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The effect of partially stabilized zirconia on the mechanical properties of the hydroxyapatite–polyethylene composites

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The effect of partially stabilized zirconia (PSZ) on the mechanical properties of the hydroxyapatite–high density polyethylene composites was studied by investigating the effect of hydroxyapatite and the simultaneous effect of hydroxyapatite and PSZ volume fractions on fracture strength, modulus of elasticity, and absorbed energy in the composite samples. The results showed a decrease in fracture strength, and absorbed energy with an increase in the volume fraction of hydroxyapatite content in the hydroxyapatite–polyethylene samples. Partial replacement of hydroxyapatite with PSZ particles was beneficial in the improvement of both the fracture strength and failure energy values in the composite samples. A transition from ductile to brittle behavior was observed as the volume fraction of ceramic filler particles increased in the samples.

1. Introduction

Hydroxyapatite–high density polyethylene (HA/HDPE) composites have been developed as bone replacement materials. The ceramic particles stiffen the ductile polyethylene and provide the bioactive phase while the polyethylene toughens the composite. The mechanical properties of this composite and the biological response to it have been studied extensively by a number of researchers [1–12]. In cell culture studies with human osteoblasts, the cells were shown to grow and spread over the composites, attaching themselves to the hydroxyapatite particles on the sample surface [5, 13–16]. However, the strength of this composite material is below the lower bounds for cortical bone, so that its clinical use has been limited to minor load-bearing applications such as middle ear or orbital floor implants [1, 11]. Therefore, considerable research effort is focussed on HAPE composites with the aim of raising their strength and toughness to a level necessary for hard tissue replacement implants. In some of these studies use is made of chemical coupling agent to improve the ductility and tensile strength in the composite samples [17, 18]. In another publication it was shown that the alignment of the polymer chains in a hydrostatic extrusion process led to an improvement of ductility in the extrusion direction [19]. It is well known that the mechanical properties of the oxide ceramics can be improved by introducing partially stabilized zirconia (PSZ) particles, which undergo a tetragonal to monoclinic transformation under mechanical stress. The latter process is accompanied by 3–5% volume expansion and as a result suppresses crack propagation in the microstructure. Earlier work with zirconia in the hydroxyapatite system have been positive to some extent [20–22]. For instance, zirconia–hydroxyapatite coating on titanium showed higher bending strength compared to its pure hydroxyapatite counterpart [21, 22]. The primary objective of this study was to investigate whether altering the content of PSZ particles would have any significant effect on the mechanical properties of HA/HDPE composite bulk samples.

2. Experimental

2.1. Materials and specimen preparation

Hydroxyapatite powder (Merck, 102196) was used as the filler material for the preparation of HA/HDPE composites. The matrix polymer was a high density ($0.944\,\mathrm{g/cm^3}$) polyethylene (supplied by Arak Petrochemical Co., Iran). The as-received hydroxyapatite powder was calcined at 1200 °C for 2 h prior to use. Table I shows the HA particle size distribution used in the preparation of composite samples.

Partially stabilized zirconia was synthesized by adding 4 wt % CaO into high purity (99.8%) chemical grade monoclinic zirconia powder. Disk-shaped samples were prepared from this mixture and were heat treated at 1400 °C in an electric furnace. Samples were cooled down to room temperature after 3 h of soaking at this temperature. The spectrum XRD of the calcined sample is shown in Fig. 1. It can be seen that the addition of CaO to zirconia has led to the formation of a multiphase

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TABLE I Particle size distribution of particulate hydroxyapatite used to prepare composite samples

