Thermal and dynamic mechanical properties of grafted kenaf filled poly (vinyl chloride)/ethylene vinyl acetate composites

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ABSTRACT

The effects of kenaf and poly (methyl methacrylate grafted kenaf on the thermal and dynamic mechanical properties of poly (vinyl chloride), PVC and ethylene vinyl acetate, EVA blends were investigated. The PVC/EVA/kenaf composites were prepared by mixing the grafted and ungrafted kenaf fiber and PVC/EVA blend using HAAKE Rheomixer at a temperature of 150 °C and the rotor speed at 50 rpm for 20 min. The composites were subjected to Differential Scanning Calorimetric (DSC), Thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), Fourier transform infrared (FTIR) and Scanning Electron Microscopy (SEM) studies. The DSC data revealed that the crystallinity of the EVA decreased with the addition of 30% grafted and ungrafted kenaf fibers. TGA and derivative thermogravimetric (DTG) curves displayed an increase in the thermal stability of the composites upon grafting of the fiber. Studies on DMA indicate that the T_g of the PVC and EVA in the PVC/EVA/kenaf composites has been shifted to higher temperature with the addition of the kenaf fiber. The presence of PMMA on the surface of grafted kenaf fiber was further confirmed by the analytical results from FTIR. The morphology of fractured surfaces of the composites, which was examined by a scanning electron microscope, showed the adhesion between the kenaf fiber and the PVC/EVA matrix was improved upon grafting of the kenaf fiber.

1. Introduction

The blending of two or more polymers has become an increasingly important technique for improving the cost performance ratio of commercial plastic in order to reduce the cost of an expensive engineering thermoplastic and also to improve the processibility, product uniformity and scrap reduction. The characteristic of a polymer blend is highly dependent upon the method of preparation where it can be manufactured by melt blending, solution blending or dispersion or latex blending. Commercial blends may be homogenous, phase-separated or a bit of both.

PVC is one of the major thermoplastic materials with an enviable and continuing growth. As a hard thermoplastic, PVC offered many useful outdoor applications such as in the building materials, pipe, plumbing and many other applications. With the addition of elastomer, the PVC can be made softer and more flexible which is suitable in electrical wiring. Besides, it is an efficient way to overcome the migration of low molecular weight plasticizer from the PVC and it can also extend the service life of the PVC. EVA copolymers are widely used as a long-lasting life plasticizer for PVC applications where these copolymers have a higher moduli than standard elastomers and can be easily processed without the need to vulcanize. An investigation of miscibility, fracture behavior, surface properties and mechanical properties of PVC/EVA blends were previously reported [1–3].

Abu-Abdeen and Elamer [4] investigated the mechanical behavior of the blend of acrylonitrile butadiene rubber (NBR) and polyvinyl chloride (PVC). Both the elastic modulus and the tensile strength increased with increasing PVC loadings while the elongation at brake recorded a linear decrease. A study on the influence of fiber content on mechanical of untreated bast fiber reinforced poly(vinyl chloride) (PVC) /thermoplastic polyurethane (TPU) polyblend was carried out by El-Shekeil et al. [5]. Poor fiber/matrix adhesion and interfacial bonding were observed in this composite. However, addition of kenaf had enhanced its thermal stability at the higher temperatures. Abu Bakar et al. [6] reported EFB-filled unplasticized poly(vinyl chloride) (PVC) composites. They found

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that the incorporation of EFB slightly enhanced the glass transition temperature but it decreased the thermal stability of the composites. Ratnam et al. [7] investigated the effect of oil palm empty fruit bunch (OPEFB) fiber and poly(methyl acrylate) grafted OPEFB on the thermal and structural properties of PVC/ENR blends. Their studies of dynamic mechanical analysis (DMA) indicate that the T_g of the PVC/ENR composite is shifted to higher temperature with the addition of the OPEFB fiber.

Most polymer blends are immiscible on molecular scales which affect their properties. There are several methods available to chemically modify lignocellulose and polymers. Imparting hydrophobicity to the fiber or hydrophilicity to thermoplastic matrix turned out to be the most appealing methods of chemical alteration. The later approach is been applied to natural fiber plastic biocomposites because of the ease of application, specifically maleated polymer is co-compounded with a base polymer together with wood fiber to form products with improved mechanical and water absorption properties. Various coupling agents such as polymeric isocyanates, silanes, and acid anhydrides have been evaluated and have shown improvements in mechanical properties of the final product. Modification of cellulose by graft copolymerization techniques allows one to chemically change the cellulose chain by introducing polymeric chains that confer different structural characteristics of the initial material, which has led to new cellulosic products with improved or new properties.

