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Morphological and Mechanical Properties of Natural Zeolite-High Density Polyethylene Composite

Purnomo[1,2], Rudy Soenoko[3], Yudy Surya Irawan[3], Agus Suprapto[4]
[1] PhD Student of Mechanical Engineering Brawijaya University, Malang-Indonesia
[2] Universitas Muhammadiyah Semarang, Mechanical Engineering Department, Engineering Faculty, 50273, Semarang-Indonesia
[3]Brawijaya University, Mechanical Engineering Department, Engineering Faculty, 65145, Malang Indonesia
[4] Merdeka University, Mechanical Engineering Department, Engineering Faculty 65115, Malang Indonesia
E-mail address: purnomo@unimus.ac.id

Abstract

This study focused on the morphology and mechanical properties of novel implant skull reconstruction from the natural zeolite-high density polyethylene (HDPE). The composites were formed through injection molding techniques. Scanning electron microscopy (SEM) was used to investigate the morphology of composites. The composite morphology showed the present of aggregate. An increase in the content of the particles resulted in lower the inter-particle distance. Ductility and yield stress decreased with increasing content of zeolite. On the other hand, Young's modulus increased in line with the increasing zeolite content. Tensile stress increased with addition of zeolite content of 5 wt.% and decreased in further additions. This indicated that the highest adhesion strength of the interface occurs at a concentration of 5 wt.% zeolite. Therefore, the mechanism of stress transfer from the matrix to the filler occurs effectively.

Keywords: morphology, mechanical properties, high-density polyethylene, zeolite, composites

Introduction

High density polyethylene (HDPE) is a biocompatible, inert, non-toxic and has been widely used in the fields of orthopedics such as skull reconstruction implant to repair the skull defect. However, HDPE has limitations in the use of, for example, the low stiffness and low strength. To overcome its limitation in the low stiffness, rigid particles possessing a Young's modulus much higher than the polymer is added as a filler in order to form a composite that has a stiffness greater than the neat matrix [1, 2, 3, 4, 5]. Bioactive particles such as hydroxyapatite were used as filler [6, 7, 8, 9] to obtain bioactive composite. To avoid the occurrence of accelerated degradation, HDPE should be kept out of direct ultraviolet radiation [10].

To respond to these problems, it is very important to develop a new filler material that is capable to increase resistance of HDPE matrix to ultraviolet radiation and in accordance with the requirements as biomaterials are biocompatible, bioactive and non-toxic. Both natural and synthetic zeolite are the right material to be used because they have all the requirements, i.e., biocompatible and non-toxic [11], bioactive [12, 13, 14] and are able to protect the polymer matrix from degradation due to ultraviolet radiation [15]. Another advantage of the use of zeolite is its abundant availability in nature with low prices that reduce the cost of making. However, the zeolites have a negative thermal expansion coefficient [16, 17, 18] and no information about the structure and mechanical properties of natural zeolite-filled HDPE is available. Research on the mechanical properties of bone implants performed through characterization of the tensile strength and stiffness [19, 20, 21]. The low mechanical properties causes the material can only be used for low load-bearing applications [22]. For load-bearing implants such as skull reconstruction implants, it is important to increase the stiffness and strength of materials [23]. In this study, the zeolite-filled HDPE was investigated as skull reconstruction implants. As novel biomaterials for bone implant applications, it is necessary to understand the mechanical properties of zeolite-filled HDPE. In this study, the morphological and mechanical properties of zeolite-filled HDPE were investigated as skull reconstruction implants. As novel biomaterials for bone implant applications, it is necessary to understand the mechanical properties of zeolite-filled HDPE. The morphology is very important to learn in order to support the analysis of the mechanical properties of the composite.

Material and Methods

Materials and Sample Preparation

Commercial high density polyethylene (HDPE) was used as the matrix, while the natural zeolite was used as filler. Natural zeolite composed of 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%). Natural zeolite powder with particle size distribution as shown in Figure 1 was calcined at a temperature of 300_oC for 3 hours. The HDPE powder with particle size 177-250 µm was mixed with calcined zeolite powder. The zeolite and HDPE powder were mixed in dry conditions and the mass ratio of zeolite to HDPE was set as 0/100, 5/95, 10/90, 15/85 and 20/80. The blend powders were injection-molded into dumbbell shape by using injection molding machine. The injection parameters were set at barrel temperature of 160_oC. The blends in the barrel were held for about 2 minutes prior to injection. Composites were cooled in air atmosphere and maintained no contact with direct ultraviolet light.

