

MECHANICAL PROPERTIES AND WATER ABSORPTION OF KENAF POWDER FILLED RECYCLED HIGH DENSITY POLYETHYLENE/NATURAL RUBBER BIOCOMPOSITES USING MAPE AS A COMPATIBILIZER

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The performance of kenaf powder (KP) filled recycled high density polyethylene (rHDPE) /natural rubber (NR) blends with and without a compatibilizer, maleic anhydride grafted polyethylene (MAPE), were investigated. The composites with different filler loading (0 to 40 phr) were prepared with a Haake internal mixer. Increasing the KP loading in rHDPE/NR/KP biocomposites reduced the tensile strength and the elongation at break but increased the stabilization torque and the tensile modulus. The addition of MAPE as a compatibilizer increased the tensile strength, elongation at break, and modulus of the composites. This might be attributed to the enhanced adhesion between the filler and polymer matrix, as evidenced from the morphology, using scanning electron microscopy. The incorporation of compatibilizer also reduced the water absorption of the composites.

Keywords: Recycled HDPE; Kenaf; Biocomposites; Mechanical properties; Water absorption; Compatibilizer

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INTRODUCTION

Remarkable attention has been paid to thermoplastic elastomers (TPEs) from both practical and scientific points of view. Due to their unique microstructure, TPEs are promoted for their attractive elastic properties at room temperature, their flowability at high temperature, and their ability to be remelted for recycling use (Ismail et al. 2001b). A further benefit of TPEs is that they provide high value-added products if the components are derived from waste sources ('upcycling') (Grigoryeva et al. 2004).

The incorporation of various types of filler into a TPEs matrix has been carried out either to improve properties or further reduce the cost of materials or to achieve both objectives simultaneously. Recently, fillers (bio-fibers or powders) derived from renewable natural resources such as banana, sisal, hemp, jute, pineapple, bamboo, cotton, coconut, rice husk, and kenaf have become strong competitors to inorganic fillers. These fillers offer several advantages including low density, low cost, relative non-abrasiveness, high filling levels, recyclability, biodegradability, and renewable nature (Bledzki et al. 1999). Kenaf (*Hibiscus cannabinus*) is well known as a cellulosic source having econ-

omical and ecological advantages. Kenaf is widely used as an alternative raw material to wood in the pulp and paper industries for avoiding destruction of forests and also used as non-woven mats in the automotive industries, textiles, fibreboard (Nishino et al. 2003; Ashori 2006; Ashori et al. 2007). For the last few years, many studies have been reported on the utilization of kenaf as reinforcement material for polymeric composites (plastics as well as elastomers). However, as far as TPEs are concerned, very limited studies have been made on the use of kenaf core powder as a filler in HDPE/NR composites.

The mechanical properties of TPEs composites are dependent strongly upon dispersion of the filler in the matrices and the adhesion at the filler/matrix interface. Because of its hydrophilic nature, the filler does not wet or interact with hydrophobic polymers due to the difference in surface energies (Buggy et al. 2005). It is necessary to use compatibilizers to improve the compatibility between fiber and matrix. Many researchers (Oksman et al. 1998; Felix et al. 1991; Mohanty et al. 2006; Han et al. 2008) have shown that the interaction at the fiber-matrix interface can be improved by adding a small amount of a grafted matrix. Among the different compatibilizers, maleic anhydride is the most commonly used.

In this study, kenaf core powder was used as a filler to produce biocomposites based on recycled HDPE/natural rubber blend. The effect of filler content and a compatibilizer, maleic anhydride grafted polyethylene (MAPE), on the mixing, tensile properties, and water absorption of the reinforced biocomposites was investigated.

EXPERIMENTAL

Materials

rHDPE was obtained from Zarm Scientific and Supplies Sdn Bhd, Penang with melt flow index of 0.237 g/10 min (at 200⁰C and 5 kg load). Natural rubber used was SMR L grade from the Rubber Research Institute of Malaysia (RRIM). MAPE with appropriately 3 wt% level of grafting was supplied by Aldrich Chemical Company, Inc. (Milwaukee, WI). Kenaf powder was produced by grinding kenaf core in a table-type pulverizing machine and sieved to obtain the powder size in range of 32 to 150 μ m.

