Improved mechanical properties of HIPS/hydroxyapatite composites by surface modification of hydroxyapatite via *in-situ* polymerization of styrene

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High impact polystyrene (HIPS)/hydroxyapatite (HA) composites are potential biomaterials for bone replacements due to their good biocompatibility and adequate mechanical properties. At the present work, the surface of the micron-sized hydroxyapatite (HA) particles was modified by *in situ* polymerization of styrene (St), then compounded with HIPS. The effect of the modification of HA surface on morphology and mechanical properties of HIPS/HA composites were investigated. The results showed that the HA particles does not inhibit the polymerization of St. The PS segments coated on the HA surface by *in situ* polymerization of St enhances the compatibility between HA and HIPS, improves the dispersion of HA particles in HIPS matrix, and enhances the interfacial adhesion between HA and matrix. Thereby, the stiffness, tensile strength and notch impact strength of HIPS/HA composites are improved at the same time. And there is a critical coating thickness of PS on the HA surface for the optimum mechanical properties of HIPS/HA composites.

Introduction

Recently the bioactive polymer-matrix composites have attracted more attention since Bonfield introduced a bone substitute by reinforcing a bio-inert high-density polyethylene (HDPE) matrix with a bioactive hydroxyapatite (HA) ceramic in early 1981 [1]. The combination of bioactive, stiff, but brittle HA, and low-elastic modulus, ductile polymer allows the composite having a good biocompatibility and adequate mechanical properties. Unlike the conventional implant materials such as metals and ceramics, the polymer/HA composites match the mechanical properties (i.e. stiffness and strength) of cortical bone. Thereby, it avoids the bone resorption and subsequent implant loosening [2]. At the same time, the polymer/HA composites mimic the bony tissue by generating a biological response that promotes bone growth on the implant due to the addition of HA. Up to now, various polymer matrices have been investigated, which includes unbiodegradable HDPE [3–8], polyetheretherketone (PEEK) [9–11], polysulfone [12, 13] and poly(amide 66) (PA66) [14], and biodegradable poly(D,L-lactide) (PDL-LA) [15–18], starch [19–24], polyhydroxybutyrate [25–28] and hydroxybutyrate–hydroxyvalerate copolymer [26, 29].

Polystyrene (PS) has been widely used as the materials for culturing cells since 1980 [30]. In order to enhance adhesion and growth of cell line on PS substratum, many techniques, such as chemical modification [31, 32], grafting or blocking polymerization [33, 34], plasma deposition [35–39] are used to modified the surface structure of PS for improving the hydrophilicity of PS [40, 41]. In 1993, Callen and his co-workers [42] reported the behavior of primary bone-cells on PS surfaces. Glant *et al.* [43] found PS particulates stimulated the bone-resorbing activity. High-impact polystyrene (HIPS) is one of the first toughened systems in which the brittle polystyrene becomes more ductile with the addition of an elastomer. Bucknall [44] proposed in the mid-1970s that toughness enhancement of HIPS is due to the generation and efficient termination of crazes by the rubber particles. In other word, HIPS is easy to generate the crazing under tensile, compression

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and impact processes [45–49]. The crazes are crack-like defects which differ from cracks, however, in that they are filled with porous fibrillar materials and so remain load-bearing [50]. As Walboomers *et al.* [51] reported the rat dermal fibroblasts (RDF) can be growth oriented on the microgrooved PS substrates, we believe that the porous structure of crazes in HIPS will be useful for bone cells to grow on the surface of HIPS.