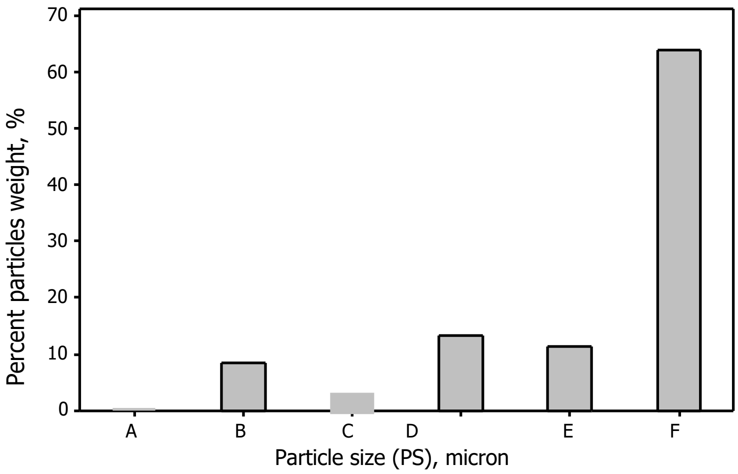

Figure 1: Particles size distribution of zeolite, where A, B, C, D, E and F are 177≤PS<250, 149≤PS<177, 125≤PS<149, 99≤PS<125, 74≤PS<99 and PS<74, respectively.

Tensile Testing

Mechanical properties of zeolite/HDPE were evaluated by tensile testing on dumbbell shaped specimens. The tests were conducted according to ISO 527 using a universal testing machine at a cross head speed of 2 mm/min. All composites were given a tensile load to a complete failure and the elongation of the specimen is calculated from the crosshead displacement. All mechanical tests were performed at room temperature.

Morphological Analysis

The distribution and dispersion of zeolite particles in HDPE were examined using light microscope (LM). The specimens taken after injection molding were prepared included sectioning, mounting and polishing. The morphological analyses of the tensile fracture surface were carried out by FEI Inspect S50 scanning electron microscope. Samples were cut from the fracture tensile surface and sputter-coated with thin gold layer before investigation.

Results and Discussion

Zeolite Distribution in HDPE

Distributions of zeolite particles in the composite specimens were observed using a light microscope as shown in Figure 2. It appears that zeolite particles are well distributed in the HDPE matrix. However, the particles are not dispersed well. Aggregate particles present and increase in number with the increasing amount of zeolite content.

