Enhancement of PVC/ENR Blend Properties by Poly(methyl acrylate) Grafted Oil Palm Empty Fruit Bunch Fiber

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ABSTRACT: Effect of oil palm empty fruit bunch (OPEFB) fiber and poly(methyl acrylate) grafted OPEFB on several mechanical properties of poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) blends were studied. The composites were prepared by mixing the fiber and the PVC/ENR blends using HAKEE Rheomixer at the rotor speed of 50 rpm, mixing temperature 150°C, and mixing period of 20 min. The fiber loadings were varied from 0 to 30% and the effect of fiber content in the composites on their ultimate tensile strength (UTS), Young's modulus, elongation at break, flexural modulus, hardness, and impact strength were determined. An increasing trend was observed in the Young's modulus, flexural modulus, and hardness with the addition of grafted and ungrafted fiber to the PVC/ENR blends. However the impact strength, UTS, and elongation at break of the composites were found to decrease with the increase in fiber loading. An increase in elongation at break and UTS and decrease in the flexural and Young's modulus was observed with the addition of PMA-*g*-OPEFB fiber compared to ungrafted fiber. This observation indicates that grafting of PMA onto OPEFB impart some flexibility to the blend. The morphology of cryogenically fractured and tensile fracture surfaces of the composites, examined by a scanning electron microscope shows that the adhesion between the fiber and the matrix is improved upon grafting of the OPEFB fiber. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 368–375, 2008

Key words: grafting; OPEFB fiber; poly(methyl-acrylate); PVC/ENR blend; mechanical properties

INTRODUCTION

Studies on natural fibers as fillers or reinforcement agents to thermoplastic elastomers have recently attracted interest of many researchers.[1] The use of fiber as filler offers several advantages over inorganic fillers with regard to their lower density, less abrasiveness to processing equipment, environmentally friendly and lower cost. Oil palm empty fruit bunch (OPEFB) fiber is one of the promising readily available, nonwoody natural fiber in Malaysia. OPEFB fiber is a by product from the oil palm industry. It is extracted by retting process of the empty fruit bunch. Retting is the process of extracting fiber from the OPEFB. The available retting processes are as follows: mechanical retting (hammering), chemical retting (boiling and applying chemicals), steam/vapor/dew retting, and water or microbial retting. Among them, the water retting is the most popular process in extracting OPEFB fibers. OPEFB consists of 65% of cellulose and 19% of lignin.[2] These fibers are hard and tough. These properties made OPEFB as an important lignocellulosic raw material for the preparation of cost effective and environmental friendly composite material. However the presence of the hydroxyl group made OPEFB hydrophilic, which cause poor interfacial adhesion with hydrophobic polymer matrices and lead to low compatibility. This had caused poor mechanical and physical properties to the OPEFB fiber composite. Thus modification of OPEFB by graft copolymerization of hydrophobic vinyl monomer is an alternative way to increase the fiber matrix compatibility.

Studies on the blends of poly(vinyl chloride), PVC, and epoxidized natural rubber, ENR, revealed that the two polymers are miscible at all composition range.[3] This quality has generated interest in further modifications of the blend properties.[4–6] PVC is expected to impart high tensile strength and good chemical resistance, whereas ENR acts as a permanent plasticizer to PVC.[7–9] The potential modification of PVC/ENR blend by electron beam irradiation was highlighted by Ratnam and coworkers[4–7] in

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TABLE I
Formulations of 50/50 PVC/ENR Blend Composites

	Formulation (%)						
Material/batch	1	2	3	4	5	6	7
ENR	47	47.5	45	42.5	40.0	37.5	35.0
PVC	47	47.5	45	42.5	40.0	37.5	35.0
TBLS[a]	6	6	6	6	6	6	6
OPEFB	0	5	10	15	20	25	30

[a] Parts per hundred of PVC.

their series of publications. They have studied the effect of irradiation with doses ranging from 20 to 100 kGy on various PVC/ENR blend ratio and concluded that electron beam irradiation enhances the mechanical properties of the blend in a relatively mild manner.[4,5] The aim of this study is to investigate the effect of OPEFB fiber and poly(methyl-acrylate) grafted OPEFB fiber on the mechanical properties of PVC/ENR blend.

