

The effect of reinforcement volume fraction and particle size on the mechanical properties of β -tricalcium phosphate–high density polyethylene composites

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Abstract

The mechanical properties of the tricalcium phosphate–high density polyethylene (β -TCP/HDPE) composite samples have been investigated by looking at the effect of particle size and volume fraction of tricalcium phosphate on the fracture strength, modulus of elasticity and failure energy in the composite samples. A decrease in both the fracture strength and failure energy was observed with an increase in the volume fraction of the tricalcium phosphate. Both properties decreased further with the use of larger β -TCP particles. Increase in the tricalcium phosphate content led to an increase in the modulus of elasticity values in the composite samples. However, a lesser increase in modulus of elasticity was observed when larger β -TCP particles were used in the preparation of the composite samples. SEM analysis of the fractured surfaces showed a transition from ductile to brittle type of failure as the volume fraction of the tricalcium phosphate increased in the samples. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

The mechanical properties of the hydroxyapatite reinforced polyethylene composite has been studied extensively.^{1–6} The combination of bioactive, but brittle hydroxyapatite and ductile high density polyethylene allows a good biocompatibility and adequate mechanical properties in the composite samples.^{1–6} On the other hand, to our knowledge there is no published data on the mechanical and biological properties of the tricalcium phosphate reinforced high density polyethylene composite samples.

Depending on the specific stoichiometry of the calcium phosphate compounds, they are classified as permanent, partially biodegradable, or completely biodegradable in the biological environment. The chemical composition of the hydroxyapatite makes it more stable against resorption. Tri-

calcium phosphate (TCP), on the other hand is partially resorbable.^{4,7–9,11} When a bone suffers a trauma, a temporary support is often desired to allow the use of the bone while natural healing occurs. It is in these types of application that biodegradable bioactive materials such as TCP are used.^{4,9,10} The choice of β -TCP is due to its lower solubility and better overall performance in the physiological environment in comparison to the α -form^{7,9,11,12}.

The objective of this study was to examine the effect of β -TCP particle size and volume fraction on the mechanical properties of the TCP/HDPE composite samples.

2. Experimental procedures

Medical grade tricalcium phosphate powder (Merck) was used as the ceramic filler material. The matrix polymer was a high density (0.944 g/cm³) polyethylene (supplied by Arak Petrochemical Co. in Iran). Particle size distribution in the

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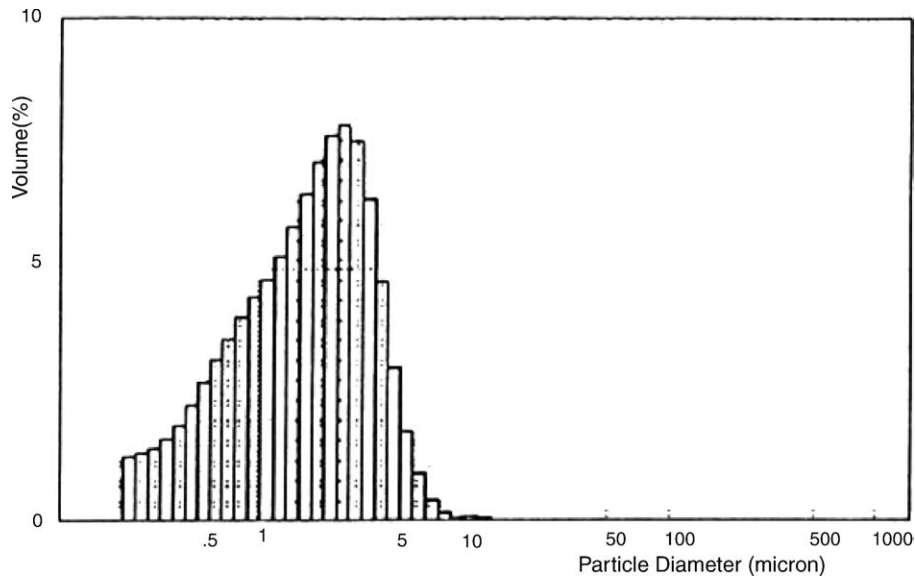


Fig. 1. Particle size distribution in the as-received TCP powder.