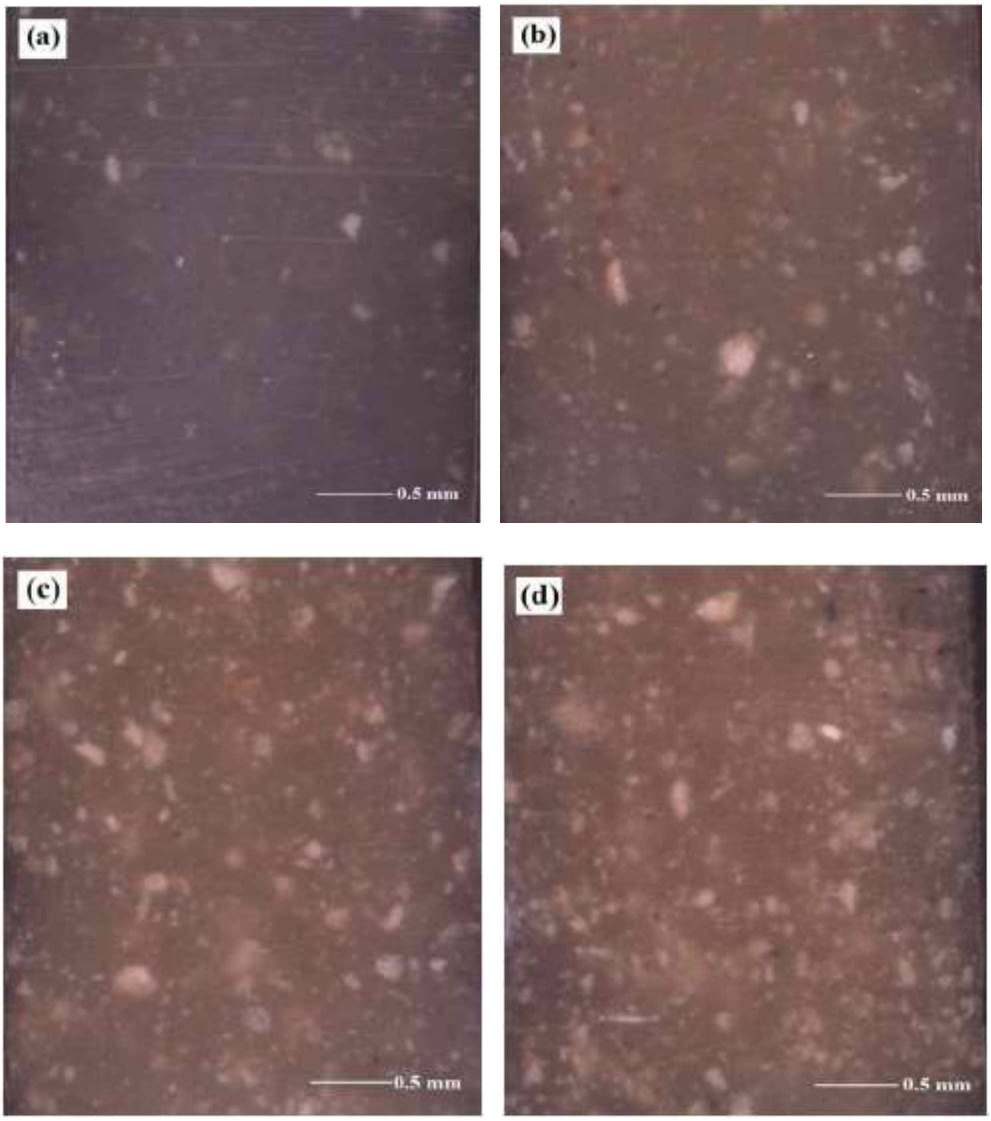

Figure 2: Zeolite/HDPE composite cross section which showed the distribution of the zeolite in after injection on zeolite content variations: (a) 5 wt.%, (B) 10 wt.%, (C) 15 wt.%, And (d) 20 wt.%.

Tensile Properties

The effects of adding zeolite content on elongation at break are shown in Figure 3. It can be seen clearly that the addition of zeolite content reduces the maximum displacement. The ratio of elongation at break (x_b) to the maximum load (F_{max}) is also shown in Figure 3. It is clearly shown that increasing the zeolite content lowers the elongation per applied load, which means a decline in the composite ductility. These results indicate that the increased of zeolite content causes a gradual transition behavior from ductile to brittle.

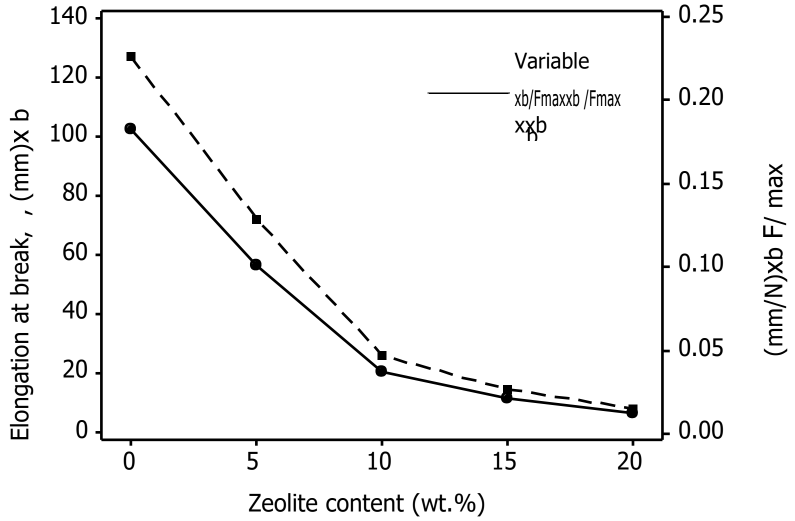

Figure 3: Zeolite Content Influence on The Elongation At Break And X_b/F_{max} Ratio

