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Properties of Kenaf Bast Powder-Filled High Density Polyethylene/Ethylene Propylene Diene Monomer Composites

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High-density polyethylene (HDPE)/ethylene-propylene-diene monomer (EPDM) blend was prepared by mixing HDPE and EPDM in an internal mixer. Kenaf fibers were then added to the mixture with a few minutes of mixing. The tensile properties of the HDPE/EPDM/kenaf composites were investigated using tensile testing and scanning electron microscopy. Treated kenaf bast powder was prepared using hydrochloric acid (HCl). Hydrolysis was carried out to study the effect of HCl on the structure, composition, and properties of the fibers. HCl treatment removed the impurities in the fibers, resulting in smooth fibers with a small particles size. Fourier transform infrared analysis showed a reduction in lignin, wax, and hemicellulose but no modification in surface chemical composition. The treated filled HDPE/EPDM composites had high tensile strength, elongation at break, and modulus than the untreated filled HDPE/EPDM composites.

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INTRODUCTION

The decline in petroleum resources has motivated researchers to seek alternative resources that are sustainable, low in cost, renewable, and environmentally friendly. In the past decade, natural fibers have become potential fillers in green composites and biodegradable materials. These fibers consisting mainly of cellulose, hemicellulose, and lignin have received attention as potential replacements for synthetic reinforcing materials because of their light weight, low cost, low energy consumption, biodegrade-ability, and renewability (Ahmad and Luyt 2012; Sherely *et al.* 2008; Bai and Li 2009).

Thermoplastic elastomers (TPEs) are a class of polymers with the combined properties of rubber and thermoplastics. TPEs can be stretched, and unlike rubber-like elastomers, they can be processed without curing or vulcanization because they are true thermoplastics. Conventional thermoplastic techniques such as injection molding, blow molding, and extrusion may be used in TPE processing (Chang *et al.* 2006; Puskas *et al.* 2010; Le *et al.* 2003; Papke and Karger-kocsis 2001; Asami and Nitta 2004). Blends of thermoplastics such as HDPE and amorphous soft rubber such as EPDM are usually found in packing, kitchenware, toys, furniture, and electronics (Maysa *et al.* 2011).

Despite their promise as potential reinforcing materials, natural fiber still have some drawbacks, such as low thermal stability and high moisture absorption. These fibers are usually treated to improved their thermal stability and tensile strength. The cementing region composed of lignin, wax, and some hemicelluloses is removed through acid

hydrolysis to increase thermal stability crystallinity and crystallite size (Bai and Li 2009; Mohamed and Mohammad 2007; Leandro *et al.* 2012).

Kenaf (*Hibiscus cannabinus* L.) stems have three distinct fiber types: bast, core, and wood (Charles *et al.* 1999; Dan *et al.* 2010). Previous studies investigated the tensile and flexural strengths of kenaf fiber in kenaf-fiber reinforced polylactic acid (PLA) composites, and found that these composites possess promising biodegradability (Nishino *et al.* 2003; Ochi 2008). Kenaf fiber received attention because of its superior properties over other natural fiber, such as oil palm (Chin and Yousif 2009). Kenaf bast consists of 31 to 39% cellulose, 21.5% hemicellulose, and 15 to 19% lignin (Yao *et al.* 2008). Compared with kenaf core fibers, kenaf bast fibers have higher crystallinity index, lower moisture content, higher bulk density, and higher tapping density when treated with HCl (Wang *et al.* 2010; Mohanty *et al.* 2000).