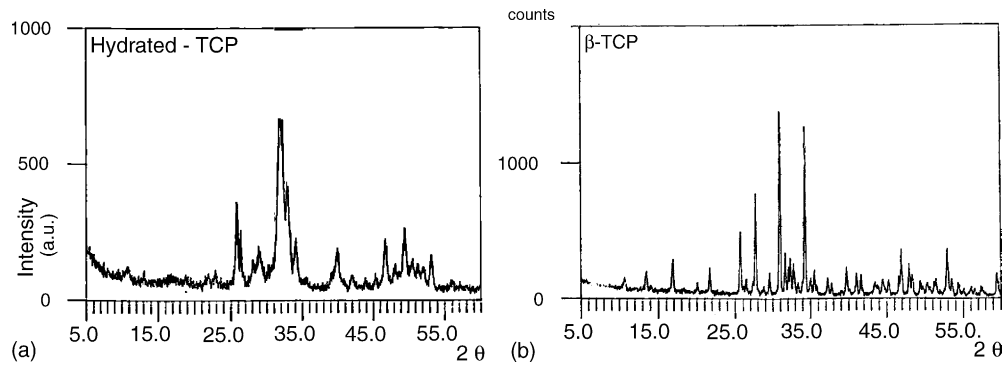


Fig. 2. XRD patterns for the: (a) as-received powder; (b) TCP powder sintered at 1250 °C for 2 h.

as received powder was determined by particle size analysis (PSA) using Fritsch particle size analyzer (Fig. 1). As shown in this figure the majority of particles were less than 5 μm in size. The only phase present in the as received powder was hydrated tricalcium phosphate (Fig. 2a) as determined by XRD analysis (JEOL, JDX-8030). The conversion of the as received powder into β -TCP form was

done by pressing the powder into cylindrical shape at an applied pressure of 28 kg/cm^2 and sintering the pressed samples at 1250 °C for 2 h. After cooling and grinding, two different particle size distribution; namely 80–100 and 120–140 mesh size were chosen for further studies. These powders were used in the preparation of β -TCP/HDPE composite samples. β -TCP/HDPE composite samples were

Table 1
Characteristics of the composite samples prepared in this study

Sample code	TCP volume fraction (%)	Particle mesh size	TCP mass (g)	PE mass (g)	Composite mass (g)	Composite density (g/cm^3)
A	10	80–100	9.82	26.97	36.8	1.15
B	10	120–140	9.82	26.97	36.8	1.15
C	20	80–100	19.64	23.87	43.52	1.36
D	20	120–140	19.64	23.87	43.52	1.36
E	30	80–100	29.5	21.1	50.61	1.58
F	30	120–140	29.5	21.1	50.61	1.58
G	40	80–100	39.29	17.98	57.28	1.79
H	40	120–140	39.29	17.98	57.28	1.79
I	50	80–100	49.12	14.88	64	2
J	50	120–140	49.12	14.88	64	2

prepared by first blending and compounding the ceramic and polyethylene powder to produce a homogenous composite mixture. These preforms were compression molded into plates 160 mm × 100 mm × 2 mm in dimensions. Compression molding was carried out at 200–250 °C and an applied pressure of 300 kg/cm². The compositions of the samples prepared in this manner are given in Table 1. Ceramic filler distribution in the composite samples was investigated by examining the samples under SEM. Small pieces were cut out of the molded plates and mounted in an epoxy resin. The exposed surface was fine polished and gold coated before examining by SEM.

Samples for the tensile test were prepared following the procedure described in ISO 527. A 2 ton ADAMEL tensile testing system was employed in this study. The samples were strained at the rate of 1 mm/min in the tensile test. Fracture strength, modulus of elasticity, and absorbed energy in the samples with different compositions were determined using the results of this test. Based on the initial sample dimensions, the instrument makes use of a computer software to determine parameters such as Young's modulus and absorbed energy by measuring the slope in the linear region and the area under the stress-strain curve, respectively. The results reported are an average value from the five samples tested for each composition. Fracture surfaces of the selected samples with various volume fraction were examined using a scanning electron microscope at an operating voltage of 20 keV.

