Environmental Durability of Vinyl Ester Composites Filled with Carbonized Jatropha Seed Shell

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The durability of vinyl ester composites filled with carbonized jatropha seed shell was investigated in 5% NaOH solution, 5% HCl solution, and distilled water for 12 months. The environmental durability of the composites was determined by measuring weight changes, flexural properties, and tensile properties. Results showed weight gain and changes in the mechanical properties of the composites due to the soaking time in alkaline, acidic, and neutral environments. It was observed that vinyl ester composites had the highest tensile properties in alkaline environments. The highest flexural properties of the vinyl ester composites were observed in an alkaline environment. Scanning electron microscope image analysis revealed that the surface of the vinyl ester composites was rough and that the original luster was lost after soaking in alkaline solution, acidic solution, and distilled water for 12 months.

Keywords: Carbon fiber; Composite; Jatropha seed shell; Vinyl ester composite; Carbon filler

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INTRODUCTION

Polymeric composites have been widely used in civil engineering applications due to their unique characteristics such as corrosion resistance, transparency to radar waves, ability to absorb impact, and damping of vibrations (Reis 2009; Murthy *et al.* 2010). As a polymeric matrix, the use of vinyl ester resin in composite, particularly in civil engineering applications, is growing because of the polymer's superior chemical stability, ease of installation, low maintenance requirements, and flexibility in design (Ku *et al.* 2006; Murthy *et al.* 2010). However, the poor durability of vinyl ester composites in harsh environments, especially in alkaline or acidic environments, has hindered its widespread application in civil engineering. Therefore, the improved durability of vinyl ester composites, especially in corrosive environments, is in high demand (Figovsky 2010). Studies have reported that the degradation of polymeric composites in a corrosive environment is mainly caused by the weakening of the matrix interfacial bonding, which is generally caused by the ingress of moisture, alkalines, or acids (Ziębowicz *et al.* 2009; Al-Hassaniand Areef 2010; Abdul Khalil *et al.* 2013).

Carbon as a filler has been widely used in polymer-matrix composites as reinforcements or fillers because of its good mechanical, electrical, and thermal

properties (Abdul Khalil *et al.* 2013; Sri Aprilia *et al.* 2014). In addition, carbon fiber improves the strength and stiffness properties of the polymer-matrix. Hence, the durability of vinyl ester composites can be improved by adding carbon fiber into the composite (Marouani *et al.* 2012). Due to a higher carbon content, jatropha seed shell has the potential to produce carbon fiber for use as a filler in polymer-matrix composites (Abdul Khalil *et al.* 2013). In our previous study, carbon fiber was used as a filler in vinyl ester composites with various loading percentages (Sri Aprilia *et al.* 2014). Results showed that jatropha seed shell carbon fiber enhanced the mechanical, thermal, and morphological properties of vinyl ester composites. In that study, 10 wt.% carbon fiber loading into vinyl ester composites had the highest mechanical, thermal, and morphological characteristics (Sri Aprilia *et al.* 2014).

In the present study, vinyl ester composites were prepared by adding 10% carbonized jatropha seed shell. Durability of the prepared vinyl ester composites was evaluated on percentage weight gain, tensile, flexural, and morphological properties after exposure to 5% NaOH, 5% HCl, and distilled water at room temperature (25±1 ^{o}C) for 12 months.

EXPERIMENTAL

Materials

Jatropha curcas L. seed shell was obtained from Aceh Province, Indonesia. Commercial vinyl ester with 42% styrene monomer content, methyl ethyl ketone peroxide (MEKP), and cobalt napthenate were supplied by Zarm Scientific & Supplies Sdn. Bhd., Malaysia. The analytical grade NaOH and HCl used in this study were purchased from Titan Chemical® Co., Malaysia.

Methods

Durability test of vinyl ester composites filled with 10% carbon particles

Carbon particles from jatropha seed shells and vinyl ester composite were prepared following the similar method as described elsewhere (Sri Aprilia *et al.* 2014). The environmental durability testing of the vinyl ester composites was conducted following the standard method of ASTM C581 (2003). The prepared composites were cut into 210 mm x 70 mm samples and immersed in glass bottles containing 5% NaOH, 5% HCl, and distilled water. Weight changes, as well as flexural and tensile properties were measured once in every 3 months for a period of 12 months. The corrosion medium was replaced at each withdrawal to maintain solution strength. The percentage weight change of the composite panels were determine based on Eq. 1,

$$W = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W is the percentage weight of composite panel, W_0 is the weight of the untreated composite panel, and W_t is the weight of the treated composite panel at the time t (months).

