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Fracture Behavior of Zeolite-filled High Density Polyethylene Based on Energy Partitioning Work of Fracture

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Abstract

Novel biomaterials from natural zeolite-filled high-density polyethylene (HDPE) have been successfully formed through injection molding techniques at a barrel temperature of 160^{O}C and with a barrel holding time of 2 minutes. Fracture behavior of a quasi-static state was investigated using the method of essential work of fracture (EWF) in a double edge-notched tensile test. The results showed that the fracture behavior depend on the zeolite content mixture. The fracture specific essential work to initiation of composites is lower than original HDPE without any material additions. Increasing the zeolite percentage causes a fracture specific work to crack propagation and energy dissipation during crack propagation decreased. However, the energy dissipation during yielding increases upon the addition of 15 wt.% zeolite and subsequent decline gradually. In a case of adding a 5 wt.% zeolite, fracture occurred in the state of transition to ductile, but the zeolite addition above 5 wt.% resulted a fracture behavior leading to brittle which was characterized by the work to initiate crack higher than the work in the plastic deformation zone.

Keywords: high-density polyethylene, fracture and fatigue, zeolite, facture toughness, essential work of fracture

Introduction

Many studies on the use of high density polyethylene (HDPE) as bone implant materials, such as skull implants [1, 2], has been developed broadly. HDPE is highly biocompatible, inert, stable in the human body [3,4,5] and it is radiolucent on CT scan activity [2]. Good biocompatibility and flexibility of HDPE makes this material an excellent alternative to be the skull bone implants [6]. Bonfield *et al.* [7,8] has developed a hydroxyapatite (HA) reinforced HDPE composites. It has a combination of HA properties, namely, bioactive, rigid and brittle and also has a HDPE characteristic which has a low modulus of elasticity and it is ductile [9]. The study of HA-HDPE composites have been carried out [9,10,11]. The existences of hydroxyapatite causing the HA-HDPE composites become bioactive. However, HA is very expensive so it is necessary to find a new material that could replace the role of HA and of course can reduce product cost.

Zeolite is the right material that could be used to respond to the needs of this kind of new material. Zeolite is an inorganic alumino-silicate crystalline which is composed by a tetrahedral of SiO_4 and AlO_4^-. Many years, natural zeolites are widely used in chemistry because zeolite has an ability of ion exchange and separation properties [12,13]. During its development to the present, either the natural or the synthetic zeolites are widely used as biomaterial because they has a biocompatible [14] and bioactive [15,16,17] characteristic. The existence of zeolite in polymer matrix composites could protect the polymer from a degradation process due to the ultraviolet influence [18]. Another researcher [19] using zeolite as an antimicrobial agent combined with polyurethane and silicone rubber to form a biomedical application composite.

Zeolite particles composed with a high-density polyethylene is a new biomaterial as an alternative material to replace the currently existing biomaterials, namely titanium and its alloys, poly-methyl methacrylate (PMMA) and HA-HDPE composites. As a new biomaterial for skull bone reconstructions, it is necessary to investigate the material fracture behavior [9,11]. This is associated with the skull function to protect important parts in human body, which is protecting the brain from head injuries that could endanger human life due to head fractures [11]. In this study, fracture behavior of zeolite filled in high-density polyethylene was investigated in a quasi-static condition using the essential work of fracture (EWF) method. The fracture behavior has been investigated in the zeolite content variation up to 20 wt.%. Investigation was performed at room temperature.

Material and Methods

The material used in this research is a natural zeolite deposits obtained from Malang, East Java, Indonesia. This zeolite composition are SiO_2 (72.6%), Al_2O_3 (10.55%), Fe_2O_3 (2.58%), TiO (0.16%), CaO (1.40%), MgO (1.00%), K_2O (2.45%) and Na_2O (1.29%). Zeolite rocks was crushed and then strained until 100 mesh size. Zeolite powder was calcined for 3 hours long at a temperature of 300°C and then cooled by means of contacting the zeolite powder directly to the surrounding air. An Injection molding grade HDPE granule supplied by PT. Lotte Chemical Titan Nusantara Indonesia was transformed into powder by a mechanical process. The HDPE powder was then strained to 80 mesh size. The calcined zeolite powder and HDPE powder were mixed together in a dry condition with a zeolite composition of 0 wt.%, 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%. The double edge notched tension (DENT) composite specimen dimensions is 80 mm x 50 mm x 3 mm were formed by injection molding techniques. The injection process was done in line with the specimen axis at a 160°C barrel temperature and holding the specimen product about 2 minutes in the mold for a cooling process. The injection process time is about 2 minutes and 10 seconds. The DENT specimen length variation is 9, 10.5, 12, 13.5 and 15 mm.