There is still a lack of comparative studies in the literature to show the effect of kenaf as reinforcement fillers to existing PVC/EVA commercial blends which are commonly used for automotive industry applications. Nur Fatimah et al. [8] reported the effect of methyl methacrylate grafted kenaf on mechanical properties of polyvinyl chloride/ethylene vinyl acetate composites. The use of kenaf fiber is favored because it is a cheap, effective and efficient method to modify the properties of the base material. Chemical composition, structural parameters and properties of kenaf fiber as compared to some selected natural fibers are shown in Tables 1 and 2.

Thermal analysis and dynamic mechanical analysis play an important role in the field of fabrication and application of the composites which need a better understanding to determine the interfacial characteristic of polymeric systems. Graft copolymerization of polymethyl methacrylate (PMMA) on kenaf fiber will change the thermal stability patent of the fiber. In thermal analysis, thermogravimetry has been used to study the thermal degradation and thermal stability of the composites while differential scanning calorimetry has been used to characterize transitions such as crystallization and melting. In amorphous (PVC) and semi-crystalline (EVA) polymer, the types and the amounts of the amorphous and the crystalline phases are related to linear viscoelastic response during dynamic loading. In the present investigation, the thermal and the viscoelastic behaviors of PMMA grafted kenaf fibers reinforced PVC/EVA composite will be studied.

2. Materials and method

2.1. Materials

Poly (vinyl chloride), PVC with *K*-value 70 was purchased from P.T. Asahimas Chemical, Anyer, Indonesia and the PVC stabilizer, tribasic lead sulfate (TBLS) (TS-100M) were purchased from Lonover Scientific Supplier Ltd., London. Ethylene vinyl acetate, EVA with 15% vinyl acetate content was purchased from Polyolefin Company, Singapore (grade COSMOTHENE EVA H2020). The kenaf fiber, grade V36 (a variety of kenaf species that planted in Malaysia), obtained from National Kenaf and Tobacco Board (Lembaga Tembakau Negara), Kelantan State, was used as reinforced materials. The untreated whole stem (core and bast) of kenaf fiber (length 2–6 mm) was prepared by chopping then flaking and followed by the grinding and sieving process to obtain fiber diameter with the size between 100 and 150 μm, the tensile strength is ranged between 50 and 180 MPa. The fiber received was chopped and flecked. Methyl methacrylate (MMA) was purchased from Fluka Chemie (Buchs, Switzerland). It was purified by passing through a column packed with an activated alumina to remove its inhibitor. The Hydrogen peroxide (H_2O_2) used was obtained from Riedel-de-Hazen (Sleelze, Germany) and ammonium ferrous sulfate (Fe^{2+}) was purchased from BDH (Poole, UK).

2.2. Grafting procedures

The primary aim of grafting of kenaf fiber is to reduce the number of hydroxyl groups and to enhance the cross-linking with the polymer matrix. Addition of PMMA results in a hydrophobic interface. Functional groups such as isocyanates [—N=C=O], maleic anhydride [—(CO)2—O—] and dichlorotriazine [—Cl—], derivatizes the polar hydroxyl group of the fibers to form a covalent bond or hydrogen bond. The chemical bonds formed by this process determine the stability of the composite. These bonds influence physical and mechanical properties of the composites. Covalent bonds are generally formed during the modification of the fibers. The polymer matrix can be tailored by graft copolymerization, which can result in better miscibility and cross-linking at the interface.

The optimum percentage of grafting on the surface of kenaf fiber obtained by using response surface methods (RSM). The detailed procedures were described in the works carried out by Nur Fatimah [10]. The process involved three variable parameters: temperature, the amount of hydrogen peroxide and the period reaction. Besides, the constant parameters are the amount of ammonium ferrous sulfate and the amount of monomer (MMA). This situation chosen as referred to the past researches [11,12] where they found that the amount of monomer and ammonium ferrous sulfate used was reached in the similar range at the optimum of percentage.

