Fabrication and Characteristics of Hydroxyapatite Reinforced Polypropylene as a Bone Analogue Biomaterial

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ABSTRACT: Composite biomaterials, which consist of a polymer matrix and a particulate bioactive phase and are hence analogous to bone microstructure, have been developed for human hard tissue substitution. In this investigation, a manufacturing route employing injection moulding was established for producing bone analogue biomaterials. Using this manufacturing technology, a potential bone replacement material, hydroxyapatite (HA) reinforced polypropylene (PP) composite (HA/PP), was made, with the HA volume percentage being up to 25%. The characteristics of the HA/PP composite were studied using various techniques including scanning electron microscopy (SEM), differential scanning calorimetry (DSC), tensile testing, microhardness testing, and dynamic mechanical analysis (DMA). It was demonstrated that with the use of the established manufacturing route, HA particles were well dispersed and homogeneously distributed in the PP matrix. Properties of the composite were affected by the amount of HA incorporated in the composite. The melting temperature and crystallisation temperature of the composite were slightly affected by the addition of HA particles, and the crystallinity of the PP matrix polymer was decreased with an increase in HA content. Young's modulus, microhardness, and storage modulus increased when the HA volume percentage was increased from 10 to 25%, with corresponding decreases in tensile strength, elongation at fracture and loss tangent. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2780–2790, 2007

Key words: biomaterials; composites; processing; poly (propylene); mechanical properties

INTRODUCTION

In tissue replacement and regeneration, biomedical composites are designed in order to have a combination of the best characteristics of each component material (two or more materials) and to satisfy various mechanical and biological requirements. A significant number of biomedical composites have been investigated or are currently under investigation as replacement materials for diseased or damaged tissues in the human body.[1] Polymer matrix composites, metal matrix composites, and ceramic matrix composites have all been made for possible human tissue replacement. However, polymer matrix composites are the most widely studied composite materials for tissue substitution due to a number of reasons: resemblance in composition and structure to the natural tissue, good biocompatibility, relative ease of manufacture, etc. The first bioactive polymer matrix composite, hydroxyapatite (HA) reinforced high density polyethylene (HDPE), has now been used clinically for bone replacement.[2]

There are a number of polymers that can be used in the medical field.[3,4] The use of a PE matrix does not preclude the use of some other biocompatible polymers as matrix materials in bone-substituting composite materials. Polymers such as polyetheretherketone (PEEK), polysulfone (PSU), and polypropylene (PP) are good candidates as matrices. And indeed biomedical composites using these polymers were produced[5–7] and some aspects of these composites have been studied. PP, a biocompatible and biostable polymer[3] and also a stronger and stiffer polymer than PE,[4] appears suitable as the matrix material, instead of PE, for bioactive composites. Compared with PE, PP exhibits better mechanical performance in fatigue and suffers less reduction in mechanical properties at elevated temperatures, which are important for bone replacement materials because load-bearing implants must withstand millions of loading–unloading cycles and provide adequate mechanical properties at body temperature (37°C). However, the study of HA/PP composites has been very limited and nonsystematic.[7,8] Among all bioactive bioceramics, HA is the most widely studied material for hard tissue replacement and augmentation due to its close resemblance to the

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main inorganic component of natural bone and excellent biocompatibility and bioactivity (i.e., good osteoconductivity).[9,10] As HA is a weak bioceramic, it cannot be used on its own as a load-bearing biomaterial. However, with its desirable osteoconductivity, HA has been extensively used as coatings on metal implants[11] and as the bioactive secondary phase in biomedical composites.[5–8,12–16]

There are two objectives for the current investigation: (1) to conduct a systematic study of HA/PP composite as a bone analogue biomaterial for potential bone replacement applications, and (2) to establish a manufacturing route involving injection moulding for the production of biomedical composites which have heat-sensitive polymers as matrices and hence require shortest possible processing time at elevated temperatures. As was pointed out previously,[17] for a polymer matrix composite containing particulate HA, at least 20 vol % of HA must be incorporated into the composite in order for the composite to be osteoconductive. An increase in HA content in the composite leads to a higher bioactivity. On the other hand, as shown with the HA/HDPE composite,[12] higher bioactivity composite containing larger amounts of HA (e.g., 40 vol %) becomes brittle. A judicious choice has thus to be made when considering a balance between bioactivity and mechanical performance. In any case, thermal processing of polymer matrix composites containing more than 20 vol % of hard ceramic particles is not an easy task as these composites are already ''highly filled polymers'' and hence careful considerations need to be given to the use of composite processing technologies. After establishing the manufacturing route and fabrication of HA/PP composite, a variety of techniques were employed to determine the characteristics of the composite produced.

MATERIALS AND METHODS

Raw materials

Commercially available HA and PP were used for producing HA/PP composite. Synthetic HA in the form of fine powders (Taihei Chemicals, Japan) was used in its as-received state without further treatment. This HA was phase-pure HA and also highly crystalline and had an average particle size of 24.5 μm.[15] The theoretical density of HA, 3.16 g/cm^3,[10] was used in the current investigation. PP (H380F, SK-Corporation, Korea) was supplied in the form of large pellets. To ensure good mixing of particulate HA with PP at the compounding stage of composite manufacture, these pellets were melt-processed in a PRISM twin-screw extruder and pelletised into small granules which were then ready to be used for making HA/PP composite. The PP had a nominal density of 0.911 g/cm^3.

Manufacture of composite

HA/PP composite with nominal HA volume percentages up to 25% was produced through a manufacturing route which comprised compounding, pelletising, drying, and injection moulding. Compounding of the composite was conducted using the PRISM twin-screw extruder at 190°C. The extruded strands were pelletised into small granules using a PRISM pelletiser for subsequent injection moulding. Before injection moulding, all compounded materials were dried overnight in an oven at 70°C. Tensile specimens conforming to ASTM D638 were injection moulded at 178°C using a RAY-RAN manual injection moulding machine. Specimens for other studies were made from these as-produced tensile specimens.

Microstructural analysis

The dispersion and distribution of HA particles in the PP matrix was studied after injection moulding. The specimens were prepared through sectioning, cold-mounting in an acrylic resin, grinding, polishing, ultrasonic bath cleaning, and drying. Specimens were polished progressively using a series of silicon carbide paper ending at the #1200 grit paper. The polished composite surfaces were examined under a Leica 360 scanning electron microscope (SEM) at an accelerating voltage of 20 kV after the specimens had been sputter-coated with a thin layer of gold.

