FRACTURE TOUGHNESS AND FAILURE MECHANISM OF POLYMER–INTRODUCED POROUS HAP COMPOSITES

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ABSTRACT

Polymer–introduced porous hydroxyapatite (HAp) is developed for a substituting material of human bones. Firstly, Methylmethacrylate monomer containing polymerization initiator is introduced into the open pores in the HAp ceramics under a reduced pressure. The monomer is polymerized inside the pore by heating it at 60°C for 48 hours. By using the above process, the polymethylmethacrylate, often used as a biocompatible polymer because of its stability in body fluids, well fills the pore of the porous HAp ceramics. ALP activity test and inplant test in rabbit bone show good biocompatibility of above HAp/PMMA composite. The effect of the molecular weight of PMMA polymer on the fracture toughness is studied by using compact tension (CT) test method. The toughness is improved by the introduction of the PMMA polymer into the pore compared to that of pure HAp ceramic. A large inelastic deformation is observed in the CT test before final failure. The toughness has not clear tendency about the molecular weight of the polymer. The toughening mechanism by introducing the compliant polymer is proposed. The estimated toughness agrees well with the toughness of the present composite.

Key Words

Biomaterial, HAp, PMMA, Toughness, Composite

Introduction

Hydroxyapatite (HAp) ceramic material attracts great attention as a bone substitute for its good biocompatibility, because it is same material as animal bone major ingredient. However, the properties of the HAp ceramic is not sufficient to use as bone substitute because of its high elastic modulus as well as low fracture toughness compared to the bone. If the high toughness and lower elastic modulus without loss of biocompatibility is attained, it will be a promising material for human artificial bone. Bonfield[1] developed

a polyethylene containing HAp particles and Kikuchi [2] proposed TCP/copoly-L-lactide composite.

By introducing biocompatible polymer into the porous HAp ceramic developed by Aizawa et al.[3], the tougher and more compliant composite was proposed[4]. In the present paper, the toughness measured is reported and the toughening mechanism is proposed.

Fabrication of HAp/PMMA composites

After formed to arbitrary shape by a pressure of 30~40MPa at a room temperature, the fibrous HAp particles was sintered to fabricate porous HAp ceramic at 1200°C for 5 hours. MMA monomer containing azobis (isobutyronitrile) (AIBN) was repeatedly introduced in the open pores of the HAp ceramic in Nitrogen gas condition. The introduced PMMA was polymerized inside the pores by heating at 60°C for 48 hours. The PMMA polymer filled well the pore as shown in Fig.1. The molecular weight of the PMMA was controlled by changing the amount of AIBN from 1/100 to 1/10000 to investigate the effect of the introduced polymer.
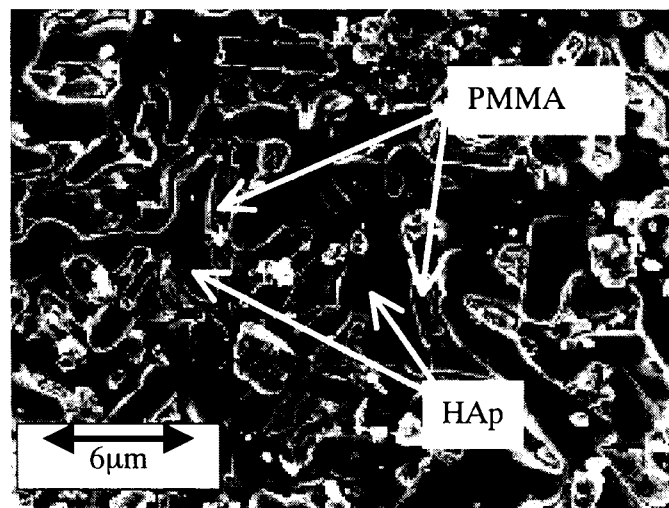

Fig.1 HAp/PMMA composite.