Tensile strength of composites on different content of zeolite is shown in Figure 4. It is clearly shown that the tensile strength of composite increased slightly by the addition of 5 wt% of zeolite into HDPE matrix. However, the addition of zeolite content above 5 wt%, the tensile strength decreased gradually. This indicates the good adhesion at the interface of zeolite particles/HDPE on the weight fraction of 5 wt% zeolite. Adhesion strength at the interface causes an effective stress transfer mechanism from the HDPE matrix to the zeolite particle. The addition of zeolite particles above 5 wt% encourages the formation of many aggregates of zeolite particles in the HDPE matrix. The aggregates have poor bonded so that the particles will undergo de-bonding and not capable to carry the load. This causes a decrease in the strength of the material by increasing the content of the zeolite.

The yield stresses are plotted as a function of zeolite content as shown in Figure 5. Yield stress decreased sharply (57.65%) by the presence of the zeolite particles. Furthermore, addition of zeolite content more than 5 wt% did not cause significant changes in the yield stress. The decrease of the yield stress was due to the early de-bonding of the filler particles from the host matrix.

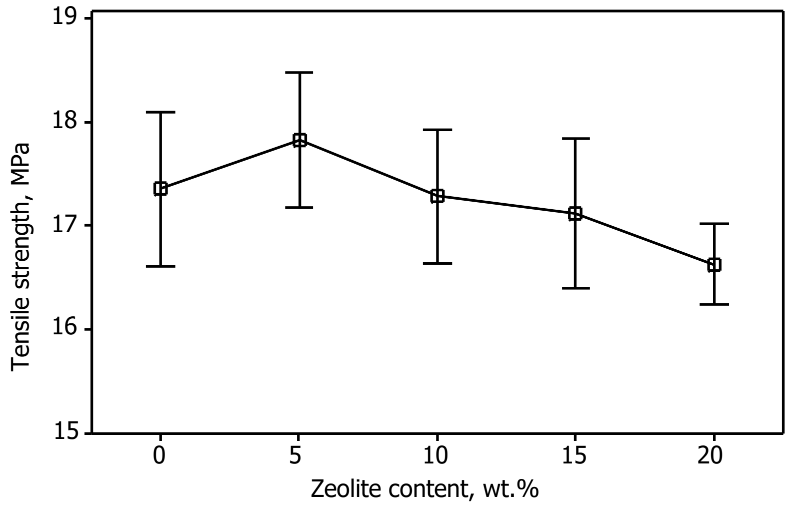

Figure 4: The Influence of Zeolite Content on The Tensile Strength of Composite

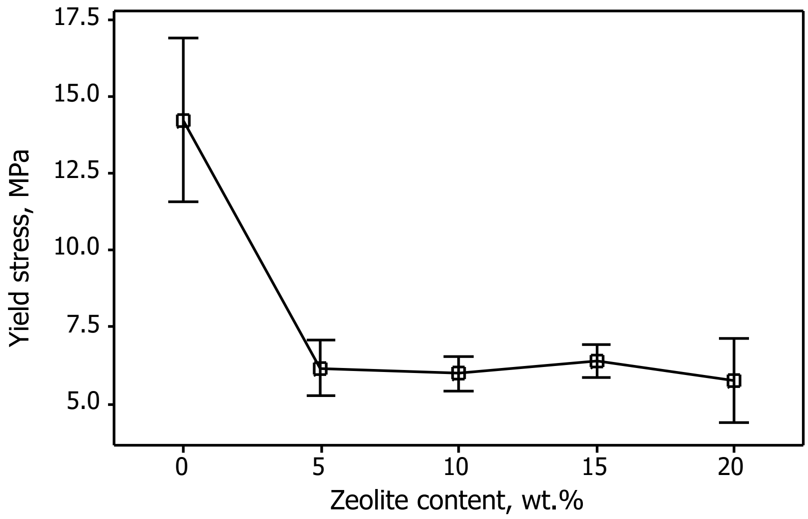

Figure 5: Composites Yield Stress At Different Filler Content.

