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Impact behavior of hydroxyapatite reinforced polyethylene composites

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Hydroxyapatite particulate reinforced high density polyethylene composite (HA-HDPE) has been developed as a bone replacement material. The impact behavior of the composites at 37 °C has been investigated using an instrumented falling weight impact testing machine. The fracture surfaces were examined using SEM and the fracture mechanisms are discussed. It was found that the fracture toughness of HA-HDPE composites increased with HDPE molecular weight, but decreased with increasing HA volume fraction. Examination of fracture surfaces revealed weak filler/matrix interfaces which can debond easily to enable crack initiation and propagation. Increasing HA volume fraction increases the interface area, and more cracks can form and develop, thus decreasing the impact resistance of the composites. Another important factor for the impact behavior of the composites is the matrix. At higher molecular weight, HDPE is able to sustain more plastic deformation and dissipates more impact energy, hence improving the impact property.

1. Introduction

Biomaterials such as metals and ceramics are commonly used in orthopaedic surgery. However, one of the major unsolved problems is their substantially higher stiffness than cortical bone, leading to bone resorption and subsequent implant loosening. Hydroxyapatite (HA) particulate reinforced high density polyethylene (HDPE) composite (HA-HDPE) has been developed by Bonfield and co-workers [1–4] as a bone substitute. The combination of bioactive, stiff, but brittle HA, and low elastic modulus, ductile HDPE allows the composite having a good biocompatibility and adequate mechanical properties. HA-HDPE composite, with 40 vol % HA (HAPEX^{TM}), has been applied successfully clinically as middle ear prostheses and orbital floor implants [5–7]. However, all of these applications are in low load bearing regions. Previous work has investigated its mechanical properties, such as stiffness, strength, creep and fatigue resistance [8–14]. For developing a further clinical application, especially in load bearing applications, for example as a skull bone implant, the impact fracture property is of great importance. However, limited work has been carried out on its impact behavior. Hogg *et al.* [15] investigated the impact behavior of HA-HDPE composites at 20 °C, and considered the effect of the volume fraction of HA filler and molecular weight of the HDPE. They found that higher molecular weight polymer had higher impact resistance. They also found that an increase in filler content produced a decrease in impact toughness and strength with medium molecular weight HDPE, but the impact strength of the composites with high and low molecular weight polymer was little affected by the HA volume fraction.

For biomaterials, mechanical properties at 37 °C are more important since the biomaterials are aimed for human implantation and will work at body temperature. In this paper, impact resistance of HA-HDPE composites at 37 °C has been investigated using an instrumented falling weight impact technique. The effects of HA volume fraction and HDPE molecular weight on the impact behavior of the HA-HDPE composite are studied and the fracture mechanisms discussed.

2. Experimental

2.1. Materials and preparation

Synthetic HA (P218R, Plasma Biotal Ltd., UK) was used as the filler material for preparing HA-HDPE composites. The particles have a median size ($d_{0.5}$) of 3.80 μm and a specific surface area of 13.54 $m^2 g^{-1}$, while the theoretical density is 3160 $kg m^{-3}$. Two grades of high density polyethylene with different molecular weights were used as the matrix. One was a blow molding grade (HDPE1, Rigidex HM4560XP), which is used for the commercial HAPEX^{TM}; and the other was an injection molding grade (HDPE2, Rigidex HD5226EA). Both grades of HDPE were supplied by BP Chemicals Ltd. The properties of the HDPE materials are shown in Table I.

Three volume fractions of HA, namely 0%, 20% and

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TABLE I Properties of HDPE (from BP data sheets)

Material	Density kg m^{-3}	Melt flow rate g (10 min)$^{-1}$)	Molecular weight M_w
HDPE1	945	6	249 233
HDPE2	953	26	48 650

40%, were composited with each grade of HDPE, giving six combinations of HA content and HDPE grade in the study. As described in greater detail in Wang *et al.* [9], the HA and HDPE powders were blended to produce mixtures with different compositions. The mixture was compounded in a twin screw extruder (Betol BTS40L, Betol, Luton, UK) to produce the HA-HDPE composite. The compounding temperatures varied according to the grade of HDPE and HA volume fraction. The extruded composites were subsequently pelletized in a Betol pelletizer. The pelletised HA-HDPE composites were powderized in an ultra centrifugal mill (Retsch powderiser). Liquid nitrogen was used as a coolant to cool and thus embrittle the composite during powderizing. The composite powders were then compression molded into plates with a size of 145 × 145 × 8.5 mm^3, followed by annealing for 8 h at 80 °C. Impact test specimens, 60 × 60 mm^2 square plates with 4.0 mm thickness, were cut from these plates. Finally, the specimens were sterilised by γ irradiation at a nominal dose of 2.5 Mrad by Isotron Plc (Reading, UK).