The reaction was carried out in the thermoset water bath at desired temperature. 1.000 g of fiber was placed in a 250 mL

Table 1
Properties of natural fibers in comparison with glass fibers [9].

Properties	Fiber type							
	Kenaf	Flax	Hemp	Jute	Ramie	Coir	Sisal	Cotton
Density (g/cm^3)	1.5	1.4	1.48	1.46	1.5	1.25	1.33	1.51
Tensile strength* 10E6 N/m^2	350–600	800–1500	550–900	400–800	500	220	600–700	400
E-modulus (GPa)	40	60–80	70	10–30	44	6	38	12
Specific (E/density)	27	26–46	47	7–21	29	5	29	8
Elongation at failure (%)	2.5–3.5	1.2–1.6	1.6	1.8	2	15–25	2–3	3–10
Moisture absorption (%)	–	7	8	12	12–17	10	11	8–25
Price/kg ($), raw (mat/fabric)	0.33–0.88	−1.5 (2/4)	0.6–1.8 (2/4)	0.35 1.5	1.5–2.5	0.25–0.5	0.6–0.7	1.5–2.2

Table 2
Comparatives of properties of some natural fibers. *source:* [11].

Type of fiber	Cellulose (wt.%)	Lignin (wt.%)	Hemicellulose (wt.%)	Pectin (wt.%)	Wax (wt.%)	Micro-fibrillar/spiral angle (Deg)	Moisture content (wt.%)
Bast jute	61–71.5	12–13	13.6–20.4	0.2	0.5	8.0	12.6
Flax	71	2.2	18.6–20.6	2.3	1.7	10.0	10.0
Hemp	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	6.2	10.8
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	7.5	8.0
Kenaf	31–39	15–19	21.5	–	–	–	–
Leaf sisal	67–78	8.0–11.0	10.0–14.2	10.0	2.0	20.0	11.00
Seed cotton	82.7	–	5.7	–	0.6	–	–
Fruit coir	36–43	41–45	0.15–0.25	3–4	–	41–45	8.0

three-necked flask containing 100 mL of distilled water and the required volume of hydrogen peroxide, arranged with magnetic stirring. Before the reaction started, nitrogen was purged through the kenaf slurry to remove the presence of oxygen then the kenaf slurry was stirred for 30 min. After time reach, the ammonium ferrous sulfate (0.1027 g) was added into the mixture and continued stirred for 5 min. Finally, 5 mL amount of monomer (MMA) was added into the vessel and the mixture was stirred at chosen reaction period.

Grafted fibers were obtained via graft copolymerization reaction. The reaction was carried out in a thermostat water bath at 62 °C. 40 g of fiber was placed in a 2000 mL three-necked flask containing distilled water and 60 mL hydrogen peroxide while stirring. The mixture was stirred for 30 min under the presence of nitrogen. After the time is reached, the ammonium ferrous sulfate (1.6 g) was added after about 5 min followed by 80 mL of monomer (MMA). The hydrogen peroxide and the ammonium ferrous sulfate were used as initiators to produce hydroxyl radicals, which initiate the reactive macroradicals to contact with the monomer (MMA) and produce a grafted side chain. The mixture was then stirred for 2 h before it is filtered and dried to a constant weight. Finally, the grafted fibers were extracted with acetone and dried again until they reached a constant weight.

The percentage of grafting (P_g) for each reaction experiments was calculated using the formulation as below:

$$P_g(\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

where W_1 is the weight of initial fiber and W_2 is the weight of purified grafted fiber.

2.3. Formulations

The formulations used to produce the PVC/EVA/Kenaf composites are given in Table 3.

2.4. Blend preparations

The PVC and its stabilizer were premixed in a tabletop high speed laboratory mixer-blender (model JE-1100 HM) at a temperature of 60 °C and 50 rpm for about 20 min. The composites were fabricated by mixing the required formulation as shown in Table 1 in a Haake Rheomix Polydrive R600/610 internal mixer at 50 rpm for 20 min. The mixed blend was compressed using an electrically heated hydraulic press, model GT-7014-A30C under a pressure 14.7 MPa at 160 °C then immediately cooled.

Table 3
Formulation of PVC/EVA/Kenaf composites.