In our point of view, filling HA in HIPS can adjust the mechanical performance of HIPS and transform HIPS from a kind of bio-inert material into bioactive material. Moreover, the generation and efficient termination of crazes by the rubber particles in HIPS may be propitious to the growth of tissue cell. However, HIPS/HA composites may exhibit poor mechanical properties, particularly the impact strength because the rigid inorganic HA particles and HIPS matrix are incompatible owing to their fundamentally different structures. How to improve the interface adhesion between inorganic particles and polymer matrix is a key problem in particle-reinforced polymer composites (PRPCs). Low molecular silane or titanate coupling agents were commonly used to modify the inorganic surfaces. Block or graft copolymers are also used to improve the adhesion of the components [52–56]. Plasma treatment of inorganic particles enables a structural change on their surfaces and increases the compatibility between particles and polymer matrix [57, 58]. However, this method is not employed in the plastics industry on a large scale. Inorganic particles were also modified by irradiation grafting of the monomer, then compounded with the polymer matrix [59, 60]. By means of *in situ* polymerization of monomer at the surface of inorganic particles [61–64], Xie and his co-workers [65–67] modified inorganic particles, such as talc and glass bead, then compounded them with polymer matrix. They found the modified inorganic particles reinforce and toughen the polymer matrix at the same time. It should be mentioned that in choosing a monomer, its miscibility/compatibility with the polymer matrix should be considered. As such, the modified inorganic particles will show good interfacial interaction with the polymer matrix.

In this study, the surface of the micron-sized HA particles were modified by *in situ* polymerization of St, then compounded with HIPS. The effects of surface modification of HA on interfacial adhesion, reinforcing and toughening effectiveness of HIPS/HA composites were investigated. According to the mechanism of wear [68, 69], the volume of wear depends upon the bulk properties of polymer material as well as the surface properties. The better the mechanical properties of polymer are, the better its wear resistance will be. Although HIPS has not yet been used for fabrication of the bone replacements, it will be expected that the HIPS/HA composites can be used as bone substitute materials due to their good biocompatibility and adequate mechanical properties.

Experimental

Materials

High-impact polystyrene resin (PH-88) was supplied by Chi Mei Corporation in Taiwan, its density is 1.05 g/cm^3. HA powder with average diameter of about 1 μm was provided by Wuhan University of Technology in China, and its density is 2.2 g/cm^3. Chemically pure grade styrene was first washed with alkali solution and deionized water, and then dried to remove the inhibitor.

Surface modification of HA

Surface modification of HA with styrene was conducted by *in situ* polymerization in a glass reactor (stirring rate 200 rpm) at 70 °C in accordance with the conditions mentioned in Tang and Xie [66]. HA particles, styrene as monomer, deionized water, sodium dodecyl sulfonate (SDS) as emulsifier were added to the reactor vessel. The mixture was heated, and stirred constantly until the reaction temperature was reached. Then the aqueous solution of ammonium persulfate (APS) as initiator was added to start the polymerization reaction. After emulsion breakage and centrifugation, the final product was dried at 45 °C in vacuum. The conversion was determined by:

$$\text{Conversion}(\%) = \frac{\text{precipitate (g)- HA(g)}}{\text{monomer used (g)}} \times 100\% \quad (1)$$

Preparation of PS-coated-HA-filled HIPS composites

HIPS was respectively compounded with 20 wt % modified or un-modified HA particles in a Barbender Plasticorder PL2000 twin-screw extruder at barrel temperature of 200 °C and screw speed of 50 rpm. The screw diameter (D) was 19.05 mm, and the length: diameter ratio (L : D) was 20. The pre-dried extrudates were injection-molded to tensile and impact specimens in a Cosmo injection-molding machine (Welltec Industrial Equipment Ltd., HK). The injection barrel temperature profile was set to 200, 220 and 220 °C.

Mechanical properties

Tensile tests were performed on an Instron 4206 machine at room temperature with a crosshead speed of 1 mm/min. Izod impact strength was measured by a Ceast pendulum impact tester. Blunt notches with a tip radius of 0.25 mm were inserted in the impact specimens with a Ceast notching device. The results reported were the average values from five samples.

Morphology observations

The freeze-fractured surfaces at liquid nitrogen temperature were observed using a S-300 scanning electron microscope (SEM). All surfaces were coated with a thin layer of gold prior to SEM examination.

