritics Gemini II 2370 Surface Area Analyser). Table 1 shows that the HA1 and HA2 have similar median particle size. However the specific surface areas are a factor of more than ten different which is the result of the different particle morphologies shown in Fig. 2.

Composites production

Three different volume fractions (20, 30, and 40%) hydroxyapatite reinforced polyethylene composites (HA-HDPE) were used in the study. The production procedure has been described previously [6], consisting of blending, compounding, pelletizing, powderising and compression moulding. After annealing for 8 h at 80 °C, the impact test samples, 60 × 60 × 4 mm^3 square plates were machined from compression moulding plates. Finally, the samples were gamma irradiated at a nominal dose of 2.5 Mrad (Isotron Plc, Reading, UK).

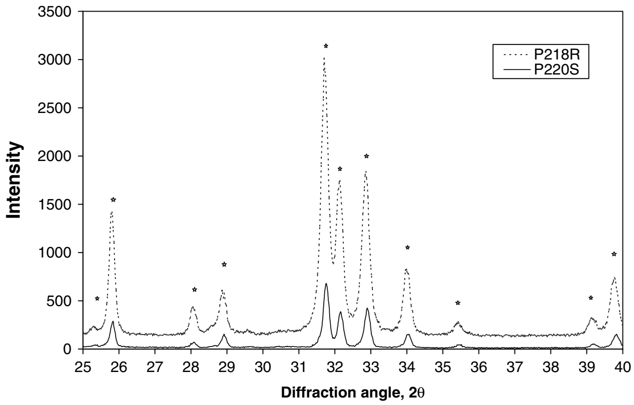
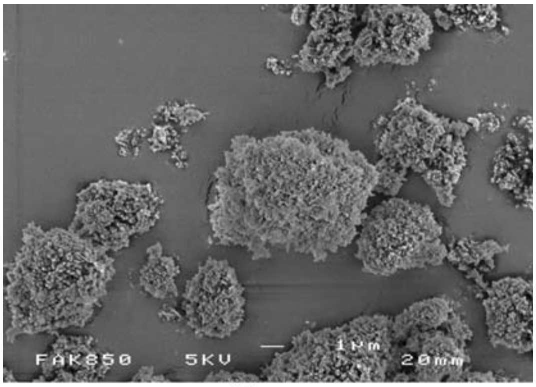
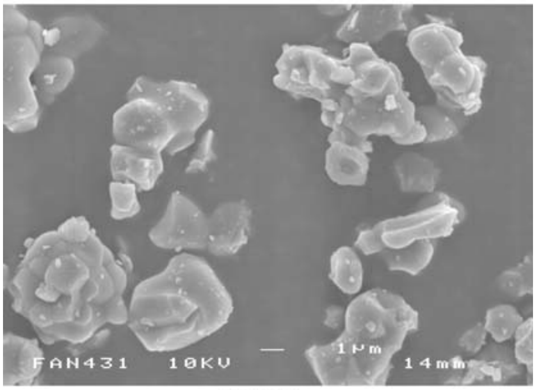


Fig. 1 X-ray diffraction patterns of the two grades of hydroxyapatite



(a) HA1



(b) HA2

Fig. 2 Particle morphologies of HA1 and HA2 (marker bars = 1 µm)

Table 1 Physical properties of two grades of hydroxyapatite

HA grade	Density (kg m^{-3})	Particle size (μm)			Specific surface area (m^2 g^{-1})
		$d_{0.1}$	$d_{0.5}$	$d_{0.9}$	
HA1	316	0.99	3.80	6.23	13.536
HA2	316	0.76	4.46	11.12	0.965

Impact testing

A CEAST instrumented falling weight impact tester (Italy) was employed in this study to investigate the impact behaviour of the HA-HDPE composites. The falling striker has a mass of 15.8 kg. A hemispherical tip of 20 mm diameter is attached to the striker, while the support ring, which is a horizontal platform, has an internal diameter of 40 mm and is in an environmental chamber which has a temperature range of –70 °C to 100 °C. The test configuration is in compliance with ISO 6603/2.