Differential scanning calorimetry analysis

The melting and crystallization behavior of HA/PP composite and crystallinity of the PP matrix polymer were studied using a Perkin–Elmer differential scanning calorimetry (DSC) thermal analyzer employing three thermal cycles between 30 and 200°C. A heating and cooling rate of 10°C/min and a sample weight of around 9 mg were maintained for all tests which were conducted in a nitrogen atmosphere.

Tensile testing

The injection moulded tensile specimens (standard ASTM D638 specimens: dumbbell specimens with 80 mm in length and 2 mm in thickness) were used to evaluate main mechanical properties of the composite. Tensile tests were conducted on a Lloyd LR-5K testing machine at a crosshead speed of 0.5 mm/min. Young's modulus, tensile strength, and elongation at fracture were determined from the recorded

stress–strain curves. At least five specimens were used for each composition of the composite.

Microhardness testing

The Vickers hardness of the composite was measured using a BUEHLER microhardness tester. For each composition of the composite, a rectangular specimen of the dimensions 10 mm × 5 mm × 2 mm was cut from an injection moulded tensile specimen. The specimens were first mounted in an acrylic resin and then ground and polished on silicon carbide papers for obtaining scratch-free surfaces. An indentation load of 50 g was applied to the polished surface for 15 s and Vickers hardness number (VHN) was obtained. Each specimen was indented at least 15 times and each indentation was at least two indentation diameters away from adjacent indentations. All indentations were made avoiding edges of specimens.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) of the composite was performed on a Rheometric Scientific DMA IV machine using a three-point bending measuring system. Dimensions of DMA specimens were 18 mm × 5 mm × 2 mm. Tests were conducted in a temperature range of 30–180°C and at a heating/cooling rate of 4°C/min. Assuming the physiological frequency (the normal walking speed of a man) was 1 Hz, all DMA tests were conducted at this frequency. The viscoelastic properties, viz., storage modulus E′, loss modulus E″ and loss tangent (tan δ), were recorded as a function of temperature. A total of five specimens were tested for each composition of the composite.

Analysis of deformed surfaces and fracture surfaces of composite

Following two types of mechanical testing, composite surfaces were examined under SEM after these surfaces were sputter-coated with a thin layer of gold. With microhardness testing, small indentations were made on composite surfaces and they were imaged. With tensile testing, fracture surfaces of the composite were obtained and subsequently analyzed using SEM.

RESULTS AND DISCUSSION

Defect-free tensile specimens of HA/PP composite (Fig. 1) were produced employing the current manufacturing route with the use of injection moulding, which is different from the previous technology which used compression moulding.[7] Using either injection moulding or compression moulding for the final product may not be a very important issue for biomedical composites such as HA/HDPE or HA/PP whose polymer matrices can withstand, to some extent, the high thermal processing temperature for a relative long duration without oxidation or thermal degradation. The composites based on HDPE matrix did not experience significant thermal degradation during composite manufacture,[18–20] even though compression moulding was used, which took much longer time for the composites to stay at the processing temperature of around 200°C[12] than injection moulding would. However, polymers such as polyhydroxybutyrate (PHB) are very heat-sensitive and suffer thermal degradation at temperatures just around the melting temperature[21,22] and hence any efforts to make PHB-based biomedical composites should avoid a long processing time of the composites at elevated temperatures. It was found out previously that the manufacturing route employing compression moulding was not satisfactory for producing PHB-based composites,[23] as cracked composite plates had resulted due to prolonged heating time during compression moulding. With current manufacturing route, PHB-based composites could avoid long heating time through injection moulding which minimizes thermal degradation of the PHB matrix. This new manufacturing route has indeed led to the production of high-quality biomedical composites based on PHB and its copolymers.[24]

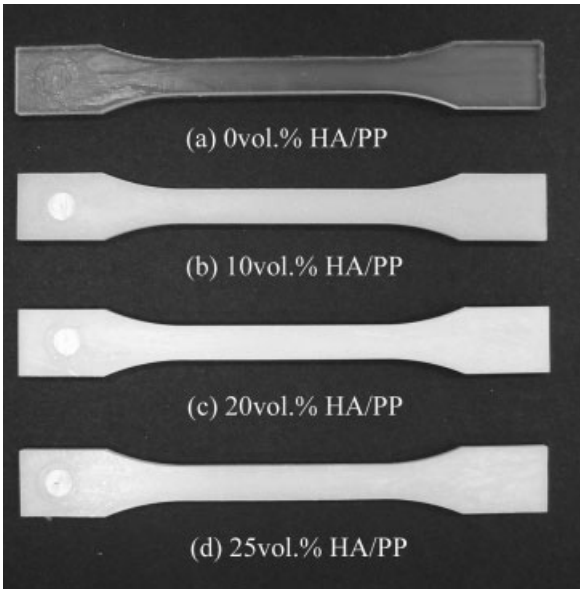
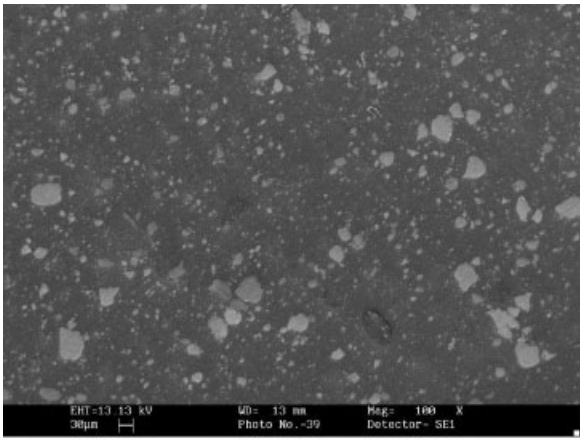


Figure 1 Injection moulded tensile specimens of HA/PP composite (From top to bottom: 0, 10, 20, 25 vol % HA/PP).