Mechanical properties

Tensile tests were performed using the INSTRON 5582 Universal Testing Machine (USA). A rectangular composite sample with dimensions 120 mm x 20 mm x 7 mm was used as per the ASTM D638 (2007) standard. Tensile properties, including tensile strength, tensile modulus, toughness, and elongation at break, were acquired from the recorded data. In each case, five specimens were tested and the average value was tabulated. Flexural properties including strength, tensile modulus, and toughness were determined by following the three-point flexural testing method in accordance with the ASTM D790 (2007) standard. The crosshead speed was 2 mm/min.

Scanning electron microscopy

The tensile fractured surface morphology of the composites was determined by scanning electron microscopy (SEM) (model EVO MA10, Carl-ZEISS SMT, Germany) at an accelerating voltage of 20 KV. The fractured surfaces of specimens were mounted on aluminum stubs and sputter coated with a thin layer of palladium and gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Weight Gain after Chemical Degradation

Figure 1 shows the percentage weight change of the vinyl ester composite filled with 10% carbonized *Jatropha* seed shell in acid and alkaline environment for a duration of 12 months. It was observed that the weight of the composite increased by increasing the soaking time up to 3 months, and gradually decreased therafter. The highest weight gained of the composite was observed in 5% NaOH solution, followed by the 5% HCl solution, and then in distilled water. It can be concluded that weight change for vinyl ester composites filled carbonized jatropha seed shell was due to solution uptake. The weight gain of the composite occurred probably due to the moisture penetration into the composite materials (Nosbi *et al.* 2010). The trend was observed to be similar for all solutions considered in the present study. The rate of water absorption might slow down after a certain period of time and reached saturation level at 3 months soaking time. However, the weight loss of the vinyl ester composite filled with carbonized J*atropha* seed shell might have occurred due to swelling and dissolution of polymer matrix in the composite (Naveen *et al.* 2014). Swelling occurs when the liquid diffuses within the composite matrix and is absorbed by the composite matrix. The solute molecules fit into and occupy positions among the polymer molecules. Thus, the macromolecules are forced apart so that the vinyl ester composite expands or swells. Therefore, a wide variety of reactions and diverse consequences are possible for material polymer composites degradation (AL-Hassani and Areef 2010). The highest weight changes of the vinyl ester composite filled with 10% carbonized *Jatropha* seed shell was observed in alkaline solution, followed by the acid solution and then distlled water. This trend can be related to the rate of the hydrolysis mechanisms of carbonized *Jatropha* seed shell of the composite matrix in alkaline solution, acid solution, and distilled water. Anionic charges in the presence of an alkaline medium can influence the diffusion process (Nosbi *et.al*. 2010), which can make the carbonized *Jatropha* seed shell swell with the cationic charge. The cationic charged ions can interact between COO^- and OH^- groups of carbonized particle. It is expected that alkaline medium holds a higher anionic charge than acid

medium, followed by distilled water (Nosbi *et al.* 2010). Such considerations may explain why the highest weight changes was observed in alkaline solution than acid solution, followed by distilled water.

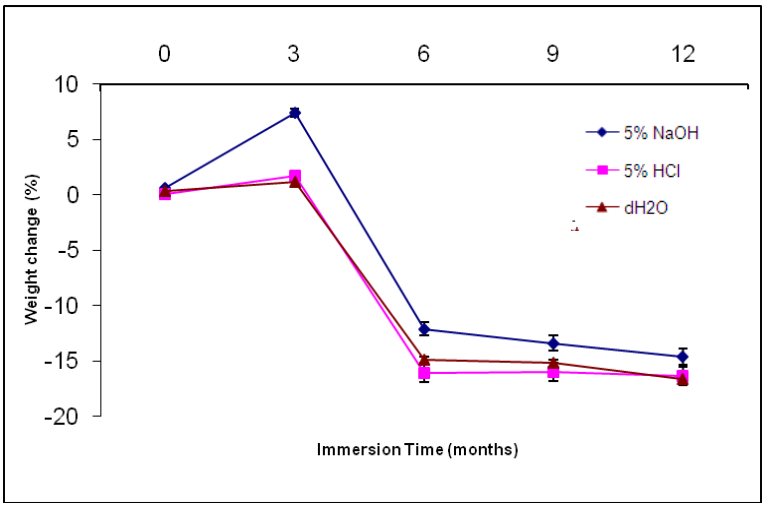

Fig. 1. Percentage weight change (± standard deviation) of vinyl ester composite filled with carbonized *Jatropha* seed shell in 5% NaOH solution, 5% HCl solution, and distilled water