Compounding and Processing

Formulations of KP filled rHDPE/NR composites are given in Table 1. Prior to compounding, rHDPE and KP were dried by using a vacuum oven at 80⁰C for 24 h. The composites were prepared by melt mixing using an internal mixer at 165⁰C with the rotor speed of 50 rpm. The rHDPE was first charged into the mixer and melted for 3 min. NR was added at third minute. The MAPE and KP were added at sixth min, respectively. The blend was allowed to further mixing for another 6 min to obtain the stabilization torque. The total mixing time was 12 min for all samples. The composites were then compression-molded at 165⁰C into 1 mm sheets for preparing test samples.

Tensile Measurement

The tensile properties were measured using an Instron 3366 machine at a cross-head speed of 50 mm/min at 25 \pm 3⁰C according to ASTM D 412. Tensile strength,

tensile modulus and elongation at break of the each sample were obtained from the average of five specimens.

Morphology Study

The tensile fracture surface was investigated with a Supra-35VP field emission scanning electron microscope (SEM). The samples were coated with gold/palladium by a sputter coating instrument (Bio-Rad Polaron Division) for 45 minutes to prevent electrostatic charging during evaluation.

Water Absorption

A water absorption test was carried out by immersing the samples in distilled water at room temperature (25°C). The water absorption was determined by weighing the samples at regular intervals on an electronic balance. The percentage of water absorption, M_t , was calculated by,

$$M_t = 100 \times (w_t - w_o)/w_o \quad (1)$$

where w_o and w_t are the original dry weight and weight after exposure, respectively.

Table 1. Formation of KP filled rHDPE/NR biocomposites*

Materials	Composition (phr)
Recycled high density polyethylene (rHDPE)	70
Natural rubber (SMR L)	30
Kenaf powder (KP)	0, 10, 20, 30, 40
MAPE ^a	5

Note: (phr)-part per hundred resin

^a 5% of KP

* Similar biocomposites but without MAPE were also prepared.

RESULTS AND DISCUSSION

Mixing and Stabilization Torque

The torque-time curves of composites are shown in Fig. 1. A similar pattern of torque curves was observed for all composites (except for the control sample). There were three torque increments due to the material loading. An initial torque increase and the second one at the third minute were detected corresponding to rHDPE and NR charging, respectively. The last was registered for addition of KP. These maximum torques after rHDPE and NR addition showed a decreasing trend from 0KP to 40KP due to the decrease of polymer matrix quantity used for mixing. In contrast, the third maximum torque increased from 10KP to 20KP, 30KP, and 40KP due to the higher filler loading in composites. There was a decrease in torque observed at the sixth minute, which originated from the addition of MAPE. The decrease was shown from 10KP to

40KP, reflecting the dosage of MAPE in composites. This was because MAPE acted as an external lubricant, which reduced the viscosity of compounds as the time it added (Liu et al. 2003). Upon completion of filler dispersion, the torque started to decrease gradually, which might be due to a reduction in viscosity as the stock temperature increased.

Figure 2 shows the stabilization torque at the end of mixing stage (12 min) of rHDPE/NR/KP biocomposites with and without MAPE. It can be seen that stabilization torque increased gradually with increasing filler loading. This was due to the higher the filler content the higher the interfacial interactions occurred between filler and matrix, which caused the reduction of the mobility of polymer chains and thus increased the viscosity and stabilization torque (Ismail et al. 2001b). The addition of MAPE resulted in the higher stabilization torque in the compatibilized composites, which improved the filler-matrix interfacial bonding, leading to an increase of viscosity of the mixtures.