Results and Discussion

Reaction kinetics of *in situ* polymerization of St in the presence of HA particles

Fig. 1 shows the reaction kinetics of the *in situ* polymerization of St in the presence of HA particles at three different temperatures. The weight ratio of HA and St is 2 : 1. The results indicate that temperature significantly affects the polymerization rate of St. The higher the temperature, the earlier the auto-acceleration occurs and the shorter the time to achieve equilibrium conversion. For three temperatures used, the last conversions all approached 98%. It can be concluded that HA particles do not inhibit the polymerization of St.

Morphology

Figs. 2 and 3 respectively present SEM photographs of freeze-fractured surfaces of HIPS/HA composites containing un-modified HA and modified HA by *in situ* polymerization of St with the weight ratio of styrene and HA = 1/12. It is seen that the unmodified HA particles tend to aggregate (see Fig. 2(a)), and the surface of the un-modified HA is very clean and a clear gap exists with HIPS (see Fig. 2 (b)), indicating poor interfacial adhesion. However, after the HA particles are modified with styrene by *in situ* polymerization, the modified HA particles are uniformly distributed in HIPS matrix almost as single particle with the average size of 1 μm (see Fig. 3(a)), and their surfaces become very rough (see Fig. 3(b)). These indicate that the PS coated on the HA surface by *in situ* polymerization of St enhances the compatibility between HA and HIPS, improves the dispersion of HA particles in HIPS matrix, and enhances the interfacial adhesion between HA and matrix.

Mechanical properties

The variation of Young's modulus and tensile strength for HIPS/unmodified or modified HA composites (with 20 wt % filler content) are plotted against the coating thickness of PS on the surface of HA in Figs. 4 and 5, respectively. It is worthy noted that the coating thickness of PS on the surface of HA is very difficult to determine, and the conversion of St during *in situ* polymerization is up to 98%, so the weight ratio ($W_{\mathrm{St}}/W_{\mathrm{HA}}$) of styrene and HA during the *in situ* polymerization, can be used to characterize the thickness of PS on the surface of HA. Apparently, the Young's modulus and tensile strength of the composites were enhanced because of the PS surface coating on the surface of HA. They increased with increasing the PS coating thickness. When the PS coating thickness is up to $W_{\mathrm{St}}/W_{\mathrm{HA}} = 1/12$, both modulus and tensile strength started to decrease. In other words, there is a critical PS coating thickness for tensile properties of the composites.

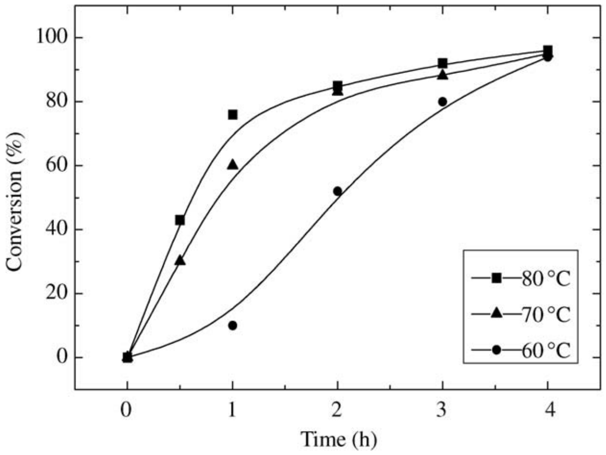

Figure 1 Reaction kinetics curves of *in situ* polymerization of styrene in the presence of HA particles at three different temperatures.