Change in Mechanical Properties

Tensile properties

The tensile strength of vinyl ester composites was decreased with increased soaking time in acid solution, alkaline solution, and distilled water, as shown in Fig. 2. It was observed that the tensile strength decreased 24.93%, 49.61%, and 70.61% for 5% NaOH, 5% HCl, and distilled water at a soaking time of 12 months. However, the loss of the tensile strength of the composite might be due to the weakening of the interfacial region between the vinyl ester matrix and *Jatropha* seed shell particle filler.

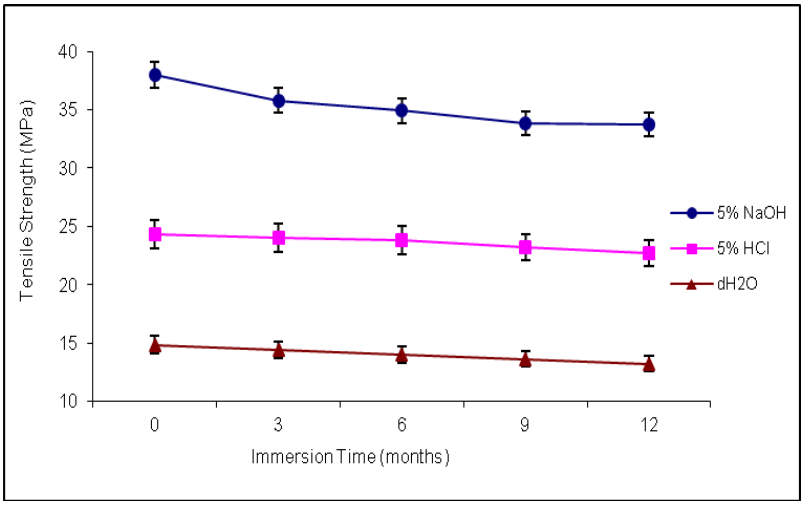

Fig. 2. Influence of the corrosion media on tensile strength of vinyl ester composite filled with carbonized *Jatropha* seed shell. The tensile strength of untreated composite panel was 44.92 MPa. Data presented as the mean ± standard deviation.

The chemical reactions, and the subsequent release of energy as a result of the different corrosion media, affected the vinyl ester matrix by rupturing the covalent bonds. This covalent bond rupture increased the degree of cross linking of the vinyl ester chains, thus decreasing the tensile strength. However, vinyl ester composites has a good chemical resistance in alkaline and acid solutions. Similarly, Chibber *et al.* (2006) reported that the decrease in the tensile strength and the change in percentage of tensile strength was due to the effect of vinyl ester matrix hydrothermal and the carbonized particle strength.

Tensile modulus

Figure 3 shows the change in tensile modulus of vinyl ester composites filled with carbon fiber of *Jatropha* seed shell at various soaking times in 5% NaOH, 5% HCl, and distilled water. The decrease of the tensile modulus in alkaline solution was minimal. The tensile modulus of the composite did not change considerably at 3 months of soaking time, whereas the tensile modulus decreased rapidly with increasing soaking time from 6 months to 12 months. Within the maximum observation time, it was revealed that the highest tensile modulus loss was about 8%, 25%, and 28% in 5% NaOH, 5% HCl, and distilled water, respectively. Results indicates that the carbnozied *Jatropha* seed shell-filled vinyl ester composites have the high potency to be used in civil engineering materials in alkaline and acidic environments. Thang *et al.* (2010) explained that pure matrix polymer reinforced filler composites are immersed in chemical environments, especially acids; they are unstable in sodium hydroxide solutions. The surface layer in case of matrix and composites with acids contains some micro-cracks.

