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Effect of particle morphology and polyethylene molecular weight on the fracture toughness of hydroxyapatite reinforced polyethylene composite

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Fracture toughness testing has been performed on hydroxyapatite–polyethylene composites. Sintered and unsintered grades of hydroxyapatite and two grades of high-density polyethylene were used to make 40 vol % hydroxyapatite composites. Compact tension testing was performed at both room temperature and at 37 °C and at three strain rates. The effect of increasing the loading rate from 2 to 200 μm s^{-1} was to increase the fracture toughness. Increasing the testing temperature or decreasing the surface area of the reinforcing particles also increased the fracture toughness. However, using a lower molecular weight, injection moulding, grade of polyethylene reduced the fracture toughness. Thus for higher fracture toughness, a low surface area sintered hydroxyapatite in a high-molecular weight polyethylene is required.

1. Introduction

Composites of hydroxyapatite in polyethylene (HA–PE) have been used clinically for bone augmentation for over 15 years [1]. Bone itself is a composite, consisting of a collagen matrix and short HA reinforcing crystals [2]. In bone, mechanical properties such as strength and toughness are largely determined by the collagen content, whereas properties such as stiffness and hardness are due to the presence of bone mineral, which is a substituted HA. Similarly, in particulate composites such as HA-PE, strength and toughness is provided by the PE matrix, whilst stiffness is given by the reinforcing particles.

The clinically used grade of HA–PE composite is known as HAPEX and is an analogue material designed to replace bone [3]. It consists of 40% synthetic HA particles embedded in a high-density polyethylene (HDPE) matrix [4]. Clinically, this material is used for minor load bearing applications such as orbital floor prostheses for patients suffering from post-enucleation socket syndrome [1] and in middle ear implants [5].

The mechanical properties and performance of HAPEX have been extensively investigated. Abrams *et al.* [6] and Wang *et al.* [7] amongst others reported the effect of volume fraction and size of the HA particles on the tensile properties. Other properties investigated include impact strength [8, 9], creep [10] and uniaxial and biaxial fatigue [11, 12]. *In vitro* biological and mechanical assessments have been carried out [13]. *In vivo* implantation has shown that bone grows up to the composite [14] with the mineral phase being deposited epitaxially onto the HA crystals in the composite [15]. However, the fracture toughness of HAPEX and factors that causes it to vary have not been reported.

Although HAPEX currently only has minor weight bearing applications, understanding its behaviour in the presence of a crack, that is, fracture toughness, is important, as this enables better predictions of service life, with adequate safety factors.

2. Materials and methods

2.1. Materials

Hydroxyapatite powders (Fig. 1) were blended with cryogenically grounded HDPE pellets and then compounded in a co-rotating twin extruder (Betol BTS40L, Luton, UK) as described by Wang *et al.* [16]. The extrudate was produced in rod form and was cooled by passing through a water bath at room temperature, pelletised and finally powderised with liquid nitrogen as a coolant. From the powder, 145 mm square and 8.5 mm thick plates were compression moulded. Compact tension specimens to ASTM D 5045-96 (Fig. 2) were machined from these plates.

Different grades of composite were manufactured using two grades of injection moulding grade HDPE, Rigidex HD4556EA, molecular weight, Mw 240 000 mol g^{-1} and Rigidex HD5226EA Mw, 48 650 mol g^{-1} both with density of 953 kg m^{-3} (BP Chemicals Ltd., UK). The synthetic HA were a sintering