Studies on HDPE/EPDM blends, especially those using natural fibers, are lacking. Varma *et al.* (1989) reported that the crystallization rate of HDPE is influenced by the addition of EPDM, which improves TS and impact properties. The use of $CaCO_3$ on HDPE/EPDM blends was reported (Mohamed *et al.* 2011). In EPDM/polypropylene (PP) blends, PP viscosity affects both morphology and phase inversion during dynamic vulcanization (Antunes *et al.* 2011). PP/EPDM-kenaf has better tensile, flexural, and impact properties than TPNR-kenaf (Anuar and Zuraida 2011). The present study aims to evaluate the effect of kenaf bast powder on the properties of HDPE/EPDM with different filler loadings. The tensile fracture surface of untreated and treated kenaf powder-filled HDPE/EPDM composites was analyzed using scanning electron microscopy (SEM). Chemical composition and fiber properties vary with different stages of the growing season. With maturity, the average length of bast and core fibers increases, whereas the crystallinity, protein content, and ash content of kenaf fibers decrease (Rowell and Stout 2007). Kenaf fibers are strong materials with initial modulus but low recoverable elasticity (Rowell and Stout 2007; Liu and Sun 2010).

EXPERIMENTAL

Materials

HDPE with a density of 0.961 g/cm^3 was supplied by Titan Chemicals, Malaysia. EPDM VISTALON 2504 was supplied by ExxonMobil Chemical. Kenaf bast fibers were obtained from Lembaga Kenaf and Tembakau Negara, Kelantan, Malaysia. Kenaf bast was ground to powder using a table-type pulverizing machine at a speed of 2850 rpm and then sieved (70 mesh) to remove foreign materials.

Kenaf Bast Powder Treatment

Kenaf bast fiber was supplied by Lembaga Kenaf and Tembakau Negara. The fiber was ground and sieved to remove foreign materials, such as sand and dust, and produce kenaf bast powder. Kenaf bast, the size of 100 μm, was soaked in 7.5% sodium hydroxide for 24 h before being hydrolyzed with acid to remove impurities and soften the fibers. Kenaf bast powder was then hydrolyzed with 2M HCl for 3 h under heat and mechanical stirring. The hydrolyzed fibers were thoroughly washed with distilled water and then dried at 70 °C. Kenaf powder was stored in a desiccator until compounding. The size of treated kenaf bast is 67.8 μm.

Composite Preparation

Composites were prepared by melt blending a 70/30 ratio of HDPE/EPDM with different filler loadings using a Haake Rheomix 600 mixer with a fixed rotor speed of 50 rpm at 155 °C. Untreated fibers served as the control. The HDPE pellets were introduced first in the mixer before the EPDM rubber. Mixing was carried out for 12 min. The composites were compression-molded into 1 mm thick sheets through a hydraulic hot press Gotech Testing Machine. Subsequently, they were preheated for 6 min at 155 °C, compressed for 3 min at the same temperature, and then cooled under pressure for 2 min.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy was used to investigate the functional groups and chemical characteristics of the fibers. FTIR spectra were obtained through a Perkin Elmer spectrometer (USA). Thin pellet samples of untreated and treated kenaf bast powder were prepared by grinding the powder with potassium bromide.

Tensile Test

An Instron Universal Testing Machine (model 3366) was used to determine the tensile properties of the composites. Dumbbell-shaped samples were prepared using a Wallace die cutter from a 1 mm mold sheet. Tensile testing was carried out according to ASTM D 638 with a crosshead speed of 50 mm/min. TS, tensile modulus (E), and elongation at break (ε) were all automatically recorded.