EXPERIMENTAL

Materials

Epoxidized natural rubber, grade "Epoxyprene 50" with 50% epoxidation level was supplied by Guthrie Polymer Ltd, Siliau, Malaysia as a free sample; poly(vinyl chloride), PVC with K value 70 was purchased from Industrial Resin (M) Ltd. Johore Bahru, Malaysia. The PVC stabilizer used, tribasic lead sulfate (TS-100M) was purchased from Lonover Scientific Suppliers Ltd., London, United Kingdom. Methyl acrylate (MA) used in this study was purchased from Fluka Chemical Company, Ronkonkoma, New York, United States of America. It was passed through a column filled with chromatographic grade activated alumina to remove the inhibitor and strored at −10°C. Hydrogen peroxide (Riedel-de-Hazen, Seelze, Germany), ammonium ferrous sulfate (BDH, Poole, United Kingdom) and other chemicals of analytical grades were used as received. OPEFB fibre was obtained from Sabutek (M) Sdn. Bhd, Kuala Lumpur, Malaysia. To remove the excessive wax and other impurities, the OPEFB was washed by soaking in distilled water for 24 h. The fiber was then rinsed with hot water at 60°C and acetone respectively, prior to drying at 60°C in air oven. The particle size of the fibers was reduced to 100–250 μm by using crusher machine.

Sample preparation and formulations

Grafting procedure

Graft copolymerization reaction was carried out at 75°C in a thermostat water bath using hydrogen peroxide and ferrous ammonium sulfate as initiators in an aqueous system. About 40 g of fiber was placed in a 1000-mL three-necked flask containing distilled water and hydrogen peroxide. This mixture was stirred and continuously heated for 15 min under nitrogen atmosphere. Then, 0.9 g of ferrous ammonium sulfate was added into the mixture and stirred for 5 min. Finally 100 mL of MA was added into the vessel containing the reactant mixture and the mixture was stirred for 3 h. Then the crude products were filtered and dried to a constant weight at 60°C. The dried products were extracted with acetone.

Formulations

The recipes used to prepare the PVC/ENR blend composites are given in Tables I and II.

Blend preparations

PVC and the stabilizer were premixed at room temperature in a tabletop high-speed mixer at 1200 rpm for 10 min. Melt blending was carried out at 150°C and 50 rpm rotor speed in a Haake mixer having a mixing cam attachment. The blending was done as follows.

When the desired temperature was reached, ENR was charged into the mixing chamber and mixed for 1 min. The PVC compound was then added and allowed to melt in the mixer for 4 min before OPEFB fiber is charged. The mixing was continued for another 15 min.

The blends from the HAKEE mixer were then compression molded into 1-, 3-, and 6-mm thick sheets under a pressure of 14.7 MPa at 160°C. The sheets were immediately cooled between two plates of a cold press at 25°C. Test pieces were cut from these sheets in accordance to standard procedures stated in the proceeding sections.

Tensile properties

The ultimate tensile strength (UTS), elongation at break, Young's modulus, and modulus at 100% elongation were measured with a Instron Universal

TABLE II
Formulations of 70/30 PVC/ENR-OPEFB Blend Composites

	Formulation (%)						
Material/batch	1	2	3	4	5	6	7
ENR	70	66.5	63	59.5	56	52.5	49
PVC	30	28.5	27	25.5	24	22.5	21
TBLS[a]	6	6	6	6	6	6	6
Fiber	0	5	10	15	20	25	30

[a] Parts per hundred of PVC.

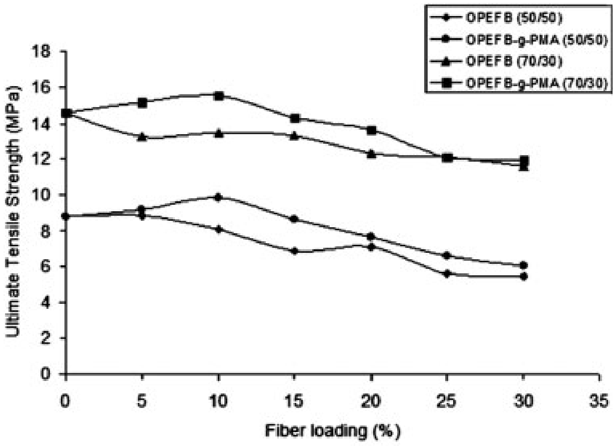

Figure 1 Effect of fiber loading on the ultimate tensile strength of 50/50 and 70/30 PVC/ENR blends.

Testing Machine using a crosshead speed of 50 mm/min in accordance to BS6746. Altogether, seven samples were used for the tensile test and an average of five results was taken as the resultant value.

Flexural modulus

The flexural modulus was determined using Instron Model 4301 machine in accordance with ASTM D 790-97 standard. The flexural test was performed using a 3-point bending method. Five rectangular bar shaped specimens were tested for each composition with a thickness of 3 mm and their average values were calculated.