2.2. Impact testing

Falling weight impact tests were performed at 37 °C according to ISO 6603/2. A CEAST system (Italy) instrumented falling weight impact tester was employed in this study. The striker mass was 15.8 kg and strike tip was a hemisphere with a diameter of 20 mm. Samples were lightly clamped onto a ring support of 40 mm in diameter. The support is in an environmental chamber, which has a temperature range of − 70–100 °C. The impact speed used was 3.13 m s^{-1}, with an impact energy of 77.47 J, for all materials except the unfilled blow mounding grade HDPE1. For this material, in order to penetrate the sample completely, a higher impact speed was used, which was 4.43 m s^{-1} giving an impact energy of 154.95 J. The striker is instrumented with a semi-conductor strain gauge. During impact test, signals were acquired by a computer using DAS4000 software. Thus the force–time curve was recorded and the energy absorption was calculated from the area under force–time curve.

2.3. Scanning electron microscope

Fracture surfaces were examined using a scanning electron microscope (SEM) (JEOL JSM6300). Samples were cut from the impacted specimens and gold-coated before examination.

3. Results

Figs. 1 and 2 show the effect of HA content and HDPE grade on the total absorbed energy and peak impact force. It can be seen that both the total absorbed energy and the peak impact force decreased with increasing HA content. For the composites with HDPE1 polymer matrix, the total absorbed energy and the maximum impact force dropped dramatically from 93.6 J and 5452.9 N for the unfilled HDPE1 to 26.0 J and 2637.8 N for the 20% HA-HDPE1 and to 7.6 J and 1155.6 N for the 40% HA-HDPE1, respectively. The higher molecular weight HDPE1 has much higher impact resistance than the lower molecular weight HDPE2. The fracture toughness and the maximum impact force decreased from 93.6 J and 5452.9 N for the unfilled HDPE1 to only 5.1 J and 927.7 N for the unfilled HDPE2, respectively.

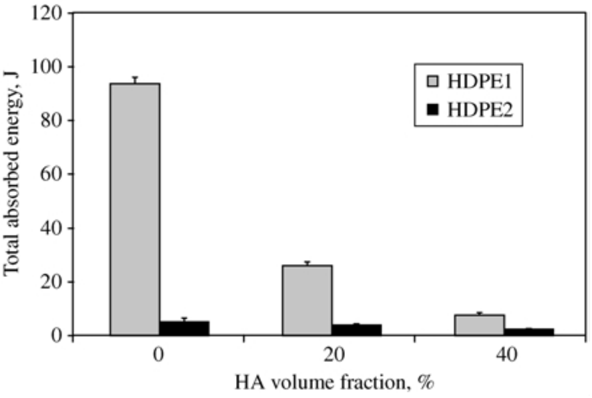

Figure 1 Effect of HA volume fraction and type of HDPE on the total absorbed energy.

Present results are consistent with previous results of Hogg *et al.* [15] in the general trend and the results with HA-HDPE2 composites are comparable with theirs. But the present results show much higher peak force and total absorbed energy for the composites with HDPE1 matrix. Many factors can affect the impact properties of HA-HDPE composites and explain the differences, among which are the molecular weight of the matrix, the filler material, processing route, sample thickness, testing temperature and testing parameters.

Post impact examination of the specimens revealed different failure modes. Figs. 3 and 4 show images of the impacted specimens of the HA-HDPE1 and HA-HDPE2 composites. The damaged area of the unfilled HDPE1 (Fig. 3(a)) is a small hole with large plastic deformation, showing ductile fracture. For the unfilled HDPE2 (Fig. 4(a)), however, the impact striker produced a clean

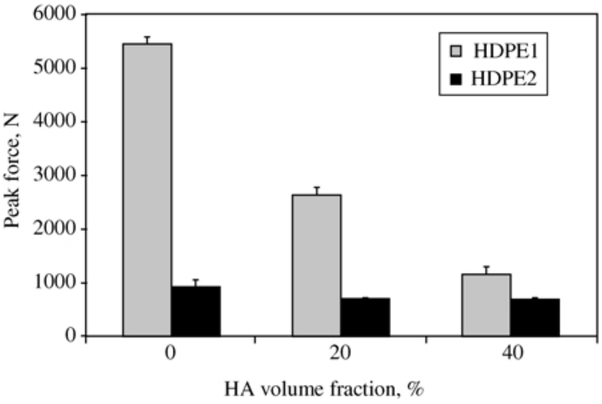

Figure 2 Effect of HA volume fraction and type of HDPE on the peak force.