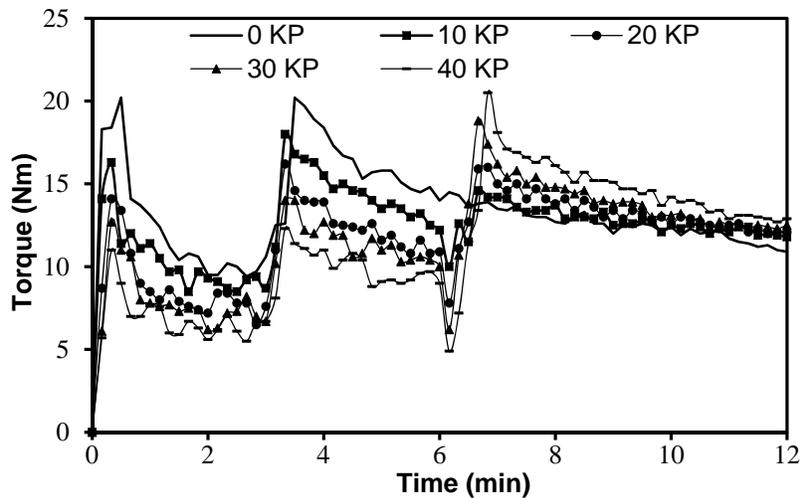


Fig. 1. Torque development for rHDPE/NR/KP biocomposites with MAPE as a compatibilizer

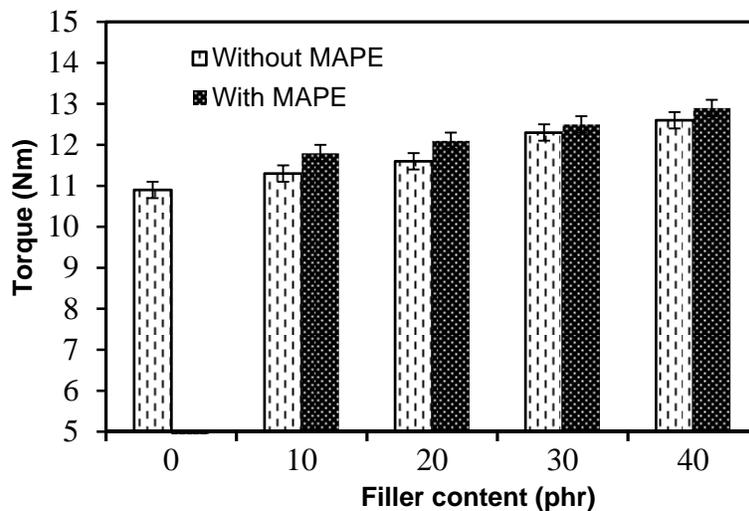


Fig. 2. Stabilization torque at 12 min of rHDPE/NR/KP biocomposites

Tensile Properties

Figure 3 shows the effect of KP content on tensile strength of the rHDPE/NR/KP biocomposites. Tensile strength dropped with the incorporation of KP. The reduction of tensile strength might be due to poor adhesion between KP and matrix. In addition, the other reason was the irregular shape of KP, because of which their capability to support stress transmitted from the polymer matrix is rather poor (Fig. 4). The decreasing trend in tensile strength could be also explained by the agglomeration of filler particles and dewetting of the polymer at the interphase (Ismail et al. 2001a).

The addition of MAPE showed higher tensile strength for the rHDPE/NR/KP biocomposites. Percentage increase in tensile strength was between 6% and 9.6%. The results could be explained in term of the better adhesion at the fiber-matrix interface due to the presence of compatibilizer, as shown later in morphology study. The interfacial adhesion was improved through forming hydrogen bonding between succinic anhydride moieties from MAPE and hydroxyl groups on the KP surfaces (Lu et al. 2005). The better interfacial bonding reduced the interfacial stress concentration and might prevented fiber-fiber contact.