Particle size (μm)	< 45	45–75	75–100	100–125
Wt%	50.86	21.93	26.56	0.65

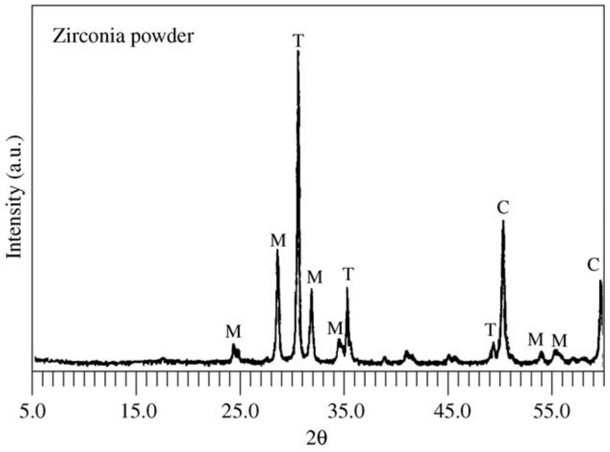

Figure 1 XRD plot for the zirconia powder calcined at 1400 °C for 3 h. C, cubic; M, monoclinic; T, tetragonal phase.

material consisting of tetragonal zirconia as the major phase, with monoclinic and cubic phases as the minor phases in the microstructure. Powdered zirconia samples with determined particle size distribution (Table II) were used in the processing of the composite samples. Results of the XRF chemical analysis for the heat treated zirconia powder is given in Table III.

Compression molded HA/PE and HA + PSZ/PE composite samples were prepared by first blending and compounding the ceramic and polyethylene powders to produce a homogeneous composite mixture. The powders were then compression molded into plates $160 \times 100 \times 2\,\mathrm{mm}^3$ in dimensions. Fourteen different compositions were prepared in this manner. The composition of the samples are summarized in Table IV.

2.2. Filler distribution

Ceramic filler distribution in the composite specimens 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 using abrasive papers. The specimen were gold-coated before examining by scanning electron microscope (SEM).

2.3. Mechanical testing

Samples for the tensile test were prepared following the procedures given by ISO 527. A two ton ADAMES 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.

TABLE II Particle size distribution of particulate zirconia

Particle size (μm)	< 45	45–75	75–100	100–125
Wt%	59.81	19.93	19.70	3.56

2.4. Fracture surface

Fracture surfaces of the selected samples were examined using a SEM at an operating voltage of 20 kV.

3. Results and discussion

The hydroxyapatite distribution in the composite samples containing 20 and 40 vol% HA particles are presented in the SEM micrographs shown in Fig. 2(a) and (b), respectively. Except for a few areas with agglomerated particles, there is a rather uniform distribution of filler particles in the polyethylene matrix.

Fig. 3 shows the effect of HA content on the fracture strength of HA/HDPE composite samples. It can be seen that the fracture strength of the composite samples decreased with the increase in the HA content.

The general trend observed in this study is consistent with the previous studies done on this system [1, 2, 4, 7, 17]. However, the strength values determined in this study are slightly lower than the previously reported values. Major factors contributing to this difference may be the smaller filler particles and/or better interface coupling achieved by the previous investigators [17–19]. The reduction in strength with 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 on to filler particles while cooling the samples from the compounding temperature. Thus, an increase in the HA content led to increase in the total weak filler/matrix interface area with the overall effect of reducing the strength in the composite samples. It is also shown that in a particulate filled polymer composites having a weak interface, the applied load is carried mainly by the polymer matrix [23, 24]. In such a case, the strength of the composite samples may be stated as follows:

$$\sigma_c = \sigma_m(1 - \varphi) \tag{1}$$

where σ_c and σ_m are the strengths of the composite and the matrix polymer, respectively, and is the volume fraction of the ceramic filler. According to Equation 1, with an increase in the ceramic content there will be a decrease in the composite strength which is in agreement with what was observed experimentally (Fig. 3). The

TABLE III XRF chemical analysis for the partially stabilized powder

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	TiO_2	Fe_2O_3	ZrO_2	HfO_2
Wt%	0.13	0.35	0.12	< 100 ppm	0.093	4.0	0.20	0.032	95.1	< 100 ppm

