Tensile Properties of a Poly(vinyl chloride) Composite Filled with Poly(methyl methacrylate) Grafted to Oil Palm Empty Fruit Bunches

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ABSTRACT: The influence of oil palm empty fruit bunch (OPEFB) fiber and oil palm empty fruit bunches grafted with poly(methyl methacrylate) (OPEFB-*g*-PMMA) on the tensile properties of poly(vinyl chloride) (PVC) was investigated. The OPEFB-*g*-PMMA fiber was first prepared with the optimum conditions for the grafting reaction, which were determined in our previous study. To produce composites, the PVC resin, OPEFB-*g*-PMMA fiber or ungrafted OPEFB fiber, and other additives were first dry-blended with a laboratory blender before being milled into sheets on a two-roll mill. Test specimens were then hot-pressed, and then the tensile properties were determined. A comparison with the composite filled with the ungrafted OPEFB fiber showed that the tensile strength and elongation at break increased, whereas Young's modulus decreased, with the incorporation of 20 phr OPEFB-*g*-PMMA fiber into the PVC matrix. The trend of the tensile properties obtained in this study was supported by functional group analysis, glass-transition temperature measurements, and surface morphological analysis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 91–98, 2010

Key words: graft copolymers; mechanical properties; poly-(vinyl chloride) (PVC); reinforcement; renewable resources

INTRODUCTION

Poly(vinyl chloride) (PVC) is intrinsically more ductile than other thermoplastics such as polystyrene, and in comparison with polyethylene and polypropylene, it is more rigid and stronger. Besides that, PVC is an important commodity thermoplastic resin that plays an important role in many construction applications. The success of PVC includes its good formulating versatility, chemical and weathering properties, nonflammability, and low cost, and for the last few years, researchers have concentrated their efforts on developing natural-fiber-reinforced PVC composites.[1]

Oil palm empty fruit bunches (OPEFBs) from the oil palm plant *Elaesis guineenis* are highly attractive for use as reinforcement fibers for fiber-filled thermoplastic composites because of the consumer trend of requiring products made from ecofriendly and natural waste. Even though natural fibers offer several advantages, certain drawbacks, such as the incompatibility of the fibers with the polymer matrix, greatly reduce the potential of these fibers to be used as reinforcements. The drawbacks (particularly incompatibility) lead to low fiber–matrix adhesion, which can cause a reduction in the mechanical performance of composites. To improve the fiber–matrix adhesion, therefore, the graft copolymerization of poly(methyl methacrylate) (PMMA) onto OPEFBs with a fiber length of less than 75 μm was first conducted, and the results were characterized. On the basis of our previous study,[2] the optimum reaction period, reaction temperature, monomer concentration, and initiator concentration were 60 min, 50°C, 47.15×10^{-3} mol, and 3.92×10^{-3} mol, respectively. In this study, these optimum conditions were used to prepare OPEFB fibers grafted with methyl methacrylate (MMA) and reinforced into a PVC matrix. In contrast to our previous studies, the OPEFB fiber was untreated with a chemical surface reagent, whereas the PVC matrix was impact-modified with an acrylic impact modifier to improve the mechanical properties of OPEFB-filled PVC composites.[3–5]

Recently, OPEFB fiber was chemically modified with benzoyl chloride, and it was reinforced into a PVC matrix.[6] The benzoylated OPEFB fiber was able to improve the tensile properties and impact strength of PVC composites in comparison with untreated fiber. Meanwhile, OPEFB grafted with poly(methyl acrylate) reinforced into a PVC/

TABLE I
Specifications of PVC Suspension Resin MH-66

Appearance	White powder
Degree of polymerization	1000 ± 50
K value	66
Specific gravity	1.4
Bulk density (g/cm^3)	0.50 ± 0.05
Volatile matter, maximum (%)	0.5
Foreign matter (grain/100 g)	15
Particle size retained at 250 μ, maximum (%)	0.3

epoxidized natural rubber (ENR) blend has also been investigated by other researchers.[7] Increases in the elongation at break and tensile strength and decreases in the flexural and Young's moduli have been observed with the addition of OPEFB fibers grafted with poly(methyl acrylate) in comparison with ungrafted fibers. Benzoylation and grafting techniques are used to improve the compatibility of the hydrophilic OPEFB fiber with the hydrophobic PVC matrix by the introduction of other chemical surface reagents able to interact with the fiber and polymer matrix.