Morphology

Morphological analysis was performed with a Leo Supra-3SVP field emission SEM. The specimens were mounted on aluminum stubs and sputter-coated with a thin layer of gold to prevent electrostatic charge during examination and provide better resolution.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of the untreated and treated kenaf bast powder are shown in Fig. 1. At 1730 and 1246 cm^{-1}, the untreated kenaf bast showed some characteristics that are lacking in the treated kenaf bast. The peaks at 1730 and 1246 cm^{-1} can be ascribed to hemicelluloses and lignin that are present in the untreated kenaf fiber (Mwaikambo and Ansell 2002). The peak at 1730 cm^{-1} can be attributed to the C=O valence vibration of acetyl or COOH groups (Adel *et al.* 2010). The peak at 1246 cm^{-1} corresponded to C=O and C-O vibrations. The C=O group may also be present in the fiber as traces of fatty acids (Mwaikambo and Ansell 2002). Kenaf bast fiber consists of three main components: lignin, hemicellulose, and cellulose. Lignin, which is located at the outside layer of the fiber, acts as an adhesive that holds cellulose fibrils together. After HCl treatment, lignin was almost completely removed by Cl, in which a soluble chloro-lignin complex was formed (Rowell and Stout 2007). As lignin was removed, hemicellulose content also reduced, and cellulose fibrils were separated from the bundle to form small fibril fibers (Fig. 5B). The disappearance of the peak 1246 cm^{-1} treated kenaf spectrum indicates the removal of hemicelluloses region. This implies that hemicelluloses can be removed by acid hydrolysis. The peaks at 3399 and 3368 cm^{-1} can be attributed to

hydrogen-bonded O-H stretching. The peak at around 2900 cm^{-1} can be attributed to C-H stretching (Spoljaric *et al.* 2009; Colom *et al.* 2003; Behera *et al.* 2012). New peaks related to asymmetric C-O-C bridge stretching, anhydroglucopyronose ring, C-OR stretching, and C-O-C pyronose ring skeletal vibrations were found in the treated kenaf bast at 1112, 1032, and 1161 cm^{-1} (Leandro *et al.* 2012; Poletto 2011).
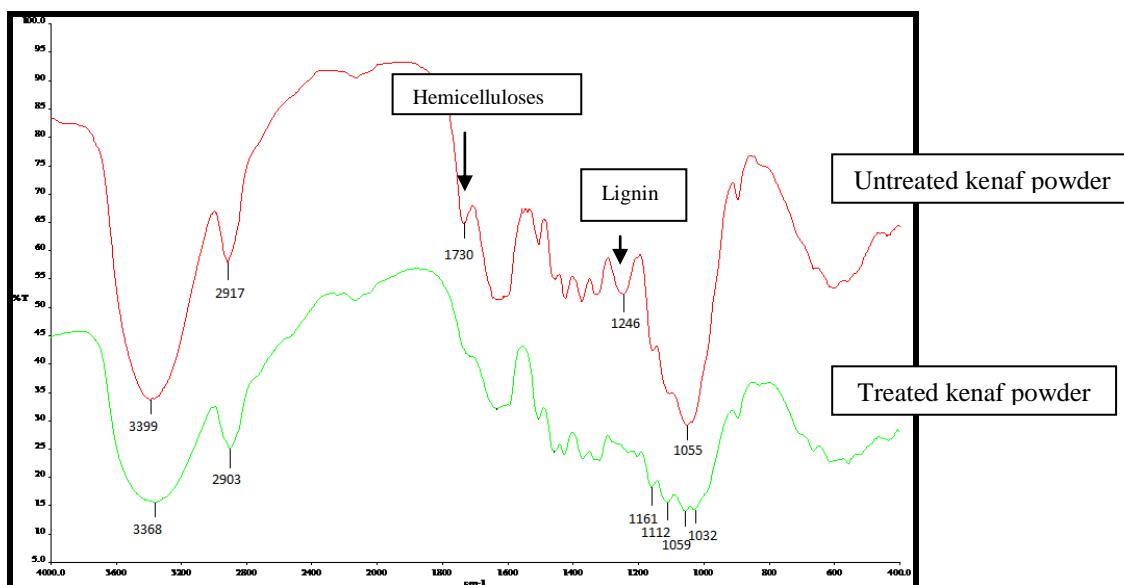
Fig. 1. FTIR spectra of untreated and treated kenaf powder