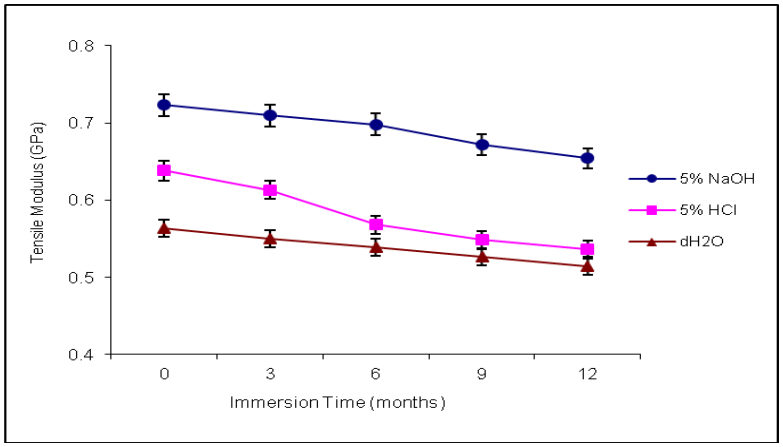

Fig. 3. Influence of the corrosion media on tensile modulus of vinyl ester composite filled with carbonized *Jatropha* seed shell. The tensile modulus for untreated composite was 0.715 GPa. Data presented as the mean ± standard deviation.

Elongation at break

Figure 4 shows the change of elongation at break for vinyl ester composites at various soaking times in 5% NaOH, 5% HCl, and distilled water. The highest degradation in elongation at break of vinyl ester composite occurred in distilled water then 5% HCl solution, followed by 5% NaOH solution. Percentage elongation at break decreased 12.2% for immersion vinyl ester composites in 5% NaOH, 7.55% in distilled water, and 9.23% in 5% HCl at a soaking time of 12 months. According to the results of percentage loss of elongation at breaking of carbonized *Jatropha* seed shells filled with vinyl ester composites and immersed in different chemical solutions, 5% NaOH is the

most aggressive environment relative to distilled water and 5% HCl for carbonized particle vinyl ester composites.

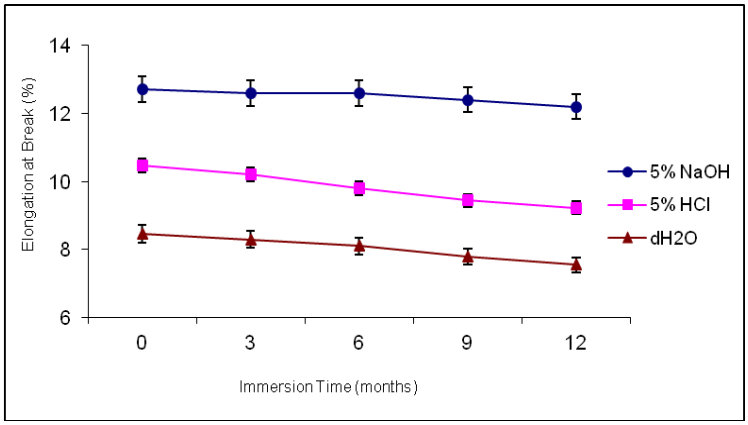

Fig. 4. Influence of the corrosion media on percentage loss in elongation at break of vinyl ester composite filled with carbonized *Jatropha* seed shell. The percentage elongation at break for untreated composite was 12.4%. Data presented as the mean ± standard deviation.

Flexural modulus

Figure 5 shows the change of flexural strength of vinyl ester composites at various soaking times in 5% NaOH, 5% HCl, and distilled water. It was observed that the flexural strength decreased with increasing soaking time of the composite. The degradation of percentage loss in flexural strength of vinyl ester composite at immersion time of 12 month was 49.57%, 62.18%, and 73.11% in 5% NaOH, 5% HCl, and distilled water, respectively. The flexural strength of vinyl ester composites in different chemical solution reveals that 5% NaOH was the more aggressive environment relative to 5% HCl and distilled water. The change in the flexural properties with soaking time was most obvious for the carbonized *Jatropha* seed shell filled vinyl ester composites. Similarly, Zhu *et al.* (2011) and Almussalam *et al.* (2012) observed that the mechanical properties of vinyl ester composite decrease with an increased soaking time in chemical solution.