3. Results and discussion

The XRD pattern for the pulverized sintered powder is shown in Fig. 2b. As shown in this figure, the heat treatment condition adopted in this study was sufficient in converting the as-received powder into β -tricalcium phosphate. The powder particles are shown in SEM micrographs of (Fig. 3a

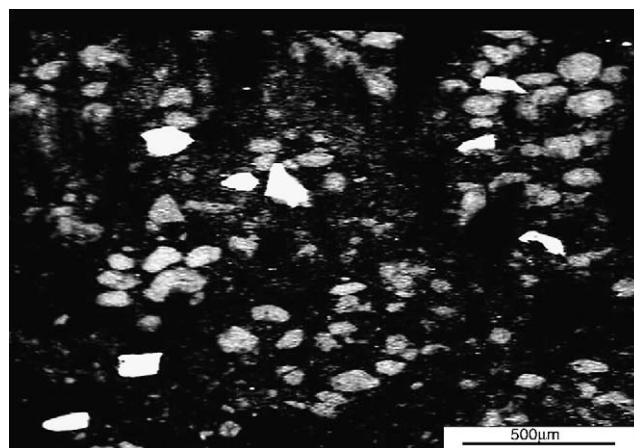


Fig. 4. SEM micrograph showing the distribution of the TCP particles in the polyethylene matrix (sample E with 30 vol.% TCP).

and b). The rough nature of the particle surface is considered to be an advantage in the bone forming process¹³.

The distribution of β -TCP particles in the polymer matrix is shown in Fig. 4. As illustrated in this figure, a good distribution of ceramic particles in the polyethylene matrix was achieved in the mixing process.

Fig. 5 exhibits the effect of ceramic content on the fracture strength of the β -TCP/HDPE composite samples. It can be seen that the fracture strength of the composite samples decreased with the increase in the β -TCP content. In addition, it is seen that the use of larger particles (80–100) in the composite samples led to lower fracture strength values in the composite samples. The reduction in strength with the increase in the filler content may be explained by the presence of a weak bond at the particle–matrix interface. This type of interface forms as a result of a mechanical interlocking produced by the shrinkage of the polymer matrix around the filler

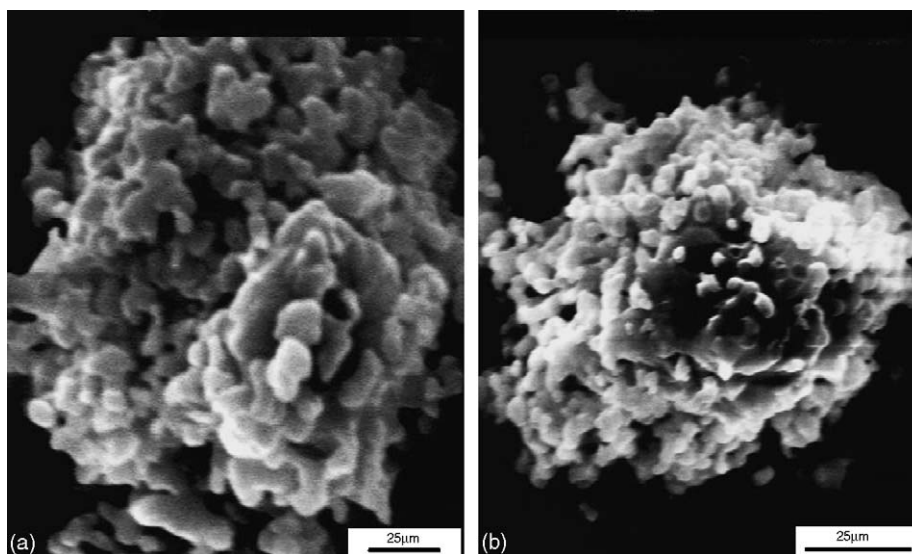


Fig. 3. SEM micrographs of aggregate particles in two size distributions: (a) 80–100 mesh size; (b) 120–140 mesh size.