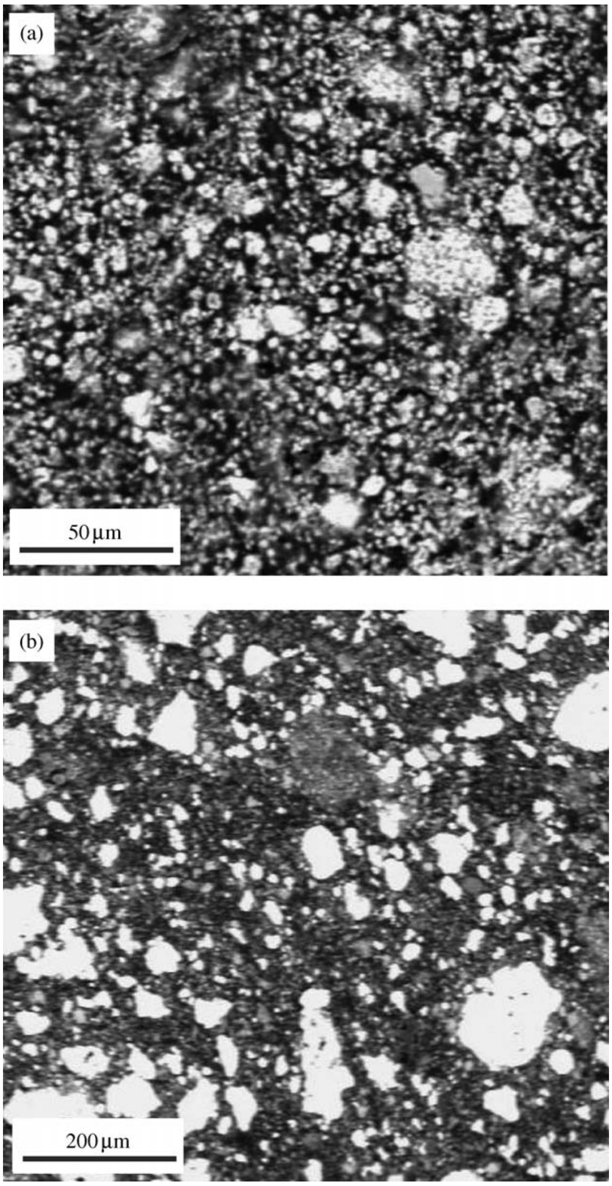

Figure 2 SEM micrographs showing the distribution of the filler particles in the polymer matrix: (a) Sample containing 40 vol % HA particles; (b) sample containing 20 vol % HA + 20 vol % PSZ.

effect of replacing a part of the hydroxyapatite with PSZ is shown in Fig. 4.

Comparison of Figs. 3 and 4 shows that the strength of the composite samples containing PSZ was slightly higher than the samples without it. As was mentioned previously, there is a weak bond at the interface between the ceramic particles and the polymer matrix. The stress concentration at this weak interface makes it less effective in resisting crack propagation than the matrix itself. Therefore, the existing crack can grow much more easily along the particle–matrix interface. The improvement in the strength with partial substitution of HA by PSZ particles may be the result of tetragonal to monoclinic phase transformation taking place in the PSZ particles. The volume expansion associated with this transformation inhibits or retards the advancing crack, thereby improving the strength values in the composite samples. Figs. 5 and 6 show the effect of filler

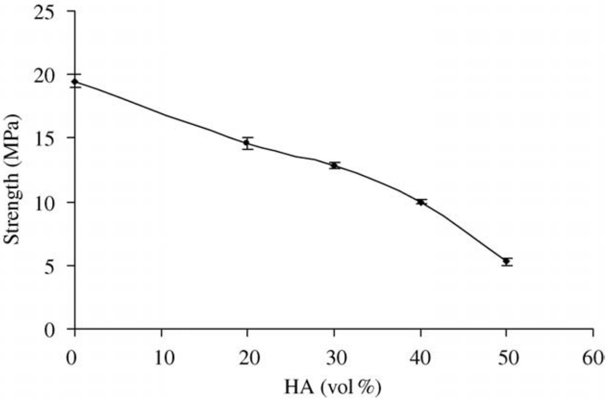

Figure 3 Variation of strength with HA volume percent.