Figure 2 displays micrographs of polished surfaces of cross-sections of injection moulded HA/PP tensile specimens. All specimens showed homogeneous distribution of HA particles in the composite,



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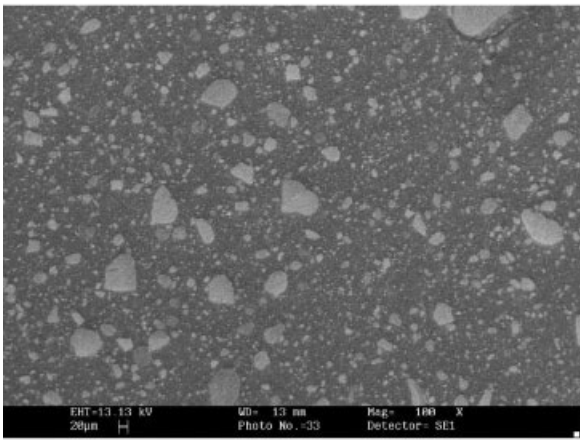

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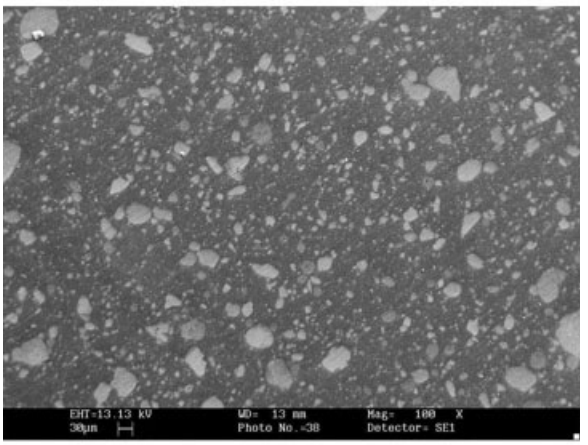


(c)

Figure 2 SEM micrographs showing the microstructure of HA/PP composite: (a) 10 vol % HA/PP, (b) 20 vol % HA/PP, (c) 25 vol % HA/PP.

demonstrating that after the compounding process HA particles in HA/PP composite were well dispersed and pore-free HA/PP composite could be successfully injection moulded. The uniform distribution of HA particles in bioactive composites is essential for mechanical as well as biological performance of implants.[1] In previous studies of HA/PP composites, the microstructure of the composites was either not reported[7] or if reported, showed unsatisfactory distribution of HA particles in the composite.[8] In the study conducted by Ramirez et al.,[8] probably due to their inexperience in manufacturing bioceramic-polymer composites and also because of the compounding technology that they used, the particulate HA was shown to have formed streaks of agglomerates in the composite, which would not yield high performance biomedical composites. Their observation of the unexpected ''brittle behaviour'' of their HA/PP composite during tensile testing can be correlated to this inhomogeneous distribution of HA particles in the composite.

Bone is a natural nanocomposite consisting of nano-sized bone apatite and collagen matrix.[1] The HA/PP composite produced in the current investigation is analogous to bone structure at the lowest microscopic level, albeit the size of HA particles in the composite is much larger than that of apatite in natural bone. Efforts have been made to mill down the as-received HA to a much smaller size for making HA/PHB composites and it appears that the current manufacturing route for producing HA/PP composite can still be used to make these new HA/PHB composites.[25]

Thermal properties, such as melting temperature (T_m), crystallization temperature (T_c), and heat of fusion (H_f), of the HA/PP composite containing different amounts of HA and also the degree of crystallinity of polymer matrix ($H^*(\%)$) were determined from DSC thermograms (Fig. 3) and are listed in Table I. The degree of crystallinity of the PP matrix, $H^*(\%)$, was estimated using the equation below[26]:

$$H^*(\%) = \frac{\Delta H_m/\phi_{PP}}{\Delta H_m^0} \times 100\%. \quad (1)$$

where ΔH_m is the apparent fusion enthalpy of matrix PP in the composite, ΔH_m^0 is the fusion enthalpy of the theoretically 100% crystalline PP polymer which has been reported to be 138 J/g,[27] and ϕ_{PP} is the weight fraction of matrix PP in the composite.

It can be seen from Figure 3 and Table I that T_m and T_c were slightly affected (generally increased) by the addition of HA particles. The degree of crystallinity of the PP matrix polymer generally decreased with an increase in HA amount in the composite. It appears that the presence of HA particles in the composite hindered the growth of crystallites in the polymer, leading to the decrease in crystallinity of the matrix polymer. This decrease in crystallinity is in contradiction to the common belief that the introduction of minute particles into the

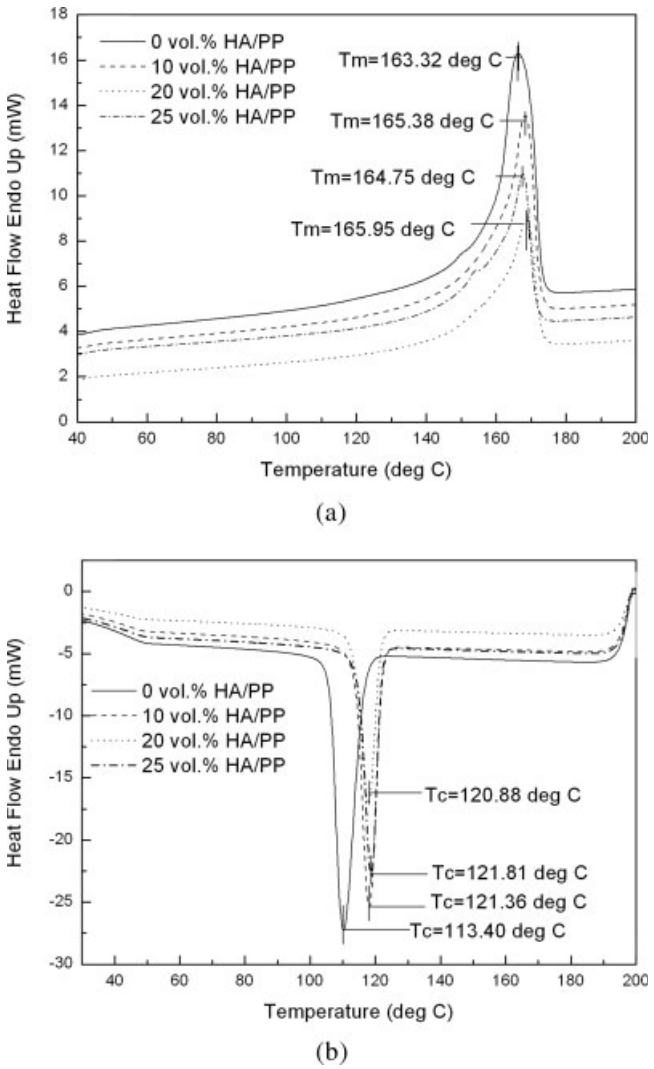


Figure 3 DSC thermograms for the melting and crystallization of HA/PP composite: (a) melting, (b) crystallization.