Tensile Properties

The TS, ε, and *E* values of the composites are shown in Figs. 2 to 4. The effects of filler loading on the TSs of the HDPE/EPDM-untreated and -treated kenaf composites are shown in Fig. 2. The HDPE/EPDM-treated kenaf composites had higher TS than the HDPE/EPDM-untreated kenaf composites because the fibrils obtained after the treatment were stronger than the untreated kenaf containing impurities. Because of the strong hydrogen bonding, bundles of cellulose molecules aggregate to microfibrils, which form highly ordered (crystalline) or less ordered (amorphous) regions (Zykwinska *et al.* 2005; Liu and Sun 2010). The microfibrils that were tied together formed a fibril bundle. Cellulose existing as microfibrils has varying degrees of crystallinity and is embedded in hemicelluloses, lignins, and wax. The ordered fiber structure provides high tensile strength and insolubility in most solvents (Liu and Sun 2010). The fibrils tied together were separated because the gel matrix in natural fibers composed of lignin and hemicelluloses was reduced, providing better tensile properties as the cellulose fibrils is stronger and stiffer. However, TS decreased with increasing filler loading. The major problem with natural fibers is their hydrophilic nature (O-H bond) that causes an incompatibility between hydrophobic HDPE/EPDM matrices. No coupling agent was used in this study. This incompatibility caused weak interfacial adhesion and non-uniform dispersion within the matrix during compounding. As a result, the mechanical properties of the polymer composites decreased (Ahmad and Luyt 2012; Mohanty *et al.* 2000; Bledzki and Gassan 1999; John and Thomas 2008; Ismail *et al.* 2001).

The changes in ε are shown in Fig. 3. The HDPE/EPDM-treated kenaf composites had higher ε than the HDPE/EPDM-untreated kenaf composites because of the stronger adhesion of the treated kenaf with HDPE/EPDM matrix (Ruksakulpiwat *et al.* 2009). As

filler loading increased, ε decreased because the composites became more rigid, which restricted the elongation, reduced the ductility, and limited the stretching of the composites (Afrifah *et al.* 2010; Oksman and Clemos 1998; Ismail *et al.* 2010).
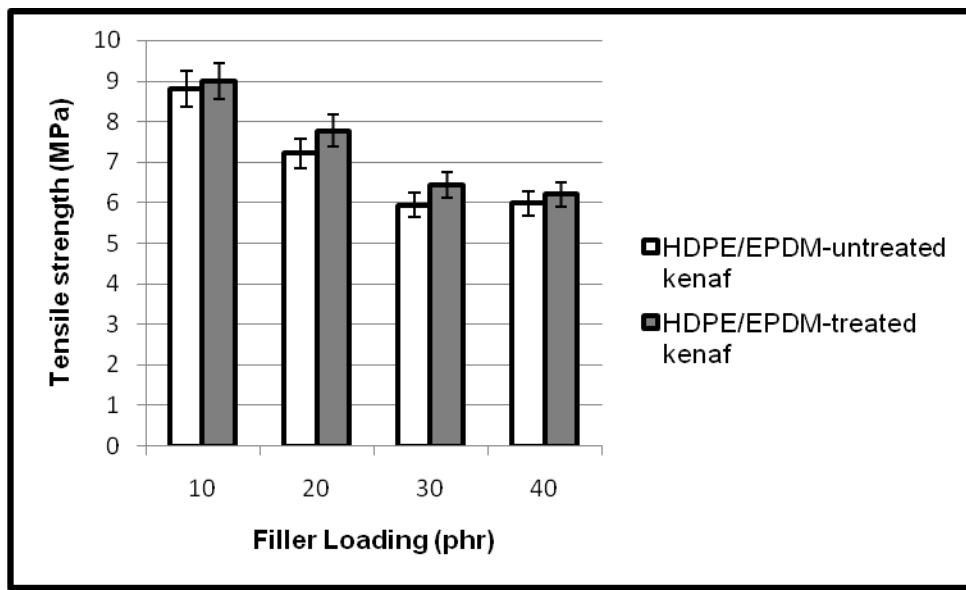
Fig. 2. The tensile strength of untreated and treated filled HDPE/EPDM composites with different filler loadings
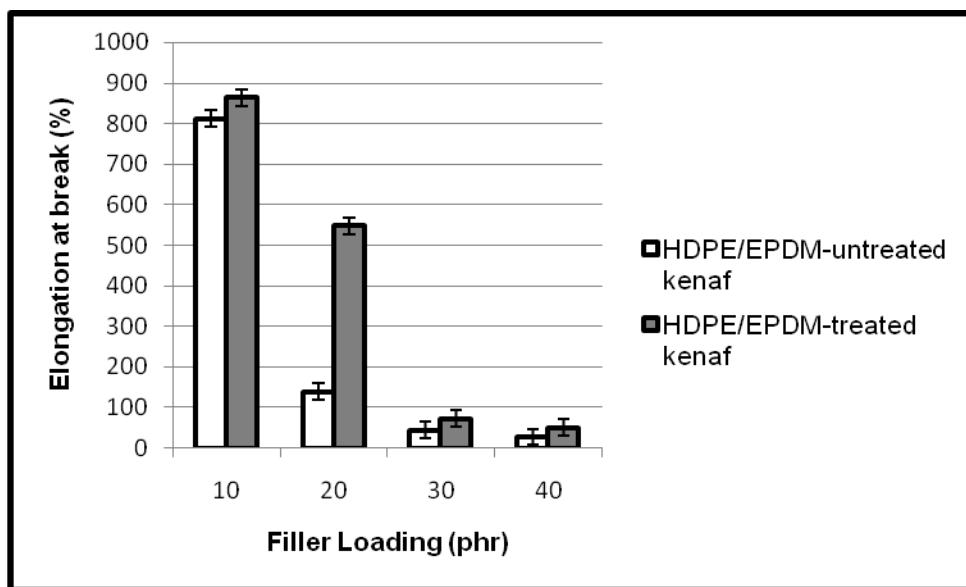
Fig. 3. The elongation at break of untreated and treated HDPE/EPDM composites with different filler loadings