Experiment

The fracture toughness of the HAp/PMMA composite was measured following a standard test method (ASTM E399). A specimen for the fracture toughness test is shown in Fig.2. A relationship between the load and displacement is shown in Fig.3. There exists a quite large inelastic deformation before the final failure. The toughness was estimated by using maximum load and the original crack length following the equation given by the ASTM standard. It may underestimate real fracture toughness of the present material. The toughness obtained is plotted against the molecular weight of PMMA in Fig.4. The measured values are
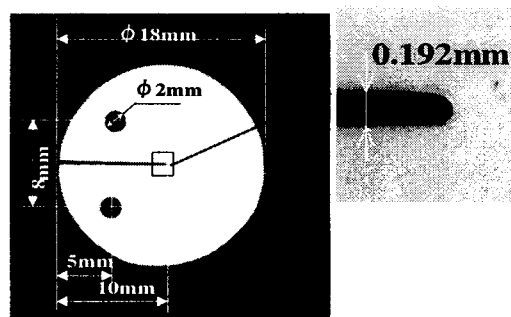

Fig.2 Test specimen (ASTM-E399)

about 1.5 MPam$^{1/2}$ throughout the molecular weight region tested. The results do not show evident dependence on the molecular weight.

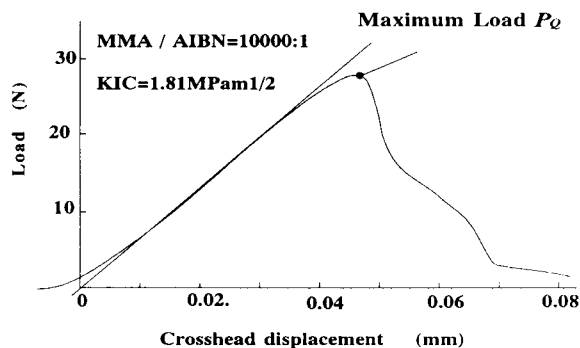
Fig.3 The relationship between the applied load and the displacement

Toughening mechanism and Toughness of HAp/PMMA composite

By introducing PMMA polymer in the open pores of the HAp ceramic, the composite becomes quite tough compared with the pure HAp ceramic. The material properties of HAp ceramic, PMMA polymer and present composite are shown in Table 1. The PMMA is very tough compared with the HAp ceramic with respect to the energy release rate. It is very important to clarify the toughening mechanism of the composite to improve the toughness.
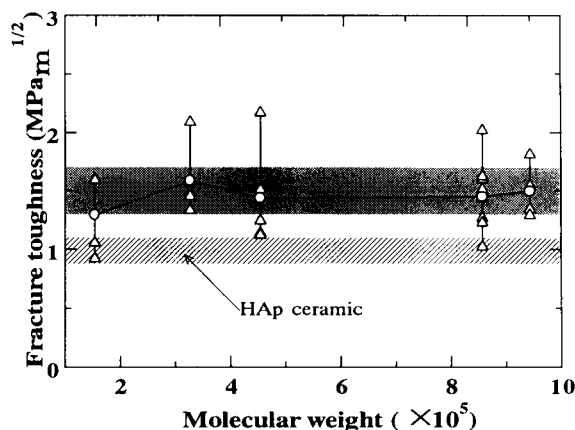

Fig.4 The toughness of HAp/PMMA composite and molecular weight of PMMA polymer.

Table 1
Material properties of HAp ceramics, PMMA polymer and HAp/PMMA composite

	HAp	PMMA	HAp/PMMA
Young's Modulus(GPa)	100	2.7~3.4	~50
G_C (J m^{-2})	10	300~400	~45
K_C (M Pa$^{1/2}$)	1	0.9~1.4	~1.6
Strength (MPa)	-	500~750	-
Elongation (%)	-	2~10	-