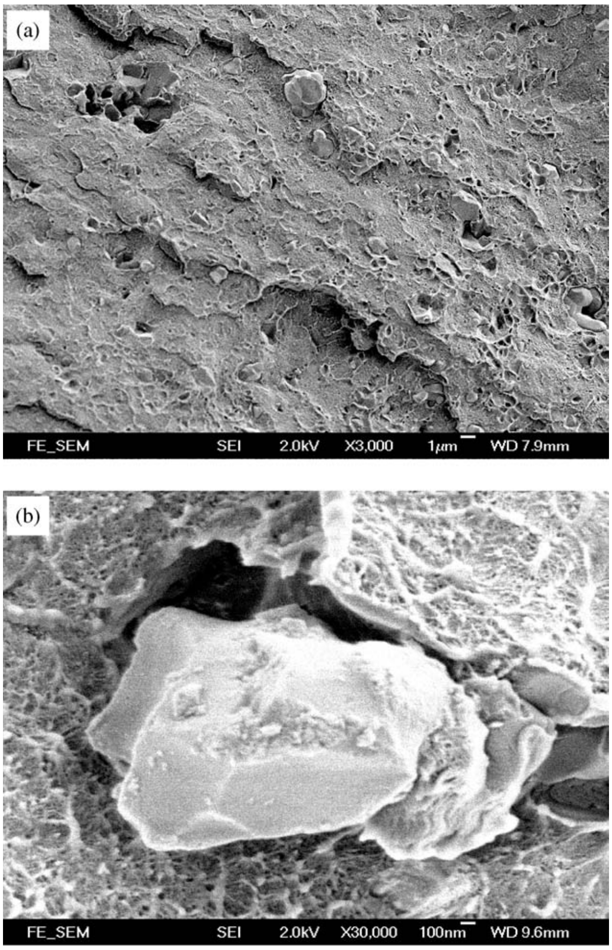

Figure 2 SEM photographs of freeze-fractured surface of HIPS/HA composites containing 20 wt % of untreated HA: (a) low magnification; (b) high magnification.

According to the composite theory, the moduli and yield strengths of particle-filled composites can be respectively predicted by Guth's equation [70]:

$$E_c = E_m(1 + 2.5\phi_f + 14.1\phi_f^2) \qquad (2)$$

and Nicolais–Narkis theory [71]:

$$\sigma_{yc} = \sigma_{ym}(1\text{-}1.21\phi_f^{2/3}) \qquad (3)$$

where (E_c, E_m) and $(\sigma_{yc}, \sigma_{ym})$ are moduli and yield strengths of composite (subscript *c*) and matrix (subscript *m*), respectively, and ϕ_f is volume fraction of particles.

Assuming the effect of surface modifications on HA density is negligible, 20 wt % of HA in HIPS composites corresponds to a volume fraction ϕ_f of 0.1066. Based on tensile experiment, the Young's modulus and tensile yield strength of HIPS are 2.43 GPa and 25.55 MPa, respectively. Thereby, the predicted values of modulus and tensile yield strength for HIPS/HA are calculated to be 3.47 GPa and 18.60 MPa. Quite clearly, when the coating thickness ($W_{\mathrm{St}}/W_{\mathrm{HA}}$) of PS on the surface of HA is up to 1/18, the moduli and yield strengths of HIPS/HA composites are higher than those predicted values.