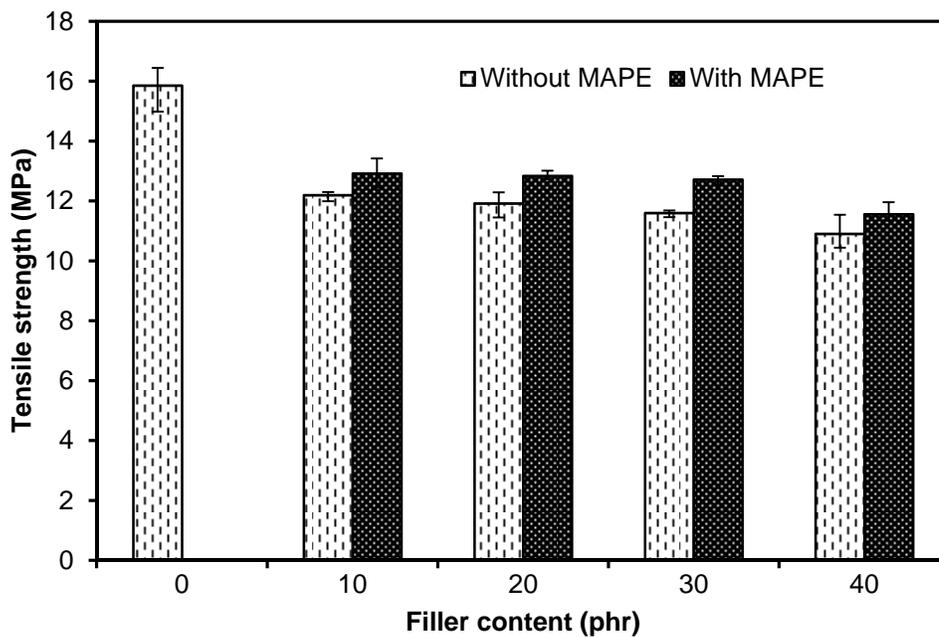


Fig. 3. Tensile strength versus KP content of rHDPE/NR/KP biocomposites

The tensile modulus of rHDPE/NR/KP biocomposites, with and without MAPE increased with increasing filler loading, is shown in Fig. 5. The addition of KP was expected to increase the modulus resulting from the inclusion of rigid filler particles in the soft matrix. However, at a similar filler loading, composites with MAPE exhibited higher tensile modulus than those without MAPE. Increase in tensile modulus varied between 4.5% and 12.3%. Again, this might be due to better interactions between matrix and filler with the presence of MAPE.



Fig. 4. SEM micrograph of irregular morphology of kenaf powder

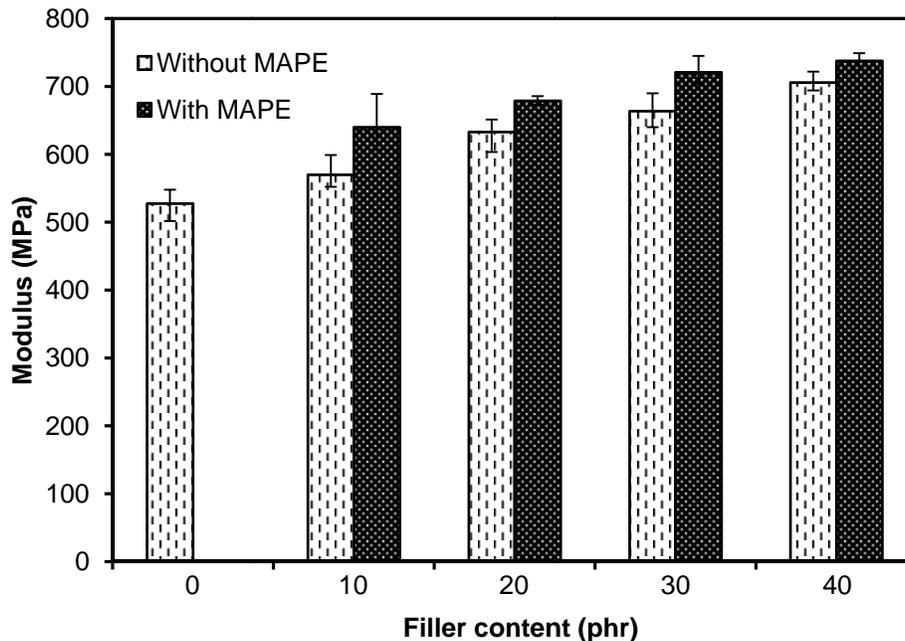


Fig. 5. Tensile modulus versus KP content of rHDPE/NR/KP biocomposites

Figure 6 depicts the variation of elongation at break of the rHDPE/NR/KP biocomposites with filler content. It can be seen that the incorporation of KP into the rHDPE/NR blend resulted in a reduction of elongation at break. This might be attributed to the decreased polymer chain mobility or deformability of a rigid interface between the filler and the matrix. With the addition of MAPE, elongation at break of the composites

was enhanced. It was found that the enhancement was strongly dependant on filler content. At 10 KP, the increment was 161%. However, it was 78.8% for 20 KP and lesser 35% for 30 KP and 40 KP. In compatibilized composites, better filler dispersion and good adhesion between filler and rHDPE/NR matrix were obtained, which would enhance the stress transfer from the matrix to the filler phase. However, at high filler loading, the stress propagation from matrix to filler was obstructed because of the irregular morphology of KP. This hindered the filler orientation during tensile test and resulted in the deterioration of elongation of the composites, especially, after 20 KP. In addition, the tensile failure was due mainly to fiber-matrix delamination, hence, lowered elongation of the composites. MAPE seemed to be less effective for elongation at break of the composites when the weight ratio of the matrix and KP reduced.