particles, while cooling the samples from molding temperature. Hence, an increase in the ceramic filler content led to an increase in the total weak filler/matrix interface area with the overall effect of reducing the strength in the composite specimens. In addition, in particulate filled polymer composites having a weak interface, the applied load is carried mainly by the polymer matrix.¹⁴ In such cases the strength of the composite samples may be stated as follows:

$$\sigma_C = \sigma_m(1 - \psi) \quad (1)$$

where σ_C and σ_m are the strengths of the composite and the polymeric matrix, respectively and $1 - \psi$ is the cross sectional area of the polymer at yield point.¹⁴ According to Eq. (1), with an increase in the ceramic content, there will be a decrease in the polymer cross sectional area which would lead to a decrease in the composite strength, in agreement with what was observed experimentally. Poor bonding at the particle–matrix interface may also be the reason for the lower strengths in the samples containing larger β -TCP particles. The presence of the larger particles led to the formation of larger defects (stress concentration points) at the interface which in turn caused further reduction in the strength of the composite samples. Hence, the composite samples with larger β -TCP particles showed lower strength as compared to samples with smaller β -TCP particles (Fig. 5).

The introduction of ceramic particles with higher modulus of elasticity is expected to increase the modulus of elasticity in the composite samples. This behavior was observed in the case of specimens containing both the small and large β -TCP particles as indicated in Fig. 6. However, a lower modulus of elasticity values was observed when larger β -TCP particles were used in the preparation of the composite samples. It should also be mentioned that because of the brittle nature of the samples, we were not able to measure the modulus of elasticity in the specimens containing high volume fraction of β -TCP powder (40 and 50 vol.%).

The dependency of modulus of elasticity on the particle size was not expected theoretically, however the experimental observation of this dependency has been reported by other

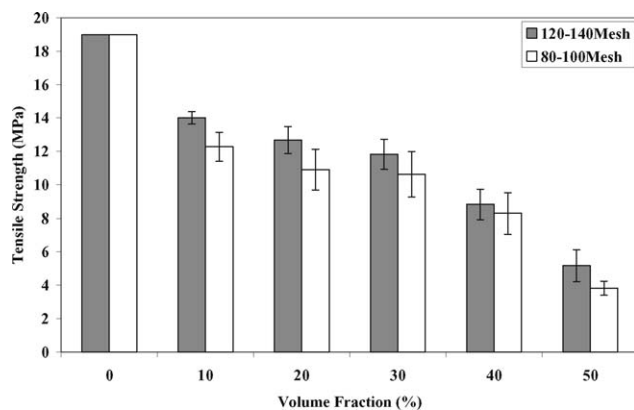


Fig. 5. The effect of TCP volume fraction and size distribution on the fracture strength of β -TCP/HDPE composite samples.

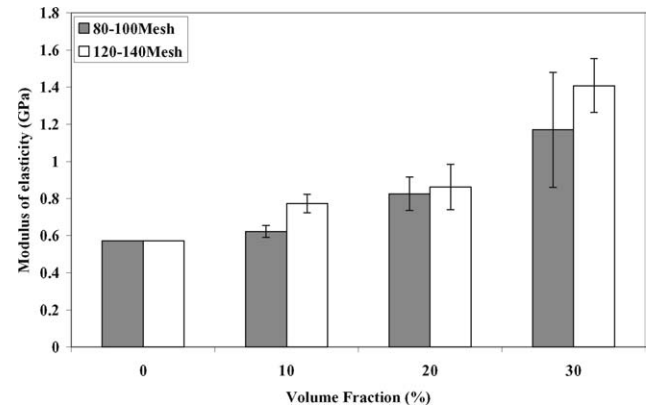


Fig. 6. The effect of TCP volume fraction and size distribution on the modulus of elasticity of β -TCP/HDPE composite samples.

researchers as well.^{14,15} The explanation offered points out to the increased surface area in the smaller filler particles. The increase in the surface area causes increased interaction at the particle–matrix interface.

One consequence of this interaction is said to be the adsorption of the polymer on the filler particle surface. The latter process has the effect of increasing the effective volume fraction of filler particles and thus increasing the modulus of elasticity values in the specimens containing smaller β -TCP particles¹⁵.

Fig. 7 shows the relationship between the absorbed energy and the β -TCP content in the composite samples. As it is indicated in this diagram, the absorbed energy decreased with the increase in the β -TCP content in the composite samples. In addition, it is observed that the energy to failure values is higher in the samples containing smaller β -TCP particles. This is believed to be due to the higher number of interfaces encountered by the growing crack in these samples. The retarding effect of the interfaces on the advancing crack has been shown to increase the amount of energy to failure in the samples prepared using smaller size β -TCP particles¹⁴.

