Exploring Material Properties of Vinyl Ester Biocomposites Filled Carbonized *Jatropha* Seed Shell

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This study investigates the influence of carbon black from carbonized *Jatropha* seed shell as a filler that was obtained by furnace method at 600 °C on the material properties of vinyl ester based biocomposites. The biocomposites were characterized for mechanical, thermal, and morphological properties. The tensile strength was enhanced at 10 wt.% loading of filler material as compared to the virgin polymer and higher loading percentage. Flexural strength decreased with an increase in the carbon black loading percentage, while the tensile modulus and flexural modulus showed an opposite trend. Thermogravimetric analysis showed enhancement in the residual content of the composite materials, thereby ameliorating thermal stability. Glass transition and melting temperatures by DSC analysis were observed to increase up to 10 wt % loading of filler but to decrease subsequently at higher loading percentage. The morphological analysis showed smooth morphology with intermittent lumps of agglomeration at higher loading percentages.

Keywords: Carbon black; Vinyl ester composites; Mechanical; Thermal; Morphology

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INTRODUCTION

Biocomposites are composite materials comprising of one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include plant fibers such as cotton, flax, hemp, jute, kenaf, and others, or fibers from recycled wood or waste paper, or even by products from food crops (Fowler *et al.* 2006), which have been investigated in biocomposites.

In recent years, agricultural by-products have received increased attention as alternative fillers because of their low cost and abundance. Agricultural by-product can be used in both thermoplastic and thermoset polymer matrices, and the choice of polymer for making composites greatly depends on the intended application of the material. The use of agriculture filler reinforcements in thermoplastics/thermoset has been gaining acceptance in many applications in the past few years. Fillers are widely used for polymer materials; they are added with the goal to enhance the nature and processing capabilities or to reduce the cost of production (Ibrahim *et al.* 2012). The filler in composite materials needs to achieve the desired processing performance and to improve product quality.

A more economical approach is to incorporate agriculture fillers into composites in the form of particulate fillers, similar to a flour, to replace the use of traditional mineral fillers such as calcium carbonate, mica, and talc.

However, the matrix also plays an important role in a composite, allowing it to be designed for specific applications by properly selecting the polymer. Vinyl ester is a thermoset plastic that is widely used for developing advanced composites due to its good stiffness, dimensional stability, chemical resistance, higher strength than polyester resins, and lower cost than epoxy resins (Suresha and Kumar 2009). They can be easily handled at room temperature and have mechanical properties similar to those of epoxy resins, especially hydrolytic stability. Further, it offers greater control over cure rate and reaction conditions than epoxy resins. Vinyl ester resin is brittle, and one approach to increasing the performance and minimizing the cost of the resin is by reinforcing it with fillers (Ku *et al.* 2012). As the structural products are cast to shape, the best option to reinforce the vinyl ester resin is to mix it with particulate fillers.

Carbon black, a type of particulate filler, is widely used for reinforcement in composites. Commercially available carbon blacks are obtained from thermal cracking of natural gas and furnace black produced by incomplete combustion of oil filled stocks. This carbon black is relatively expensive because of its dependence on dwindling supplies of crude oil (Abdul Khalil *et al.* 2010). Therefore, it is important to develop alternative sources of fillers from renewable resources such as biomass which are carbonaceous in nature and rich in organic matter. Biomass rich in lignocellulosic fibers can produce biocarbon (carbon black) after pyrolysis or carbonization because they have high fixed carbon content (Abdul Khalil *et al.* 2007).

Today, experts have achieved technological improvements in product materials by the use of carbon black. Many studies have been carried out on carbon black from biomass as a filler in composites such as bamboo (Abdul Khalil *et al.* 2010; Onyeagoro 2012; Acharya and Samantarai 2012), coconut shell, oil palm empty bunch (Abdul Khalil *et al.* 2010), and rice husk (Acharya and Samantarai 2012). These fillers are commonly used in composites to reduce cost, as well as to improve processing ability, electrical properties, fire retardancy, and mechanical properties. The effect of fillers on the properties of the composites depends on their concentration, their interaction with the matrix, filler size and shape, and filler dispersion.