Natural Zeolite and HDPE Composites Characterization

The DENT specimens were given a tensile load until the specimen break of at a 2 mm/min crosshead speed. The tests were carried out using a universal testing machine equipped with a controlled microcomputer. The tensile direction is given along the specimen axis and at a room temperature. The composite fracture behavior was evaluated by the method of essential work of fracture which dividing the total work that led to the specimen fracture (W_f) into two parts. First, is the essential work (W_e) which was happened in the fracture process zone (FPZ) to form a new fracture surface. Second, is the non-essential work (W_p) constituted the work for plastic deformation around the ligament area. This concept is expressed in the following equation [20, 21, 22]:

$$W_f = W_e + W_p = w_e.t.\,l + \beta w_p.t.l^2 \tag{1}$$

$$w_f = \frac{W_f}{t.l} = w_e + \beta w_p.l \tag{2}$$

where w_f, w_e, βw_p, l, t are the total specific work of fracture, specific essential work of fracture, specific non-essential work of fracture, ligament length, specimen thickness, respectively. The β parameter is the plastic area shape factor. Specimen load on the test was plotted against the specimen length displacement. The W_f is the area under the load-displacement curve and is obtained through the integration of the load-displacement curve. Plotting w_f against the ligament length is a straight line that the intercept on w_f at $l = 0$ and the slope are w_e and βw_p, respectively. To obtain the condition of plane stress fracture, the specimen dimensions are based on the following conditions [23, 24, 25, 26]:

$$(3\text{-}5)t \leq l \leq \min\left(\frac{W}{3} or\, 2rp\right) \tag{3}$$

where W and $2rp$ are the width of the specimen and size of the plastic zone, respectively.

Results and Discussion

The load-displacement curve typical shape in a plane stress condition of DENT with 5 % zeolite weight content filled HDPE specimen were presented in Figure 1. There was a similarity of load-displacement curve as mentioned in Mai's research [27]. Thus, the EWF method can be used to analyze this research result. From Figure 1 it can be seen that the area under the curve increased when the ligament length increase. In all test composite result, the load displacement performance for all zeolite content has always a similar curve shape as seen in Figure 1.

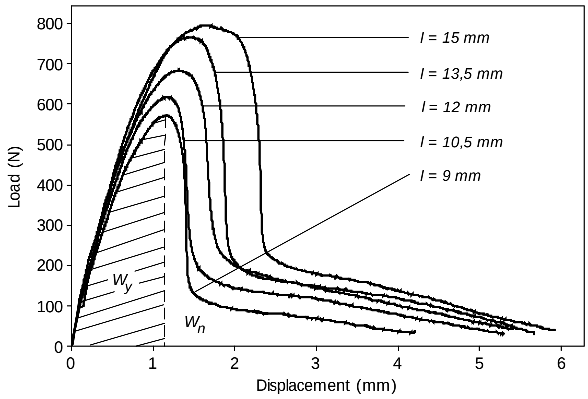

Figure 1: Load-displacement curve of 5*wt.*% zeolite

The w_f versus ligament length under a zeolite content variation plotting is shown in Figure 2. Table 1 shows the extrapolation w_f line with an intercept on zero ligament length, w_e, and the slope, βw_p.

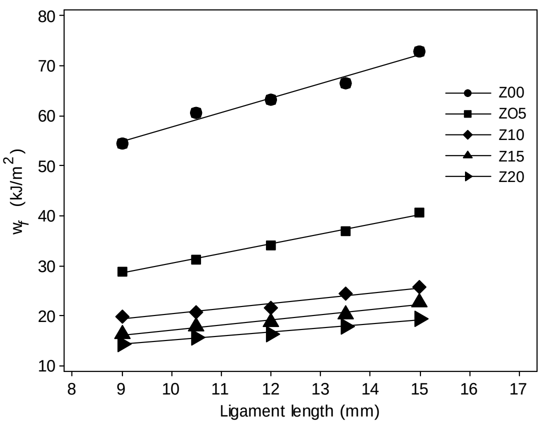

Figure 2: The specific work of fracture as a ligament length function, where Z00, Z05, Z10, Z15 and Z20 are the zeolite content of 0 wt.%, 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%, respectively.