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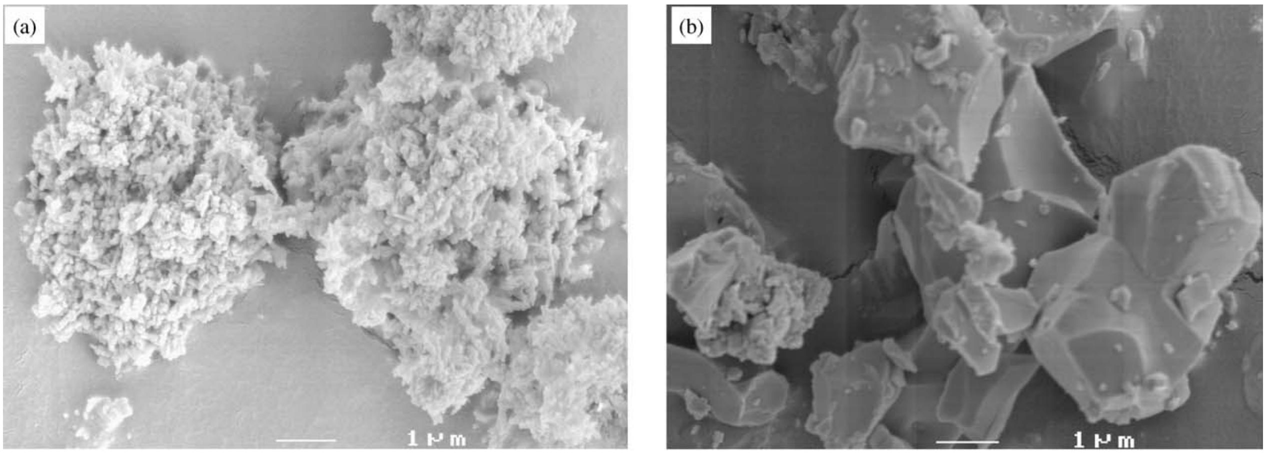

HA P205

HA P215S

Figure 1 Scanning electron micrographs (SEM) of (a) non-sintered and (b) sintered grades of HA used to manufacture HAPEX®.

grade P205 (Plasma Biotal Ltd, Tideswell, UK), which is normally used for HAPEX production, and a sintered grade P215S, which was compounded only with the HD5226EA grade of HDPE (Fig. 1). The two grades of HA were chosen to have similar particle size distributions, but a factor of 10 difference in their specific surface areas (Table I).

TABLE I Particle size and specific surface area for P205 and P215S grade HA in polyethylene

Commercial name	Density ($kg\,m^{-3}$)	Specific surface area ($m^2\,g^{-1}$)	Mean particle size (μm)		
			$d_{0.1}$	$d_{0.5}$	$d_{0.9}$
P205	3160	13.2992	0.42	4.02	11.91
P215S	3160	1.1558	0.32	3.58	9.56

2.2. Methods

Fracture toughness testing was performed using compact tension testing on an MTS MiniBionix 858 hydraulic testing machine (Minneapolis, USA) according to ASTM D 5045-96. Specimens were tested to failure and the crack length was measured using crack propagation gauges (Micro-measurements Group, Inc; model TK-09-CP A01-005) mounted on each specimen (Fig. 2). Tests were carried out in a temperature-controlled room at 21 ± 1 °C in air or at 37 ± 1 °C in saline and at actuator velocities of 2, 20 or 200 $\mu m\,s^{-1}$.

Time (t), displacement (d), load (P) and crack gauge voltage (v) data were recorded during the test by the MTS computer software package Teststar. From this