In this study, falling weight impact tests were performed at 37 °C. The impact speed used was 3.13 m s^{-1}, with an impact energy of 77.47 J. The force-time curves were recorded during impact test and the energy absorption was calculated automatically from the area under force-time curve via a series of integration steps.

SEM examination of fractured surface

Impacted fracture surfaces were examined using JEOL JSM6300 scanning electron microscope. Samples were cut from the fractured impact samples and sputter coated with gold for SEM study.

Results

A typical force-deformation curve recorded for 20 vol% HA1-HDPE composite at 37 °C is showed in Fig. 3. The peak force showed the onset of crack formation, and the total absorbed energy is the sum of the dissipated energies required to initiate and propagate the fracture. The total absorbed energy can be split into initiation (I, E_I) and propagation (II, E_P) energies from the peak point, as shown in Fig. 3. The results of impact tests for both HA1-HDPE and HA2-HDPE composites are shown in Table 2. The results indicate that the impact resistance of HA-HDPE composites is highly affected by filler HA contents. All the total absorbed energy, initiation and propagation energy decreased significantly with increasing HA volume fraction. Furthermore, the impact behaviour of HA-HDPE was markedly affected by the type of HA used. The fracture resistance was dramatically improved when the sintered grade of HA2 particles with smooth surfaces were used, compared to the spray dried grade of HA1 particles with rough surface. Both the crack initiation and propagation resistances were increased when HA2 filler was used.

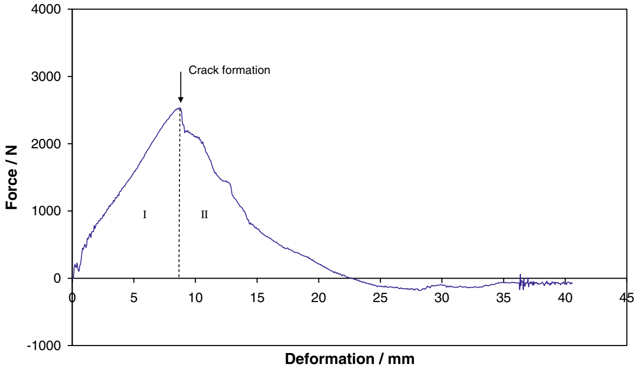


Fig. 3 Typical force-deformation curve for impact test, 20 vol% HA1-HDPE

The damaged zone of the impacted specimens (Fig. 4) revealed that the damaged area increased with increasing HA concentration for both types of HA fillers. Compared with HA1-HDPE, HA2-HDPE composites produced much smaller impacted zone with all the materials still connected together and not shattered into separate pieces, showing tougher behaviour than the HA1 filled composite. The difference can easily be seen from these images.

SEM images of impacted fracture surfaces are shown in Fig. 5 and Fig. 6 respectively for HA1-HDPE and HA2-HDPE composites. At lower HA content, more polymer matrix is available for deformation, producing more fibrils. The increase of HA filler leads to the reduction of polymer matrix and hence less plastic deformation of the matrix and less energy dissipation. It is seen clearly that longer HDPE matrix fibrils were pulled out from HA2-HDPE composite compared with HA1-HDPE composite, which indicated more matrix plastic deformation during the impact testing. For 20 vol% HA2-HDPE composite, SEM image shows that some HA particles were still wrapped inside HDPE matrix, showing the stronger interfacial bonding between particle and matrix.