polymer melt would enhance the nucleation of crystallites in the polymer upon cooling and hence improve the crystallinity of the polymer after cooling. The decrease in crystallinity has a negative effect on the mechanical properties of the polymer matrix and hence the composite, as a higher degree of crystallinity will lead to a stronger and stiffer polymer.[28] However, for the HA/PP composite, this negative effect can be negated by the presence of

TABLE I
Thermal Properties of HA/PP Composite and Crystallinity of PP Matrix

HA content (vol %)	T_m (°C)	H_f (J/g)	T_c (°C)	H_c (J/g)	H^* (%)
0	163.3	109.3	113.4	−111.6	79.2
10	165.4	71.5	121.4	−72.0	57.6
20	166.0	51.3	120.9	−51.7	46.5
25	164.8	49.3	121.8	−51.5	47.6

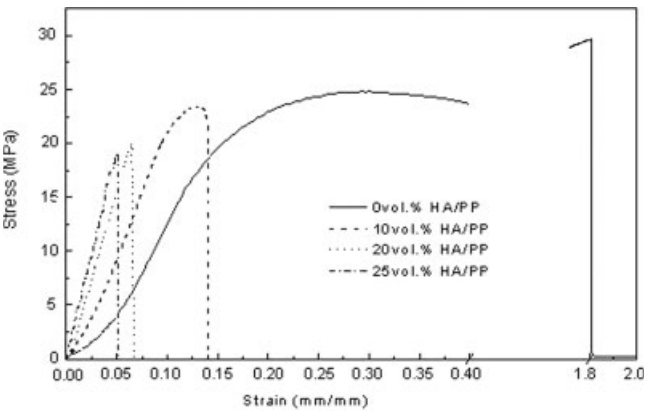


Figure 4 Typical tensile stress–strain curves of HA/PP composite.

HA particles which stiffen the composite, which is evidenced by the mechanical testing results obtained in the current investigation.

Figure 4 shows typical tensile stress-train curves of HA/PP composite containing different amounts of HA. It can be seen that the tensile strength decreases with an increase in HA content. The elongation at fracture of the HA/PP composite is much lower than that of unfilled PP. The value of elongation at fracture of 10 vol % HA/PP is significantly higher than those of 20 vol % HA/PP and 25 vol % HA/PP, whereas the elongation at fracture of 25 vol % HA/PP is only slightly lower than that of 20 vol % HA/PP. While the 10 vol % HA/PP still exhibited yielding before fracture, 20 vol % HA/PP and 25 vol % HA/PP showed near-linear stress–strain relationship up to their respective fracture points. The HA/PP composite is less ductile than unfilled PP.

The relationship between Young's modulus of HA/PP composite and HA volume percentage is shown in Figure 5. Young's modulus is an important property of a biomaterial. It can be observed that

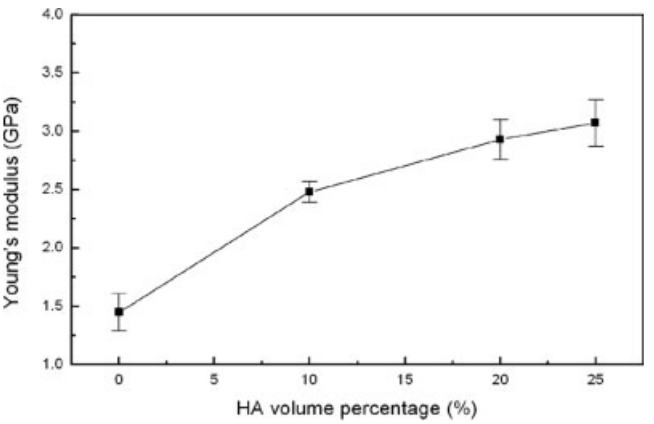
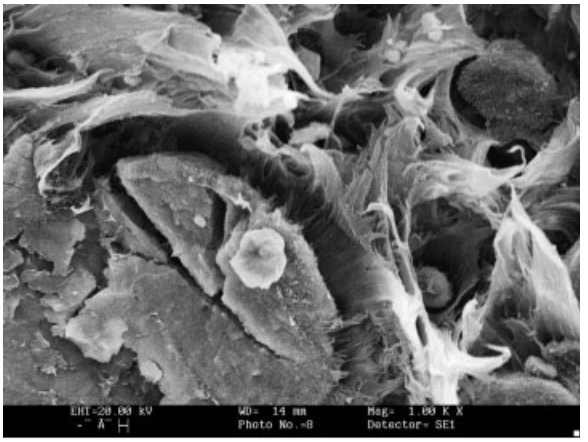


Figure 5 Effect of HA volume percentage on Young's modulus of HA/PP composite.



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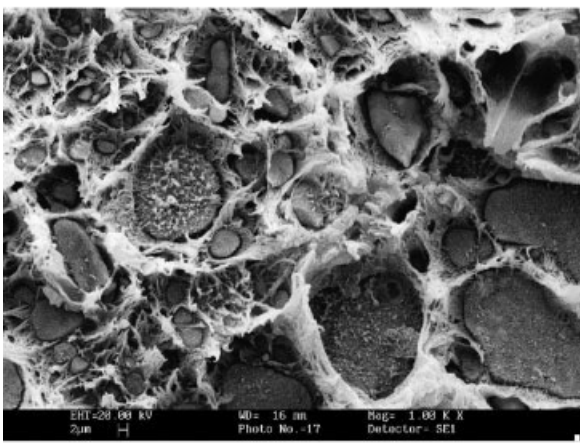

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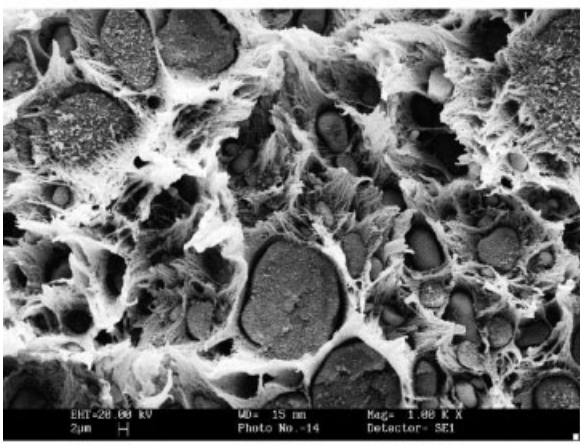


(c)

Figure 6 SEM micrographs of tensile fracture surfaces of HA/PP composite: (a) 10 vol % HA/PP, (b) 20 vol % HA/PP, (c) 25 vol % HA/PP.