Hardness

The Shore A hardness test was carried out according to ASTM D2240-89 using the Zwick Hardness Tester machine. Disk-shaped specimen with 6 mm thickness was used. The measured value of hardness was taken after 15 s of contact in Shore A indentor obtained at three different points distributed over the test piece. Three test pieces were used and their average value was determined.

Impact strength

The Izod impact test was carried out using a 4 Joule hammer on a Universal Digital Pendulum Model CEAST machine in accordance to ASTM D 256-97. A total of seven samples were used for the tensile test and an average of five results was taken as the resultant value.

Scanning electron microscopy

Selected samples were manually fractured at liquid-nitrogen temperature. The fractured surfaces were then sputter coated with gold and examined using a SEM/EDAX QUANTA 400 scanning electron microscope. SEM studies were also performed on tensile fractured samples.

RESULTS AND DISCUSSION

Ultimate tensile strength

Figure 1 depicts the effect of OPEFB loading on the UTS of the 50/50 and 70/30 PVC/ENR blends. It is apparent from Figure 1 that the UTS decrease gradually with the increase in ungrafted OPEFB loading. This trend could be associated with the poor wetting of the fiber by the polymer matrix. The poor wetting of the fiber by the PVC/ENR blends will lead to poor interfacial adhesion between the fiber and polymer matrix resulting in weak interfacial regions. With the incorporation of MA grafted OPEFB, an initial increase in UTS is observed until 10% loading. This is mainly due to improved adhesion between the fiber-polymer matrices in the presence of MA grafted fiber. The improved fiber-matrix wetting would result in reduced interfacial regions and stronger interfacial bond. It would therefore be anticipated that more efficient stress transfer would occur between the fibers as a load is applied. The higher UTS obtained for PVC/ENR blends filled with grafted OPEFB further confirm this observation. However, similar to ungrafted fiber, the addition of above 10% fiber (MA grafted) causes a gradual reduction in UTS of the composite. A further increase in fiber loadings has a deleterious effect on the UTS. This is because eventually a level is reached whereby the filler particles or aggregates are no longer as equally separated or wetted by the polymer matrix.[10] Thus, the reduction in strength may be due to agglomeration of the filler particles to form a domain that acts like a foreign body. Similar trend of UTS was also observed in white rice husk ash filled natural rubber compounds.[11] The higher UTS observed for 70/30 blend compared to 50/50 PVC/ENR blend is well illustrated by Ratnam and Zaman.[12]

Young's modulus

Figure 2 shows the effect of fiber loading on Young's modulus of PVC/ENR blends. It can be seen from Figure 2 that the Young's modulus shows a gradual increase with the fiber loading for both systems (grafted and ungrafted). Such a trend indicates that incorporation of fibers into the PVC/ENR blend matrix increases the stiffness of the PVC/ENR blend. However lower values of Young's modulus was observed for OPEFB-*g*-PMA reinforced PVC/ENR blend. This evidence that grafting of the fiber with MA reduces the stiffness of the composite. The

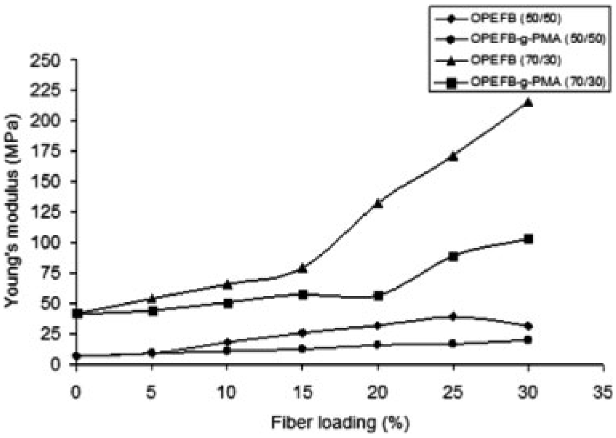

Figure 2 Effect of fiber loading on the Young's modulus of 50/50 and 70/30 PVC/ENR blends.

lower modulus of the grafted fiber reinforced composites compared to ungrafted fiber reinforced composites is associated with the elastic nature of the poly(methyl acrylate). The elasticity of the PMA is attributed to the good mobility of PMA chains ($T_g = 10°C$) at room temperature. The changes in the orientation of the fiber with the grafting may also result in reduction in modulus as reported by Manikandan et al.[13] Similar trend of result was also observed for 70/30 PVC/ENR blends.