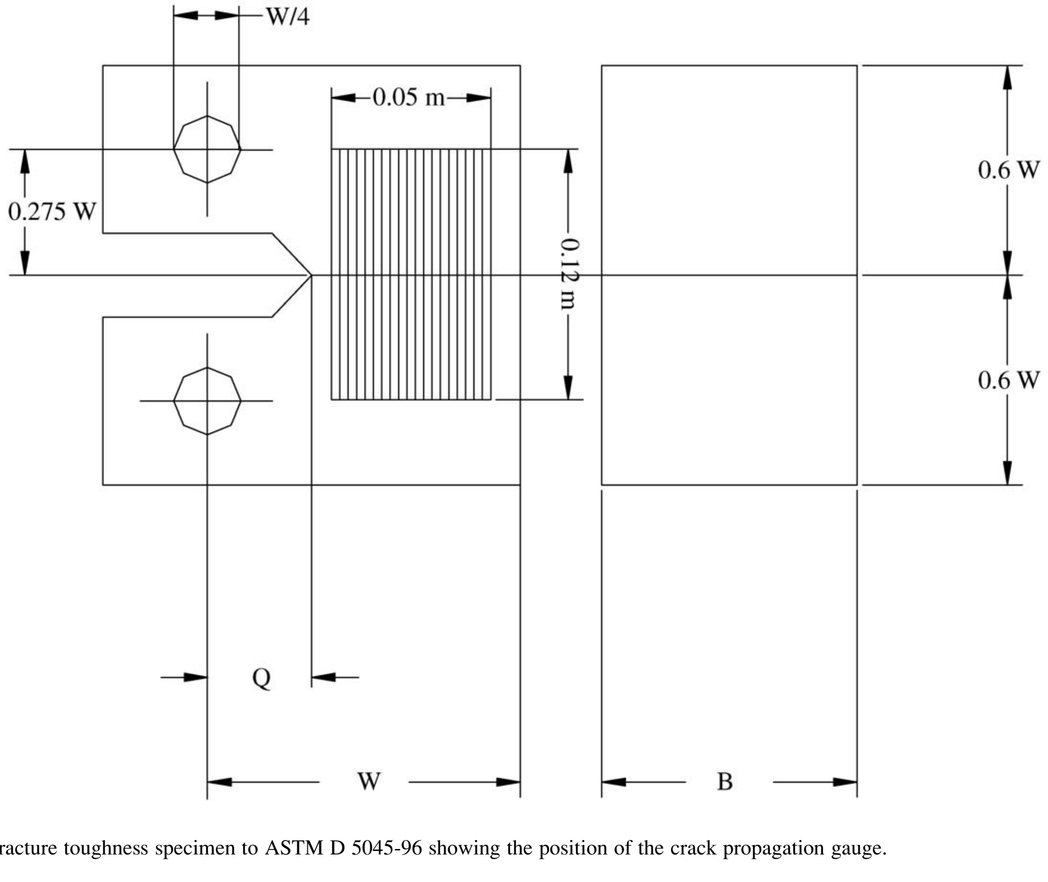

Figure 2 Fracture toughness specimen to ASTM D 5045-96 showing the position of the crack propagation gauge.

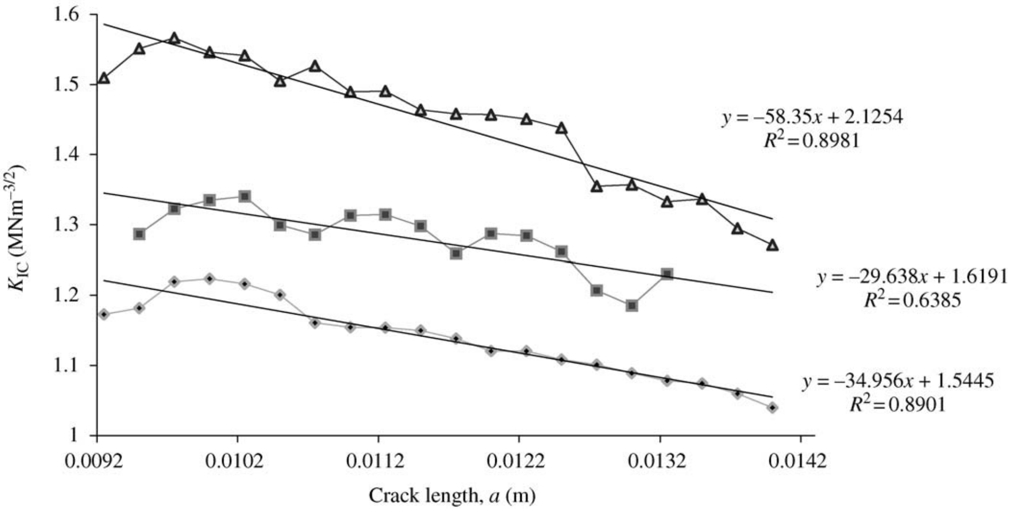

Figure 3 Fracture toughness K_{IC} versus crack length at actuator displacement rate of 2, 20 and 200 μm s^{-1}, measured at 21 ± 1 °C in air.

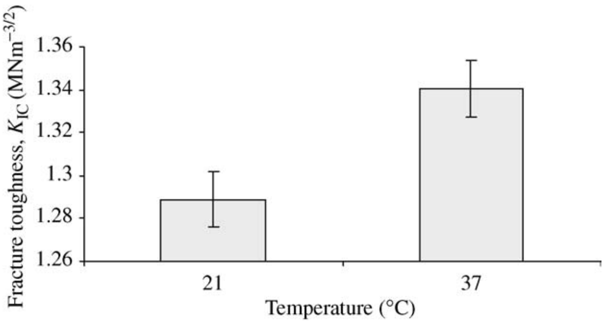

Figure 4 Mean fracture toughness at 21 and 37 °C.