Table 1: The fracture parameter of zeolite-filled HDPE in the zeolite content variation

Zeolite/HDPE (wt %)	w_e (KJ/m^2)	βw_p (MJ/m^3)	R^2
100/0	29.015	2.8729	0.9779
95/5	6.5018	0.9377	0.9954
90/10	9.7794	1.0514	0.9537
85/15	7.1687	0.9954	0.9741
80/20	6.8991	0.8154	0.9884

Refer to Figure 1 and the DENT specimen result fracture test, it is obvious that the ligament was full yielded at the maximum load and a crack initiated was also identified. After reaching this maximum load, the load decreases as the crack propagated by advanced of necking and followed by tearing until the material fractured. Furthermore, EWF concept is based on the energy partitioning work of fracture proposed by Karger-Kockis *et al.* [25, 28] and Mouzakis *et al.* [29], which is separating the total work of fracture into two work criteria. The energy for yielding that contributed to the crack initiation, W_y, and the energy for necking subsequent tearing that contributed to the crack propagation, W_n (see Figure 1). Based on the energy partitioning methods, it can be written as follows:

$$W_f = W_y + W_n \quad (4)$$

$$w_f = (w_{e,y} + \beta_y w_{p,y}.\ l) + (w_{e,n} + \beta_n w_{p,n}.l) \quad (5)$$

From equation (5), it can be concluded:

$$w_e = w_{e,y} + w_{e,n} \quad (6)$$

$$\beta w_p. = \beta_y w_{p,y} + \beta_n w_{p,n} \quad (7)$$

where $w_{e,y}$ and $w_{e,n}$ are the specific essential work for yielding/crack initiation and the specific essential work for necking subsequent tearing (crack propagation), respectively. While the $w_{p,y}$ and $w_{p,n}$ are the volumetric energy dissipated during yielding/crack initiation and the necking followed by tearing (crack propagation), respectively. The β_y and β_n are the shape factor related to the plastic form zone during the yielding/crack initiation and the tearing process. Another author used $w_{e,y}$ and $w_{e,n}$ as a resistance parameter to crack initiation and crack propagation[29].

Two terms of energy w_y and w_n are separately plotted against the ligament length, as shown in Figure 3. The work of fracture is the intercept between the zero ligament length and the specific non-essential work of fracture which is the linier regression line slope. The w_y - l and w_n - l diagram has a good linearity relationship with the R^2 value, which is about 0.94 to 0.99, as shown in Figure 3.

The specific essential work of fracture for yielding/crack initiation was decreased by the presence of zeolite, as shown in Figure 4a. The biggest specific essential work of fracture value decline (38.76%) is on the 5 wt.% zeolite addition. For all composites specimen tested, the $w_{e,y}$ value fluctuations is nearly constant by the zeolite addition up to 20 wt.%. This phenomenon indicates that the essential work for crack initiation was very sensitive to crack micro-mechanism by the presence of zeolite in the host matrix but would be insensitive for a further zeolite addition. For the zeolite content addition above 5 wt.% causes the $w_{e,n}$ value dropped sharply to 76.4% of the unfilled matrix. Further zeolite content addition 5 wt.% to 20 wt.% would gradually decreased the $w_{e,n}$ value. There is an indication that the addition of zeolite causes a decrease in energy consumption for yielding and decreased the resistance to crack initiation. Presumably it is due to an increase in the slip interface intensity between the zeolite particles and the matrix when the composite was loaded. Crack initiation represents the stress level where micro-cracking starts happening. On the other hand, the addition of zeolite particles content, which means reducing the composite matrix percentage causing a smaller distance between the zeolite particles. Voids initiated by the separation of the matrix/particle interface grew during a further elongation due to external tensile load. The small distance between the particles accelerated the coalescence of voids, crack propagation and finally the fracture time occurs earlier.

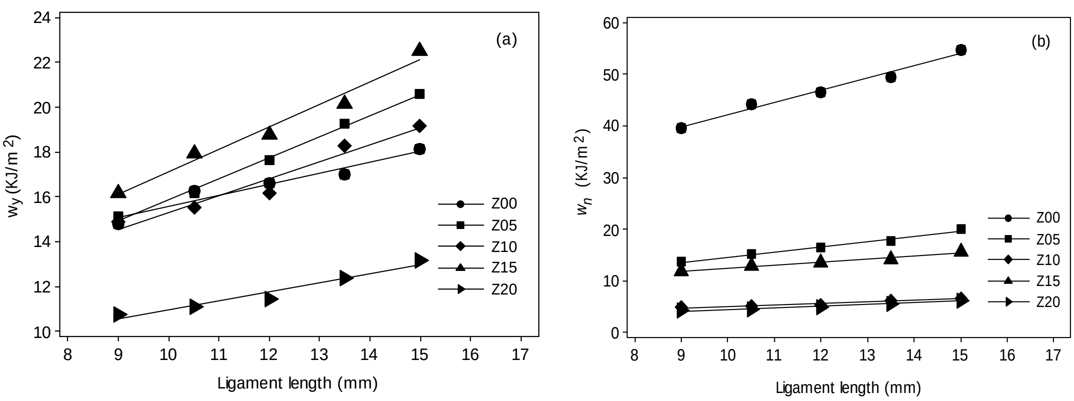

Figure 3: Specific EWF for yielding/crack initiation (a) and necking subsequent tearing (crack propagation)