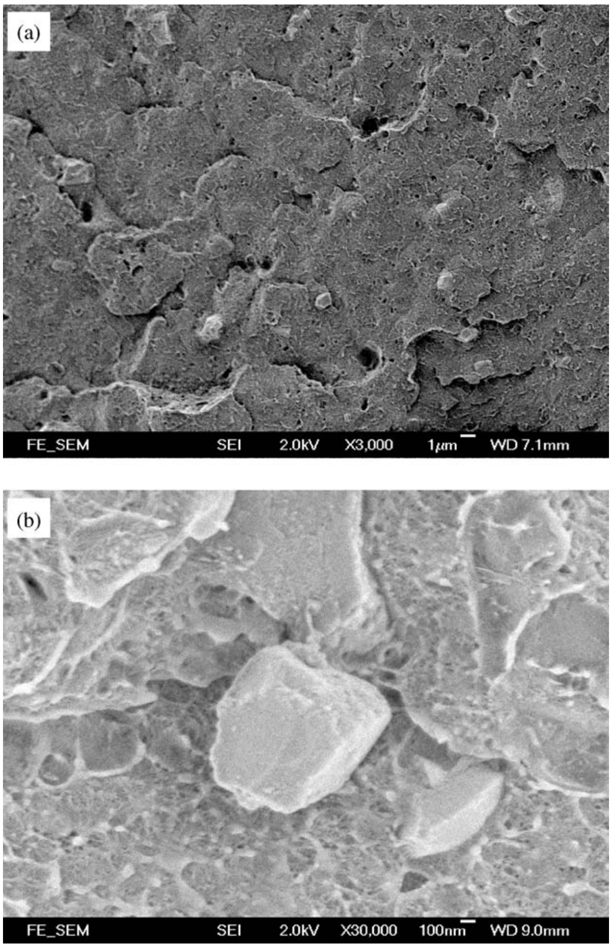

Figure 3 SEM photographs of freeze-fractured surface of HIPS/HA composites containing 20 wt % of HA modified by *in situ* polymerization of St with the weight ratio of styrene and HA = 1/12: (a) low magnification; (b) high magnification.

TABLE I $B_{\sigma y}$-value of HIPS/HA composites with different coating thickness of PS on the surface of HA

$W_{\mathrm{St}}/W_{\mathrm{HA}}$	0	1/24	1/18	1/12	1/6
$B_{\sigma y}$	2.20	2.31	2.41	2.61	2.40

The poor mechanical properties of untreated-HA/HIPS composites are due to the poor dispersion of HA in the HIPS matrix and interfacial bonding between HIPS and HA. It is well known that HIPS and PS are completely miscible. When the surface of HA is coated by *in situ* polymerized PS, the PS enhances the interaction between the HA and HIPS, and improves the interfacial adhesion. This leads to increasing Young's modulus and tensile strength of the PS-coated-HA/HIPS composites. However, when the PS coating thickness is higher than the critical value, the mechanical properties of the composites decrease. It may be related to the internal stress in the intermedium PS between HIPS and HA. The behavior is the same as the PVC/talc composites [65].

It is known that the tensile strength of polymer composites is affected by the interfacial adhesion. Turcsanyi *et al.* [72] gave a quantitative relation between tensile strength and interfacial interaction as:

$$\sigma_y = \sigma_{ym}\frac{1-\phi_f}{1+2.5\phi_f}\exp(B_{\sigma y}\phi_f) \tag{4}$$

where σ_y and σ_{ym} are yield stresses of composite and polymer matrix, respectively. ϕ_f is volume fraction of particles and $B_{\sigma y}$ is a parameter that characterizes the interfacial interaction. Generally, larger $B_{\sigma y}$ values correspond to stronger interfacial interaction.

By means of Equation 4, $B_{\sigma y}$ values for HIPS/HA composites can be calculated and listed in Table I. Whilst $B_{\sigma y}$ has no direct physical meaning, it is obviously connected with the interfacial interaction of composites. For ABS polymer filled with glass beads, $B_{\sigma y} = 0.246$ was determined and approximated the ''no adhesion'' case by Turcsanyi *et al.* [72]. For the HIPS/unmodified HA composite, $B_{\sigma y}$ value is high to 2.20 due to the small size of HA (1 μm) and large interfacial areas with HIPS matrix. When HA particles were modified by *in situ* polymerization of styrene, $B_{\sigma y}$ is increased to 2.31–2.61. And when the coating thickness $(W_{\mathrm{St}}/W_{\mathrm{HA}})$ of PS on the surface of HA is 1/12, the $B_{\sigma y}$ is up to maximum value, 2.61. For HIPS/modified HA composites, the high $B_{\sigma y}$ value indicates that the interfacial adhesion between HA particles and HIPS matrix is very strong and tends to prevent debonding at the matrix-particle interface during tensile deformation.

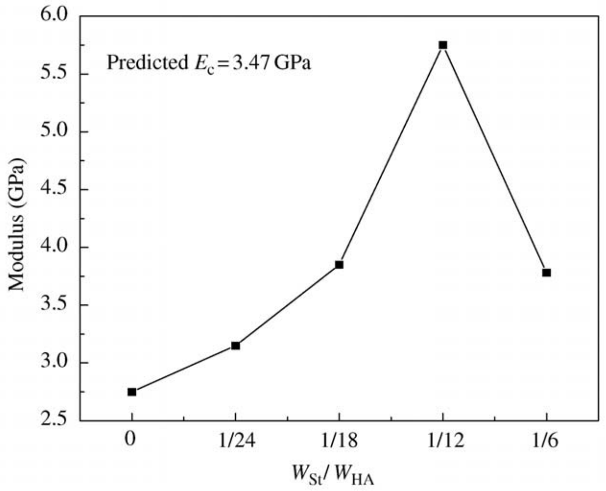

Figure 4 Relationship between Young's modulus of HIPS/HA composite and the coating thickness of PS on the surface of HA.