data, values of crack lengths (a) and fracture toughness (K_{IC}) were calculated using the following equation:

$$K_{IC} = \frac{PY_2}{BW^{0.5}} \tag{1}$$

where P is the load at crack length a, the specimen thickness is B, the width is W, and Y_2 is a shape factor given by

$$Y_2 = \frac{(2 + a/W)}{(1 - a/w)^{3/2}} * \{0.866 + 4.64\,(a/W) - 13.36\,(a/W)^2 + 14.72\,(a/W)^3 - 5.6\,(a/W)^4)\} \tag{2}$$

where (a/W) ranges from 0.2 to 1.0. Five specimens were tested per group and statistical differences between groups were assessed using Student's t-test.

3. Results

For all materials, and test velocities, a general trend was observed as the crack propagated through the specimen. Generally, there was a linear decrease in toughness with increase in crack length. However, the specimens fractured at an elevated temperature, that is, 37 °C showed the opposite trend.

TABLE II Mean fracture toughness of HAPEX specimens consisting of P205 HA and HD4556EA at different strain rates

Strain rate (μms^{-1})	K_{IC}(M Nm$^{-3/2}$)
2	1.15 ± 0.13
20	1.30 ± 0.04
200	1.34 ± 0.10

3.1. Effect of strain rate

At all three strain rates, similar trends in K_{IC} were observed as the cracks propagated through each specimen (Fig. 3), increasing the strain rate caused significant increases in K_{IC} (Table II) with a semi-log relationship between strain rate and K_{IC} given by:

$$K_{IC} = 0.042 \ln \dot{\varepsilon} + 1.1347 \tag{3}$$

where $\dot{\varepsilon}$. is strain rate.

3.2. Effect of temperature

The fracture toughness at 20 μm s^{-1} actuator velocity increased from 1.30 ± 0.04 M Nm$^{-3/2}$ to 1.34 ± 0.07 M Nm$^{-3/2}$ when the temperature was increased from 21 ± 1 °C to 37 ± 1 °C (Fig. 4). However, in contrast to the behaviour noted earlier at room temperature, at 37 °C there was an increase in K_{IC} as crack length increased (Fig. 5). That is, the materials resistance to crack propagation increased as the crack grew, making further crack growth difficult.

3.3. Effect of polyethylene grade

Determination of the effects of the grade of the polymer matrix took place at room temperature, 21 ± 1 °C and at 20 μm s^{-1} actuator displacement rate. Decreasing the molecular weight caused a decrease in K_{IC} (Fig. 6), and as before, resistance to crack propagation decreased as crack length increased (Fig. 7).

3.4. Effect of particle surface area

Fig. 8 shows that fracture toughness was lower for the high surface area HA composite. That is the composite containing sintered HA grade P215S was tougher than that containing HA grade P205, with surface area approximately a factor of 10 greater (Table I).

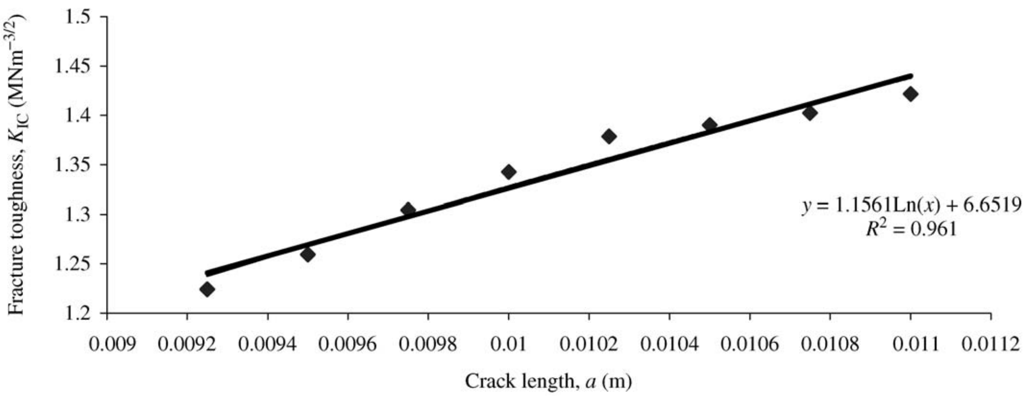

Figure 5 Fracture toughness increasing with crack length at 37 °C, at actuator displacement rate of 20 µm s^{-1}.