Young's modulus increases nonlinearly with the increasing amount of HA in the composite. This indicates that the addition of HA bioceramic stiffened HA/PP composite, which is in agreement with theories and the general observation that fillers having higher stiffness than the matrix can increase the elastic modulus of the composites.[1,29] Apart from bioactivity due to the presence of HA, the higher Young's modulus the HA/PP composite is desirable for hard tissue replacement.

Figure 6 exhibits SEM micrographs of tensile fracture surfaces of HA/PP composite. It can be seen that HA particles were held by the PP matrix, possibly through certain degree of mechanical bonding between the two phases. Debonding can be observed at the HA-PP interface on all HA/PP fracture surfaces, which may indicate that there was only mechanical bonding between HA and PP. This mechanical bonding is a direct result of the shrinkage of PP matrix around individual HA particles when the composite was cooled down from the elevated melt-processing temperature to room temperature. This weak mechanical bonding accounts for the decreasing tensile strength of the composite when the HA content is increased (Fig. 4). The fracture surfaces shown in Figure 6 also indicate that the tensile fracture process of the HA/PP composite follows the conventional process for highly filled polymers through debonding, cavitation, void coalescence, and tearing and fracture of polymer fibrils (Fig. 7), which was observed for other bioceramic–polymer composites such as HA/HDPE.[30,31]

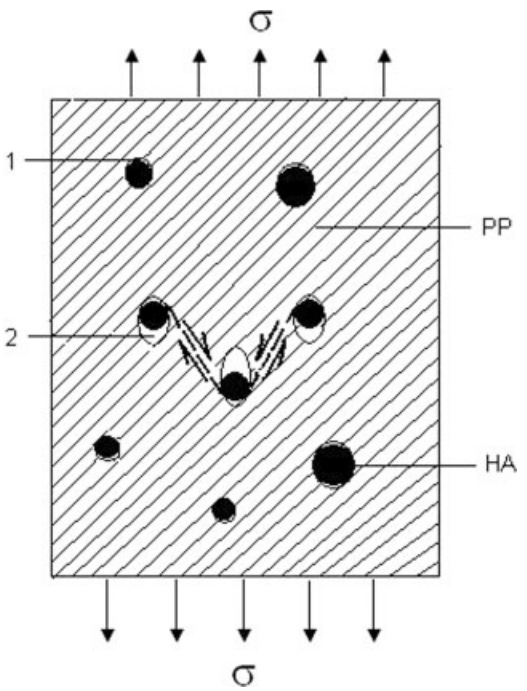


Figure 7 A schematic diagram illustrating the tensile fracture mechanism of HA/PP composite (Location 1: debonding; Location 2: cavitation; Location 3 of three adjacent HA particles with surrounding PP matrix in the middle of the diagram: tearing of polymer fibril under shear stress.)

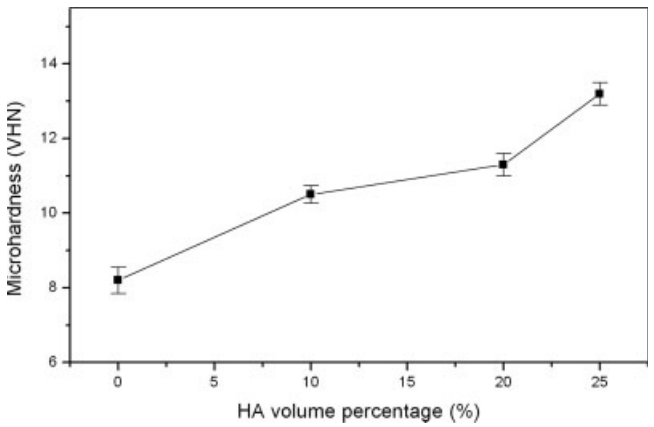


Figure 8 Effect of HA volume percentage on microhardness of HA/PP composite.

It has been reported that Vickers hardness of bioceramic–polymer composites increased with the increases in bioceramic volume in the composites.[15,20,32] Figure 8 shows Vickers hardness (VHN) for the HA/PP composite, in which an ascending trend of Vickers hardness is observed with the increase in HA volume percentage. Although the hardness of a material is actually determined by the compressive yield strength of the material,[33] it is shown to be a fairly good predictor of the Young's modulus for mineralized tissues[34] and it was observed that the relationship between Young's modulus and Vickers hardness was close to a linear one for both human cortical bone[34] and bioceramic–polymer composites.[20,32] However, it was found in the current investigation that Young's modulus and microhardness of HA/PP composite did not follow a linear relationship (Fig. 9). It is thus obvious that with regard to the relationship between Young's modulus and Vickers hardness, different composite systems need to be treated differently. As pointed out previously,[15,20] using a much simpler mechanical testing method such as microhardness testing instead of tensile testing has significant practical advantages in assessing mechanical properties of new biomaterials, especially when there is a very limited amount of the new biomaterial for characterization and evaluation. For comparison, mechanical properties of HA/PP composite obtained from tensile testing and microhardness testing are tabulated in Table II.