As biomass, *Jatropha curcas* L. is attracting a great amount of attention all over the world as a source of renewable energy as well as an alternative to fossil fuels. *Jatropha* seed shell is one part of the waste after extracting the oil. Due to high carbon content, *Jatropha* seed can be converted and used as carbonized filler (Abdul Khalil *et al.* 2013). *Jatropha* has the potential to be used as a filler material by using different parts of the plant, such as, seed, seed cake, shell, seed shell because they each contain high carbon content.

In this study, carbon black filler from *Jatropha* seed shell was evaluated to be used as a filler material for the vinyl ester composites. The characteristics of the carbon black filled vinyl ester composite containing various loading percentage of carbon black from *Jatropha* seed shell were compared with those of unfilled vinyl ester. The effects of carbon black fillers on the mechanical, thermal properties and morphology of composites were investigated. In addition, the properties of the biomass based carbon black used as filler for the composites were also determined.

MATERIALS AND METHODS

Materials

Jatropha curcas L. seed shell was procured from Aceh Province, Indonesia. The average proximate analysis of *Jatropha* seed shell represented in weight percent shows a moisture content of 9.68%, a volatile matter of 61.66%, fixed carbon of 24.84%, and ash content of 3.82%. Carbonized *Jatropha* seed shell was prepared by furnace method for 1 h at 600 ^{o}C. Characteristics of carbon black are shown in Table 1. 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.

Table 1. Characterization Carbon Black from *Jatropha* Seed Shell

Properties	Carbon black
Density particle (g/mL)	1.80
Bulk density (g/mL)	0.43
Iodine adsorption number (mg/g)	309.65
Moisture content (wt %)	5.68
Particle size distribution (μm)	45.05
Composition (wt% and atomic%):	
C	74.25 and 81.97
O	20.85 and 17.28

Composites Preparation

Vinyl ester-carbon black composites were prepared at different loading percentages, *i.e.* 0,10, 20, 30, and 40wt% with 1.5% w/w of MEKP used as hardener/catalyst, and 0.2 % w/w of cobalt napthenate as accelerator. Compounding matrix with fillers has been done by using a mechanical stirrer. Compounded materials were poured onto a flat surface mould (200 mm x 200 mm x 55 mm) and cured at room temperature for 24 h and post cured at 80 ^{o}C for 4 h.

Table 2. Vinyl Ester Composites Filled Carbonized Jatropha Seed Shell Designation

Composites name	Vinyl ester composition (w%)	CB *jatropha* seed shell (w%)	Co-Nathenate (w/w%)	MEKP (w/w%)
VE	100	0	0.2	1.5
VE-CB-10	90	10	0.2	1.5
VE-CB-20	80	20	0.2	1.5
VE-CB-30	70	30	0.2	1.5
VE-CB-40	60	40	0.2	1.5

Mechanical Properties

The tensile and flexural strengths were analyzed to determine mechanical properties of the composites. Tensile and flexural tests of the composite specimens were carried out according to ASTM D638 and ASTM D790 standards, respectively, using an Instron Universal Testing Machine Model 5582. An average of at least five tests per sample was performed to report tensile test and flexural test.

Thermal Analysis of Composites

Thermal analysis of composite determined with a Perkin Elmer thermal gravimetric analyzer (TG/DTA) was used to investigate the thermal stability of the

composites. The samples (±10 mg) were heated from 30 to 800 ºC under nitrogen gas atmosphere at a heating rate of 20 ºC/min. A Perkin Elmer Differential Scanning Calorimeter (Pyris 6, DSC) was used under nitrogen atmosphere to determine the glass transition temperatures of the composites. The measurements were performed from room temperature to 450 ºC at a programmed heating rate of 10 ºC/min.