As a continuation of our previous work, the optimum conditions for the grafting reaction obtained from our previous study were used for the preparation of fibers of oil palm empty fruit bunches grafted with poly(methyl methacrylate) (OPEFB-g-PMMA). The ability of these fibers to influence the tensile properties of PVC composites was mainly investigated.

EXPERIMENTAL

Materials

OPEFB fibers were bought from Sabutek Sdn. Bhd. (Teluk Intan, Malaysia) and separated into different lengths with a Restsch shaker. The vibration time used for separation was 10 min. The OPEFB fibers were less than 75 μm long and were dried in an oven at 105°C for about 24 h to a constant weight. MMA monomer, obtained from Merck Schuhardt (Hohenburnn, Germany), was grafted onto the OPEFB fiber surface. Analytical-grade hydrogen peroxide (H_2O_2), produced by QRëC (Shah Alam, Malaysia), was used as an initiator, whereas ammonium ferrous sulfate, obtained from BDH Sigma–Aldrich Chemie GmbH (Steinheim, Germany), was used as a catalyst. All solvents and other analytical-grade chemicals were used as received from the manufacturers without further purification.

Meanwhile, the suspension PVC resin used in this study, with a solution viscosity constant (K) value of 66 (trade name MH-66), was supplied by Industrial Resin Malaysia Sdn. Bhd. (Tampoi, Malaysia). Its specifications are summarized in Table I. The additives used in the PVC formulations (Table II) were also obtained from Industrial Resin Malaysia.

Preparation of PMMA-g-OPEFB

The graft copolymerization of MMA onto OPEFB fibers through a free-radical mechanism was carried out in a typical five-necked flask (250 mL) equipped with a magnetic stirrer, and it was immersed in a thermostated water bath. A Graham-type reflux condenser was attached to the five-necked flask to reduce the loss of the water medium. The reaction was carried out under an atmosphere of nitrogen. A thermometer was used to ensure that the heater maintained the temperature of 50°C. Forty grams of dried OPEFB fibers together with 100 mL of distilled water was added to the five-necked flask. Nitrogen was purged through the OPEFB slurry for 30 min to remove oxygen in the flask. Later, 80 mL of a 2.0M H_2O_2 initiator was injected into the flask, and the mixture was left for 5 min. Then, 4 g of an ammonium ferrous sulfate cocatalyst was added to the flask, and the slurry was allowed to settle for 5 min. Next, 200 mL of MMA monomer was injected into the mixture. The reaction mixture was magnetically stirred under a nitrogen atmosphere at 50°C for 60 min. When the reaction period was over, the reaction flask was immediately exposed to the ambient atmosphere, and the grafted product was filtered with a vacuum pump. The flask was washed thoroughly with distilled water to remove the grafted

TABLE II
PVC Formulations

Ingredient	PVC blend	OPEFB-filled PVC composite	OPEFB-g-PMMA-filled PVC composite
PVC resin (phr)	100.0	100.0	100.0
Tin stabilizer (phr)	2.0	2.0	2.0
Calcium stearate (phr)	0.5	0.5	0.5
Stearic acid (phr)	0.6	0.6	0.6
Acrylic polymer (phr)	1.5	1.5	1.5
Titanium oxide (phr)	4.0	4.0	4.0
OPEFB (phr)	—	20	—
OPEFB-g-PMMA (phr)	—	—	20

product stuck on the inner flask surface, and it was filtered again. Finally, the grafted product was kept in an oven at 60°C for 24 h until a constant weight was achieved. The grafted product was further treated with the Soxhlet extraction technique for the removal of PMMA homopolymer that formed during the reaction. The procedure of grafting was explained thoroughly in our previous work.[2]

The grafting percentage (% G) and grafting efficiency percentage (% E) were determined with the following formulas:

$$\% G = [(w_3 - w_2)/(w_1)] \times 100\%$$

$$\% E = [(w_3 - w_1)/(w_2 - w_1)] \times 100\%$$

where w_1 is the weight of the original OPEFB, w_2 is the weight of the grafted product after copolymerization, and w_3 is the weight of the grafted product after copolymerization and purification (extraction).