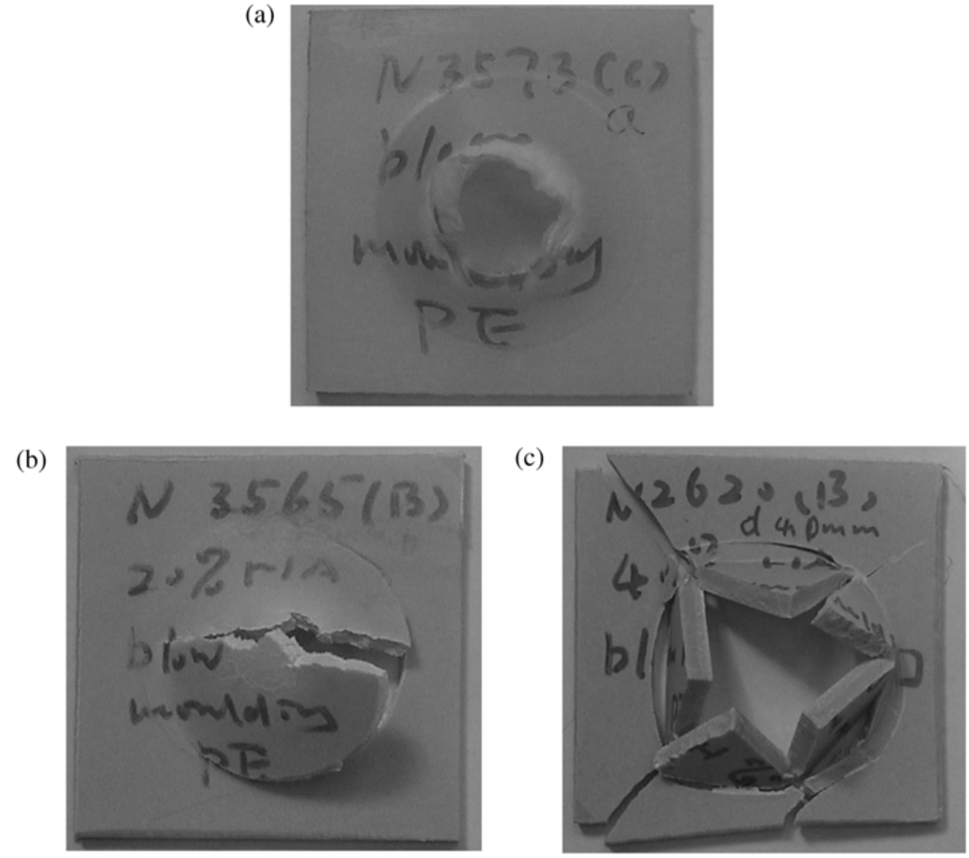

Figure 3 Damaged samples of HA-HDPE1 composites: (a) unfilled HDPE1; (b) 20 vol % HA-HDPE1; (c) 40 vol % HA-HDPE1.

punch, which indicates brittle failure with minimal plastic deformation of the matrix. Neither the 20 or 40 vol % HA-HDPE1 composites failed totally as the impacted zone is still connected with the support area of the specimens. In contrast, all the HA-HDPE2 composites produced a clean punch and the impact zone shattered into multiple small pieces. This observation indicates that the HA-HDPE1 composites are more