Elongation at break

Figure 3 shows the elongation at break of the PVC/ENR blend composites. The addition of both grafted and ungrafted OPEFB fiber to PVC/ENR blends found to reduce the elongation at break drastically. Such a decline is associated with the decreased deformability of a rigid interphase between the fiber and the matrix material. It is clear from Figure 3 that the blend shows a tendency for higher elongation at break with the addition of grafted OPEFB as compared to ungrafted one. This observation further confirms the increase in the elasticity of the PVC/ENR upon grafting of the fiber with MA, which discussed in the previous section. Comparison with the 70/30 blends was not made, as the 70/30 blends are PVC dominant blends and poses poor elongation at break.

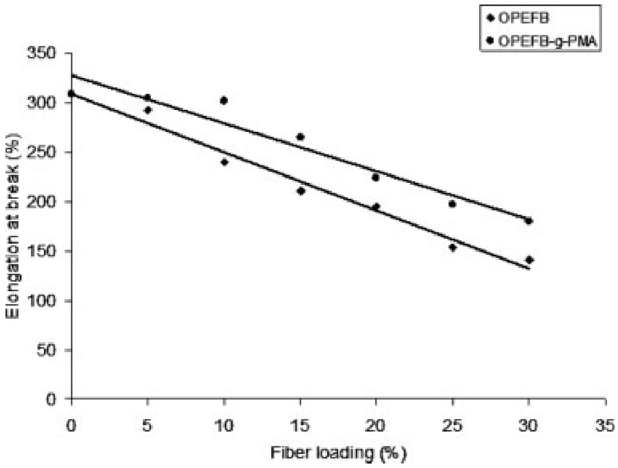

Figure 3 Effect of fiber loading on the elongation at break of 50/50 PVC/ENR blends.

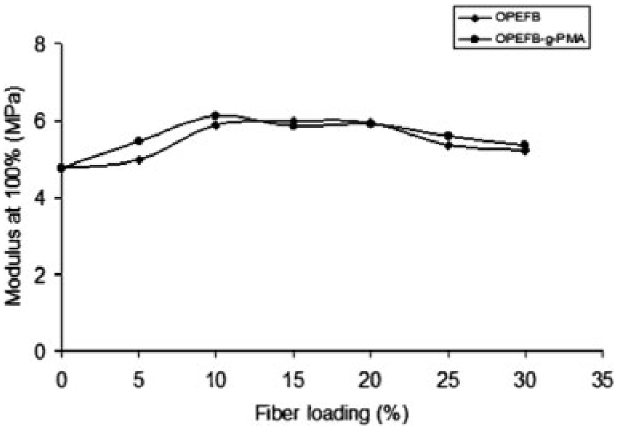

Figure 4 Effect of fiber loading on the modulus at 100% elongation of 50/50 PVC/ENR blends.

Modulus at 100% elongation

The effect of fiber loading on the modulus at 100% elongation of PVC/ENR blends are illustrated in Figure 4. The 100% elongation is found to exhibit similar trends as UTS. Modulus at 100% elongation for both grafted and ungrafted fiber increase up to10% and does not show significant changes thereafter. As the modulus indicates the stiffness of a material, the results show that the fiber imparts a greater stiffening effect to the blend. However, it is interesting to note that the changes were less pronounced compared to the changes in UTS and Young's modulus with fiber loading. This trend of results indicate that the addition of OPEFB fiber to PVC/ENR blends do not cause remarkable effect to the modulus at 100% elongation of the blends. Such observation could be attributed to the stress–strain behavior of the PVC/ENR blend that does not undergo stiffening effect at 100% elongation. Modulus at 100% elongation for the 70/30 PVC/ENR could not obtain as the sample breakage was below 100% elongation.

Flexural modulus

One of the primary intensions of filler incorporation into polymers is to increase the stiffness of the resultant material. Figure 5 shows the flexural modulus of the reinforced PVC/ENR blends. The flexural modulus was found to increase steadily with increasing OPEFB and OPEFB-*g*-PMA content. Figure 5 also indicates the flexural modulus that show

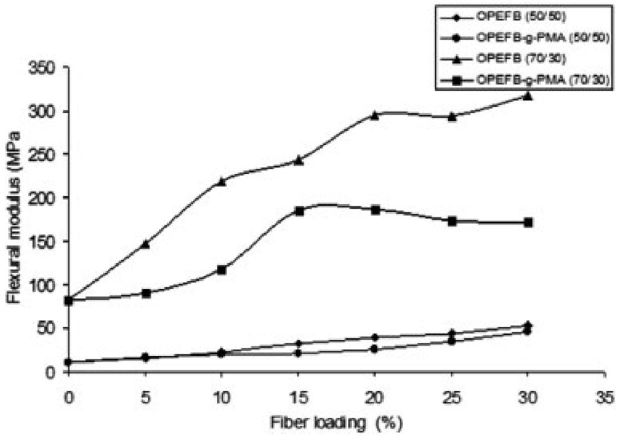

Figure 5 Effect of fiber loading on the flexural modulus of 50/50 and 70/30 PVC/ENR blends.