Figure 4 shows the *E* value of the HDPE/EPDM-untreated and -treated kenaf composites. At the same filler loading, the HDPE/EPDM-treated kenaf composites had higher *E* than the HDPE/EPDM-untreated kenaf composites. This finding may be attributed to the more active interaction between the fibril with small particles and the HDPE/EPDM matrix. The higher E of the HDPE/EPDM-treated kenaf composites was also ascribed to the stiffness of the cellulose fibrils. The fibrils in natural fibers made of

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cellulose have high crystallinity and stiffness, which provide better mechanical properties (Rowell and Stout 2007; Charles *et al.* 1999; Liu and Sun 2010; Bai and Li 2009). As shown in Fig. 4, *E* increased as filler loading increased. This finding may be attributed to natural fiber rigidity, which increased the stiffness and reduced the ductility of the composites (Santiagoo *et al.* 2011; Nourbakhsh and Ashori 2008; Li and Matuana 1998; Mohanty *et al.* 2006; Ismail *et al.* 2010).
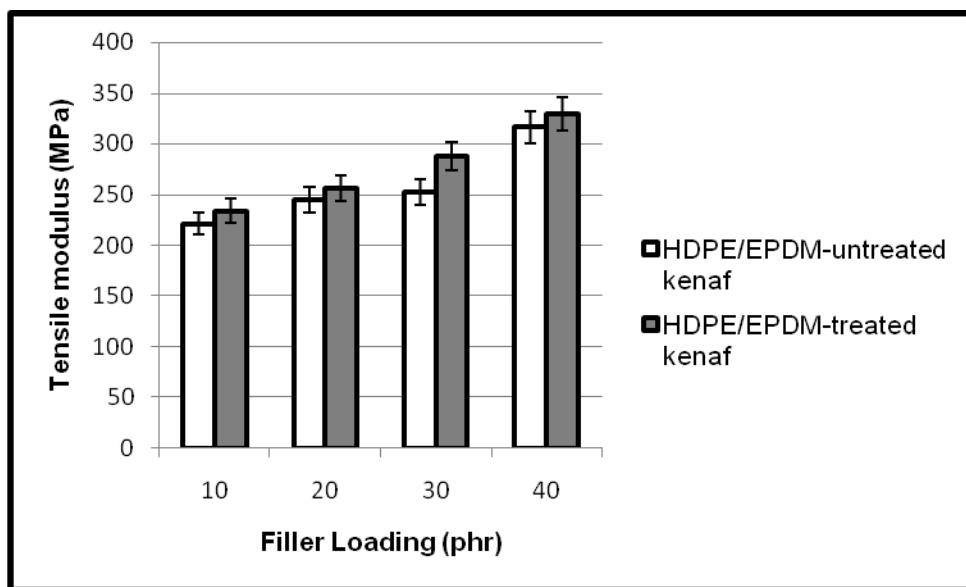
Fig. 4. The tensile modulus of untreated and treated HDPE/EPDM composites with different filler loadings