Figure 10 shows SEM micrographs of Vickers indentations made on HA/PP composite from microhardness testing. These micrographs reveal good interlock between HA particles and PP matrix for composite of all compositions. As Vickers hardness testing is basically compression testing using a pyramid-shaped diamond indenter instead of a flat-surface compression platen, the material around the sharp tip and edges of the indenter was squeezed and deformed plastically. Unlike the condition of a tensile force, such a compressive stress condition would not cause debonding at the HA-PP interface. Therefore, bioceramic–polymer composites with a weak interfacial bond such as HA/PP is better suited for the compressive loading condition than for the tensile loading condition. As the matrix is a tough polymer (i.e., PP), no microcracks were generated at the sharp corners of indentations on HA/PP composite and no material came of the composite surface during or after microhardness testing (Fig. 10). This is in drastic contrast to what was observed from microhardness testing of bulk HA. As shown in Figure 11, microcracking [Fig. 11(a), microcracks emanating from the corners of a Vickers indentation] or chipping [Fig. 11(b)] can occur in sintered HA during microhardness testing because HA is a weak ceramic (and as a ceramic, it is also brittle). (Fig. 11 is previously unpublished work conducted by M. Wang at the IRC in Biomedical Materials of the University of London, Queen Mary and Westfield Collage, London, UK. The HA discs for microhardness testing were prepared through a standardized procedure in the IRC and sintered at 1250°C. The microhardness testing of the sintered HA discs was performed using a Schimadzu microhardness tester. The average VHN of sintered HA was ~220.) The HA chips caused by the propagation of Vickers indentation-induced lateral cracks either fractured [Fig. 11(c)] or came off the HA surface easily. The provision of toughness by the matrix polymer is certainly an appealing feature of HA-containing polymer composites which overcome the shortcomings of brittleness and weakness of HA while providing bioactivity through HA.

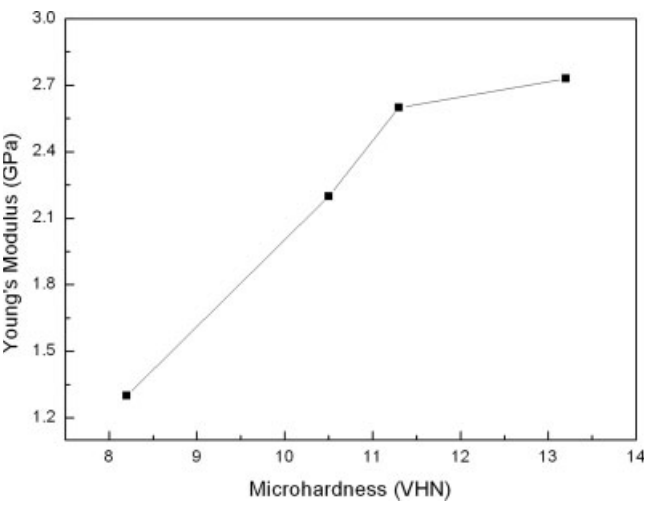


Figure 9 Relationship between Young's modulus and microhardness for HA/PP composite.

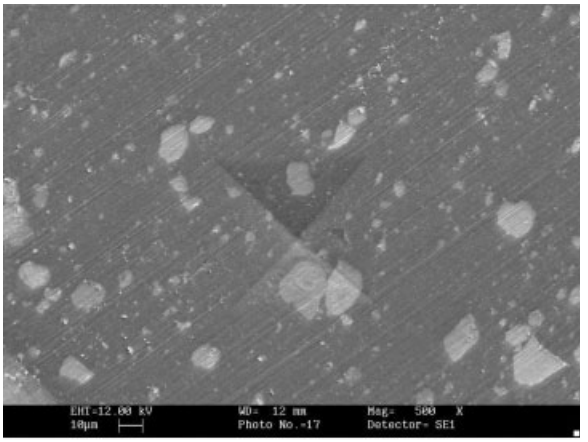
TABLE II
Mechanical Properties of HA/PP Composite

HA content (vol %)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at fracture (%)	Microhardness (VHN)
0	1.30 ± 0.16	29.55 ± 0.61	181.8 ± 5.7	8.2 ± 0.4
10	2.20 ± 0.09	26.32 ± 0.46	13.7 ± 2.6	10.5 ± 0.5
20	2.60 ± 0.27	22.34 ± 0.59	6.5 ± 3.1	11.3 ± 0.3
25	2.73 ± 0.20	20.16 ± 0.77	5.2 ± 1.7	13.2 ± 0.5

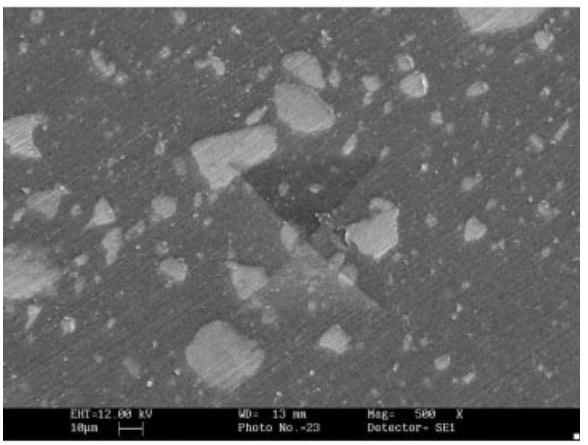
Using DMA, the viscoelastic properties were investigated in the temperature range of 30–180°C for injection moulded HA/PP composite containing 0–25 vol % of HA. It can be seen from Figure 12 that, for composite with different HA contents, the storage modulus increased with an increase in HA volume percentage and decreased with the increase in temperature. This is in agreement with observations made on other bioceramic–polymer composites.[6,15,19,23] The increase in storage modulus can be attributed to the presence of HA particles in the composite, which act as a hard reinforcement for the composite (Young's modulus of 80GPa for HA versus Young's modulus of 1.3 GPa for PP). These reinforcing HA particles restrained the movement of the PP matrix phase in the vicinity of each particle and the PP matrix transferred certain levels of the applied external load to HA particles.