lower values for the PVC/ENR blends filled with OPEFB-*g*-PMA compared to that of the blends filled with ungrafted OPEFB. It has been reported that grafting of an amorphous polymer (PMMA) onto cellulose results in a reduction of the crystallinity degree of the grafted fiber.[14] The crystalline structure of OPEFB believed to be destroyed by grafting with MA and the amorphous fiber can be easily deformed. Thus the decline in flexural modulus upon grafting with MA is associated with the reduction in crystallinity of the fiber. Similar observations were also reported by Liao et al.[15] in their report on "Influence of Modified Wood Fibers on the Mechanical Properties of Wood Fiber-Reinforced Polyethylene." Furthermore it has been shown that grafting of flax fiber with binary vinyl monomer decreases the percentage crystallinity with reduction in its stiffness and hardness.[16] Therefore it can be inferred that grafting of MA onto OPEFB reduces the stiffness of the fiber, which resulted in the increased flexibility of the PVC/ENR blend composite.

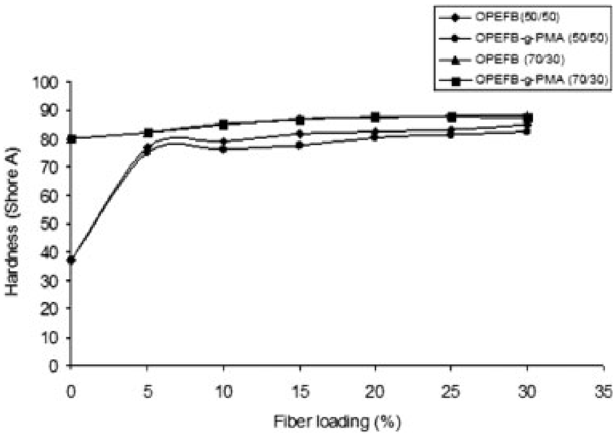

Figure 6 Effect of fiber loading on the hardness of 50/50 and 70/30 PVC/ENR blends.

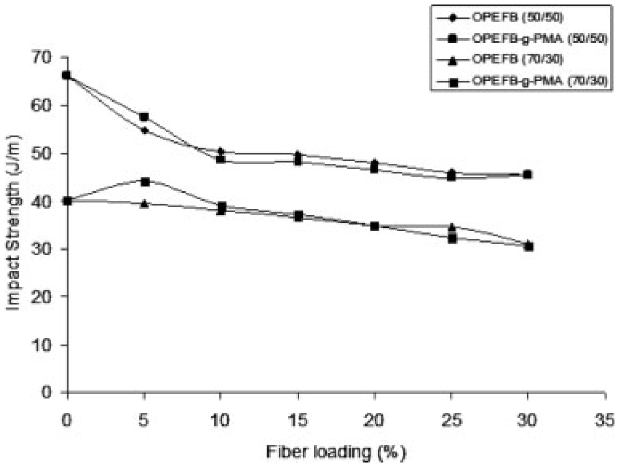

Figure 7 Effect of fiber loading on the impact strength of 50/50 and 70/30 PVC/ENR blends at liquid nitrogen temperature.

Hardness test

The variation in the hardness of the 50/50 and 70/30 PVC/ENR blends is shown in the Figure 6. Fillers that increase the modulus of composites should also increase the hardness of the thermoplastic elastomer. This statement is supported with the results shown in Figure 6. Hardness of the 50/50 PVC/ENR blends increases with increasing fiber loading (grafted and ungrafted) up to 5% as shown in Figure 6. This trend of result is expected because as more filler particles incorporated into the polymer matrix, the elasticity or flexibility of the polymer chain is reduced, resulting in more rigid blends. However beyond 5% of fiber loading, the changes in hardness, found to be marginal indicating the blend has approached the hardness of the fiber. The less pronounce increase in hardness of the 70/30 PVC/ENR blend compared to 50/50 PVC/ENR blend attributed to the higher

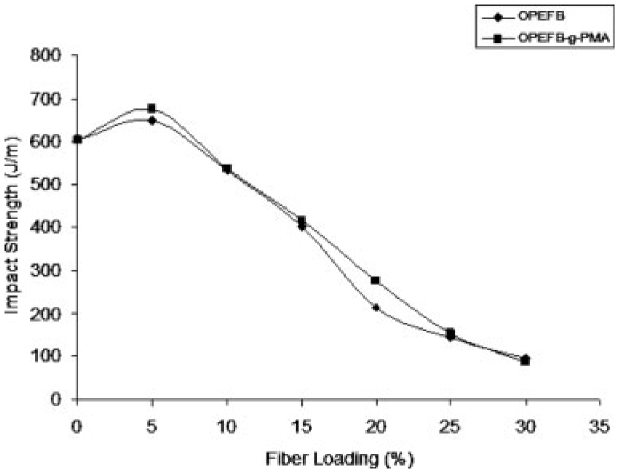

Figure 8 Effect of fiber loading on the impact strength of 70/30 PVC/ENR blend under room temperature.