The energy amount absorb for necking subsequent tearing decreased by the decrease of zeolite percentage content. This means that the material resistance to crack propagation was decreased. The $w_{e,n}$ value in the matrix without any zeolite mixed is greater than $w_{e,y}$ value. This is an indication that the resistance to crack propagation is greater than crack initiation. A contradiction occurs in composites with a zeolite content above 5 wt.%. The greatest contribution to the essential work is given by the $w_{e,y}$ than the $w_{e,n}$. It means that in HDPE mixed with zeolite, the energy absorb to initiate crack is greater than the energy required for crack growth to fracture process. The addition of zeolite increases the contact area between the particle and the matrix which promotes the voids around the particle. Cracks propagate to the point where numerous voids bunch together and finally composite become weakened and no longer could support a specific load applied.

Non-essential work of fracture for yielding and necking subsequent tearing dependent on zeolite filled could be seem in Figure 4b. The zeolite addition until 5 wt.% lead the $\beta_y w_{p,y}$ value increased to 89.2%. This means that there is a significant energy dissipated used in plastic deformation zone. By adding zeolite above 5 wt.% resulted a gradual decrease of $\beta_y w_{p,y}$ value, which means a lower energy needed for the work in the plastic deformation zone. While on the addition of zeolite content up to 10 wt.% causes the $\beta_n w_{p,n}$ value declined sharply to 87.63%. Furthermore, a zeolite content addition from 10 wt.% to 20 wt.% would give a nearly constant $\beta_n w_{p,n}$ value. In the zeolite filled HDPE, the energy dissipated during the process of ligament yielding to crack initiation is greater than the crack propagation.

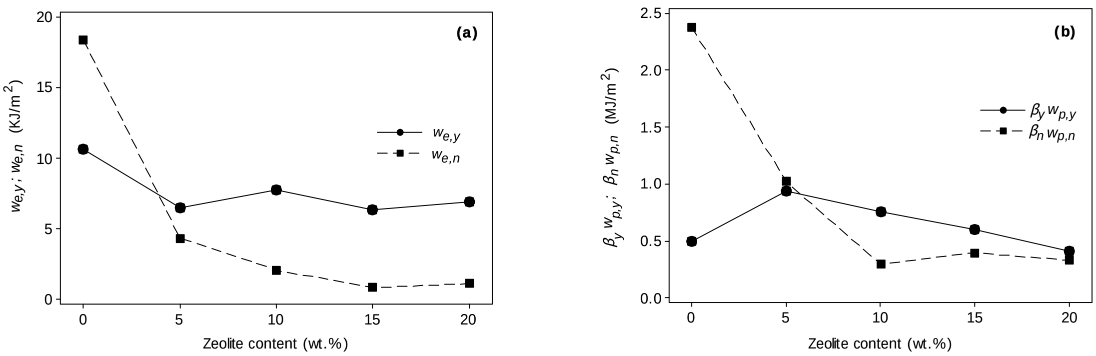

Figure 4: The influence of zeolite content on fracture parameter essential work (a) and non-essential work of fracture parameter (b).

The essential work of fracture estimation through the crack opening displacement (COD) proposed by Hashemi and O'Brien [30] with a relationship of $w_e = \sigma_y \delta_c$ where δ_c and σ_y were the COD and the material yield stress, respectively. This relationship also applies to the implementation of the fracture partitioning work concept [28, 31, 32] so that the $w_{e,y} = \sigma_y \delta_{c,y}$ and the $w_{e,n} = \sigma_y \delta_{c,n}$, where $\delta_{c,y}$ is the COD for yielding and $\delta_{c,n}$ is the COD for necking subsequent tearing. The COD is obtained from the linearity of the relationship between the displacement and ligament length. Referring to Figure 1, x_b the displacement at break, x_y is the displacement at yield point and x_n is displacement at necking subsequent tearing (x_b-x_y). Plotting x_y and x_n toward the ligament length would be a straight line with an intercept at the zero ligament length which is the $\delta_{e,y}$ and the $\delta_{e,n}$.