According to the theory of viscoelasticity for polymers,[28] unlike the loss modulus which defines the dissipation of energy per loading cycle during DMA testing, the storage modulus which defines the energy stored in the specimen due to the applied strain may be correlated to Young's modulus of the material. It was found previously that there actually existed a linear relationship between Young's modulus and storage modulus for HA/HDPE composites.[35] It is shown in the current investigation that there is also a liner relationship between these two properties for HA/PP composite (Fig. 13), even though the slopes of these two linear curves are different. (The data for plotting the linear relationship for HA/HDPE composite in Figure 13 were obtained in a previous study.[19]) Both microhardness testing and DMA use much smaller specimens than standard tensile testing (refer to the Materials and Methods section for dimensions of specimens for tensile testing, microhardness testing, and DMA) and it was demonstrated in previous studies and also in the current investigation that Vickers hardness and storage modulus could be correlated with Young's modulus for bioceramic–polymer composites, albeit sometimes these relationships are nonlinear. These findings have practical importance for biomaterials development. During the initial stage of developing a biomaterial, only a small quantity of the biomaterial may be produced due to various constraints but sometimes mechanical properties of the biomaterial need to be assessed. Another situation can arise where there is a requirement for monitoring the change of mechanical properties over a period of time (e.g., a year) in an *in vitro* study and there is a limited amount of the biomaterial for the study. In these situations, microhardness testing and DMA, instead of tensile testing, can be very useful. Using microhardness testing or DMA alone may not be totally reliable. Using both microhardness testing and DMA (and perhaps other simple testing methods as well) will provide a clear indication of properties of the material. Obviously, in situations such as determining the fracture mechanism(s) of the material, the use of tensile testing (or other destructive testing methods) is inevitable in order to generate fracture surfaces.

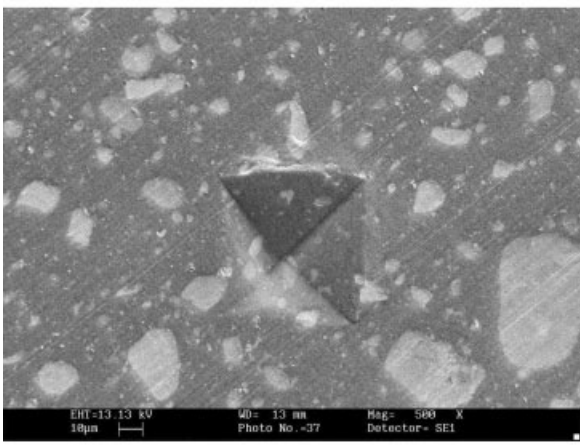
Figure 14 shows the variation of loss tangent, which is the ratio of the energy dissipated per cycle to the energy stored during the cycle, i.e., E''/E', for the HA/PP composite with different amounts of HA. It can be observed that the composite of all compositions exhibited a plateau in tan δ curves between ~ 70 and 140°C. Above 140°C, the curves rose steeply as the specimens became rubbery until they were melted at 163–166°C (Table I). For HA/PP composite with different HA contents, in the temperature range of 37–140°C, the loss tangent became lower when the HA volume percentage was increased. The loss tangent of a material gives an indication of the ability of the material to store and dissipate energy. A material that has a high tan δ value has a high damping capability and can only maintain a low dimensional stability. The incorporated HA particles in PP have limited the mobility of the molecular chain in the polymer matrix, contributing to the reduced damping capability or tan δ of the HA/PP composite. Another source contributing to the decrease in tan δ of HA/PP composite is the volume reduction of the viscoelastic phase, i.e., the PP matrix, in the composite as HA particles which are nonviscoelastic filled up the volume in the composite. An advantage of using a biomaterial having a low damping capability such as HA/PP is the maintenance of dimensional stability, which can be important to a hard tissue implant undergoing cyclic loading.



(a)



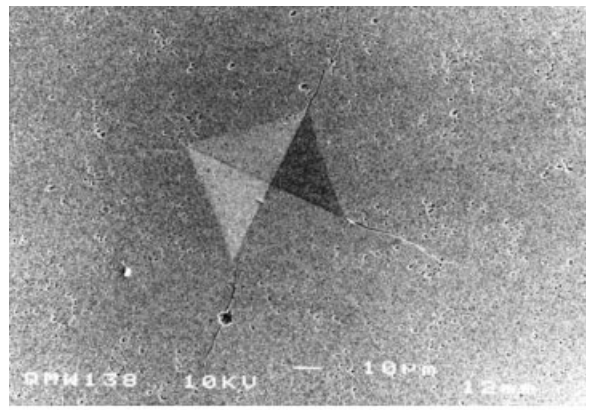
(b)



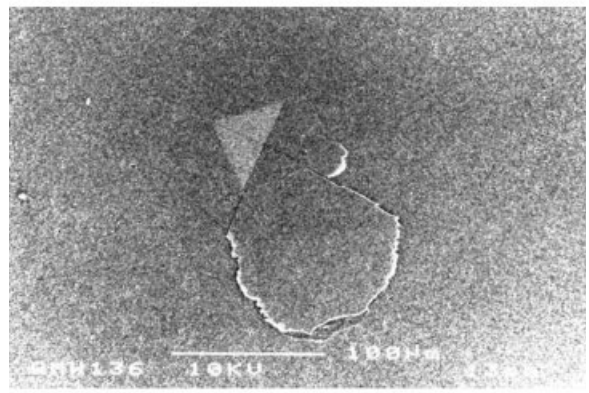
(c)

Figure 10 SEM micrographs of Vickers indentations made on surfaces of HA/PP composite: (a) 10 vol % HA/PP, (b) 20 vol % HA/PP, (c) 25 vol % HA/PP.

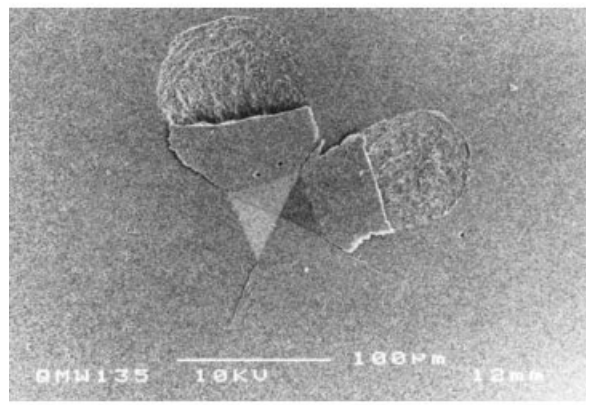
The first bioactive polymer matrix composite, i.e., HA/HDPE, for clinical use as a bone replacement material possesses lower Young's modulus values than that of human cortical bone.[12] To improve mechanical properties of conventionally processed HA/HDPE composite, the composite was hydrostatically extruded.[36] Hydrostatic extrusion caused polymer chain alignment in the extrusion direction and hence drastically increased the stiffness and strength of HA/HDPE composite in the extrusion direction. However, hydrostatically extruded HA/HDPE



(a)



(b)



(c)

Figure 11 SEM micrographs of Vickers indentations made on surfaces of sintered HA: (a) microcracking due to indentation, (b) chipping due to indentation, (c) fracture of HA chips.