Discussion

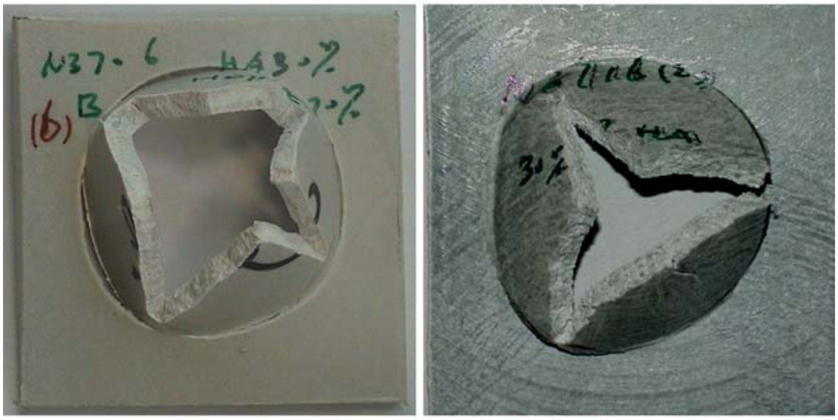
As discussed in the previous study [6], the fracture of the rigid particulate filled polymer composites undergoes particle-matrix debonding and microvoid formation at the interface. This debonding initiates a crack which propagates through the voids, connects and coalesces; finally leading to material fracture. Therefore, the strength and toughness of a particulate composite depend on the amount of filler, which is compounded with the plastic, the particle

Table 2 Impact test results of HA-HDPE composites at 37 °C, showing means ± standard deviations

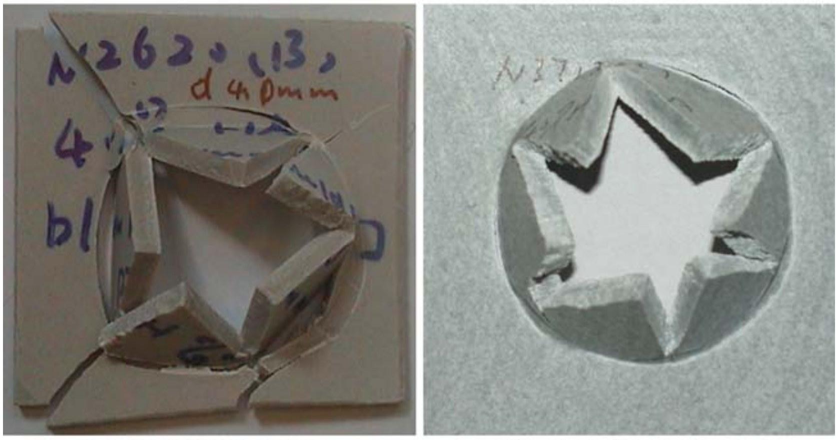
HA volume fraction (%)	Total energy (J)		Initiation energy (J)		Propagation energy (J)	
	HA1-HDPE	HA2-HDPE	HA1-HDPE	HA2-HDPE	HA1-HDPE	HA2-HDPE
20	26.0 ± 1.5	44.9 ± 2.6	13.1 ± 1.9	28.6 ± 2.0	12.9 ± 0.8	16.3 ± 0.3
30	14.0 ± 1.0	23.6 ± 2.3	3.1 ± 0.3	9.3 ± 1.7	10.9 ± 0.8	14.3 ± 0.7
40	7.6 ± 0.9	12.9 ± 0.4	1.5 ± 0.4	2.3 ± 0.2	6.1 ± 1.2	10.6 ± 0.3