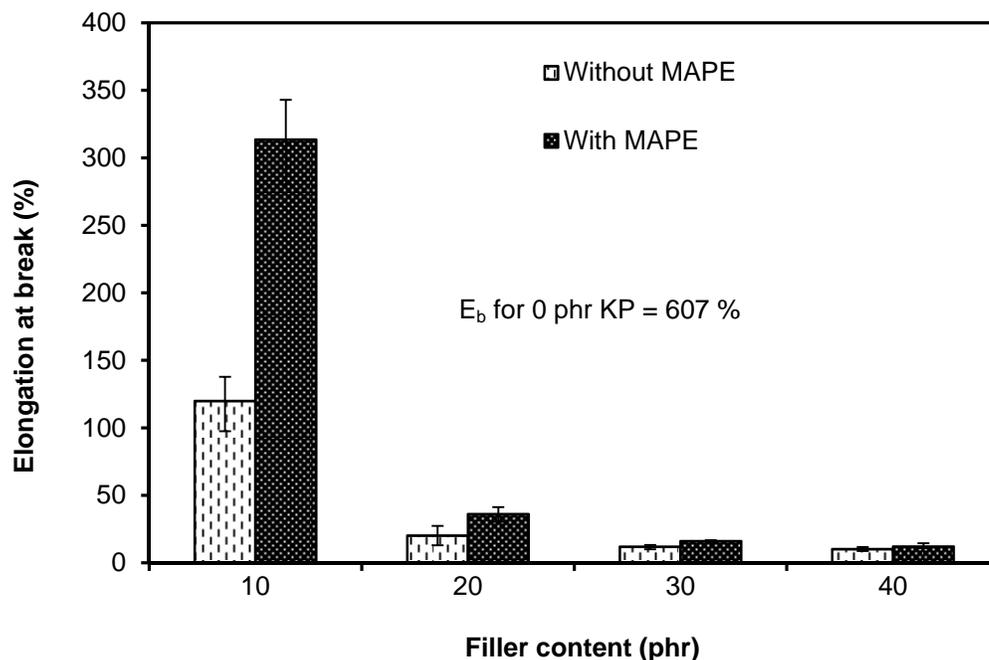


Fig. 6. Elongation at break versus KP content of rHDPE/NR/KP biocomposites

Water Absorption

Figure 7 shows the water absorption of uncompatibilized KP filled rHDPE/NR biocomposites as a function of immersion time. Obviously, the water absorption increased with increase in filler content. Natural fibers are highly hydrophilic in nature and are permeable to water. Incorporation of lignocellulosic filler into polymeric composites thus generally increases the rates of water sorption ability by forming hydrogen bonding between water and the hydroxyl group of cellulose, hemicellulose in the cell wall. As filler content increased, the number of hydrogen bonds between organic components and water molecules also increased. Higher filler content resulted in higher voids entrapped leading higher water accumulating at the interface between the fiber and the matrix (Jacob et al. 2005).

Figure 8 presents the variation of water uptake at 63 days with filler content for uncompatibilized and compatibilized rHDPE/NR/KP biocomposites. The water absorp-

tion is dependent on the availability of free $-OH$ groups on the surface of the fiber. In compatibilized composites, the number of $-OH$ groups could be reduced via the esterification between MAPE and $-OH$ of fiber. Therefore, the absorption of water became restricted (Naik et al. 2007). In addition, the voids in compatibilized composites were less due to the improvement of interfacial filler/matrix adhesion, which limited the penetration of water molecules into the composites.