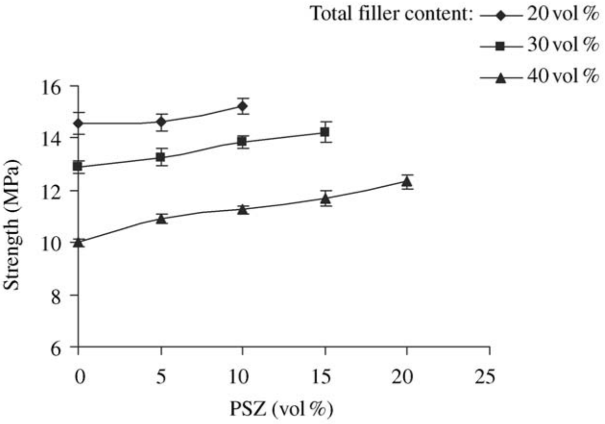

Figure 4 The effect of PSZ addition on the strength values.

T A B L E I V Composition and calculated bulk density values of the composite samples prepared in this study

Sample code	HA (wt %)	PSZ (wt %)	HDPE (wt %)	Composite bulk density (g/cm^3)
20HA	45.65	0	54.35	1.38
30HA	70.58	0	41.30	1.61
40HA	69	0	31	1.83
50HA	76.94	0	23.06	2.05
15HA5PSZ	30.88	19.93	49.19	1.53
10HA10PSZ	18.74	36.31	44.95	1.68
25HA5PSZ	44.81	17.43	37.76	1.75
20HA10PSZ	33.10	32.12	34.78	1.90
15HA15PSZ	23.14	44.63	32.23	2.05
35HA5PSZ	55.77	15.48	28.75	1.97
30HA10PSZ	44.51	28.77	26.72	2.12
25HA15PSZ	34.74	40.31	24.95	2.27
20HA20PSZ	26.03	50.57	23.40	2.42
40HA10PSZ	53.76	26.07	20.17	2.34

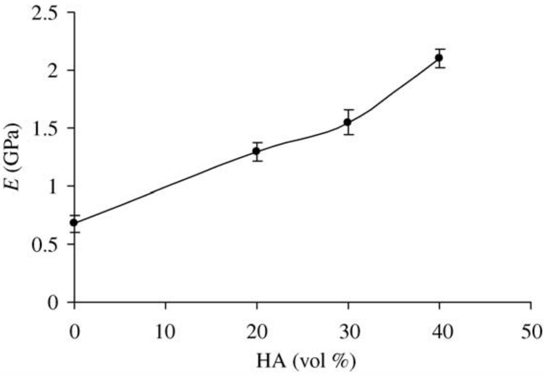

Figure 5 Variation of modulus of elasticity with HA volume percent.

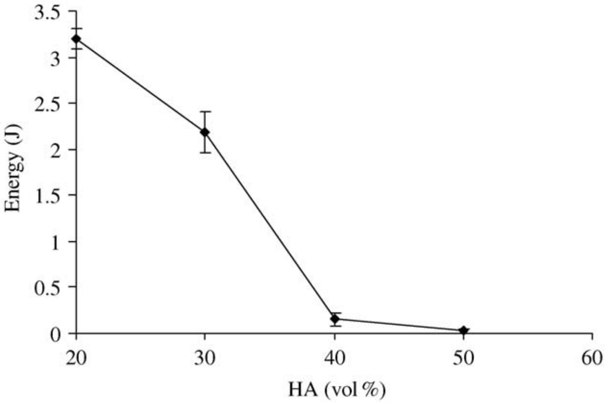

Figure 7 Variation of absorbed energy with HA volume percent.

addition on the modulus of elasticity in the HA and PSZ containing samples, respectively.

As could be expected the addition of ceramic particles with higher modulus of elasticity increased the modulus of elasticity values in the composite samples. Fig. 7 shows the relationship between the absorbed energy and the hydroxyapatite content in the composite samples.

As shown in this figure the absorbed energy decreased with the increase in the HA content in the samples. The result was not surprising, in the sense that the incorporation of ceramic particles into the polymer matrix reduces the amount of the energy-absorbing phase, thereby reducing the energy-absorbing capacity of the composite samples. The addition of PSZ particles improved the situation and led to the higher absorbed energy values as indicated in Fig. 8. The energy values were calculated for the composite samples containing 20, 30, and 40 vol % of total ceramic particles.

