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Preparation of carbon fiber fabric reinforced hydroxyapatite/epoxy composite by RTM processing

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In recent years bioactive ceramic/polymer composites have been developed as hard tissue implant materials for their good biological and mechanical performances [1–3]. Bioactive ceramic such as hydroxyapatite (HA) is combined with polymer that is generally bioinert, and renders the composite bioactive. The composite implants thus are able to form chemical bonds with the living tissue and accelerate the fixation. The ceramic at the same time increases the hardness and elastic modulus of the composite, making the composite possess elastic modulus near to that of human bone. Matching the elastic modulus between implants and bone can help avoid stress shielding and subsequent bone absorption caused by implants with high elastic modulus [4].

The current researches of bioactive ceramic/polymer composites are mainly focused on composites of thermoplastic polymer matrix, such as polyethylene, polyactide and PEEK [1–3]. Although these thermoplastic polymers have good biocompatibility, their processing techniques are complicated [3]. In the present work thermosetting epoxy resin is chosen for the simple forming processing, and the reinforcement is HA powder. It is found that HA/epoxy composite has biocompatibility but with poor mechanical properties that are far lower than those of human cortical bone. So three-dimensional carbon fiber fabric is used to reinforce HA/epoxy composite through resin transfer molding (RTM) processing, and it is found that the resulting composite has higher flexural strenth than that of human cortical bone, and its flexural modulus is quite close to that of cortical bone.

Epoxy resin WSR618 and solidifying agent phthalic anhydride were from Wuxi Resin Factory, China. Silane coupling agent KH-570 was from Nanjing Shuguang Chemical Factory, China. HA powder was synthesized by wet method, heated at 650 °C for 1 h and sieved by 400-grit sieve to get a grain size of 3–4 μm. The three-dimensional carbon fiber fabric was made of T-300 carbon fiber beam with fiber volume ratio 35%. HA powder with or without silane treatment was added into epoxy at mass ratio HA:epoxy = 20:80 or 40:60 in stirring state. The mixtures were heated at 130 °C for 1 h before the solidifying agent, dilute agent and anti-foam agent were added. The mixture was then cast into a mold, solidified and sample HE1 or HE2 was obtained. Pure epoxy sample HE0 without HA was also prepared. The mixture with mass ratio HA:epoxy = 20:80 or pure epoxy was used for preparing carbon fiber fabric reinforced HA/epoxy composite (FHE) and carbon fiber fabric reinforced epoxy sample (FE). The sample size was $10 \times 15 \times 75$ mm for all.

The flexural test was done using an electronic pull tester, and the flexural modulus was determined as the slope of the straight part of the load-displacement curve. The cross-section and the fracture were observed with scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) analysis before coating with a thin gold film to increase conductance.

Two kinds of materials, HE0 and HE2 were subjected to a cytotoxicity test with L929 fibroblasts. The samples were cut into slices of $10 \times 10 \times 1$ mm, polished, cleaned and sterilized by ultraviolet rays for 2 h. The culture was RMPI1640 culture + 10% fetus bovine serum. The samples were soaked in the culture at the ratio (culture volume/sample surface area) of 6×10^{-2} m^3/m^2 at 37 °C. The culture was filtered and the original leach was obtained after being soaked for 24 h. The original leach with 100% concentration was diluted to get 50%, and diluted again to get 25% of the original leach concentration. The positive control is the original leach of pure lead, and the negative control is cell culture without soaking samples. L929 cells were inoculated to 96-pore culture plate with cell concentration 10^{10}/m^3 and culture volume 10^{-7} m^3 for each pore. The culture was replaced by 10^{-7} m^3 leach (for the tested groups and positive control) or culture (for negative control) after being cultured for 24 h. The cell activity was checked by MTT assay after being cultured for another 3 or 6 days. The cell survival ratio was calculated by: survival ratio $= (E/C) \times 100\% \pm$ s.s $= [s_E^2 \times 1/E^2 + (s_C^2 \times E^2/C^4)]^{1/2}$ [5], in which E was light absorption of the tested group, C was light