Young's modulus of composites increased almost linearly by addition of zeolite particles containing up to 10 wt.% (Figure 6). Furthermore, a sharp increase in the content of zeolite of 15 wt.% occurred. Zeolites are much stiffer than the matrix so that the Young's modulus of the composite is sensitive to the content of the zeolite. According Vollenberg *et.al* [24] and Pukánszky [25], de-bonding stress (i.e., the stress necessary to initiate de-bonding) is proportional to the Young's modulus of the matrix and reversible work of adhesion. This means that the de-bonding stress increased by increasing the reversible work of adhesion. Meanwhile, Nilsen [26] and Kolarik *et.al* [27] argued that the Young's modulus of the composite is proportional to the matrix stiffness. By combining the opinions of these two groups, it can be concluded that the Young's modulus of the composite increased by two states, first, increasing de-bonding stress, second, decreasing reversible work of adhesion. As explained earlier, an increase in Young's modulus by increasing the zeolite content is not caused by an increase in de-bonding stress. Decrease reversible work of adhesion is a cause of increased Young's modulus of the composites.

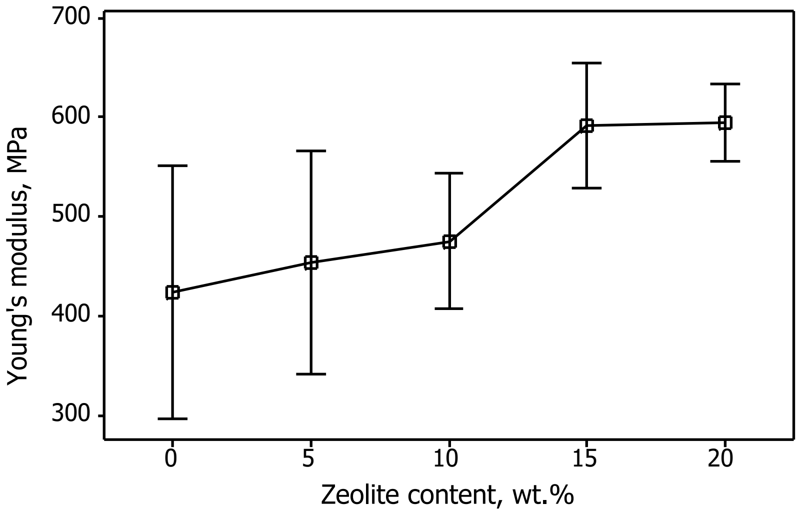

Figure 6: Young’s Modulus As A Function of Zeolite Content

Tensile Fracture Surface

The SEM analysis of the tensile fracture surfaces for all tested composites is presented in Figure 7. It reveals the influence of the presence of zeolite particles on the local deformation of the HDPE matrix. The composite with 5 wt.% zeolite as shown in Figure 7a showed clearly that matrix underwent extensive plastic deformation. This indicates that this composite has undergone ductile fracture. The morphology of tensile fracture surface containing a large number of particles pull out of the HDPE matrix is shown in Figure 7b-d. The increase of the zeolite particles more than 10 wt.% promotes extensive voids initiated at the interface of HDPE matrix-zeolite particles as shown in Figure 7c and 7d. Finally, increasing zeolite particles lead to reduced matrix deformation.