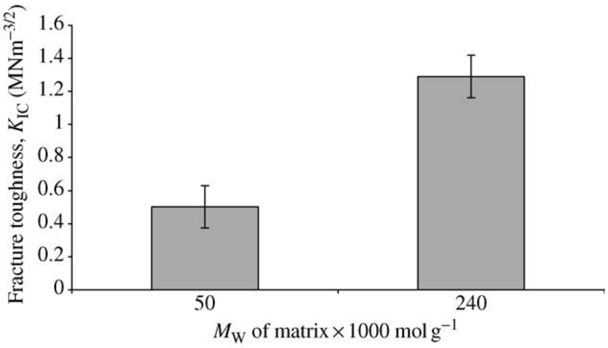

Figure 6 Effect on mean fracture toughness of HAPEX® produced by an increase in molecular weight of the HDPE matrix.

Composites made with both grades of HA, however, showed a decrease in toughness as the crack length increased when tested at room temperature (Fig. 9).

4. Discussion

The values obtained for the HA–PE composites were lower by approximately a factor of 2 when compared with the value of 3.2 M Nm$^{-3/2}$ obtained for bone by Wright and Hayes [18]. A more relevant comparison can be made between this value and that obtained by Bonfield [19]. His value of K_{IC} of approximately 2.9 ± 0.3 M Nm$^{-3/2}$ was obtained using 45% HA in HDPE. However, the HDPE used to manufacture Bonfield's material had a molecular weight (Mw) of approximately 400 000 mol g^{-1} whereas the HDPEs used in this report had Mw of 240 000 and 48 650 mol g^{-1}. Also, the HA used by Bonfield was calcined bone ash, which has a larger particle size and lower specific surface area than either of the synthetic HAs used in this study. Therefore, the combination of such factors such as HDPE grade being half that used by Bonfield and the different HA particle size and surface area would account for the lower K_{IC} values obtained.

A positive correlation was observed between K_{IC} and strain rate, that is HA–PE composite has a component of viscoelasticity in its fracture toughness. Behiri and Bonfield [20] also observed this positive correlation in bone within the strain rate limits used in this report. They reported that within the cross-head speed range of 10–3200 µm s^{-1}, K_{IC} increased from 2.8 to 6.3 M Nm$^{-3/2}$.

At slow crack rates, microcracks are generated around the main crack. The behaviour seen was momentary suspension of crack growth, then a sudden increase by a significant length, that is, series of lengthy periods where crack growth ceases, followed by several crack gauge wires breaking at once. This behaviour is similar to that reported by Vashishth *et al.* [21] for bone. Generating microcracks dissipates energy, increasing the fracture toughness. These microcracks were observed on the fracture surfaces under scanning electron microscopy (SEM) (Fig. 10) and by the systematic variations about the fracture toughness trends lines seen in Figs. 3, 5, 7 and 9.

4.1. Temperature

Temperature was found to increase the toughness of the composite from an average of 1.30 ± 0.04 at 21 ± 1 °C to 1.34 ± 0.07 at 37 ± 1 °C. This increase is a similar to

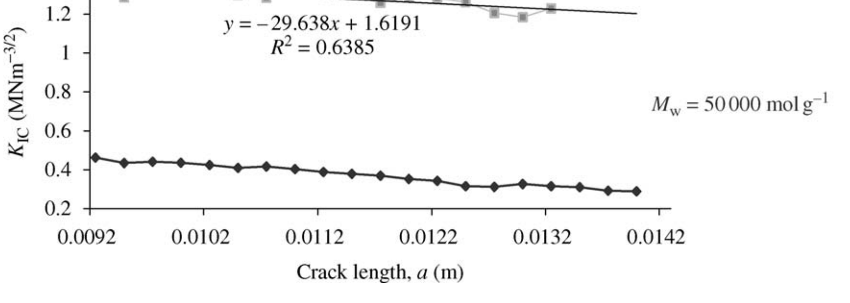

Figure 7 Effect of polyethylene molecular weight on fracture toughness versus crack length at 21 °C.