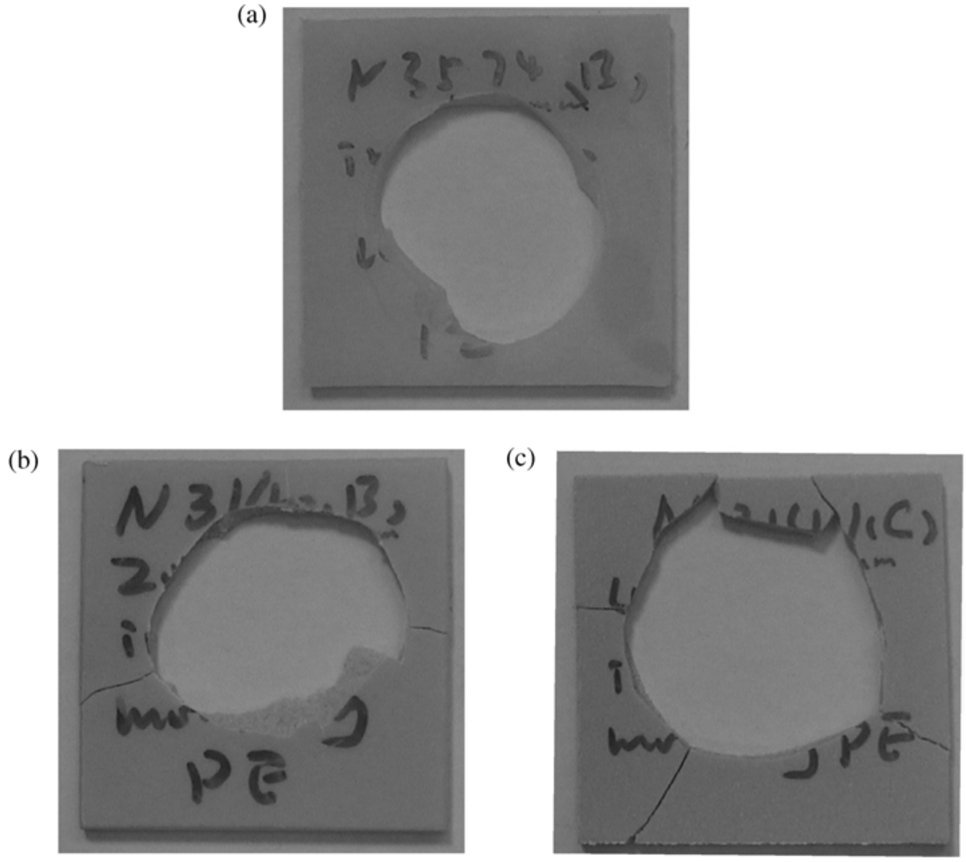

Figure 4 Damaged samples of HA-HDPE2 composites: (a) unfilled HDPE2; (b) 20 vol % HA-HDPE2; (c) 40 vol % HA-HDPE2.

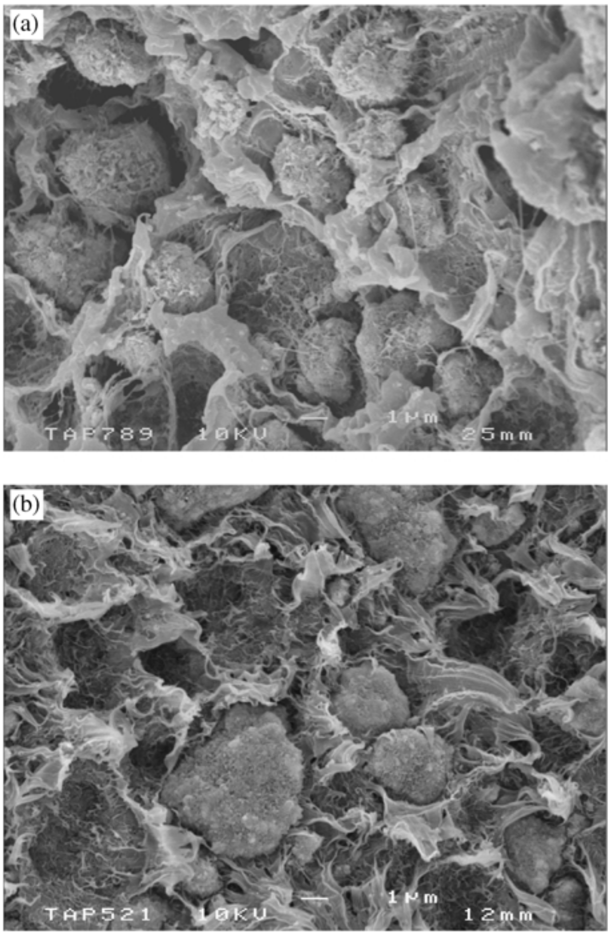

Figure 5 SEM micrographs of fractured surfaces showing debonded particles: (a) 20 vol % HA-HDPE1 and (b) 20 vol % HA-HDPE2.