Preparation of the PMMA-*g*-OPEFB/PVC composites

The dry-blend formulations, as shown in Table II, were first dry-blended with a laboratory high-speed mixer for 10 min to homogenize the blends. The dry-blended formulations were then melt-blended and sheeted with a laboratory two-roll mill at 165°C for 10 min. The milled sheets were then placed into a mold with five cavities and hot-pressed at 180°C and 1.2 kPa, respectively, for 5 min. The mold was cooled for 5 min before the specimens were removed.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was used to identify the related functional groups present in samples. A small quantity of a sample was thoroughly mixed with dry potassium bromide (KBr) powder in a mortar and then pressed at 6 bars for 2 min to form a moisture-free, thin disc of KBr. The thin disc was placed in a sample cup of a diffuse reflectance accessory and was then scanned from 4000 to 370 cm^{-1} 16 times to reduce the noise/signal ratio. All the spectra of samples were obtained by the attenuated total reflection technique with a Nicolet 5700 FTIR apparatus (USA).

Differential scanning calorimetry (DSC)

A DSC study was carried out with a PerkinElmer (Worcestershire, UK) DSC7 according to ASTM D 3418–2 at a heating rate of 10°C/min from 30 to 200°C. Liquid nitrogen was used at a steady rate of 50 mL/min. A sample was placed in a sealed alumi-num pan, and an empty pan was used as the reference. The tangent method was used to determine the glass-transition temperature (T_g) of the sample. The midpoint of the first endothermic baseline shift in the DSC heating curve was taken to be T_g.

Scanning electron microscopy (SEM)

Studies of the surface morphologies of ungrafted OPEFB, grafted OPEFB, and PVC composites filled with ungrafted or grafted OPEFB fibers were performed with a Zeiss Supra 35 (Amsterdam, Netherlands) PFE scanning electron microscope. Samples were mounted on the stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during the examination.

Tensile testing

The tensile property assessment was carried out on a dumbbell-shaped sample according to ASTM D 638 with an Instron (London, UK) model 5567 machine with a 20-kN load cell. The crosshead speed was set at 10 mm/min, and the test was carried out at room temperature (25 ± 2°C) and at a relative humidity of 50 ± 5%.

RESULTS AND DISCUSSION

Graft copolymerization reaction analysis

The optimum conditions for the grafting reaction obtained from our previous study[2] were used to produce OPEFB-*g*-PMMA fibers. The grafting and grafting efficiency percentages were found to be about 177 and 59%, respectively. These results were similar to the grafting and efficiency percentages at the reaction time of 60 min and at the temperature of 50°C, as reported in our previous study,[2] although other optimum conditions such as the monomer, initiator, and cocatalyst concentrations were scaled up according to the amount of OPEFB fiber required. This showed that MMA monomer was grafted successfully onto the OPEFB fiber surface, and this fiber was called OPEFB-*g*-PMMA.