Scanning Electron Microscope

The tensile fractured surface morphology of the composite was determined by scanning electron microscope (SEM) model EVO MA10, Carl-ZEISS SMT, Germany at an accelerating voltage of 20 kV for carbon blacks. 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

Mechanical Properties of Composites

In this study, the tensile properties, which included tensile strength and tensile modulus of vinyl ester composite filled with carbon black of *Jatropha* seed shell, were investigated, and the results are shown in Fig. 1. The tensile strength showed a slight increase when 10 wt.% of carbon black was loaded as compared to the virgin vinyl ester, and further increase in loading percentage of 20, 30, and 40 wt.% showed a decrease in tensile strength. Ojha *et al.* (2012) also investigated in their study that the tensile strength decreases after a maximum at 10 wt.% loading of coconut shell char in polyester matrices.

The tensile strength decreased beyond 10 wt% loading due to increase in the particle concentration of the filler material, thereby increasing agglomeration, which makes composite material brittle. Ibrahim *et al.* (2012) and Obayi *et al.* (2008) in their studies state that this occurs due to the agglomeration of particles, which reduces the compatibility of filler in the matrix. It was also shown that their capability to support stress transmitted from the matrix is relatively poor. The decrease of strength may also be due to the highly porous structure and agglomeration of filler in the matrix to form a domain that acts like a foreign body, or simply the result of physical contact between adjacent aggregates (Jamil *et al.* 2006). Agglomeration and incorporation between particles and matrix were the main factors for the trend. The higher tensile strength at 10 wt% loading might be attributed to better dispersion of carbon black in the matrix, better wettability and interfacial bonding.

On the other hand, the tensile modulus increased when carbon black was added from 10% to 20, 30, and 40% respectively. Jamil *et al.* (2006), in their study showed that the addition of filler is expected to increase the tensile modulus resulting from the inclusion of rigid filler particles in the matrix. According Ibrahim *et al.* (2012), the relative stiffness of a material is indicated by its modulus. It is well known that the incorporation of filler imparts greater stiffness to the composites. The incorporation of carbon black from *Jatropha* seed shell improved the stiffness of the vinyl ester matrix, since the tensile modulus of the composites increased as carbon black filler loading percentage was increased.

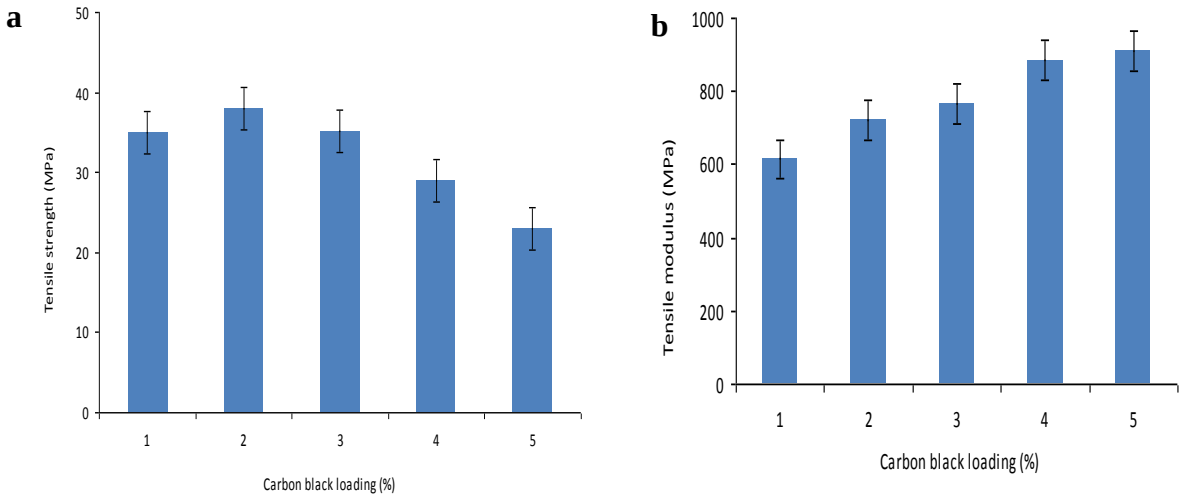

Fig. 1. Tensile properties of vinyl ester-carbon black composites: a. tensile strength and b.tensile modulus