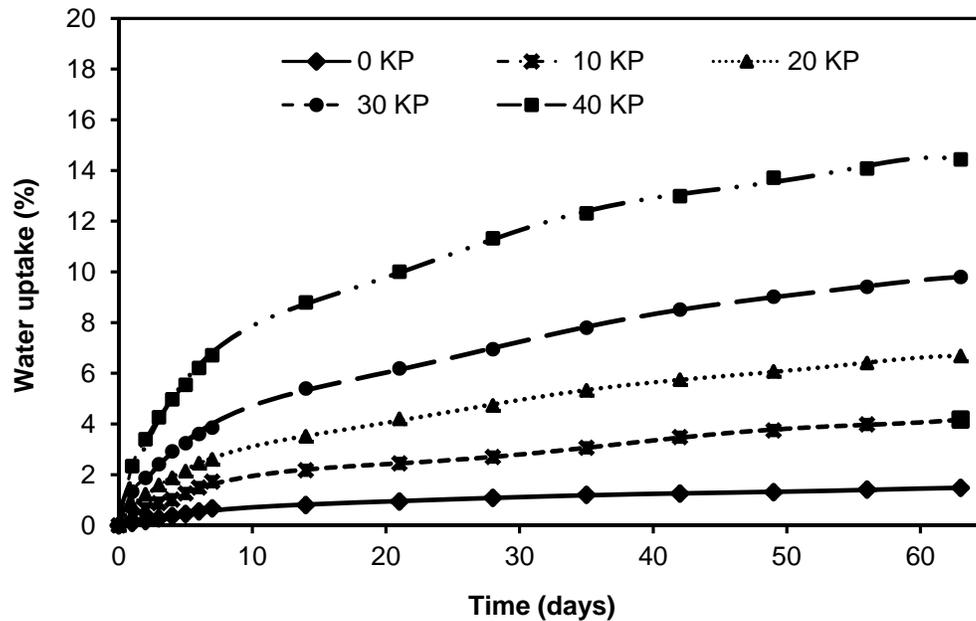


Fig. 7. Water absorption versus immersion time of uncompatibilized rHDPE/NR/KP biocomposites

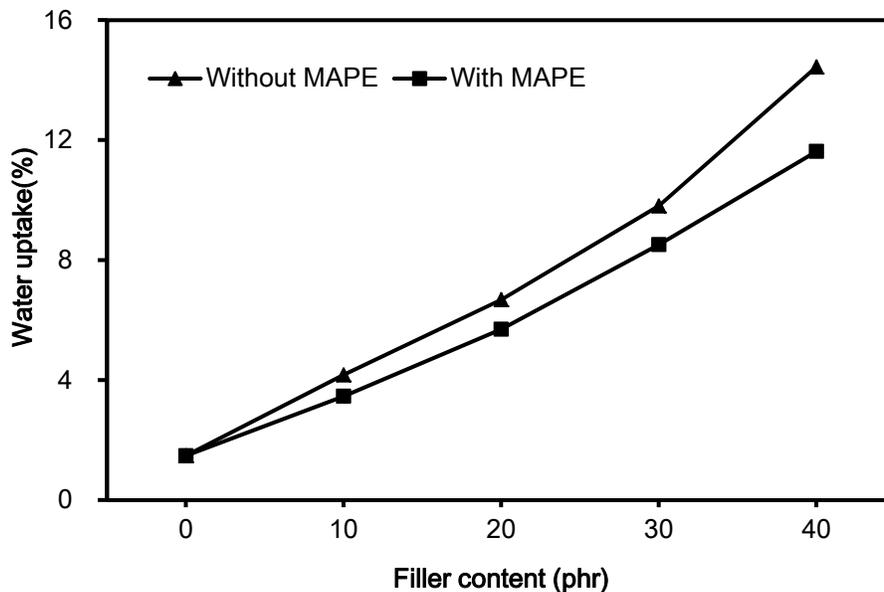


Fig. 8. Equilibrium water uptake at 63 days of rHDPE/NR/KP biocomposites with and without MAPE

Morphology

Scanning electron microscopy (SEM) was used to examine the tensile fracture surface of rHDPE/NR/KP biocomposites. SEM micrographs of the fracture surface of KP filled rHDPE/NR biocomposites at 10, 30, and 40 phr of KP are shown in Fig. 9 (a), (b), and (c), respectively. It can be observed that at lower filler content, the sample had high fibrillation and deformed in ductile mode. At higher filler loading, the presence of fiber was more visible. As shown in Figure 9(b) and (c), fibers were arranged in a disoriented manner and most of the KP fibers directly contacted one another, thus resulting in agglomeration. Some of fibers were pulled out or remained loosely with matrix. Furthermore, voids were also present, as shown in Fig. 9(c). These features were evidences of poor interfacial adhesion between fiber and matrix. Therefore, lower tensile strength and elongation at break as well as higher water adsorption were obtained for composites with higher filler loading.