Fig. 4 Impacted samples of HA1-HDPE and HA2-HDPE composites

(a) 20vol%HA1-HDPE **(b)** 20vol%HA2-HDPE



(c) 30vol%HA1-HDPE **(d)** 30vol%HA2-HDPE



(e) 40vol%HA1-HDPE **(f)** 40vol%HA2-HDPE

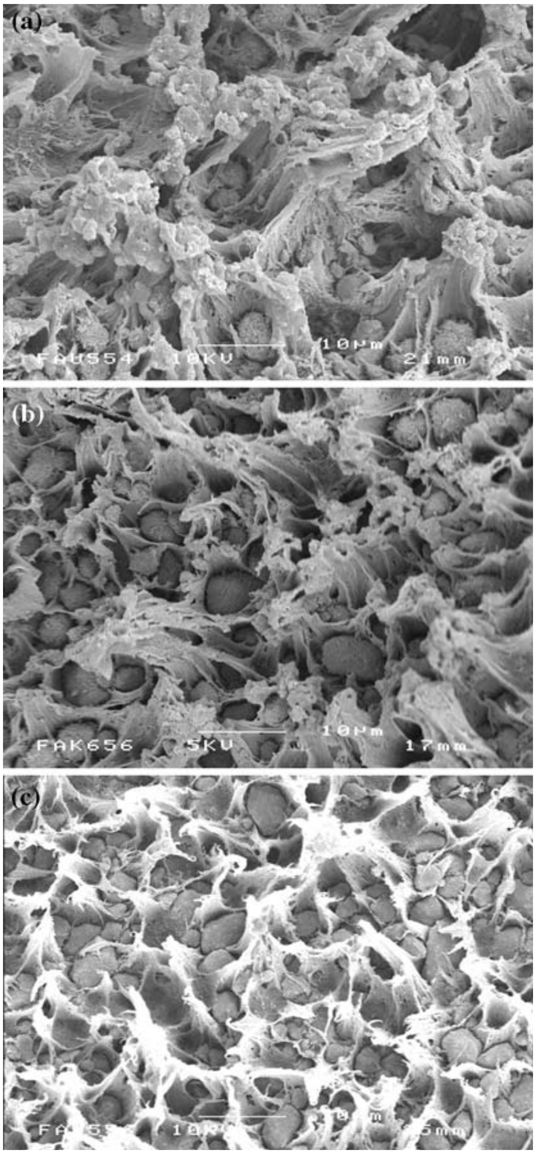


Fig. 5 SEM micrographs of the fracture surfaces of HA1-HDPE composites after falling weight impact test with HA of (**a**) 20 vol%; (**b**) 30 vol%; and (**c**) 40 vol% (marker bars = 10 µm)

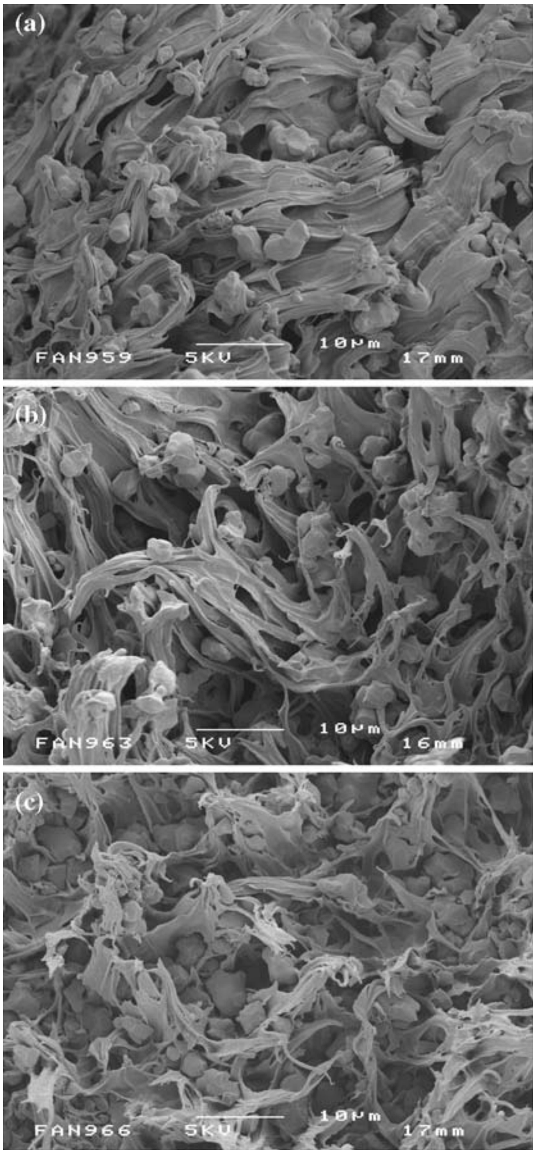


Fig. 6 SEM micrographs of the fracture surfaces of HA2-HDPE composites after falling weight impact test with HA of (**a**) 20 vol%; (**b**) 30 vol%; and (**c**) 40 vol% (marker bars = 10 µm)

size and shape, the bonding between the filler and the plastic, the toughness of the plastic, and the toughness of the filler. Among them, the interface strength between particulate filler and polymer matrix plays a critical role for the composite fracture mechanisms.