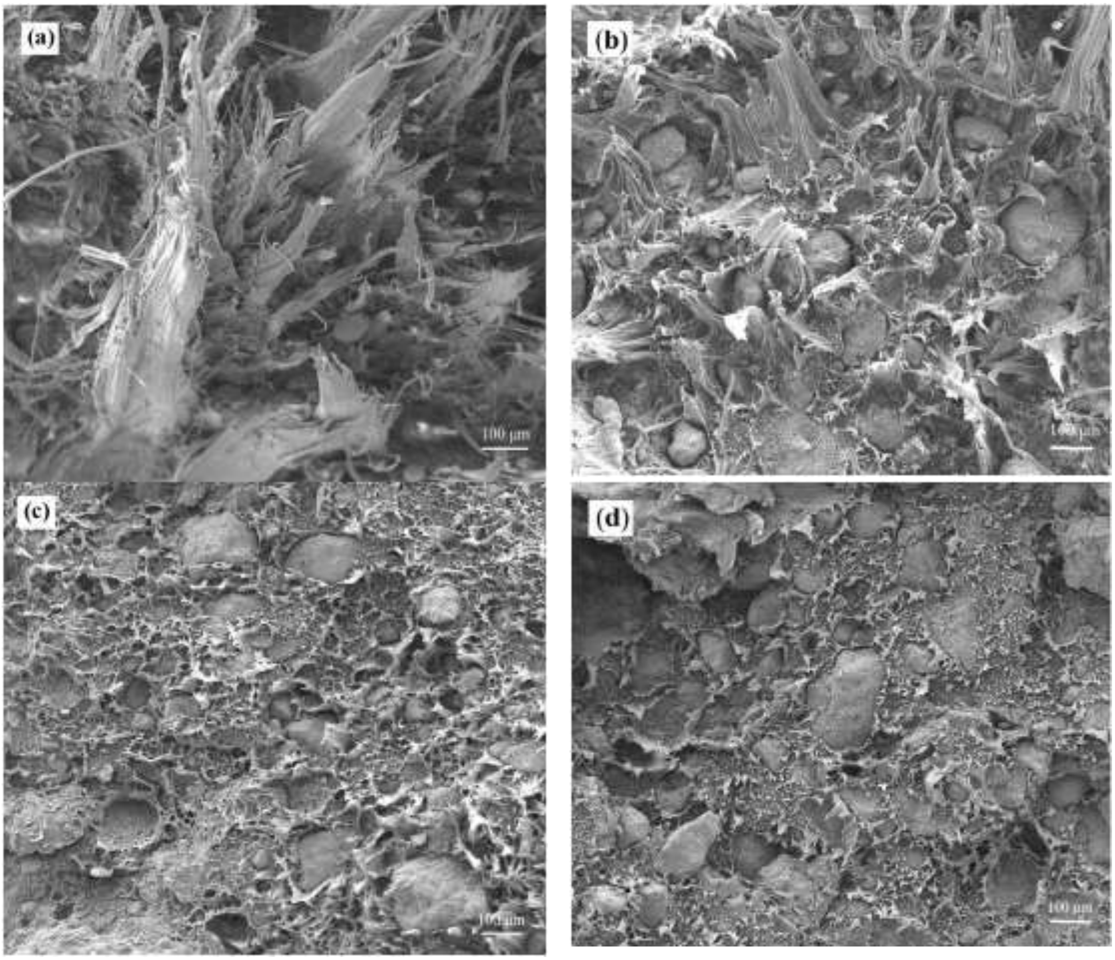

Figure 7: The Tensile Fracture Surface SEM micrographs of zeolite/HDPE composites: (a) 5 wt.% zeolite, (b) 10 wt.% zeolite, (c) 15 wt.% zeolite, (d) 20 wt.% zeolite.

The HDPE matrix network in the zeolite particles is depicted in Figure 8 which shows the gap between the HDPE matrix and the zeolite particles. Stress concentration due to the tensile load during test led to the voids formation as a result of particles de-bonding from the matrix. Furthermore, the voids grow in the tensile stress direction (Figure 9a). On the other hand, craze febrile network can be observed as shown in Figure 9b. The crazes formation was initiated when the plane strain led to a microscopic void to open up under appropriate state of local stress created by particles [28].