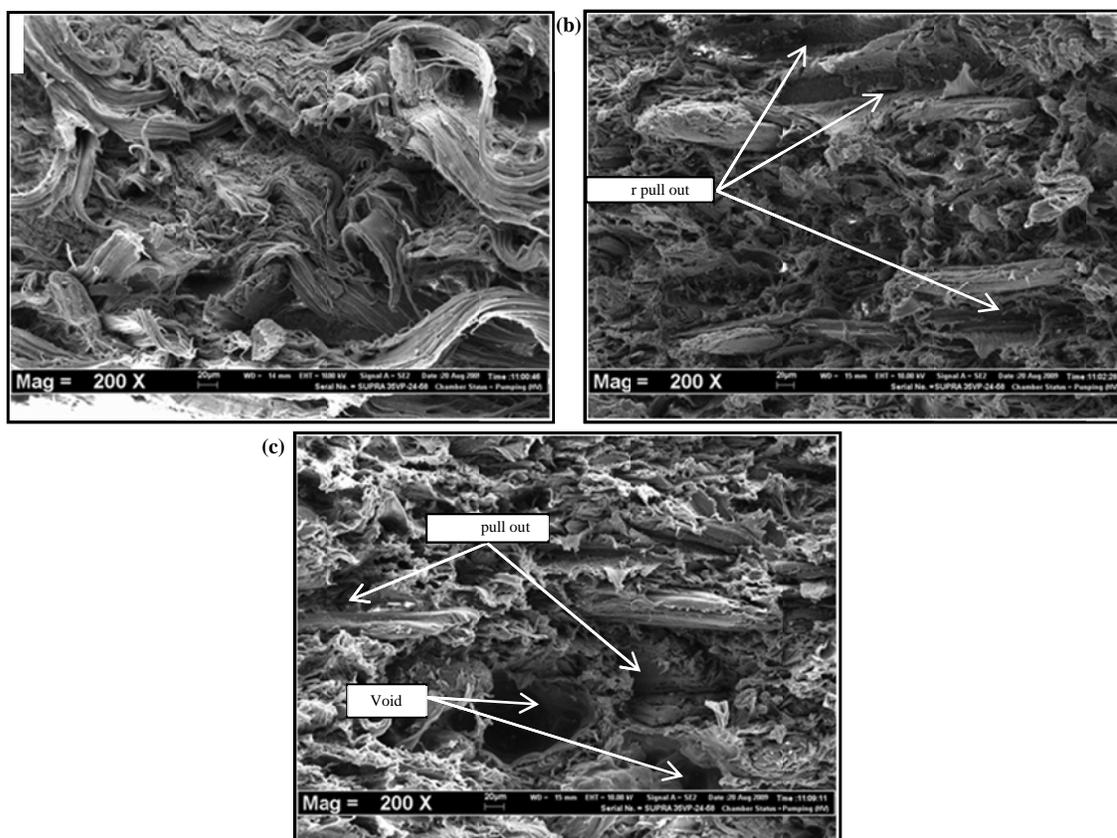


Fig. 9. SEM micrographs of rHDPE/NR/KP biocomposites (200X) at different filler content: (a) 10 phr, (b) 30 phr, and (c) 40 phr

The incorporation of compatibilizer improved adhesion of the matrix to the fibers. Figure 10 (a), (b), and (c) shows the microstructure of KP filled rHDPE/NR composites with MAPE at 10phr, 30phr, and 40phr, respectively. The morphology showed more fractures and higher toughening effect compared to the uncompatibilized composites. The better fiber-matrix adhesion resulted in less fiber pulling-out and fiber-fiber contact (filler agglomeration). The adhesion was strong enough so that the fiber was instead broken or

even torn under tensile load. Matrix fibrillation took place, and more smaller filaments were observed. This finding was a strong indication of good interfacial adhesion between the fiber and the matrix (Demir et al. 2006). The improved interfacial adhesion explained the improvement in not only tensile strength and modulus, but also elongation at break. This proved that MAPE was an effective compatibilizer for this composite.