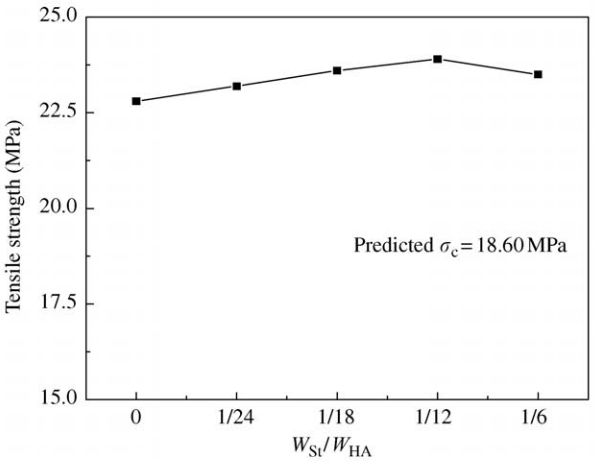

Figure 5 Relationship between tensile strength of HIPS/HA composite and the coating thickness of PS on the surface of HA.

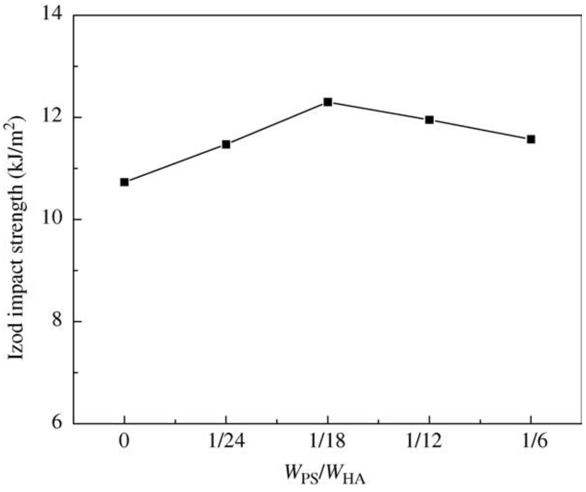

Figure 6 Relationship between Izod impact strength of HIPS/HA composite and the coating thickness of PS on the surface of HA.

Interestingly, notch impact strength of HIPS/unmodified HA composite was substantially improved by surface modification of HA particles (see Fig. 6). The impact strength of HIPS/unmodified HA composite is 10.73 kJ/m^2. After HA particles were treated by *in situ* polymerization of styrene, the impact strengths of these composites increased obviously. When the coating thickness (W_{St}/W_{HA}) of PS on the surface of HA is 1/12, the impact strengths of HIPS/HA composite is up to maximum value, 12.30 kJ/m^2. Obviously, PS segments on HA surfaces improve compatibility and interfacial adhesion between HA and HIPS matrix. Improved compatibility enables uniform dispersion of HA particles and dissipation of impact energy. Thus, addition of rigid HA particles to HIPS imparts excellent toughness with improvements in both stiffness and strength. This is far more effective than adding rubber to polymer matrix because the toughness improvement is at the expense of significant losses in both stiffness and tensile strength.

Conclusion

Based on the outcomes and results obtained in this study, we can draw some definitive conclusions. HA particles does not inhibit the polymerization of St. The PS segments coated on the HA surface by *in situ* polymerization of St enhances the compatibility between HA and HIPS, improves the dispersion of HA particles in HIPS matrix, and enhances the interfacial adhesion between HA and matrix. Thereby, the stiffness, tensile strength and notch impact strength of HIPS/HA composites are improved at the same time. And there is a critical coating thickness of PS on the HA surface for the optimum mechanical properties of HIPS/HA composites.

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