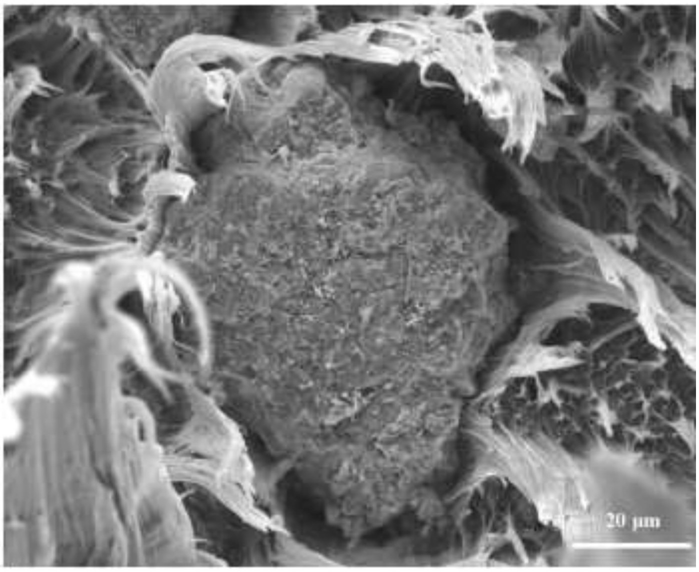

Figure 8: SEM micrograph of tensile fracture surfaces showing polymer network in the zeolite particles of composite with 10 wt.% zeolite

Further deformation of HDPE matrix led to void coalescence (Figure 9b) prior to composites fracture. Increase in the zeolite content shortens the distance between the particles in the host matrix. This resulted in a decrease in the strain required for growth and coalescence of voids and hence an increase in the content of the zeolite particles causing the fracture behavior of composites in transition from ductile to brittle. This mechanism resulted in the appearance of the fracture surface as shown in Figure 7 which reveals a change in the fracture behavior of the composite as previously discussed.

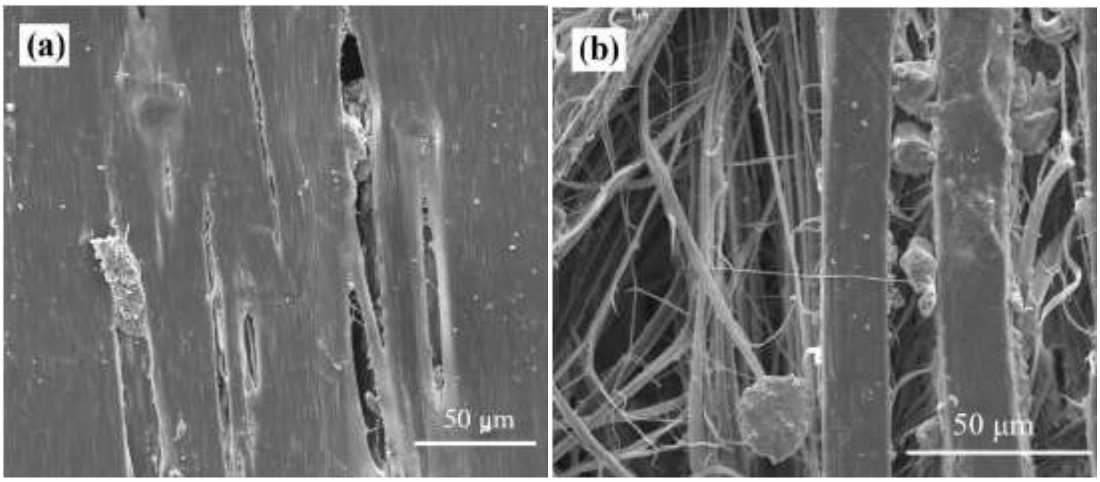

Figure 9: SEM images showing the fracture process of 5 wt.% zeolite/HDPE (a) voids grow in tensile stress direction (b) voids coalescence and the crazing formation.

Conclusions

Study on morphology and mechanical properties of novel composites has been discussed in this paper. Aggregates were observed and found in more locations with increasing zeolite content. The particles in the aggregates have poor bonding so that the particles are de-bonded early. Therefore, the de-bonding stress (i.e., stress necessary to initiate de-bonding) decreased. The voids created by the de-bonded particles can serve as precursor for crack during tensile loading. Aggregate lowers the ductility behavior of composites. Stress transfer from the matrix to the particles is effective on the addition of 5 wt% zeolite characterized by increased tensile strength. On the other hand, the load stress lead to an increase in the intensity of irreversible slip on the surface of the particles and the matrix are characterized by a decrease in the yield stress of the composites

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