In order to study the failure behavior in the samples, the fracture surface of the selected samples were observed

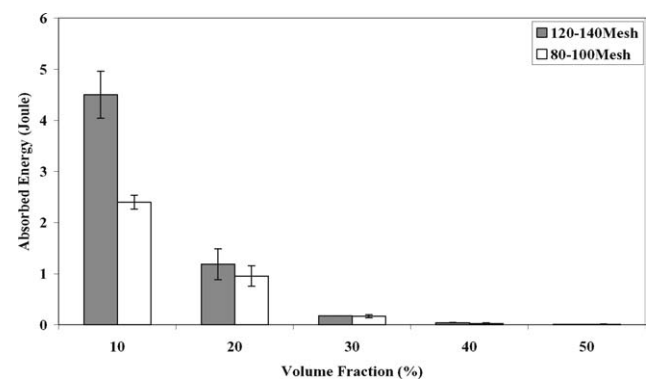


Fig. 7. The effect of TCP volume fraction and size distribution on the absorbed energy values of β -TCP/HDPE composite samples.

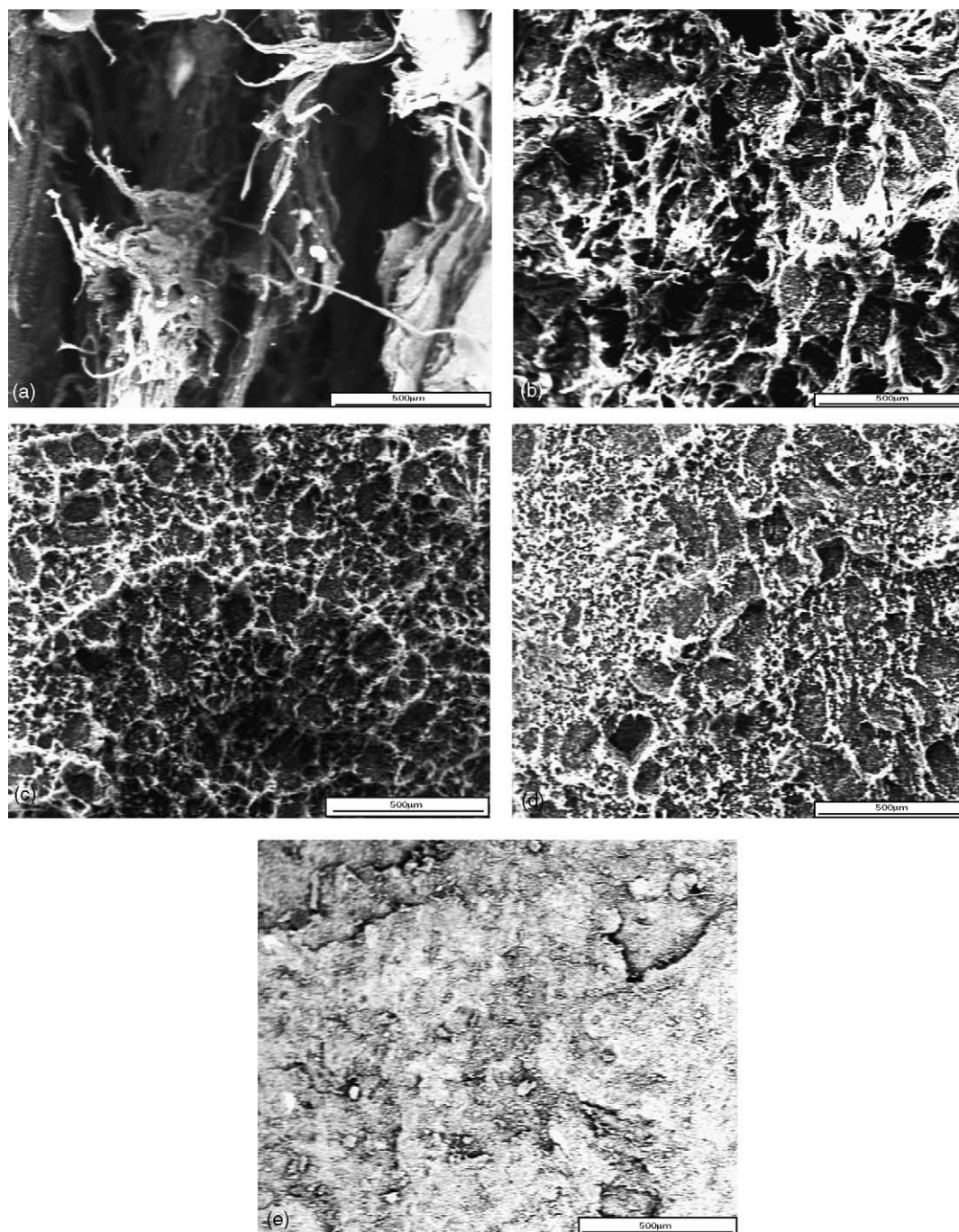


Fig. 8. SEM micrographs of fractured surfaces: (a) sample A, 10 vol.% TCP; (b) sample C, 20 vol.% TCP; (c) sample F, 30 vol.% TCP; (d) sample G, 40 vol.% TCP; (e) sample J, 50 vol.% TCP.

under SEM. Fig. 8a–e show the SEM micrographs for the samples containing 10–50 vol.% β -TCP, respectively. The presence of the debonded particles shown in the micrographs may be the result of stress concentration at the weakly bonded β -TCP/HDPE interface which makes it easy for the particles to detach themselves from the polymer matrix. This process may be seen more clearly in the SEM micrograph shown in Fig. 9. Another point is that there was no sign of failure in the exposed parti-

cles in the samples studied. Thus, particle–matrix debonding, crack formation and propagation at the interface seems to be the major cause of failure in these composite samples.