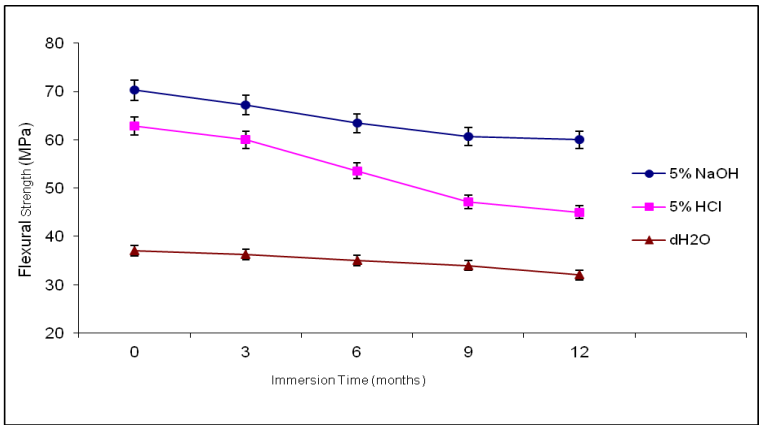

Fig. 5. Influences of the corrosion media on flexural strength of vinyl ester composite filled with carbonized *Jatropha* seed shell. Flexural strength of untreated composite panel, 119 MPa. Data presented as the mean ± standard deviation.

Flexural modulus

Figure 6 shows the change in flexural modulus of vinyl ester composites at various soaking times in 5% NaOH, 5% HCl, and distilled water. The highest degradation of percentage loss in flexural modulus of vinyl ester composite occurred after an immersion of 12 months. Flexural modulus decrease at 12 months soaking time of 6.40%, 17.75%, and 45.63% in 5% NaOH, 5% HCl, and distilled water, respectively.

The decrease of the mechanical properties including tensile and flexural properties might have occurred due to swelling and dissolution of polymer matrix in the composite. The reason for the degradation of the mechanical properties of vinyl ester composites at various soaking times in 5% NaOH, 5% HCl, and distilled water was similar as discussed in terms of weight gain after chemical degradation. Analyses of the mechanical properties of the prepared vinyl ester composite filled with carbonized *Jatropha* seed shell revealed that the carbonized Jatropha a seed shell has the potential to be used as filler in composite. The slow degradation of mechanical properties (tensile and flexural) after 12 months soaking time of vinyl ester composite filled with carbonized *Jatropha* seed shell indicate that carbonized *Jatropha* seed shell had improved the rigidity of the vinyl ester composite. Based on the results, the vinyl ester composite filled with carbonized *Jatropha* seed shell showed the highest rigidity in 5% NaOH solution, in comparison with 5% HCl solution, and then followed by the distilled water.

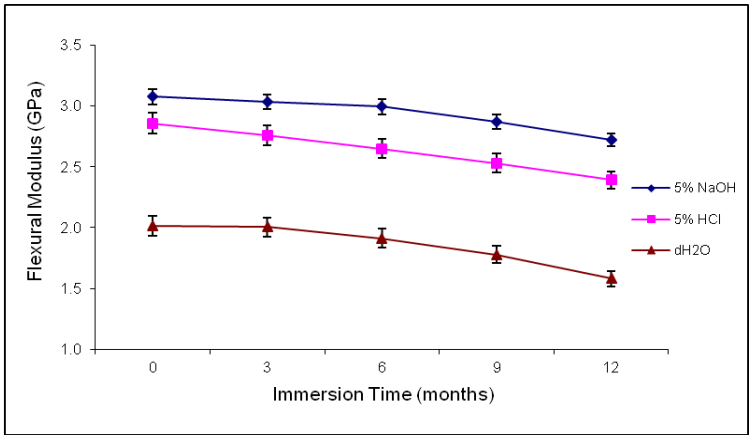

Fig. 6. Influence of the corrosion media on flexural modulus of vinyl ester composite filled with carbonized *Jatropha* seed. The flexural modulus for untreated composite was 2.91 GPa. Data presented as the mean ± standard deviation.

Change in Morphology

SEM images in Figure 7 shows fracture surfaces of carbonized *Jatropha* seed shell filled with vinyl ester composite before and after immersion in 5% NaOH, 5% HCl, and distilled water for 12 months. The surface fracture of carbonized particle vinyl ester composites was smooth before immersion in a chemical solution (Fig. 7a) and became rough and lost original luster after immersion in the chemical solutions. Accordingly, the carbonized *Jatropha* seed shell filled with vinyl ester composites showed that surface fracturing weakened the adhesion between the carbonized particle and the vinyl ester matrix. Additionally, the vinyl ester matrix started to deteriorate more as the soaking time was increased. The effect of the chemical degradation on the surface fracture of the composites was observed on the damage pattern in these composites. This damage occurs because the chemical solutions penetrate the interface through the micro-voids and

micro-cracks. The trapped solution damages the interfacial region (Marouani *et al.* 2012). It is clear from the SEM images that decreasing the strength of the bond has a strong correlation with reduction in tensile strength (Murthy *et al.* 2010).