The results for flexural strength and flexural modulus of the vinyl ester composites filled with carbon black from *Jatropha* seed shell at different loading percentage are presented in Fig. 2. In general, the graph of flexural strength shows a decreasing trend as the carbon black filler loading percentage is increased. This trend could be because of this fact that the surface adhesion between vinyl ester matrix and carbon black filler was rather poor (Melo and Santos, 2009). In other words, there was less interfacial interaction between filler and the vinyl ester.

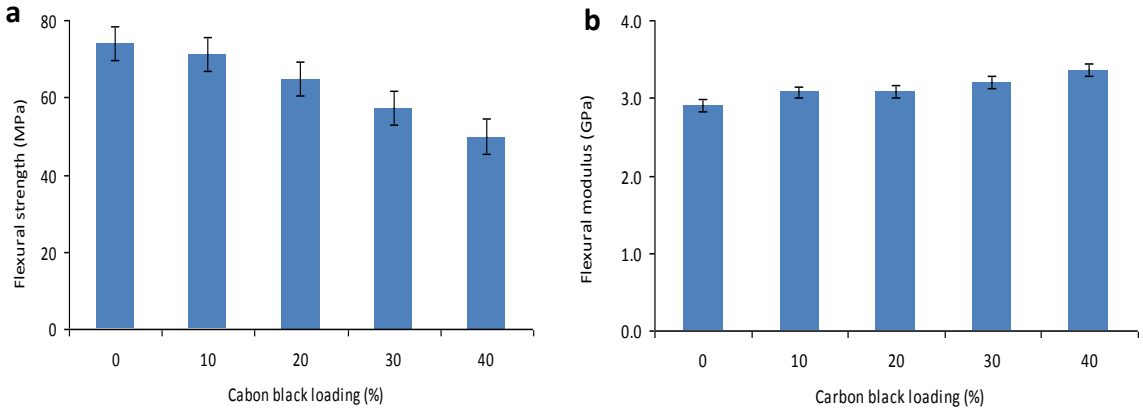

Fig. 2. Flexural properties of vinyl ester-carbon black composites: a. flexural strength and b. Flexural modulus

Thermal Properties of Composites

The thermal stability of vinyl ester composites filled with carbon black from *Jatropha* seed shell was analyzed by TG and derivative thermogravimetry (DTG) to evaluate of the effect of carbon black content in matrix vinyl ester. The thermal stability curves of carbon black filled vinyl ester composites are presented in Fig. 3, and the results are summarized in Table 3. The observed results showed that the highest degradation temperature was for VE, and the degradation temperature decreased with the increase in the loading percentage of carbon black at VE-CB10, VE-CB20, VE-CB30, and VE-CB40 composites, respectively. It can be seen that the decomposition of carbon

black-filled vinyl ester composites and virgin vinyl ester started at 350 °C. This result indicated that the carbon black filled composites possessed lower degradation temperatures as compared to the pristine polymer. The degradation of 10% weight loss was observed at a temperature of 382 to 367 °C. The degradation of 50% weight loss was observed at temperature of 427 to 420 °C. Thus, it was observed that increasing the carbon black filler content in vinyl ester composites also increased the residue content, as shown in Table 2. A lower residue content at 800 °C was observed for virgin vinyl ester, and at the same temperature, composites showed higher residue content with the increase in the carbon black filler content (Mengeloglu and Karakus 2008). Weight residue increase illustrates successful incorporation of higher filler content into the matrix material and ultimately increases its thermal stability (Ahmad *et al.* 2012). Ray *et al.* (2004), in their study suggested that the vinyl ester resin degradation peak was more prominent than the fiber composites degradation peak. The DTG peak of vinyl ester composites is the thermal decomposition of composites with different concentration of carbon black content.