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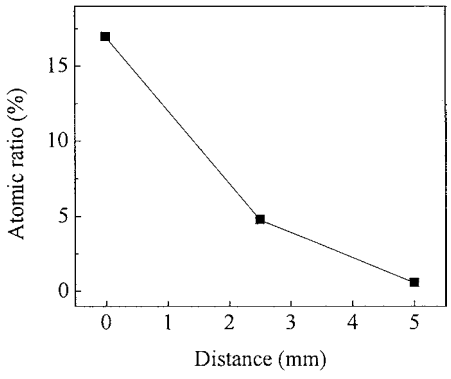

Figure 1 Atomic ratio of calcium from the surface to center of sample FHE.

absorption of the negative control, s was the standard error, s_E was the standard error of E, and s_C was the standard error of C.

It was found that HA particles without coupling agent treatment agglomerated seriously and unevenly in the epoxy matrix and the size of the aggregates was more than 10 μm in samples HE1 and HE2, while the size decreased to less than 5 μm if HA particles were treated by KH-570 silane coupling agent. Silane coupling agent was reported to improve the compatibility of HA particles with polyethylene matrix [6]. In the case of KH-570 silane coupling agent. it is speculated that the hydrophilic silane terminals have good compatibility with HA and the hydrophobic methyl methyl acrylate groups have good compatibility with epoxy resin, which result in the improved dispersion of HA particles in epoxy matrix.

Epoxy resin and HA-containing epoxy resin can impregnate the carbon fiber fabric except small defects such as gas cavities in epoxy matrix were observed at the cross-sections. The fibers are intersected in the composite, and form the integration with resin matrix, which is quite different from the structure of uni-directional fiber reinforced composite. EDX analysis was done along the cross-section of sample FHE from the surface to the center to determine the distribution of HA. The detected elements were C, O, Ca and P, and Ca was enriched at the surface (Fig. 1). The gradual distribution of HA in the composite along the depth direction may be due to the hinderance of the fabric to HA particles during the flow of the epoxy resin in the RTM process. The distribution of HA has influenced mechanical properties of the FHE sample, as will be described later.

The flexural strength and flexural modulus of HE samples are lower than those of human cortical bone (Fig. 2a, [7]), therefore HE composites cannot be used as bone implant material at load bearing conditions. The flexural strength of FE and FHE samples (Fig. 2a), although the addition of HA has decreased the flexural strength, is high compared with other commonly used implant materials, and is far higher than that of cortical bone.

The flexural load-deformation curves of samples FE and FHE are illustrated in Fig. 3. For sample FE, the curve in the initial loading stage was linear, but subsequently yield occurred with the increase of load when partial fibers and the matrix at the outer layer cracked in

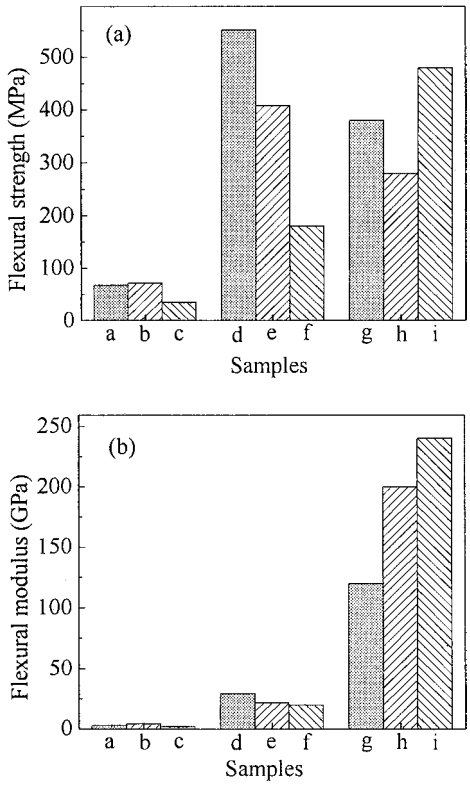

Figure 2 Flexural (a) strength and (b) modulus of samples HE, FE and FHE compared with those of several commonly used implant materials and human cortical bone. a: HE0, b: HE1, c: HE2, d: FE, e: FHE, f: human cortical bone, g: titanium alloy, h: stainless steel, i: CoCr alloy [7].