First, we assume that the both materials absorb the mechanical energy at the fracture surface as they exist independently. This assumption corresponds to the case that the polymer size is sufficiently large compared to the inelastic region in the polymer just ahead of the crack tip as shown in Fig.5. In this case the absorbing energy may satisfy the rule of mixture and be expressed as

$$\left(G_C\right)_{\text{composite}} = \left(G_C\right)_{\text{HAp}}V_{\text{HAp}} + \left(G_C\right)_{\text{PMMA}}V_{\text{PMMA}} \tag{1}$$

where V_{HAp} and V_{PMMA} are volume fractions of HAp and PMMA, respectively. G_c is critical energy release rate. If the PMMA is perfectly introduced into the pore, $V_{\text{HAp}}+V_{\text{PMMA}}=1$. The Young's modulus is assumed to be expressed the following expression, which is based on the assumption that the cubic polymer is uniformly distributed in the HAp ceramic.
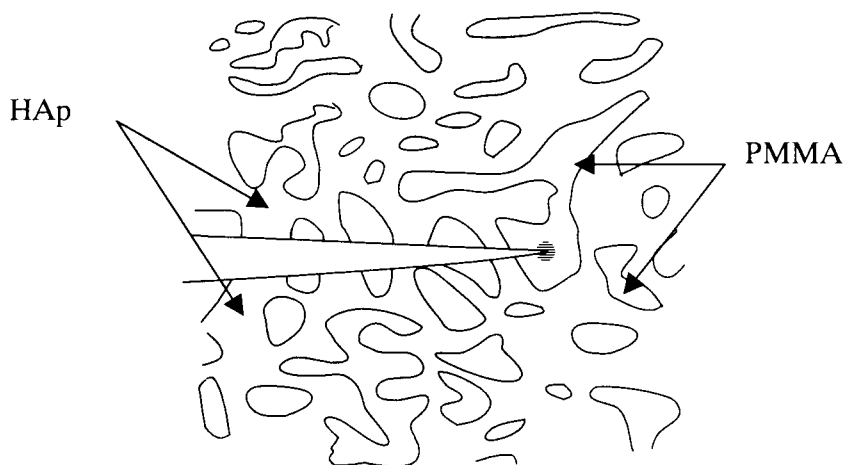

HAp

PMMA

Fig.5 A failure model when the pour size is large compared with the inelastic region

$$E = \cfrac{1}{\cfrac{\sqrt[3]{V_p}}{E_p\sqrt[3]{V_p^2} + E_{HAp}\left(1 - \sqrt[3]{V_p^2}\right)} + \cfrac{1 - \sqrt[3]{V_p}}{E_{HAp}}} \tag{2}$$

The estimate of Young's modulus is more accurate than the simple rule of mixture. K_{Ic} can be obtained from the critical energy release rate G value and Young's modulus E.

$$K_{IC} = \sqrt{EG_C} \tag{3}$$

The estimated toughness and Young's modulus are plotted against the volume fraction of the HAp V_{HAp} in Fig.6. The estimated Young's modulus agrees well with the experimental results. However, the toughness is well below the estimated value, which might be thought to be a rough estimate of its lower bound because it is obtained without any consideration of complex coupling of the polymer and HAp ceramic in fracture process.

When the pore size is small and the polymer is ductile, the polymer bridges the crack surface as shown in Fig.7, because the strongly deformed region in front of the crack tip is larger than the pore size. The possible energy absorbed by a unit volume polymer is
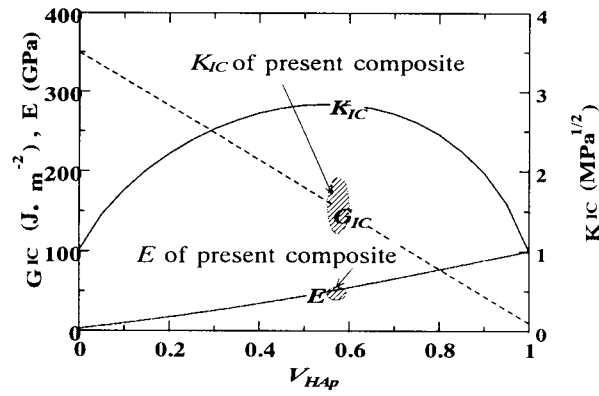
Fig.6 The estimated material properties with respect to volume fraction V_{HAp}.