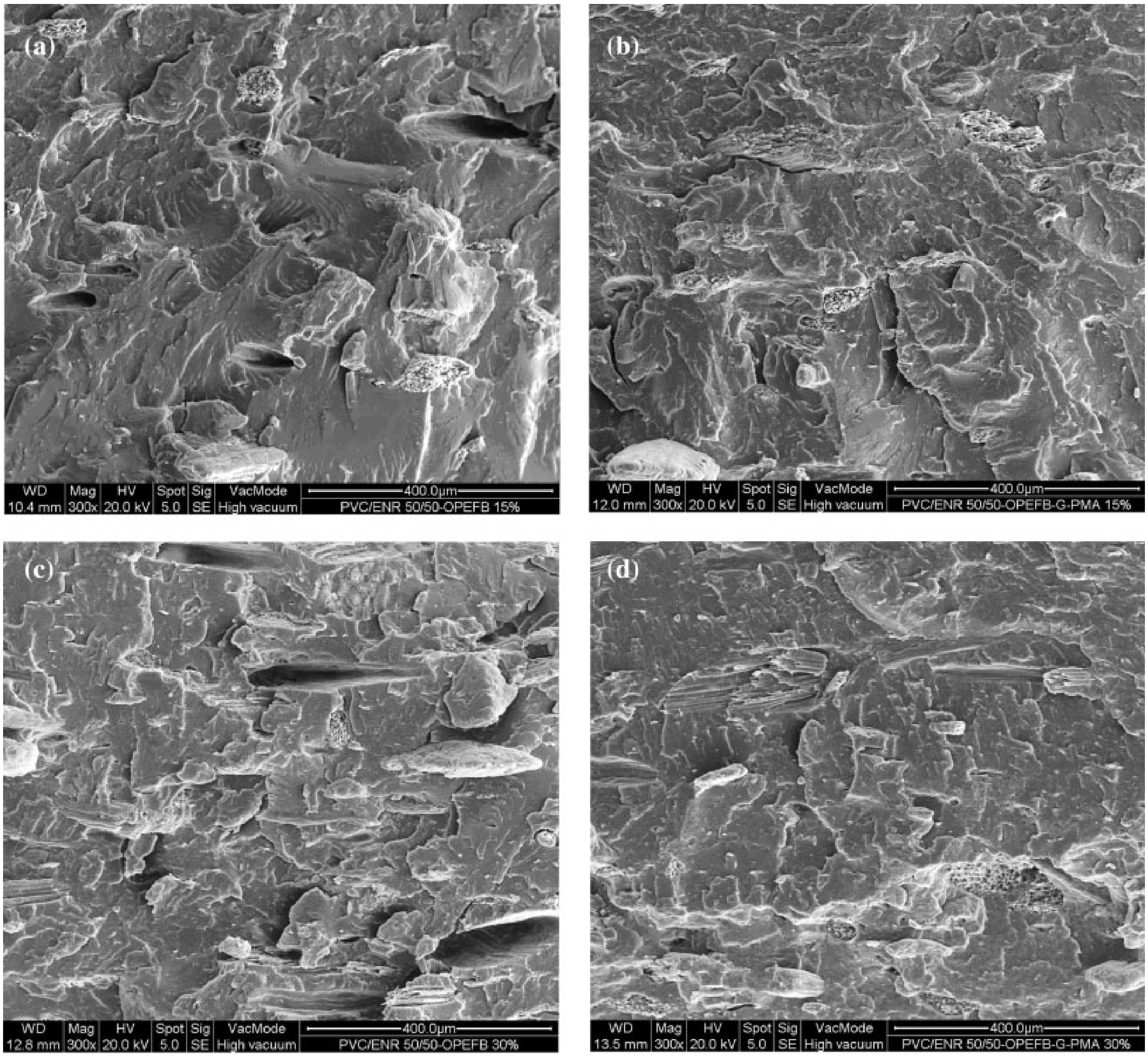

Figure 9 SEM micrographs of the fractured surface of the 50/50 composites (×300). (a) PVC/ENR-OPEFB 15%, (b) PVC/ENR-OPEFB-*g*-PMA 15%, (c) PVC/ENR-OPEFB 30%, (d) PVC/ENR-OPEFB-*g*-PMA 30%.