FTIR analysis

FTIR spectroscopy has been used in the study of interactions in polymer composites, although it is not sensitive technique for providing detailed information. In the OPEFB-*g*-PMMA-filled PVC composite, the resonance structures of the ester group in the PMMA chemical structure may be responsible for both interactions with PVC and OPEFB. Aouachria and Belhaneche-Bensemra[8] described the interaction of PMMA and PVC in detail and reported that the
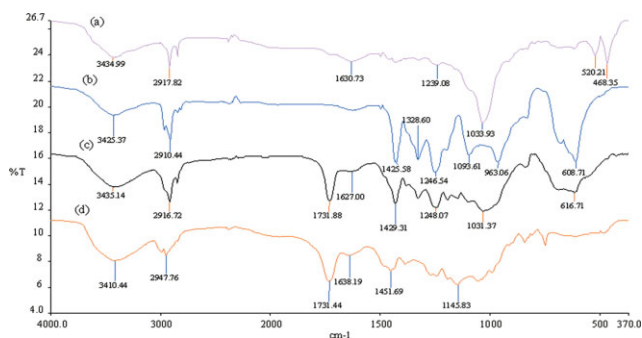
Figure 1 FTIR spectra of (a) the PVC composite filled with ungrafted OPEFB, (b) the PVC, (c) the PVC composite filled with OPEFB-*g*-PMMA, and (d) the OPEFB-*g*-PMMA fiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

carbonyl groups around 1729 cm^{-1} corresponded to the hydrogen-bonded carbonyl groups in the PVC/PMMA blend. In this work, the FTIR analysis performed on the OPEFB-*g*-PMMA-filled PVC composite showed the absorption of the carbonyl band of PMMA at 1730 cm^{-1} (Fig. 1). In comparison with the spectrum of the ungrafted composite, there was a very pronounced absorption band appearing at 1730 cm^{-1} for the grafted composite. However, the position of the C=O peak remained constant, and this suggested that an interaction between PVC and PMMA in this study was insufficiently strong to perturb the local environment of the oscillating carbonyl bond and to shift the peak toward a lower wave number.[9] It was characterized by a weak dipole–dipole interaction between PVC and PMMA in the composites. The broad and small peaks in Figure 1 at 1630 cm^{-1} are due to the interaction of acid chlorides produced by PVC during the composite preparation with the PMMA chains.[10] Besides that, absorption peaks for the grafted composite were found at 1731 (assigned to C=O of PMMA),
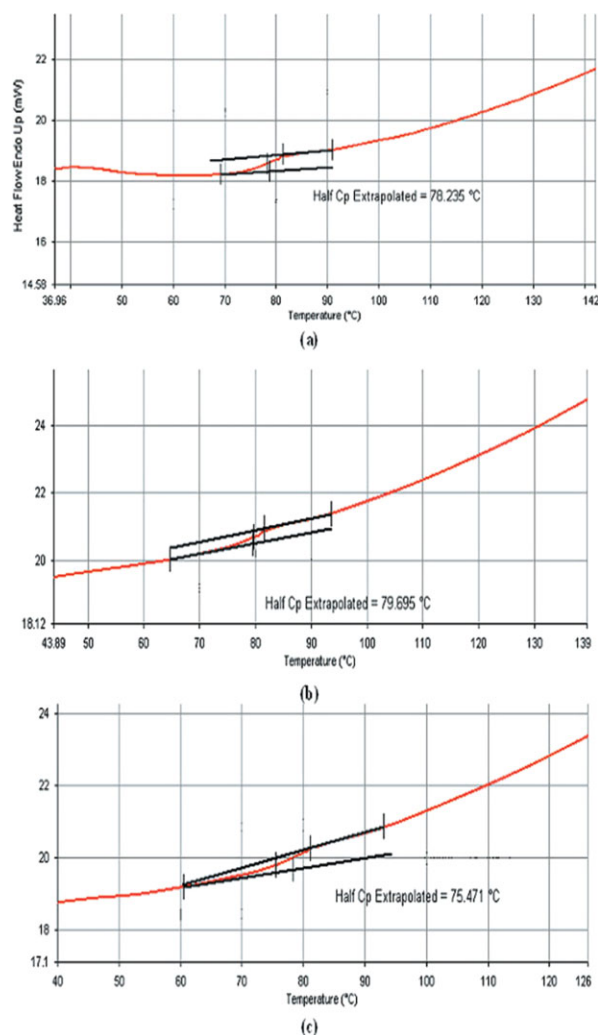