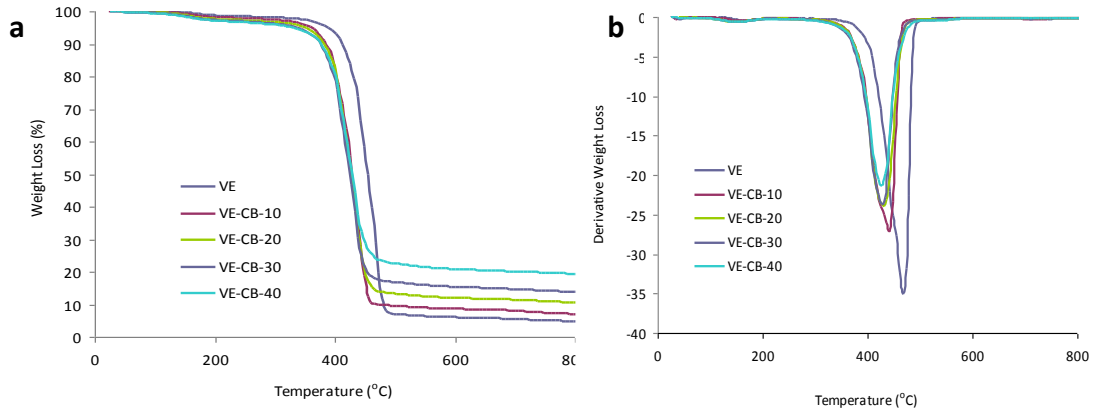

Fig. 3. a. TGA and b. DTG of vinyl ester-carbon black composites

Table 3. Thermal Properties of Vinyl Ester-Carbon Black Composites from TGA and DTG

Composites	Degradation temperature (°C)		Residual weight at 800 °C (%)	DTG Peak Temperature (°C)
	T10%	T50%		
VE	407	453	4.75	427
VE-CB-10	382	427	6.96	400
VE-CB-20	379	424	10.53	394
VE-CB-30	373	422	13.74	392
VE-CB-40	367	420	19.27	394

Glass transition temperatures (T_g), heat capacities (ΔC_p), melting temperatures (T_m), and enthalpies (ΔH) of VE and various VE-CB composites were measured by DSC, and results are shown in Fig. 4 and summarized in Table 4. T_g is the base line of degradation of materials. It is clear from the DSC figure that the T_g of vinyl ester composites decreased slightly with the increase of carbon black loading percentage. Work by Jamil *et al.* (2006) showed that a lower temperature with increase of filler indicates the immiscibility of the composites due to agglomeration and interfacial adhesion. The heat capacity of the VE-CB composites increases with rising temperature.

Cecen *et al.* (2009) found that an endothermic transition for a devitrification state that corresponding to an increase in the enthalpy is indicated as a peak in the downward direction.

The sudden increase in heat capacity starting at the devitrification region continues within the temperature interval where the mentioned endothermic transition has been detected, and it reaches its maximum value within this interval. According to Cecen *et al.* (2009), the increase in heat capacity on devitrification is caused by the beginning of large-amplitude motion that is characteristic of the liquid or rubbery state. They also implied that three major types of large-amplitude motion are possible: translation of the molecule as a whole (also called positional motion), orientational motion (also based on motion of the whole molecule), and conformational motion (the internal rotation of the various segments of flexible molecules).