Material/batch	Formulation (%)								
	1	2	3	4	5	6	7	8	9
PVC	50	45	42.5	40	35	45	42.5	40	35
EVA	50	45	42.5	40	35	45	42.5	40	35
TBLS[a]	6	6	6	6	6	6	6	6	6
Kenaf	–	10	15	20	30	–	–	–	–
Kenaf-g-PMMA	–	–	–	–	–	10	15	20	30

[a] Parts per hundred of PVC.

2.5. Differential Scanning Calorimetric (DSC)

Examination of the fractured surfaces was performed using a scanning electron microscope, Mettler Toledo model DSC822e, with masses of approximately 7.5 mg under a nitrogen atmosphere. The samples (sized 3 mm width × 6 mm length × 1 mm thickness) were cryogenically fractured using liquid nitrogen. All samples were examined after first sputter coating with gold to avoid electrostatic charging and poor image resolution.

It is necessary to obtain a reliable and reproducible DSC trace by ensuring the sample is in good thermal contact with the base of the sample pan. This can be ensured by first melting the sample in the pan on a hot stage and slowly cooling it to room temperature. The samples were then heated from 25 °C to 200 °C at a rate of 20 °C/min, then cooled to −50 °C at 10 °C/min and reheated under the same condition. By subjecting the sample to controlled heating-up and cooling-down cycles, any prior thermal history is erased and thus the sample is standardized for thermal analysis. The thermal history could induce the complexity of the melting behavior of samples [13]. The result was taken from the second scanning process.

The percentage of crystallinity, X_c, of EVA in the blend was calculated as [14]:

$$X_c = \frac{\Delta H_{f,i}}{\Delta H_f^o} \times 100 \quad (2)$$

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where $\Delta H_{f,i}$ is the heat of fusion of the sample measured at mass fraction of EVA, i and ΔH_f^o is the heat of fusion of perfectly crystal EVA, equal to 41.05 J/g [15].

2.6. Thermogravimetric analysis (TGA)

The thermal degradation for measuring weight loss was done by using TGA 851 Mettler Toledo thermogravimetric analyzer. Approximately 10 mg of samples was analyzed under the temperature range of 30–600 °C at a heating rate of 10 °C/min with nitrogen gas flow rate of 50 mL/min.

Table 4
DSC data for the composites.

Specimens	T_c (°C)	ΔH_f (J/g)	$T_{m,\,EVA}$ (°C)	X_c (%)
PVC/EVA	65.82	18.28	88.05	44.53
PVC/EVA/KNF10u	66.82	22.95	87.25	55.91
PVC/EVA/KNF30u	66.28	14.15	87.42	34.47
PVC/EVA/KNF10g	68.00	20.53	85.89	50.01
PVC/EVA/KNF30g	67.95	14.15	85.92	34.47

2.7. Dynamic mechanical analyzer (DMA) analysis

The determination of storage modulus and damping behavior in dynamic stress–strain were done on TA Instrument Q800 dynamic mechanical analyzer using a three-point bending mode in the temperature range of −100 °C to 150 °C. The frequency used was 1 Hz and the heating rate was 5 °C/min.

2.8. FTIR spectroscopy

The infrared spectra were obtained on a Fourier transform infrared (FTIR) spectrometer Perkin Elmer Spectrum 2000 instrument with the diamond attenuated total reflectance (ATR) techniques. The data were recorded in a wave number range of 4000–280 cm^{-1}.

2.9. Surface electron microscopy (SEM)

The surface morphology of the samples were examined by using a scanning electron microscope model Hitachi S-3400N, Thermo Scientific. The samples were cryogenically fractured using liquid nitrogen and were examined after first sputter coating with gold to avoid electrostatic charging and poor image resolution.

3. Results and discussion

3.1. Differential scanning calorimetric (DSC)

Fig. 1(a) and (b) shows the respective DSC cooling and heating curves of PVC/EVA composites. The data obtained from the thermal analysis curves for PVC/EVA composites are summarized in Table 4. The endothermic and exothermic regions of the curves in Fig. 1(a) and (b) indicate the melting and crystallization of EVA. By integrating the area under the endothermic region of the curves, heat of fusion for each of the composite compositions was calculated. Thermal glass transitions seem to occur for PVC around 100 °C, although the transitions are somewhat ambiguous. A much clearer indication of T_g in PVC/EVA/kenaf composites was observed via a strong tan δ maxima in the DMA measurements reported subsequently.