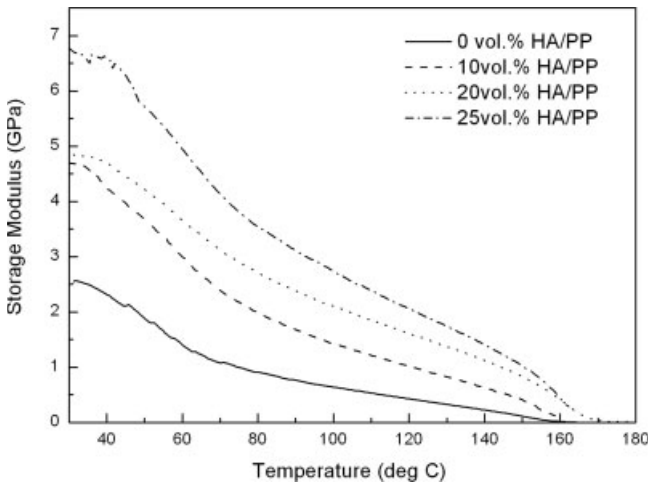


Figure 12 Storage modulus versus temperature for HA/PP composite.

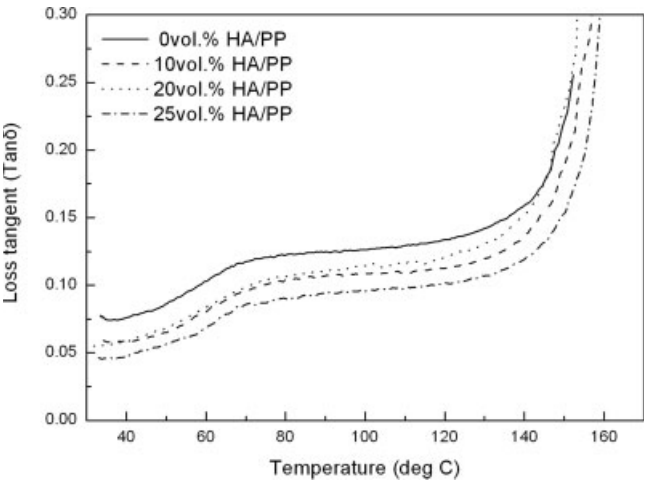


Figure 14 Loss tangent versus temperature for HA/PP composite.

composite is anisotropic: strong and stiff in the extrusion direction but not so in the direction perpendicular to the extrusion direction. Furthermore, hydrostatic extrusion equipment is not readily available in the plastics processing industry and there exist technical problems in extruding polymer composites having high volume percentages of bioceramic particles and in extruding large-diameter products of these composites. It has been shown through previous studies[5–7] and the current investigation that using biocompatible polymers such as PEEK, PSU, and PP which have higher Young's modulus and strength values than PE, bioactive composites having mechanical properties comparable to bone can be made. These bone analogue materials are potential bone replacement materials.

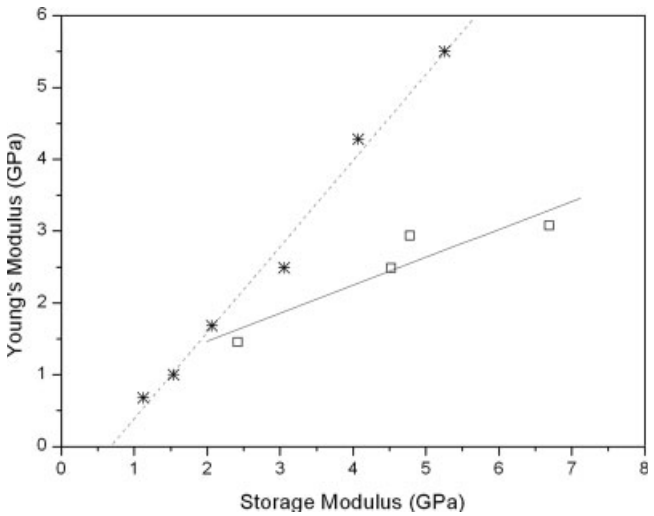


Figure 13 Relationship between Young's modulus and storage modulus for bone analogue biomaterials (□: HA/PP; *: HA/HDPE).

To minimize possible biocompatibility problems, during the development of biomedical composites such as HA/HDPE, HA/PSU, and HA/PP, no chemical coupling agents were intentionally used. With such a strategy, the tensile strengths of biomedical composites are lower than those of the matrix polymers, as shown in previous studies[12,20,30] and in the current investigation (Table II). To enhance the tensile strength of composites, it is a common practice that compatibilizers are used when producing particulate reinforced polymer composites for general engineering uses. However, in developing a biomedical composite, biocompatibility of the composite is the paramount consideration. Apart from concerns on biocompatibility, the use of a coupling agent for the particulate bioceramic reinforcement and polymer matrix can lead to reduced bioactivity of the composite or even render the composite nonbioactive as the particulate bioactive HA will be covered with the coupling agent, resulting in the loss or partial loss of bioactivity of these particles. Despite the avoidance of use of coupling agents in biomedical composites, for scientific research, however, chemical coupling between HA particles and HDPE matrix was investigated.[30,37] It was found that the use of a silane coupling agent facilitated HA/HDPE composite manufacture and improved bonding between HA particles and HDPE matrix. As a result, chemically coupled HA/HDPE composite possessed enhanced ductility and tensile strength.[30]

CONCLUSIONS

1. A manufacturing route employing injection moulding has been established for producing high-quality bone analogue biomaterials. This route significantly reduces processing time for

biomedical composites. More importantly, it is suitable for producing composites based on heat-sensitive biopolymers such as PHB and can minimize thermal degradation of these composites during composite manufacture.
2. Using the established manufacturing route, HA/PP composite containing up to 25 vol % of HA was successfully fabricated. A satisfactory dispersion and distribution of HA particles in the composite was achieved.
3. The thermal and mechanical properties of HA/PP composite were affected by the amount of HA in the composite. The incorporation of HA particles caused a decrease in crystallinity of the PP matrix polymer.
4. The storage modulus and microhardness of HA/PP composite could be correlated to its Young's modulus, which has practical importance in biomaterials development.

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