Figure 2 DSC curves of (a) the PVC, (b) the PVC composite filled with ungrafted OPEFB, and (c) the PVC composite filled with OPEFB-*g*-PMMA. C_p, heat capacity at constant pressure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
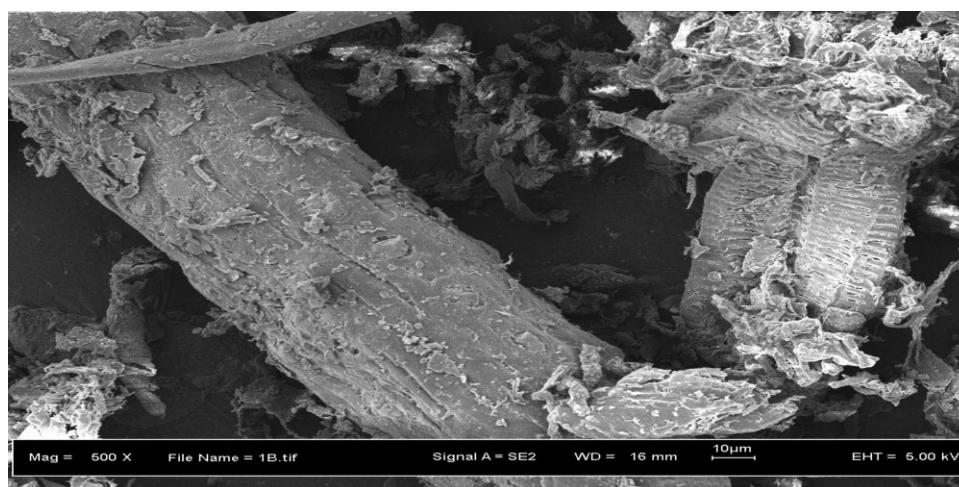

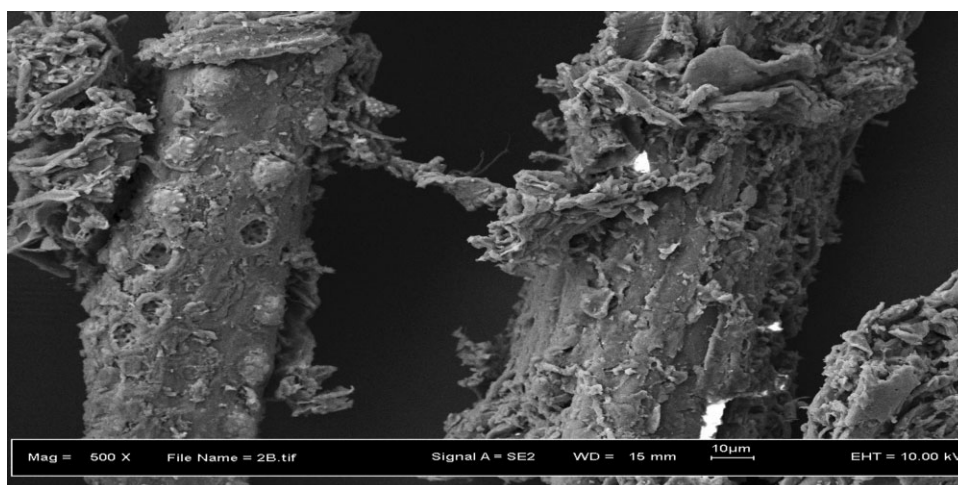**Figure 3** SEM micrograph of the untreated OPEFB fiber.

Figure 4 SEM micrograph of the OPEFB-*g*-PMMA fiber.