Many studies have been carried out in order to improve the interface adhesion between filler and matrix, for example, filler surface modification with coupling agents. However, coupling agents are material dependent: effective for some materials, but ineffective for others. Furthermore, a biomaterial must be biologically compatible with surrounding tissue, which further restricts the choice of coupling agents. Deb *et al.* [16] reported that the fracture behaviour of HA-HDPE material with 40 vol% HA was not improved substantially by increased interfacial bonding using silane coupling. In the present study, there is only mechanical interlock existed between the HA and the HDPE as no surface treatment has been used, resulting in weak interface bonding. However, when the sintered grade HA2 filler with smoother particle surfaces was used to replace the rougher HA1, the impact resistance was found to be improved markedly. SEM examination revealed that the improvement was due to stronger interface bonding between HA and HDPE, which lead to more and larger matrix fibrils being pulled out during impact testing and resulted in more impact energy being absorbed. This stronger interface adhesion between HA2 filler and HDPE matrix resulted from the composite manufacture process. During processing, the HDPE matrix could not completely fill all the cavities on the rough surface of the HA1 due to the poor wettability of HA to HDPE while the smooth surface of HA2 leads to increased contact between the two phases. More voids or weak points are present in HA1 filled composites compared to HA2 filled composites, which leads to poorer adhesion and a weaker interface between the HA1 particles and HDPE. During impact testing, the voids or weak points initiate the formation of cracks, making HA1 particles much easier to debond from the matrix. Therefore less plastic deformation of the matrix occurs before fracture, resulting in less absorbed impact energy and lower fracture toughness. SEM images (Fig. 5) showed that the interfacial bonding between HA1 and HDPE matrix has failed totally and the HA1 fillers were totally separated with matrix, and the HA1 particles were observed clearly. On the other hand, due to the smooth surface of HA2 particles, less curved gaps and cavities exist which needed to be filled during composite processing. Therefore there were fewer holes and weak points to initiate fracture of the materials during impact test. SEM images (Fig. 6) show that the interface between HA2 and HDPE was not totally debonded during impact testing, with some HA particles still wrapped inside HDPE matrix, which is obvious at low HA fraction (20 vol%). For this material, the fracture toughness of the HDPE matrix plays a more important role in the impact resistance of the composite than in the HA1 filled composites. Much longer HDPE matrix fibrils were pulled out from HA2-HDPE composite compared with HA1-HDPE composite due to stronger interfacial bonding, which indicated more matrix plastic deformation and more energy absorption during the impact testing.

Joseph and Tanner [17], and Eniwumide *et al.* [18] found that the HA2 filled HDPE composites had higher fatigue and quasi-static fracture properties compared to HA1-HDPE composites. They assumed that the larger surface area (HA1 particles) needs more HDPE matrix to wet the surface and form an immobile layer on the HA particles during processing, hence leaving less matrix available for flow during deformation, resulting in less energy dissipation. SEM images of impacted fracture surfaces in this study clearly revealed the interface difference between those composites based on these two grades of HAs, which shows that the sintered HA2 filled composites have better adhesion and stronger bonding, resulting in higher interfacial strength and better fracture resistance. Joseph and Eniwumide's explanation that more matrix in HA2-HDPE is available for plastic deformation leading to further energy absorption, may also contribute to the improvement.

Conclusions

It was found that HA surface morphology strongly influences the impact resistance of HA-HDPE composites. The total absorbed energy increased significantly when smooth surfaced HA replaced rough surfaced HA filler. The polymer matrix can produce a stronger interfacial bonding with smooth surface HA filler than with rough surfaced HA during composite manufacturing, which leads to more energy dissipation and the improvement in impact resistance. This study also indicates other methods than coupling agents for interfacial strength improvement of biocomposites.

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