Morphology

Figure 5 shows the SEM micrographs of untreated (A) and treated (B) kenaf bast at 300× magnification. The presence of lignin and impurities in the untreated fiber is shown in Fig. 5A (Sherely *et al.* 2008). Hydrolysis reduced fiber diameter, which resulted in the formation of small particles. HCl treatment removed the wax, lignin, and fatty acids on the fiber surface. The removal of lignin and hemicellulose was demonstrated with the FTIR analysis. As cementing materials were removed, the fibril bundle inside the fiber was separated. The microfibrils that were tied together were also observed in the fibril bundle. After HCl hydrolysis, the SEM results showed that the surface of the fibers appeared smooth without impurities (Fig. 5B). According to Sherely *et al.* (2008), hydrolysis treatment with acid leads to better packing of cellulose chains because of the removal of cementing materials.

The SEM micrograph in Fig. 6 shows the tensile-fractured surface of the untreated and treated kenaf bast filled HDPE/EPDM composites. The interaction of the treated kenaf with the HDPE/EPDM blend was better than that of the untreated kenaf (Fig. 6C). This result may be attributed to the penetration of the HDPE/EPDM matrix into the fiber hole between the microfibrils. The HDPE/EPDM matrix was obviously present on the fiber surface. The untreated kenaf bast appeared to be free of any matrix interaction (Fig. 6C). No physical contact was found between the untreated kenaf and the matrix; the untreated kenaf was completely separated from the HDPE/EPDM matrix.
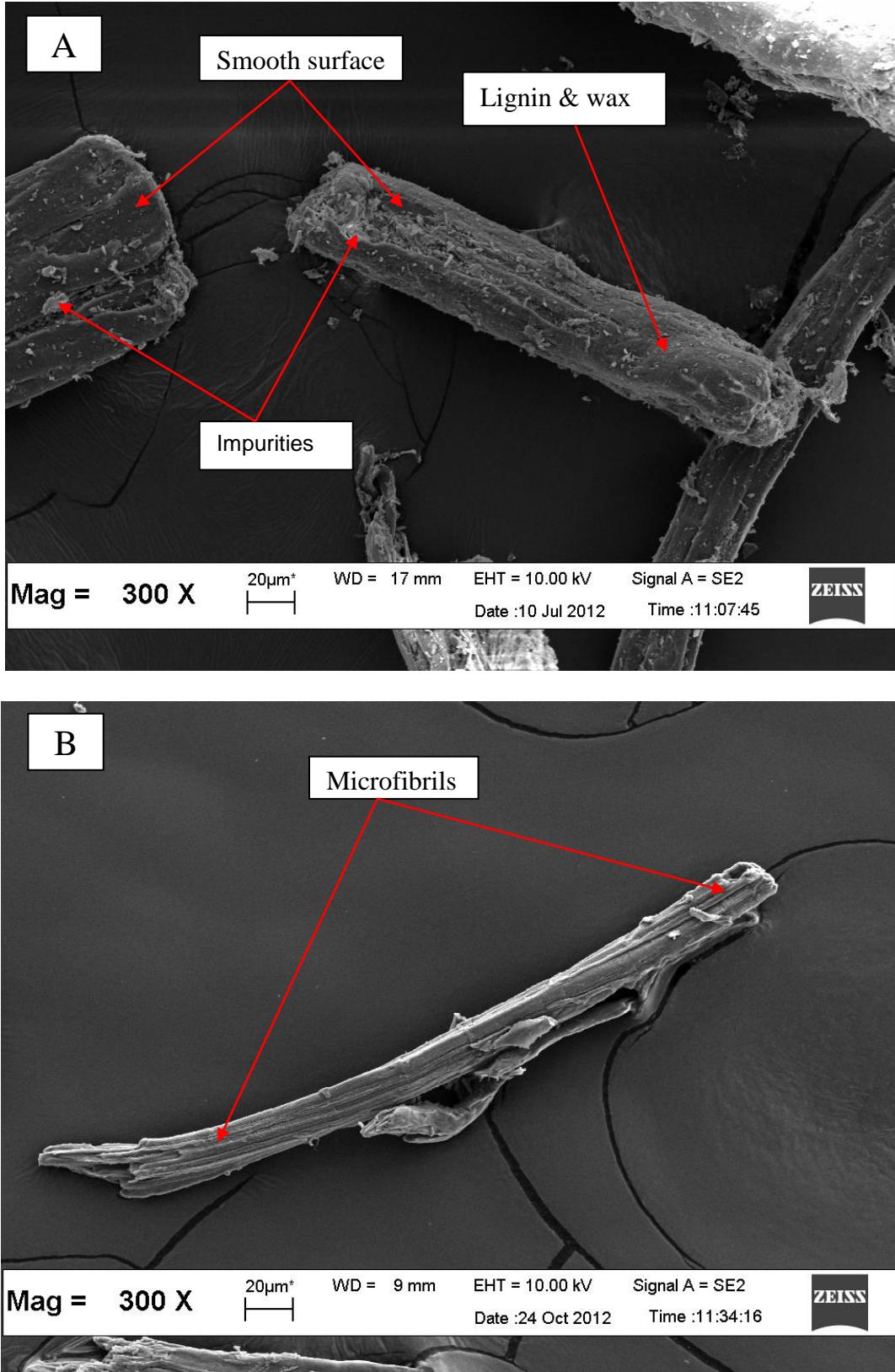
Fig. 5. The micrographs of untreated (A) and treated (B) kenaf bast 300X magnification
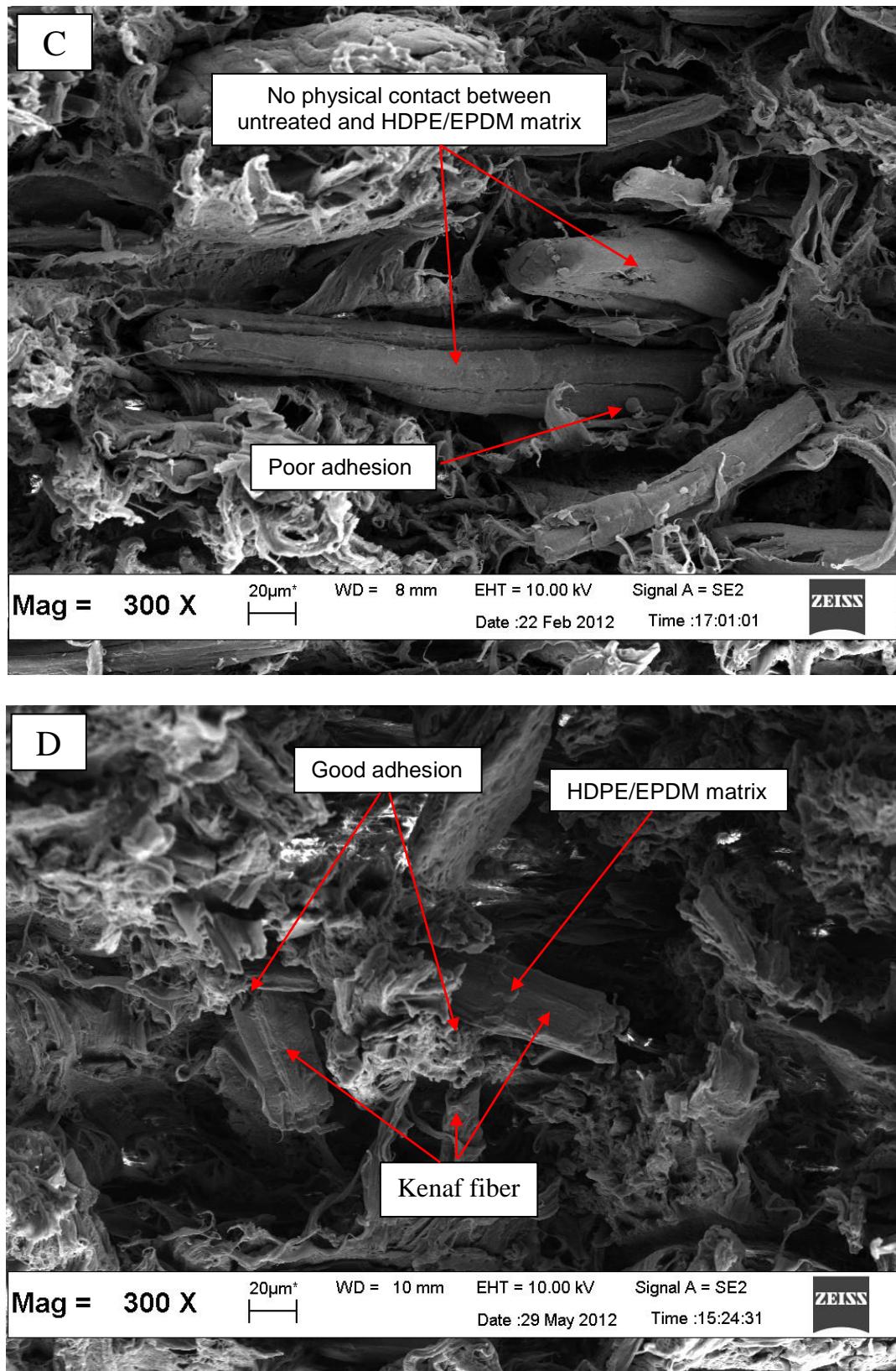
Fig. 6. The micrographs of tensile fracture surfaces of HDPE/EPDM-untreated kenaf (C) and HDPE/EPDM-treated kenaf (D) composites at 300X magnification

CONCLUSIONS

1. Treated kenaf bast powder was successfully prepared using HCl hydrolysis.

2. FTIR results showed that the treatment with acid removed lignin, wax, and hemicellulose, resulting in kenaf bast fibers with small particles and smooth surfaces, as it can be seen in SEM micrograph Fig 5B.

3. The HDPE/EPDM-treated kenaf composites had higher TS, ε, and E values than the HDPE/EPDM-untreated kenaf composites even though TS decreased because of non-polar matrices and polar natural fibers. Overall, the treated filled HDPE/EPDM composites showed higher tensile properties than the untreated filled HDPE/EPDM composites, which is evident from an SEM micrograph (Fig. 6D) of strong interaction between treated kenaf and HDPE/EPDM matrix.

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