1429 (assigned to CH_2 of PVC), 1248 (assigned to CH of PVC), and 1031 cm^{-1} (assigned to C—O of PMMA).[9] All these peaks also verified that PMMA had interacted on the OPEFB fiber surface.[2]

DSC analysis

Figure 2 shows the DSC curves of PVC, the PVC composite filled with ungrafted OPEFB fiber, and the PVC composite filled with PMMA-*g*-OPEFB fiber. The T_g values of PVC, the PVC composite filled with ungrafted OPEFB fiber, and the PVC composite filled with grafted OPEFB fiber were 78.2, 79.7, and 75.5°C, respectively. The results indicated that the incorporation of the grafted fiber into PVC lowered T_g of PVC, whereas the ungrafted fiber increased T_g of PVC. The lowering of T_g could be explained reasonably by the influence of PMMA on the rigidity of the PVC matrix and the degree of

crystallinity of the OPEFB fiber. PMMA could act as plasticizer to reduce the rigidity of PVC because PMMA has been proved to have excellent compatibility with PVC[11] and possibly diffused into the PVC matrix.[6] Similar changes in T_g of the polymers due to the incorporation of treated fibers have also been reported by other researchers.[12] Besides that, the crystalline structure of OPEFB, believed to be destroyed by grafting of PMMA and the fiber, could be easily deformed. Similar observations have been reported by other researchers.[13,14] Canche-Escamilla et al.[13] found that the degree of crystallinity of cellulose was reduced after grafting with PMMA, whereas Kaith and Susheel[14] in their study reported that the grafting of flax fiber with binary vinyl decreased the crystallinity percentage with a reduction in its stiffness and hardness. Consequently, it can be deduced that the grafting of PMMA onto the OPEFB fiber surface reduced the rigidity of the PVC
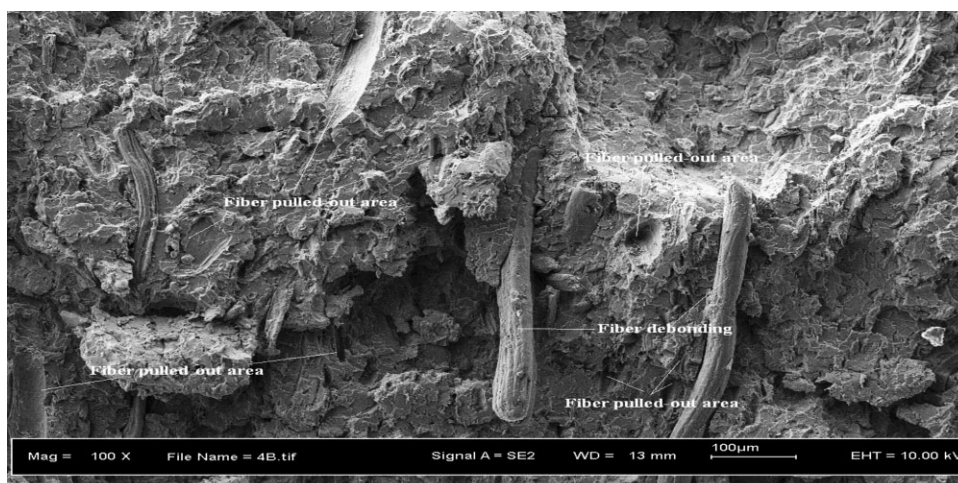

Figure 5 SEM micrograph of the fractured surface of the PVC composite filled with ungrafted OPEFB. Fiber pullout and fiber ends are shown.
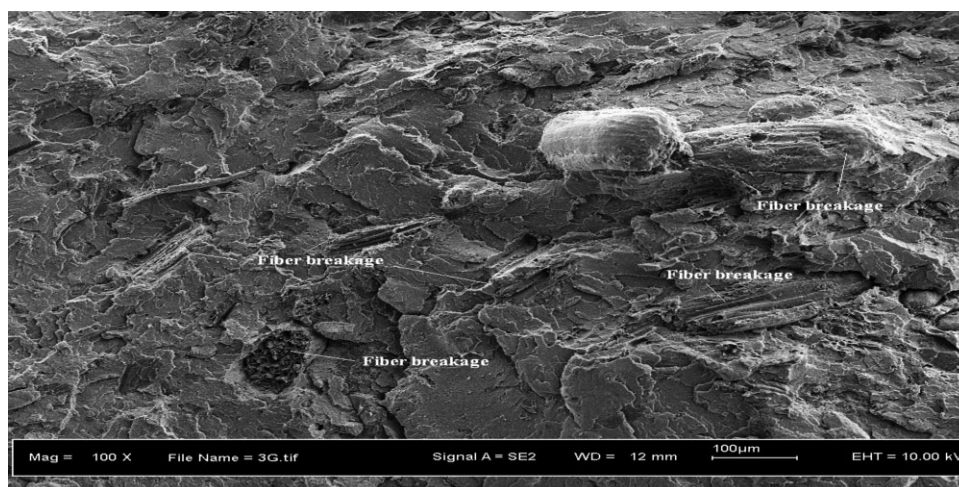
Figure 6 SEM micrograph of the fractured surface of the OPEFB-*g*-PMMA-filled PVC composite. Fiber breakage is shown.