$$U = \int_0^{\varepsilon_{max}} \sigma d\varepsilon \qquad (4)$$

The average volume of a strongly deformed region of a bridging polymer may be written as

$$v = kd \times \pi d^2 / 4 = k\pi d^3 / 4 \qquad (5)$$

where $\pi d^2/4$ and kd are the area and the length of the strongly deformed region of the polymer cut by the propagating crack as illustrated in Fig.7. The factor k may be a function of interface strength and size and shape of microstructure. The expected number of the bridging polymer may be given as

$$N = \frac{V_p}{\pi d^2 / 4} \qquad (6)$$

The expected energy possible to be absorbed at the crack surface is given as

$$G_c = G_{HAp} V_{HAp} + NvU = G_{HAp} V_{HAp} + V_p kdU \qquad (7)$$
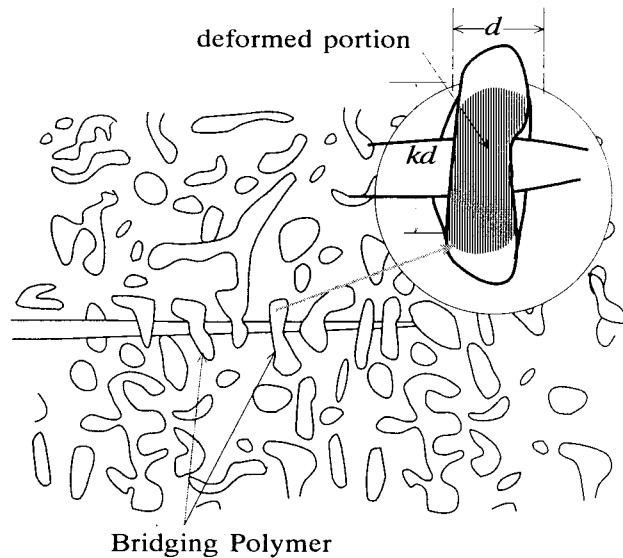

Fig.7 A Failure model with bridging polymers.

From the strength and elongation of the PMMA shown in Table 1, the energy absorbed by a unit volume U is estimated to be about 5×10^6. As the shape of the polymer filling the pore is not circle, size of the pore is difficult to say. Most of the polymer sizes in the SEM micrograph of Fig.1 are among 1~5μm. The estimated toughness by using the value $U=5\times10^6$ is plotted in Fig.8 against the polymer size d. Though the toughness of the present HAp composite 1.5~2 MPa/m$^{1/2}$ is a little higher than the estimated value, this theory well predicts the toughness of the HAp composite.
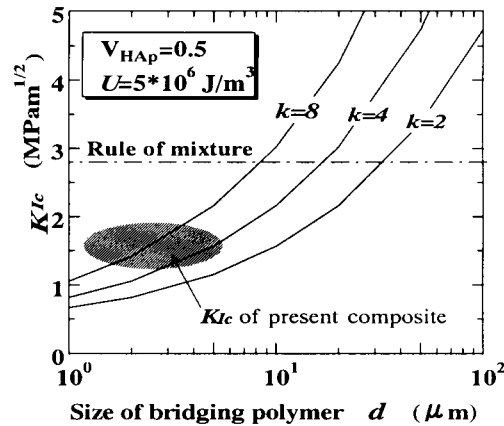

Fig.8 Effect of the size of the bridging polymer on the toughness

SUMMARY

A tough, low modulus and biocompatible composite material (1.5~2 MPam$^{1/2}$, about 50 GPa) is fabricated by introducing polymer into the open pores of porous hydroxyapatite. A toughening mechanism is proposed and the toughness estimated well agrees with the experimental results. The possibility of more toughening by increasing the pore size is suggested from the present theoretical .

ACKNOWLEDGEMENT

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