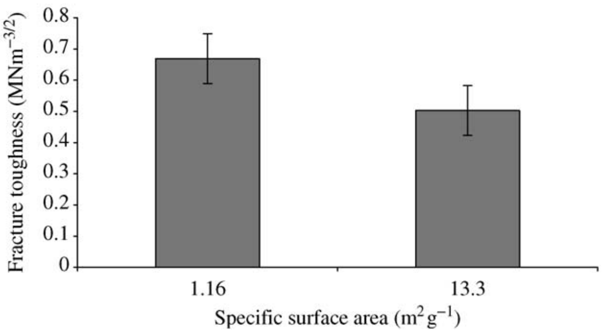

Figure 8 Mean fracture toughness for two different HAs in 50 000 mol g^{-1} polyethylene.

that observed as the strain rate was increased by a factor of 10 at room temperature.

The difference in trend observed between fracture toughness and crack propagation at both these temperatures is similar to the rate effect seen in bone as discussed by Vashishth *et al.* [21]. Their explanation considered a brittle-to-ductile transition somewhere between the two temperatures and that flaws or microcracks exist in the material, which contributes to the observed behaviour. Loading brittle materials results in an increase in stress around any pre-existing flaws, which produces unsteady crack propagation and failure once the critical value is reached. Ductile materials however, undergo crack propagation due to the formation of a plastic zone around the crack tip. The plastic zone grows as the crack advances and thereby absorbs part of the energy available at the crack tip for extension, increasing the toughness of the material [20]. At the lower temperature of 21 ± 1 °C, the material is considered to be behaving in a brittle manner, thus explaining the decline in toughness as the crack advanced. However, at 37 ± 1 °C, the material had become ductile by forming plastic zones around the crack tip and allowing the polyethylene matrix to draw. Thus, it can be concluded that HA–PE composites have a brittle-to-ductile transition temperature between 21 ± 1 °C and 37 ± 1 °C.

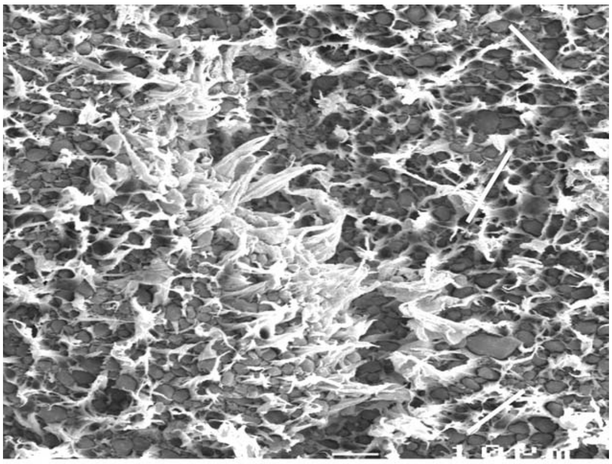

Figure 10 Scanning electron micrographs of fracture surface, showing the mechanical locking of HA and drawn PE fibrols. Ruler bar = 10 μm.

4.2. Grade of polyethylene

The same general trends observed in the standard HA–PE composite HD4556EA was observed in the HD5226EA-based material, which had a lower molecular weight. There were significant changes in fracture toughness between the grades. Compared to the work of Bonfield [19], the fracture toughness was lower by a factor of two. However, there are additional differences between the compositions of these HA–PE composites. For example, the presence of bone mineral in the matrix compared to the synthetic HA, which is found in standard HA-PE composite, is likely to increase the fracture toughness.

Similar work by Hogg *et al.* [8] and Zhang and Tanner [9] considered effect of molecular weight of HA–PE composites on their toughness. They reported impact testing of hydroxyapatite in two different ranges of HDPW composites. Their observations were that the molecular weight of the grade of polyethylene matrix was found to significantly affect both the maximum forces sustained during impact and total energy required to fracture the specimens. Similarly Joseph *et al.* [22] when