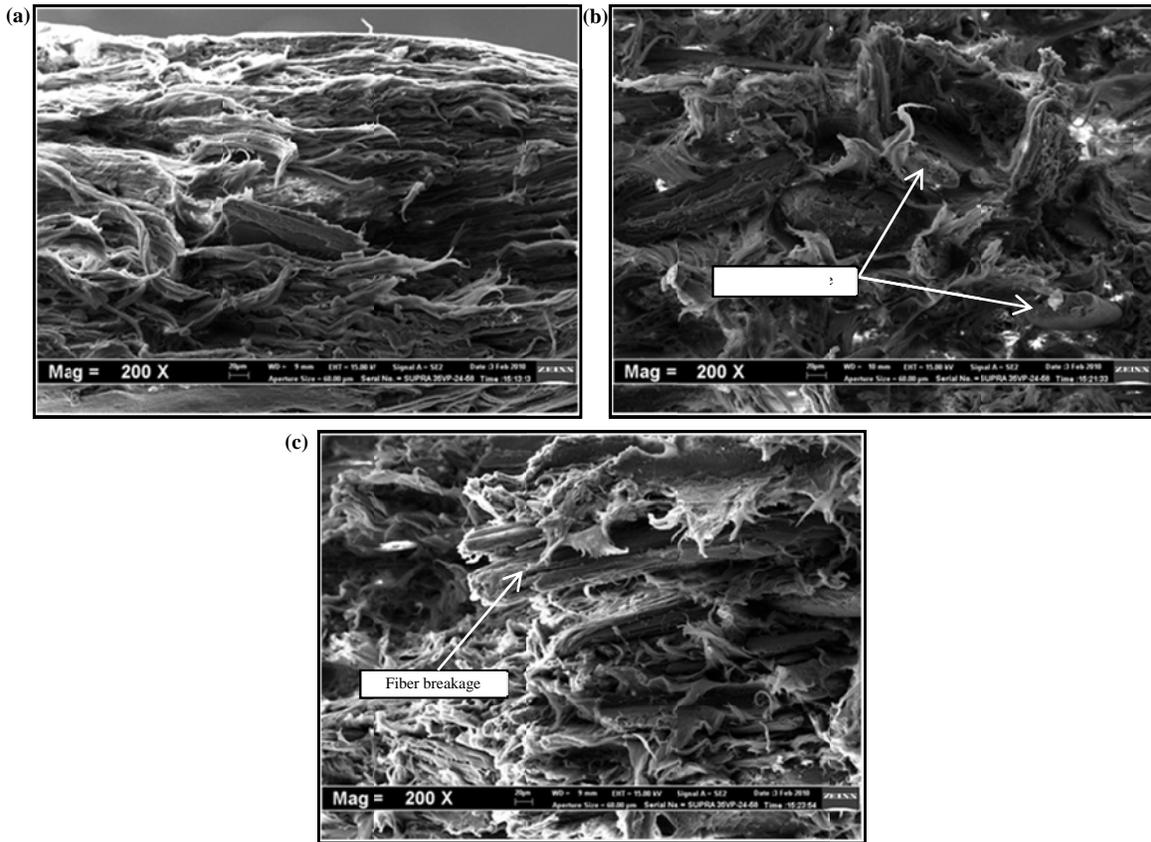


Fig. 10. SEM micrographs of rHDPE/NR/KP biocomposites (200X) with MAPE as a compatibilizer at different filler content: (a) 10 phr , (b) 30 phr , and (c) 40 phr

CONCLUSIONS

The incorporation of kenaf powder into rHDPE/NR blend increased the stabilization torque and the tensile modulus but decreased the tensile strength, and elongation at break of the biocomposites. The poor performance of ultimate properties was attributed to the poor filler-matrix adhesion. High water absorption of kenaf filled rHDPE/NR biocomposites was also observed. However, the addition of MAPE overcame this drawback of kenaf filled rHDPE/NR biocomposites. MAPE improved the interfacial adhesion between hydrophilic kenaf fiber and the hydrophobic polymer matrix, which led to enhancements in mechanical properties and reduction of water absorption compared to the uncompatibilized biocomposites.

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