To study the effect of PSZ particles, in each case up to half of the total filler content was replaced by PSZ. It is interesting to note that the improvement in the absorbed energy values was more significant at higher total filler content, i.e. compositions which are important in practical applications. As explained earlier, in the presence of a propagating crack the PSZ particles are induced to transform to monoclinic phase with an accompanying volume expansion. Consequently, the advancing crack is subjected to a compressive stress and its progress is either halted or retarded. In other words, extra energy is required to extend the crack in the PSZ, containing samples, which increases both the strength and the toughness of the samples. In order to study the failure behavior in the samples, the fracture surfaces of the selected samples were observed under SEM. Fig. 9(a)–(d) show the SEM micrographs for the samples containing 30 vol % HA, 25 vol % HA plus 5 vol % PSZ, 20 vol % HA plus 20 vol % PSZ, and finally the sample containing 40 vol % plus 10 vol % of PSZ, respectively.

The presence of the debonded particles shown in the micrographs may be the result of stress concentration at the weakly bonded HA/PE interface which makes it easy for the particles to detach themselves from the polymer matrix. This process creates gaps between the particles and polymer matrix which can be seen clearly in the Fig. 9(a), (c) and (d). Another point is that there was no sign of failure in the exposed particles in the samples studied. Thus, particle–matrix debonding, crack formation and propagation at the interface seem to be the major causes of failure in these composite samples. A closer examination of the SEM micrographs revealed that when the filler volume fraction increases there is a change in failure mode from a ductile to a more brittle type of failure. This effect may be seen, for example, by comparing the Fig. 9(a) and (d) where the filler content is 30 and 50 vol %, respectively. As can be seen, more polymer matrix is pulled out in the sample with lower amount of filler particles (Fig. 9(a)), an observation which is consistent with the results of the previous studies [11].

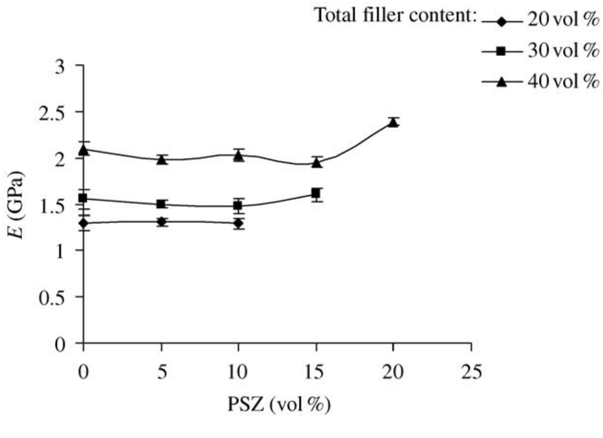

Figure 6 The effect of PSZ addition on the modulus of elasticity.

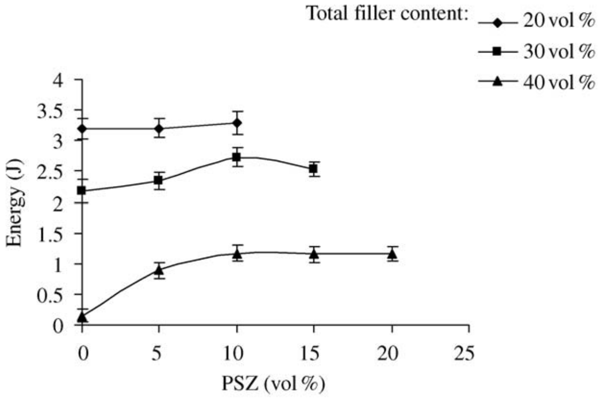

Figure 8 The effect of PSZ addition on the absorbed energy values.