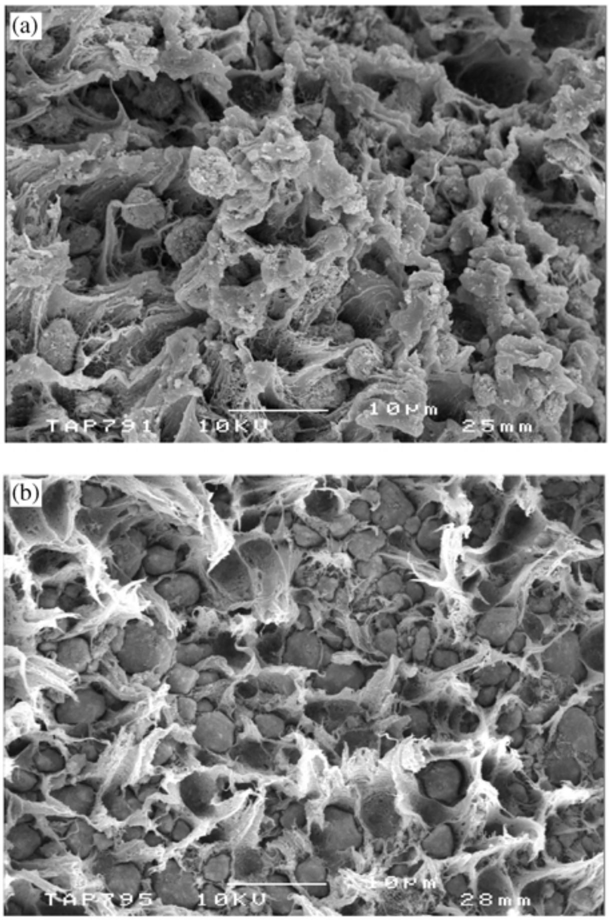

Figure 6 SEM micrographs of fractured surface of HA-HDPE1 composites with (a) 20 vol % and (b) 40 vol % HA.

ductile than the unfilled HDPE2, supporting the impact test results. When the HA volume fraction increases, the amount of ductile HDPE1 matrix decreases, leading to the decrease in impact resistance and an increase in the damaged area (Figs. 3(a)–(c)). As the HA filler increases to a critical content, the failure mode will change from ductile to brittle. For the composites with the lower molecular weight HDPE2 matrix, the decrease in the impact properties with increasing HA volume fraction is less than that for the composites with the HDPE1 matrix, which shows that polymer matrix plays an important role in the impact behavior of the HA-HDPE composites.

Fig. 5 shows SEM micrographs at high magnification of the fracture surface of the composites after the impact test. The particles can be observed clearly. There is little polymer covering the particle surfaces and gaps exist between the particles and polyethylene matrix, Furthermore, some voids are present as a result of some HA particles debonding and being pulled out during the impact test. These indicate that the interfacial bonding between the particles and the HDPE matrix are relatively weak, compared with the strength of the matrix. Figs. 6(a) and (b) show SEM photographs of the fracture surface of the HA-HDPE1 composites with 20 and 40 vol % HA, respectively. It can be seen that more polymer matrix is pulled out, producing more fibrils, in the 20 vol % than the 40 vol % composite as the increase of HA filler will lead to the reduction of polymer matrix and hence less plastic deformation of the matrix. Fig. 7 shows the fracture surface of composites with HDPE2 matrix, with 20% and 40% HA respectively at the same magnification as in Fig. 6. Comparing Figs. 6 and 7, it is clear that due to the less ductile nature of the HDPE2 matrix, smaller amounts of polymer matrix were pulled out and the plastic deformation of the matrix was reduced, leading to substantially lower absorbed impact energy and resulting in the brittle failure mode in the HA-HDPE2 composites.

4. Discussion

In a rigid particulate filled polymer composite, the main fracture mechanisms include particle-matrix debonding, void formation at particle/matrix interface, crack initiation, propagation and matrix plastic deformation [16–18]. Furthermore, particle failure may also occur, which was not observed in the present study. In general, the impact resistance of such composites decreases with the addition of the rigid particles. However, for some composites having a strong adhesion between filler and matrix, such as in composites with filler surface modification with coupling agent, the impact properties can be improved by addition of rigid particles [16–23]. But at high volume fractions, the ductility of HA-HDPE material was not improved by increased adhesion at the interface using silane coupling [24].