hardness of the 70/30 PVC/ENR blend compared to 50/50 PVC/ENR at 0% fiber content. However the OPEFB-*g*-PMA reinforced PVC/ENR blends shows a slightly lower hardness values compared to that of the ungrafted reinforced composites. Evidently, this trend of results confirms the observations made on modulus (Young's modulus, modulus at 100% elongation, flexural modulus) in which grafting of MA onto OPEFB found to increase the flexibility of the PVC/ENR blend.

Impact strength

Figures 7 and 8 show the changes in Izod Impact strength of the 50/50 and 70/30 PVC/ENR blends with addition of OPEFB and OPEFB-*g*-PMA at liquid nitrogen temperature and room temperature 25°C ± 2°C, respectively. It was unable to break the 50/50 PVC/ENR blend at room temperature. Thus the results were not shown in Figure 8. It is apparent from Figures 7 and 8 that the impact strength decreases with the addition of OPEFB fiber. This observation is due to the poor wetting of the fiber by the PVC/ENR blend, which leads to poor interfacial adhesion between the fiber and polymer matrix resulting in weak interfacial regions. The poor interfacial adhesion between hydrophobic matrix and hydrophilic filler usually results in decreased toughness.[17,18] This seems to agree with results obtained in these studies. During the impact test, the cracks