matrix and the stiffness of the fiber, and this resulted in the increased flexibility of the PVC composite. This flexibility contributed to the enhancement of the elongation at break and the reduction of Young's modulus, which is discussed in subsequent sections.

Morphological analysis

SEM micrographs were taken to characterize the ungrafted and grafted OPEFB fibers and the morphologies of the composites. Figures 3 and 4 show the ungrafted and grafted OPEFB fiber surfaces, respectively. The grafted OPEFB fiber surface was attached to PMMA. In the case of the PVC composites, the fracture surface of the ungrafted composite in Figure 5 showed fiber pullout and fiber ends, which indicated that most of the fibers came out without breaking during the fracture of the ungrafted fiber composites. This result suggested poor adhesion between the PVC matrix and OPEFB fibers. Figure 6 shows that the grafted fibers tended to break rather than pull out in the grafted composite, and this in turn indicated better interfacial strength. These results indicated that the PMMA that was attached to the surface of OPEFB enhanced the interaction between OPEFB and PVC and thus improved the adhesion and morphological structure of the PVC composites.

Tensile properties

Tensile strength

Figure 7 shows the tensile strength of the PVC and ungrafted and grafted PVC composites. The tensile strength of PVC decreased with the incorporation of the ungrafted OPEFB fibers. The hydrophobic poly-

mer did not wet or interact with the hydrophilic fibers because of the differences in their surface energy. Therefore, the aggregation of untreated OPEFB and poor compatibility between the OPEFB fibers and PVC matrix resulted in the weak interface of the PVC composites filled with ungrafted OPEFB fiber (Fig. 8). In the case of grafted composites, it is well known that PVC and PMMA are completely compatible. When the surface of OPEFB was covered by the grafted copolymer (PMMA), PMMA enhanced the interaction between OPEFB and PVC and improved the interfacial adhesion. Thus, the grafted OPEFB fibers in the composite were able to transmit the applied load to the PVC matrix. This led to the increase in the tensile strength of the grafted composite. The increment in the tensile strength with respect to the ungrafted composites was about 25%. Even though the grafted fiber was able to enhance the tensile strength of the PVC composites, the increase was less than that of PVC. As discussed in a previous section, the interaction that formed from the dipole–dipole interaction was weak
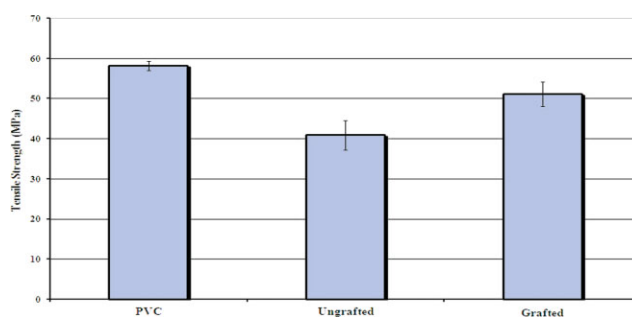

Figure 7 Effect of the ungrafted and grafted OPEFB fibers on the tensile strength of the composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8 SEM micrograph of the fractured surface of the PVC composite filled with ungrafted OPEFB. A void is shown at the fiber–matrix interface.

and insufficient to produce greater enhancement of the tensile strength of the composite. Other factors, such as the irregular shape (Figs. 4–6) and the agglomeration of OPEFB into fiber bundles (Fig. 4), also restricted the increase for the PMMA-g-OPEFB-filled PVC composite.