In the present study, the filler was not surface treated due to biocompatibility considerations, thus only a mechanical interlock exists at the particle/matrix interface. This mechanical interlock is produced by shrinkage

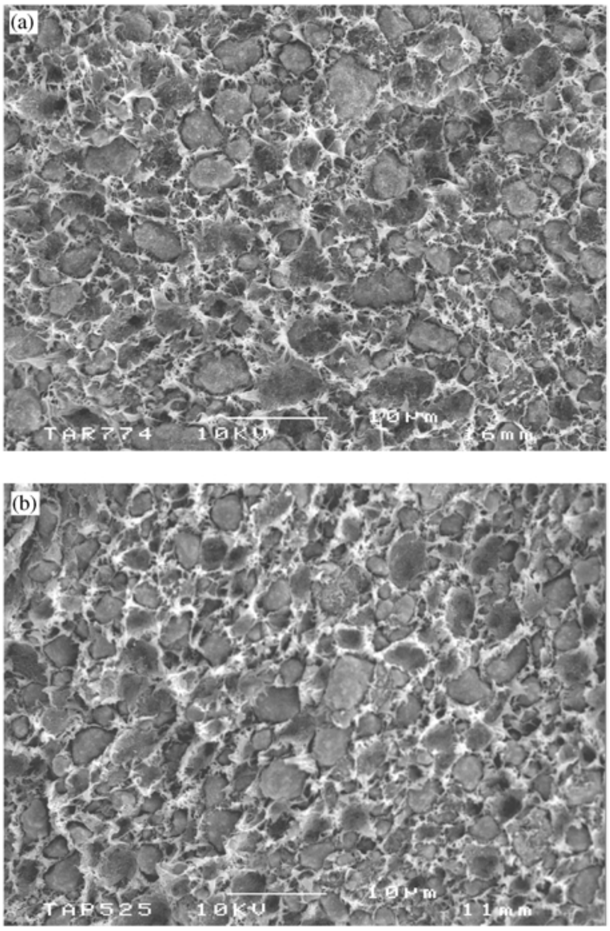

Figure 7 SEM micrographs of fractured surface of HA-HDPE2 composites with (a) 20 vol % and (b) 40 vol % HA.

of the polyethylene onto the hydroxyapatite particles during cooling from the compounding temperature. Therefore the adhesion between the filler particle and the matrix is poor, giving a weak interface bond. Predictive modelling of failure process of HA-HDPE using finite element analysis showed that the maximum direct stress is at the interface at the pole of the particle [25, 26]. The direction of this maximum direct stress is the direction of the applied stress. It is acting to pull the interface apart, leading to interfacial failure. The weak adhesion between HA and HDPE makes it easy for the particles to debond from the polymer matrix and enabling voids to form at the particle/matrix interface at the pole. The crack initiates and propagates along the particle/matrix interface more easily than through the polymer matrix since the weak interface is much less effective at resisting crack propagation than the matrix and also because of stress concentration at the interface.

As the HA volume increases, the amount of the polymer matrix is reduced, leading to less dissipation of the impact energy by the ductile matrix. Furthermore, the weak filler/matrix interface area increases and more voids are formed, again assisting crack initiation and propagation. In addition, FEA modelling has shown that the stress concentration factor increases with HA volume fraction (when HA $\geq 15\%$) [25, 26]. Even when other conditions are the same, higher HA volume fraction would lead to higher stress at the interface, making it easier to fracture. Therefore, the impact strength and the total absorbed energy decreased as HA volume fraction increased. Similar strength reduction effects from increasing the filler content have been reported in other composites with poor interfacial bonding, such as in the $CaCO_3$-HDPE system [27, 28], Kaolin-HDPE system [18], and $CaCO_3$-polypropylene composites [29]. For the composites with higher molecular weight HDPE1 matrix, the ductile matrix undergoes larger plastic deformation and dissipates more impact energy compared with the less ductile HDPE2 matrix in the HA-HDPE2 composite, resulting in better impact resistance for HDPE1 based composites.

5. Conclusions

The total absorbed energy and impact strength of HA-HDPE composites decreased with increasing HA content. The composite with higher molecular weight polyethylene matrix has higher impact resistance than that of the composites with lower molecular weight HDPE. The decrease of the impact resistance with increasing HA volume fraction is attributed to the higher stress concentration factor and the increase in weak filler/matrix interfaces which leads to easier voids formation and crack propagation, and also to the decrease in the amount of polymer matrix leading to less impact energy dissipation.

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