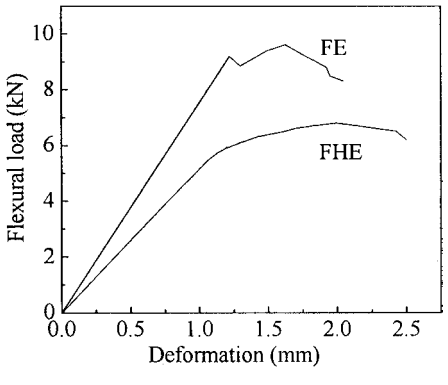

Figure 3 Flexural load-deformation curves of samples FE and FHE.

tensile stress. The remaining fibers sustained the load and made the curve increase again until the sample was destroyed. For sample FHE, there was no obvious yield point in the load-deformation curve. The reason for failure of sample FHE was probably fiber cracking followed by fiber extraction, for HA has weakened the fiber-matrix interface. However, further work still needs to be done to clarify the failure mechanism of sample FHE. There is no abrupt decrease of load in the two curves, and the destroyed samples did not fracture at the end, showing the toughening effect of the carbon fiber fabric on epoxy resin.

The flexural modulus of samples FE and FHE was calculated to be about 29 and 22 GPa, respectively (Fig. 2b). The flexural modulus of the FHE composite is very close to that of human cortical bone (average

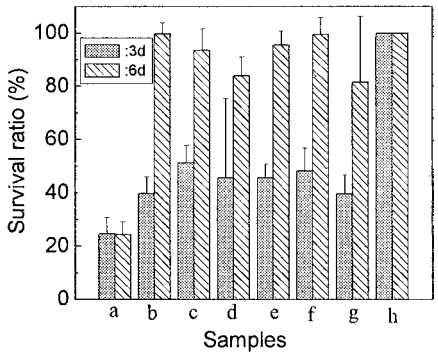

Figure 4 Viability ratio of L929 fibroblasts in leaches of samples HE0, HE2 and the controls. a–c: HE0 100%, 50%, 25%, d–f: HE2 100%, 50%, 25%, g: positive control, h: negative control.

20 GPa), and is much lower than that of commonly used implant materials (Fig. 2b). For example, the flexural modulus of titanium alloy is about 120 GPa, which is five times higher than that of human cortical bone. The match of elastic modulus between implant and human bone is favor for avoiding stress shielding and subsequent bone absorption caused by implants with high elastic modulus [4], therefore the FHE composite is expected to possess better biomechanical compatibility with human bone than the traditionally used metal implants.

Since carbon fiber has good biocompatibility [8], only HE groups were subjected to the cytotoxicity test. The viability ratio of L929 fibroblasts cultured in leaches of the samples and the controls at various concentrations was shown in Fig. 4. The HE0 group has a little toxicity to L929 fibroblasts at high leach concentration compared with the positive control group, but the toxicity was small at low leach concentration. It is also reported by Huang *et al*. that the epoxy resin-based root canal sealer exhibited a dose-dependent increase in astrocyte toxic effects *in vitro* [9]. In comparison, the HE2 group has no toxicity at all leach concentrations, indicating that the addition of HA powder in epoxy matrix has diminished the toxicity of epoxy resin and improved its biocompatibility.

In conclusion, resin transfer molding processing was used to prepare carbon fiber fabric reinforced epoxy and HA/epoxy composites. Epoxy resin and HA-containing epoxy resin impregnated carbon fiber fabric except small defects, and HA particles were distributed gradually from the surface to center of the fiber reinforced composite. The flexural strength of the fiber reinforced hydroxyapatite/epoxy composite was much higher than that of human cortical bone, and the elastic modulus was close to that of cortical bone. The cytotoxicity test with L929 cells showed that the addition of hydroxyapatite powder had diminished the toxicity of the epoxy resin.

Acknowledgments

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