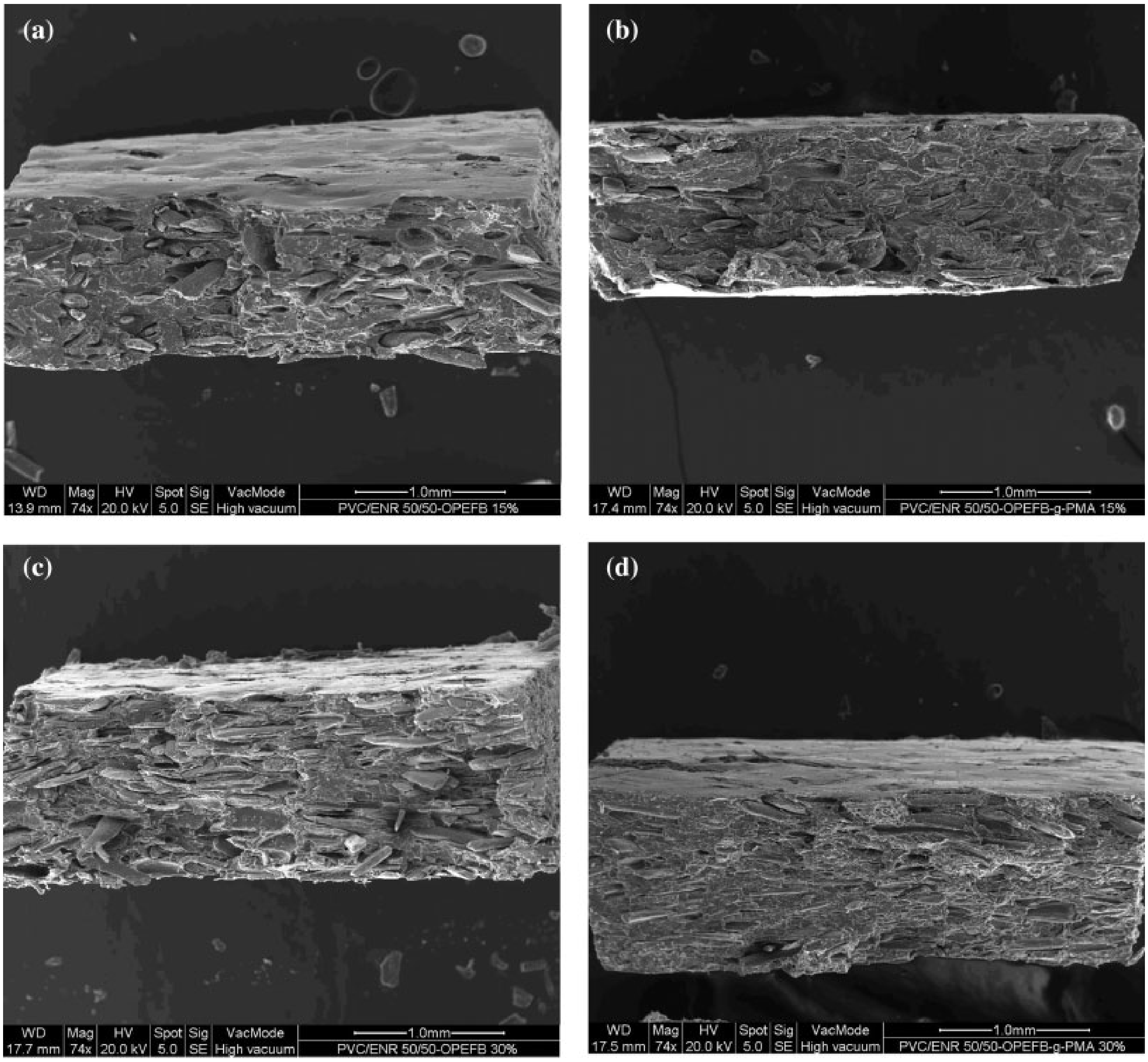

Figure 10 SEM micrographs of the tensile fractured surface of the 50/50 composite (×74). (a) PVC/ENR-OPEFB 15%, (b) PVC/ENR-OPEFB-*g*-PMA 15%, (c) PVC/ENR-OPEFB 30%, (d) PVC/ENR-OPEFB-*g*-PMA 30%.

travel through the polymer as well as along the interfacial region. The latter cannot resist crack propagation as effectively as the polymer region, hence reducing the impact strength. Thus, increasing the fiber content merely increases the interfacial regions, which exaggerates the weakening of the resulting composites to crack propagation. However, the modified fiber composites show a slightly higher impact value than unmodified fiber at 5% fiber loading. This indicates that MA grafting of the fiber improves the energy absorption,[19] implying a better interfacial adhesion between the fiber and PVC/ENR matrix been achieved. However, it can be seen in Figure 7 (50/50 PVC/ENR blend) that, at above 5% fiber loading, the impact properties of OPEFB-*g*-PMA reinforced PVC/ENR blend appear to be lower than the blend incorporated with ungrafted fiber. This trend of results could be associated with the good improvement in the fiber-matrix interaction in 50/50 PVC/ENR blend upon addition of MA grafted fiber. In view of this, Sain et al.[20] have reported that a very good interfacial adhesion between the fiber and the matrix can also result in poor impact strength, as it will lead to catastrophic brittle failure. Therefore, an optimum interaction between the fiber and the matrix is essential to have good impact strength. Similar observations were also made by Khalid et al.[21] in their studies on effect of compatibilizers on polypropylene, PP biocomposites.

Surface morphology

SEM was employed to study the cryogenically fractured and tensile fractured surfaces of the composites. Micrographs of the fractured surface of ungrafted OPEFB-PVC/ENR composite and grafted OPEFB-PVC/ENR composites are shown in Figures 9 and 10. It is apparent from Figures 9 and 10 that the fractured surface of the ungrafted fiber composites appears rougher and more brittle compared with the grafted fiber reinforced composites. A deformed surface was also noted for the ungrafted fiber. The fractured surface of the grafted fiber composites show smoother and well flow of the composite suggesting better interfacial interaction. Figure 9(a,c) show presence of holes that indicate the occurrence of the fiber pull out. This observation was believed to be due to poor adhesion between fiber and matrix. It also shows that the fibers are merely imbedded in the matrix without good adhesion or bonding at the interface. Figures 9(b,d) and 10(b,d) show fiber breakage rather than pull out which indicate better interfacial strength.[20,22] Clearly, the morphological studies support the results on impact properties of the composites. Similarly, Figure 10(a,c) of the ungrafted fiber reinforced composites show that most fibers have been pulled out without breaking during the tensile test. Therefore, it is evident that improved adhesion between fiber and the polymer matrix is achieved upon grafting.

CONCLUSIONS

In this study, the effect of OPEFB and OPEFB-*g*-PMA fiber loading on the mechanical properties PVC/ENR blends have been investigated. The results on UTS revealed that grafting of OPEFB fiber with MA could contribute to the improvement in interfacial wetting between OPEFB and PVC/ENR blend matrix. The enhancement in Young's modulus, hardness, and flexural modulus of the 50/50 PVC/ENR blend with the increase in OPEFB loading indicates that the OPEFB fiber has the potential to improve the mechanical properties of PVC/ENR blends. The lower modulus and higher elongation at break observed for blend filled with OPEFB-*g*-PMA fiber compared to the ungrafted fiber indicates the reduced stiffness and increased flexibility of the fiber with grafting. Similar observations were obtained for the 70/30 PVC/ENR blends. The improvement in interfacial adhesion between the polymer matrix and the fiber upon grafting of the fiber was further confirmed by SEM examination.

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