According to Bagheri *et al.* (2007), composite material degradation is caused by contamination of the remaining monomers, organic substances, filler particles, and ions. The depth of degradation is dependent upon a complex function of the physical and chemical characteristics of the resin, the filler, and the saline coupling. After a longer soaking time, the composites would accelerate the initiation and propagation of the micro-cracks from the surface, thus contributing to the diffusion process taking place, both within the vinyl ester matrix and within the carbonized particle-vinyl ester matrix interface. Such micro-cracks, under the combined action of chemical diffusion, accelerate the degradation process (Marouani *et al.* 2012).

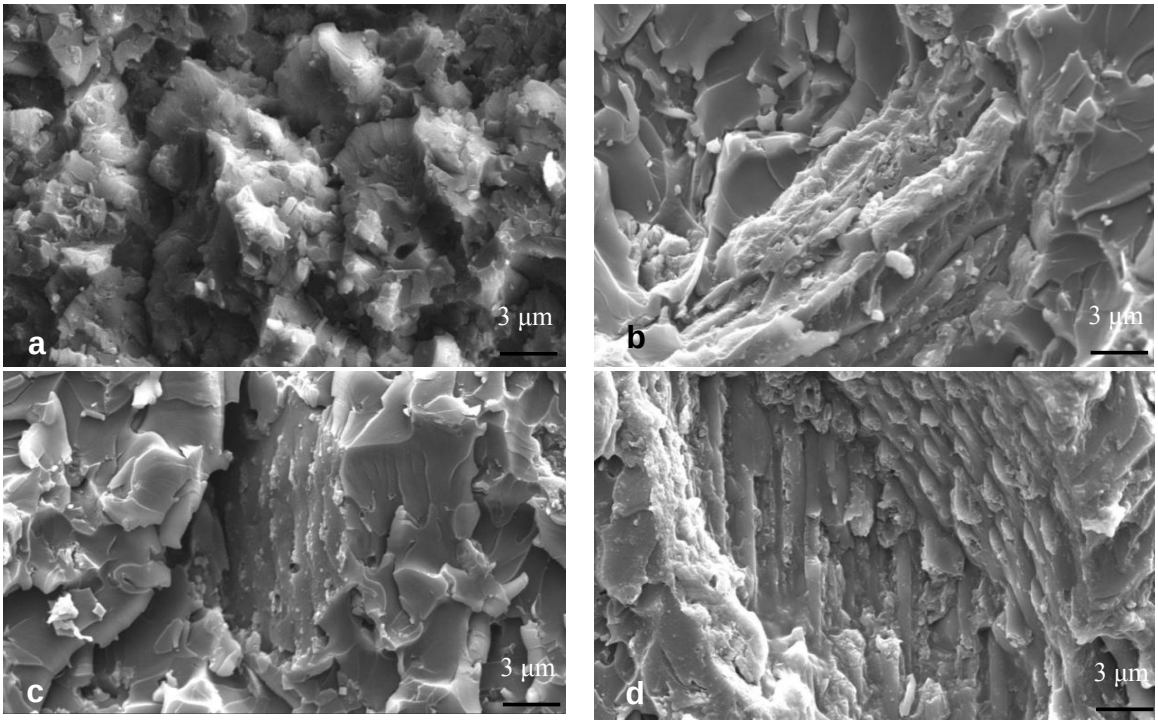

Fig. 7. SEM image of the carbon fiber of *Jatropha* seed shell filled vinyl ester composites: (a) Control (source: Sri Aprila *et al.* 2014) (b) after immersion in 5% NaOH for 12 months, (c) after immersion in 5% HCl for 12 months, and (d) after immersion in distilled water for 12 months

CONCLUSIONS

1. The weight of the carbon of *Jatropha* seed shell filled vinyl ester composites decreased after 3 months in alkaline solution, acid solution, and distilled water.
2. The mechanical properties of carbonized *Jatropha* seed shell-filled vinyl ester composites decreased after chemical degradation. The corrosive media's aggressive attack on the vinyl ester composites was manifested as changes in the structure and properties.
3. The experimental data analysis showed that carbonized vinyl ester composites offer the chemical resistance over the neat vinyl ester.

4. Results indicates that the carbonized Jarthopa seed shell has the potential to be used as filler in composite.

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