Plotting the COD as a function of the zeolite content is shown in Figure 5. The COD in the zeolite content of 5 wt.% showed a unique phenomenon. An addition of 5 wt.% zeolite lead to COD for yielding/crack-initiation decreased at the lowest value but the COD for tearing increased at the highest value. Firstly, this is an indication that the crack tip blunting effectively resist the onset of the crack propagation. Secondly, the interface adhesion zeolite particle and HDPE matrix can efficiently transfer the stress of HDPE matrix to the zeolite particle. On the other hand, COD is related to the plastic work after full yielding occurs [33]. There is a similarity between the $\delta_{e,y}$ trend in Figure 5 compare with the $w_{e,y}$ in Figure 4a. The COD could be considered as a resistance criteria toward the crack initiation [28].

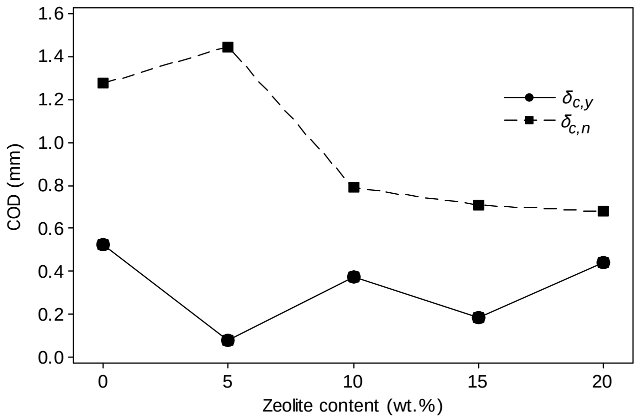

Figure 5: The influence of zeolite content on COD in zeolite-HDPE composites

The ratio between the essential to non-essential work of fracture in all the ligaments length shows a similar trend. The ratio of work of fracture on the ligament length 9 mm is shown in Figure 6. On the 5 wt.% zeolite addition, all of the energy ratio decreased and its value was lower than 1.0. It means that the energy consume for the plastic work that performed outside the plastic deformation zone is greater than energy consumed when performed inside the plastic deformation zone to create a new crack surfaces. It means that an irreversible deformation takes place in the outer fracture zone during both the crack initiation and the crack propagation process.

The energy dissipated decreases ($w_{e,y}/\beta_y w_{p,y} > 1$) by the addition of 10 wt.% zeolite above, it means that the energy used in the plastic deformation zone is lower than the essential energy to initiate the crack. During the crack propagation, the $w_{e,n}/\beta_n w_{p,n}$ ratio increased for the 10 wt.% zeolite content and for the further addition of natural zeolite would cause the energy value ratio. Energy was dissipated to non-essential work.

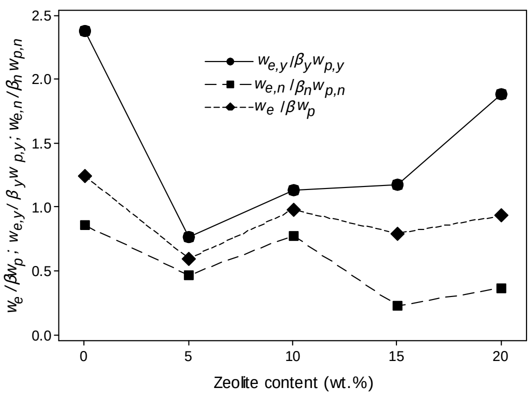

Figure 6: The essential and non-essential work of fracture ratio as a function of zeolite content

Conclusions

Energy partitioned work of fracture has been used to analyze the fracture behavior of zeolite-filled HDPE. Specific essential and non-essential works were not constant but dependent on the zeolite content. Specific essential work of the resistance to crack initiation ($w_{e,y}$) of composite is relatively constant even though its value is lower than that of unfilled HDPE. Similarities between $w_{e,y}$ and $\delta_{c,y}$ trends showed that $\delta_{c,y}$ can be used as criteria of resistance to crack initiation. Although the value of $\delta_{c,n}$ of the 5 wt.% zeolite content is greater than unfilled HDPE, the $w_{e,n}$ of unfilled HDPE is greater than the $w_{e,n}$ of composite containing 5 wt.% zeolite. This indicates that σ_y of unfilled HDPE is higher than the σ_y of 5 wt.% zeolite filled HDPE. The presence of zeolite can lead to irreversible slip between the particles and matrix interface and would occur more quickly. Increasing energy ratio indicates that the energy is used to form new crack surfaces rather than using energy in the plastic deformation zone. This is an indication that the fracture behavior of the composite is leading to a brittle fracture material condition.

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