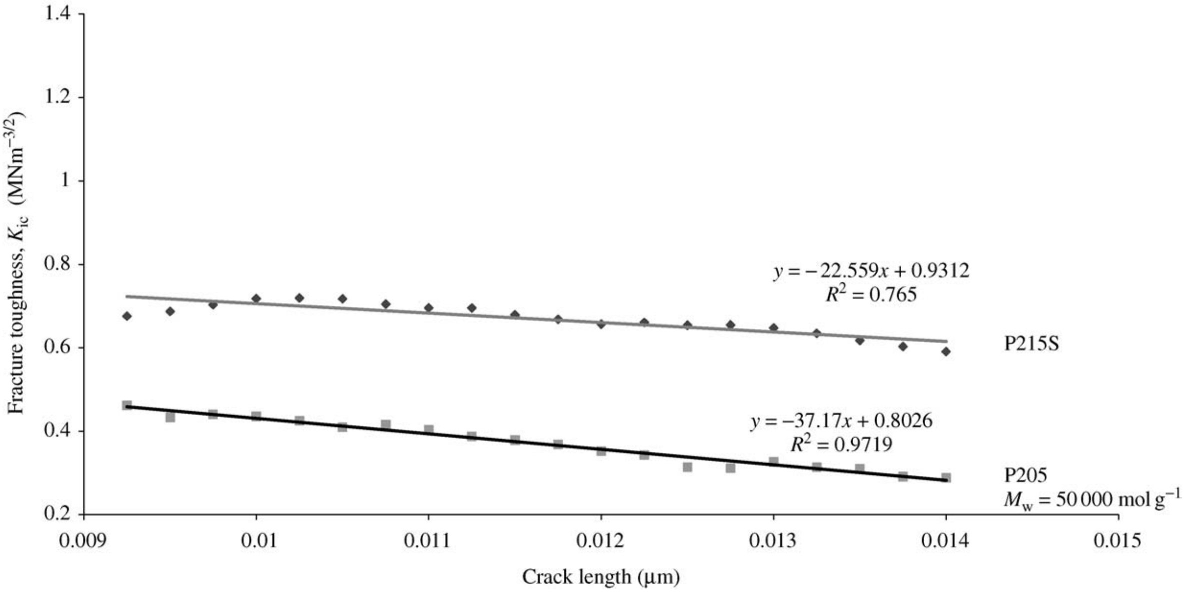

Figure 9 Effect of specific surface area on fracture toughness versus crack length at 21 °C.

tensile testing these materials found that lower specific surface area for the HA and/or higher molecular weight HDPE led to materials with higher stiffness and strength.

During tensile fractures of particulate filled polymer composites, a non-uniform state of strain exists. This strain state is generated because the filler is stiff and brittle compared to the matrix; thus the matrix provides the major contribution to the deformation and thus the toughness of the composite. Therefore, a change in the structure of the matrix leads to substantial changes in the overall toughness of the composite.

4.3. Particle surface area

As shown in Table I and Fig. 1, the two grades of HA varied significantly in specific surface area, but only marginally in particle size. Therefore, it can be concluded that change in fracture toughness of the HA–PE composite grades can be directly attributed to the differences in specific surface area of the HA particles.

The decreased specific surface area did not alter the observed trend of a decrease in resistance to crack propagation with increase in crack length (Fig. 9). The difference in surface area between the two grades caused a relatively small, but significant change in toughness. As the specific surface area was reduced by a factor of 11.5, the fracture toughness increased by a factor of 2.2. The particle/matrix interface and the resulting matrix can explain this increase in toughness. As a result of its processing route, only mechanical bonding exists between the HA particles and the HDPE matrix in HA–PE composites as they are manufactured without chemical bonding. This mechanical bonding is produced by the shrinkage of the HDPE matrix around each HA particle whilst cooling from the processing temperature [16]. Particles with lower surface area, require less matrix material in the interaction, thus more material remains to contribute to the toughness of the material.

5. Conclusions

1. There is a positive correlation between fracture toughness and log of strain rate.
2. At low strain rate, micro-cracks found on fracture surfaces are thought to be responsible for increasing toughness of HA–PE composite, similar to those found in cortical bone.
3. A positive correlation was found between temperature and toughness. This increase was similar in magnitude to that between specimens tested at 20 and 200 $\mu m\,s^{-1}$. HA–PE composite has a brittle-to-ductile transition temperature between $21 \pm 1\,^{\circ}C$ and $37 \pm 1\,^{\circ}C$.
4. A positive correlation was found between fracture toughness of HA–PE composites and molecular weight of the HDPE matrix.
5. HA–PE composites using sintered HA particles in a HDPE matrix have higher toughness. The decrease in surface area of the reinforcing particle increases only the toughness and has no observable effect on mode of failure, or resistance to cracks as they propagate through the specimens during testing.

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