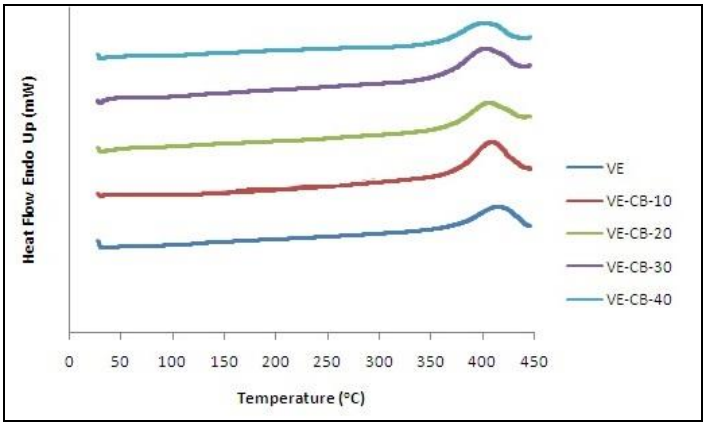

Fig. 4. DSC of vinyl ester-carbon black composite

The melting temperature was found to be higher for the pristine VE at 414 ^{o}C and tended to slightly decrease with the increase in the carbon black content, as shown in Table 4.

Table 4. Thermal Properties of Vinyl Ester-Carbon Black Composites from DSC

Sample	T_g (^{o}C)	T_m (^{o}C)	ΔC_p (J/g^{o}C)	ΔH (J/g)
VE	118	414	0.39	244.20
VE-CB-10	127	408	0.28	237.25
VE-CB-20	122	405	0.36	243.18
VE-CB-30	108	401	0.49	232.89
VE-CB-40	107	400	0.34	179.50

Rosas *et al.* (2011) observed that the thickness of the lamella enlarged at higher temperature in the ethylene vinyl acetate reinforced with ground tire rubber. It seems that particles tend to slightly decrease the thickness of the lamella, probably because of space constraints imposed by the non-crystalline reinforcement of the growth of lamellae on the crystalline side. In the vinyl ester carbon black composites system, the melting enthalpy per gram of mixture decreased with the increasing carbon black content (Table 4). The higher the content of reinforcement, the lower the content of crystallizable material (Rosas *et al.* 2011).

Morphology of Composites

Figure 5 shows micrographs of the fractured surface of vinyl ester-carbon black at a magnification 1000x. These figures show the difference of surface morphology between samples of VE, VE-CB-10, VE-CB-20, VE-CB-30, and VE-CB-40. The fracture surface of the VE was much smoother than that of the VE-CB (Fig. 6a). The roughness and aggregation on the fracture surface increased of carbon black content in order (Fig. 6: b, c, d, and e). The micrographs were taken from the tensile fracture composites in order to analyze the effect of carbon black loading and the adhesion of filler–matrix interphase of the composites. Increasing carbon black content will cause accumulation of carbon in vinyl ester, thereby reducing the strength of composites. The distribution of carbon black filler is relatively non-uniform as one increases the loading percentage of filler, whereas the matrix phase is smooth and has brittle failure fracture. This phenomenon reflected the lower filler–matrix bonding of the composites. However, blends with small loading percentage of carbon black showed better dispersion with less dewetted or undispersed carbon black agglomerates. The agglomeration may then produce discontinuity in the matrix, which subsequently creates stress concentration points in the composite samples as the amount of filler content increases in the composites (Husseinsyah and Mostapha 2011).