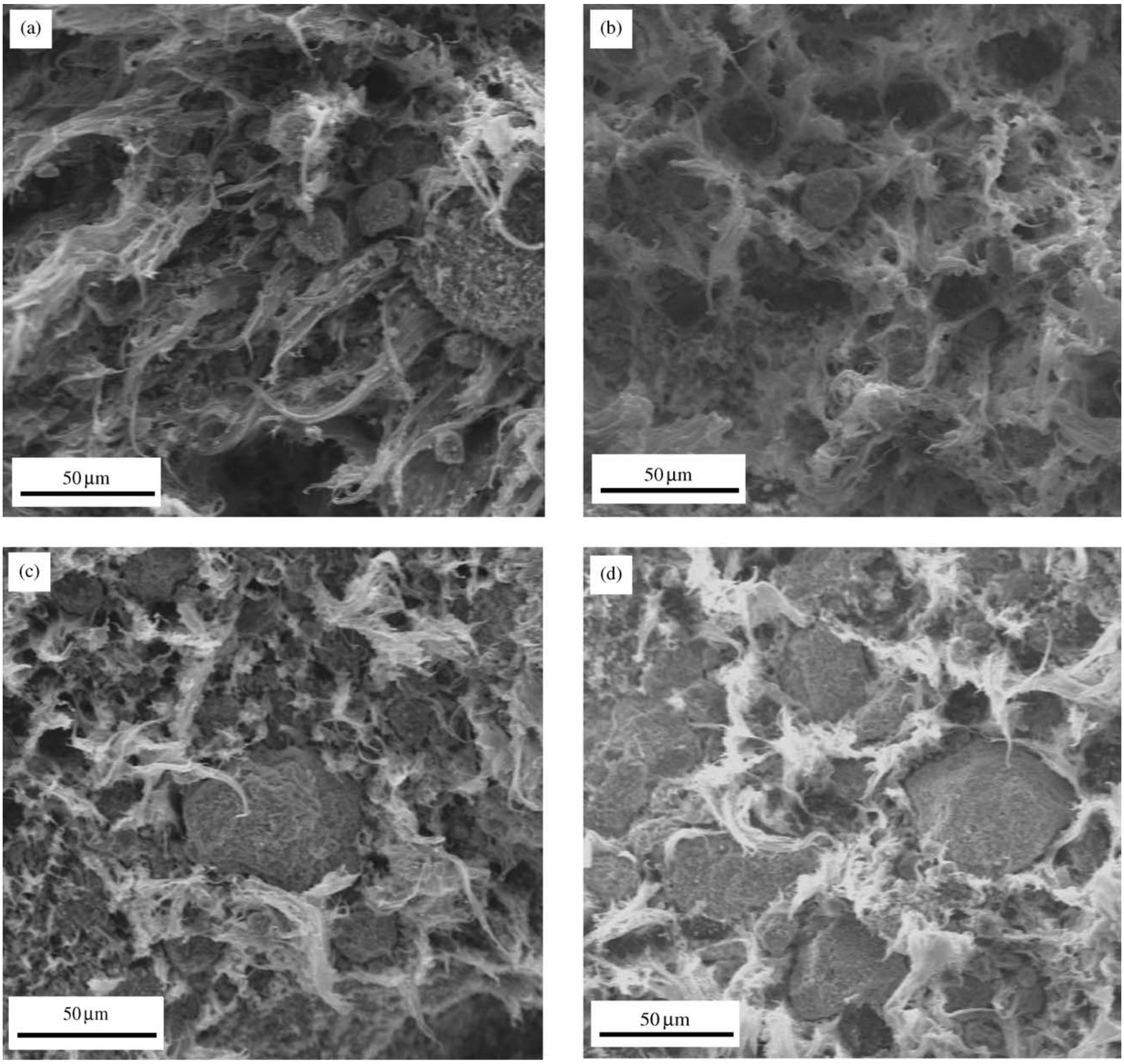

Figure 9 SEM micrographs of fractured surface: (a) 30 vol % HA; (b) 25 vol % HA + 5 vol % PSZ; (c) 20 vol % HA + 20 vol % PSZ; (d) 40 vol % HA + 10 vol % PSZ.

4. Conclusions

Partial replacement of hydroxyapatite filler particles with partially stabilized zirconia led to an increase in the strength and toughness values in HA/HDPE composite samples. The improvement in the mechanical properties was attributed to the extra energy required in extending the cracks in the PSZ-containing samples. The present study was undertaken using one particular type of PSZ particles, and additional work is underway to examine the role of PSZ particle size distribution in determining the mechanical properties.

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