Closer examination of the SEM micrographs revealed that when the filler volume fraction increases there is a change in failure mode from ductile to a brittle type of failure. This point may be seen for example by comparing Fig. 8a, b and d, e where the filler content is 10, 20, 40, and 50 vol.%,

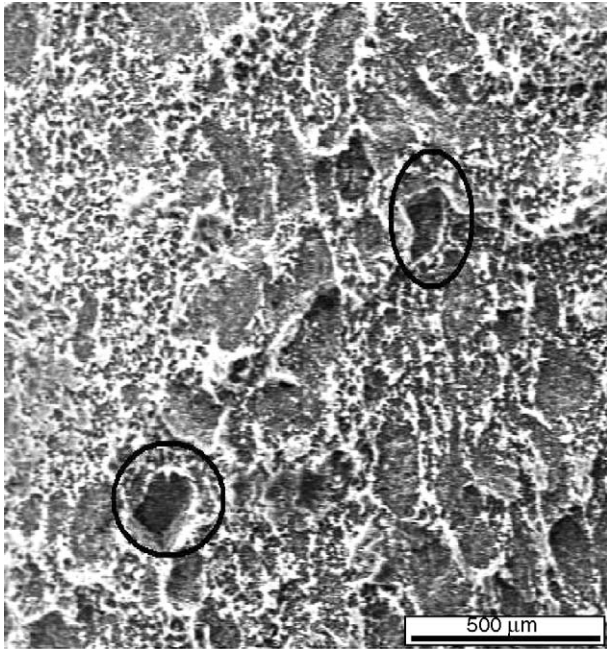


Fig. 9. SEM micrograph showing the detachment of TCP particles from polyethylene matrix in composite samples.

respectively. As shown in these micrographs there are more polymer matrix pulled out in the samples with lower amounts of filler particles (Fig. 8a and b).

4. Conclusion

The results of this study showed that both the volume fraction and size distribution of the β -TCP particles was important in determining the mechanical properties in the β -TCP/HDPE composite samples. In particular, there was a reduction in fracture strength and absorbed failure energy values with the addition of β -TCP into high density polyethylene. Both these properties decreased further in the samples containing larger β -TCP particles. We also observed a dependency of the modulus of elasticity values on the size of the β -TCP particles in the composite samples such that the modulus of elasticity was higher in the specimens with smaller β -TCP particles.

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