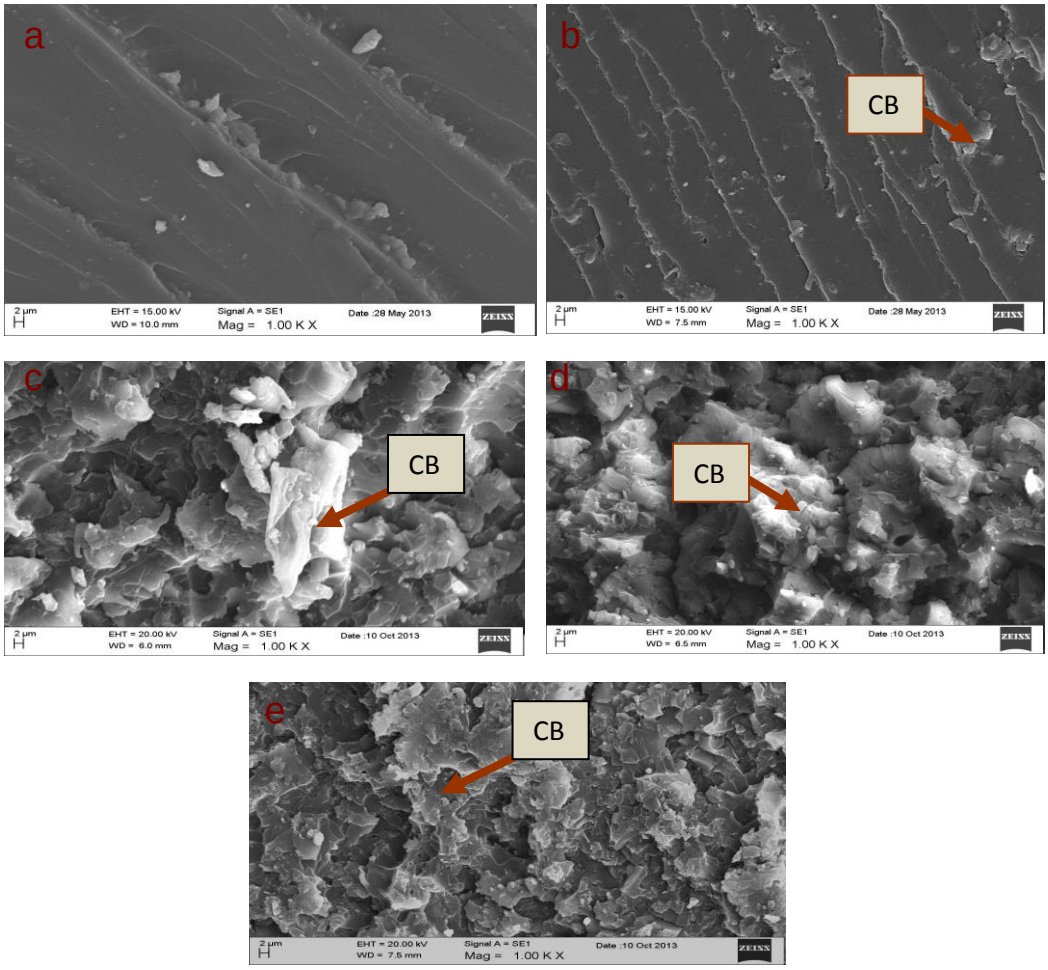

Fig. 5. SEM image fracture surface of vinyl ester composite: a. VE, b. VE-CB-10, c. VE-CB-20, d. VE-CB-30, and e. VE-CB-40, in magnification 1000x

CONCLUSIONS

1. The effects of carbon black from *Jatropha* seed shell as a filler in vinyl ester composites on mechanical properties showed that the tensile strength increased at 10% carbon black content, and decreased at 20, 30, and 40% compared with the unfilled vinyl ester matrix, but flexural strength decreased when increasing carbon black content, due to low surface interaction and non-uniformity of the stress transfer from carbon vinyl ester matrix to carbon black filler at the composites. Increasing the carbon black content also led to agglomeration of particles in the vinyl ester-carbon black composites.
2. Tensile modulus and flexural modulus in this system increased with increasing carbon black content. Vinyl ester-carbon black based composites were much more brittle and had lower elasticity compared to synthetic filler composites.
3. The thermal properties of vinyl ester-carbon black *Jatropha* seed shell from analysis TGA showed an increment in thermal stability after the addition of carbon black of *Jatropha* seed shell in vinyl ester composites. The degradation temperatures of vinyl ester-carbon black composites were decreased with an increase of the carbon black.
4. The DSC studies showed glass transition temperatures of vinyl eater-carbon black composites slightly decreased from 127 °C to 107 °C with additions of carbon black content up to 40%.
5. Morphological study has shown the effect of carbon black loading on the adhesion of filler–matrix interphases and aggregation on the fracture surface in properties of vinyl ester-carbon black composites.

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