Young's modulus

Figure 9 depicts Young's modulus of the PVC and ungrafted and grafted PVC composites. The modulus of the composite increased with the incorporation of the ungrafted OPEFB fibers into the PVC matrix. Although OPEFB fibers showed a greater tendency of self-agglomeration into fiber bundles and poor interaction with the PVC matrix (Fig. 8), the ungrafted OPEFB fibers were able to improve the stiffness of the composite. This was due to the ability of OPEFB fibers to restrict the segmental mobility of PVC molecular chains by reducing the free volume of PVC. In the case of the grafted composites, the modulus of the composites decreased with

the incorporation of grafted OPEFB fibers. The lower modulus of the grafted-fiber-filled composites compared to the ungrafted-fiber-filled composites could be reasonably explained by the plasticization effect and the reduction of the fiber crystallinity, as discussed in a previous section.

Elongation at break

Figure 10 shows that the elongation at break of PVC decreased greatly with the incorporation of both grafted and ungrafted OPEFB fibers. This reduction was correlated with the decreased deformability of a rigid interphase between the fiber and the matrix material.[7] Figure 10, however, shows that the elongation at break of the grafted composite was higher than that of the ungrafted composite. The improvement in the elongation at break, caused by grafting, could also be elucidated from the increased flexibility of the PVC composite and the improved interaction of the OPEFB and PVC matrix, as discussed in a previous section. This improvement provided a
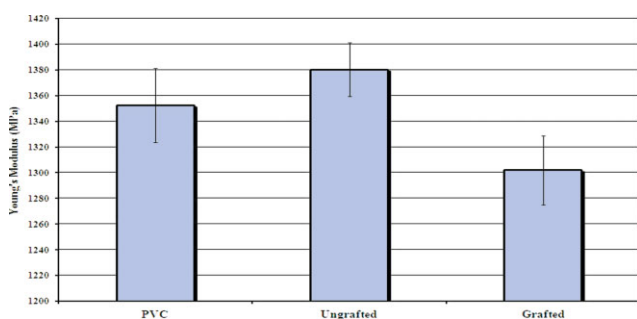

Figure 9 Effect of the ungrafted and grafted OPEFB fibers on Young's modulus of the composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
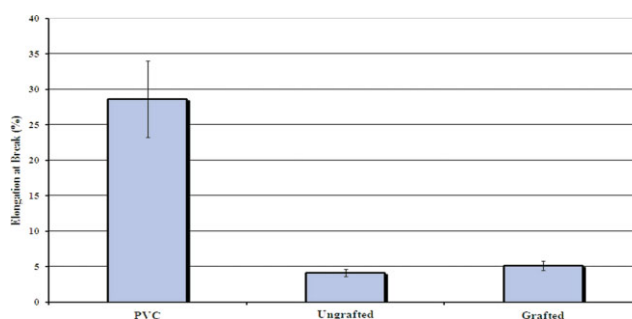

Figure 10 Effect of the ungrafted and grafted OPEFB fibers on the elongation at break of the composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

good indication of the improved impact properties of the composite.

CONCLUSIONS

This article investigated the effect of ungrafted OPEFB and PMMA-*g*-OPEFB fiber on the tensile properties of PVC. The tensile properties revealed that PMMA played an important role in enhancing the elongation at break and tensile strength and reducing Young's modulus of the PVC composites in comparison with the ungrafted one. PMMA improved the interaction between the PVC and grafted fibers, softened the PVC matrix, and reduced the fibers stiffness. The improvement in interfacial adhesion between the polymer matrix and fibers upon grafting of the fibers was confirmed by FTIR, DSC, and SEM analysis.

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