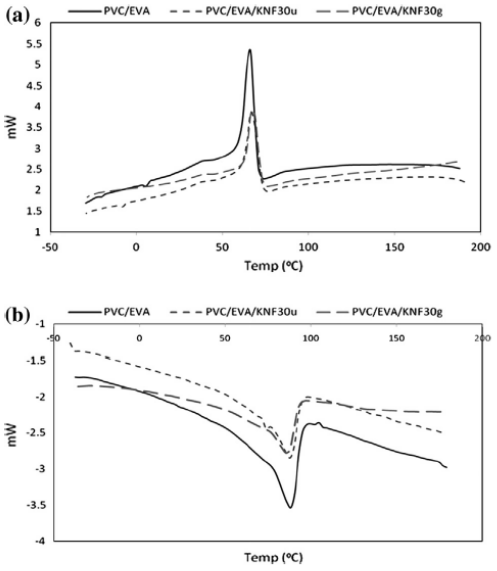

Fig. 1. DSC of PVC/EVA blend, grafted and ungrafted kenaf composites at 30% fiber loading, (a) cooling scan and, (b) heating scan.

The crystallinity of EVA was higher with lower fiber content (10% fiber) than the unfilled system, indicating that the presence of a small amount of fiber increases the crystallization of EVA. However, the degree of crystallinity of EVA was found to drop with an addition of 30% fiber to the PVC/EVA blend. It is also noted that the crystallization temperature of EVA shows an increase with the incorporation of 10% fiber and a decline with the addition of 30% fiber to the PVC/EVA blend system. Such observation suggests that as the fiber content increased, the fiber particles hinder the overall extent of EVA crystallization. From the above result, it shows that with the increase in the percentage of fiber in the bio composite the degree of crystallinty of the composite decreases. It may be concluded that with the more reinforcement, the orientation of fiber is lowered which results in the decrease in the crystallinty. Reports by Espert et al. [16] and Dikobe and Luyt [17] tend to support this observation. Dikobe and Luyt [17] reported that the decrease in heat of fusion is related to the decreasing amounts of polymer in the blend with the presence of solid filler. However, it is noticed that the grafted composites show a lower heat of fusion than the ungrafted composites at a low fiber content indicating that the crystallinity of the PVC/EVA/kenaf composites is reduced with the grafting of the fiber with PMMA. The increased interaction between the grafted fiber and the polymer matrix is believed to account for the decrease in crystallization of EVA. In agreement with this observation, it has been reported that the grafting of PMMA or poly butyl acrylate (PBA) on the cellulose fibers results in a reduction in crystallinity of the grafted fiber [18].

Barone [19] investigated the composite properties as a function of fiber properties and polymer matrix crystallinity. He found that polyethylenes with a crystalline fraction less than about 0.5 adsorb onto keratin feather fibers and remain adsorbed after melt processing and through subsequent cooling. The strong fiber/polymer interactions show that the low crystallinity polyethylenes are reinforced by the keratin feather fibers. In contrast, high crystallinity polyethylenes, i.e. with crystalline fraction greater than about 0.5, are not reinforced by keratin feather fiber. The keratin fibers inhibit crystallinity in low crystallinity polyethylenes but enhance crystallinity in high crystallinity polyethylenes. Microscopy shows increased adhesion between the fibers and the polymer for the more amorphous polyethylenes.

3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to study the thermal stability and degradation of grafted and ungrafted kenaf composites. The TGA and DTG curves of PVC/EVA blend and the ungrafted and grafted kenaf composites at 30% fiber loading are represented in Fig. 2(a). It was observed that the thermal degradation of all samples has taken place within the programmed temperature range of 30–600 °C. In case of ungrafted kenaf composite, the volatilization of moisture correlation which referred to the loss of water in the kenaf fiber still occurred at the initial temperature in the small amount due to a very low peak observed from the DTG curve. The initial mass loss from approximately 200–400 °C with a maximum at 296 °C corresponds to a weight loss of about 40%. This was due to the decomposition of cellulose and hemicelluloses. The thermodegradation of cellulose can occur by dehydration from cellulose unit, cleavage of glycosidic linkage by transglycosylation and scission of —CO and C—C bonds [12]. The second decomposition occurred in a range of 400–500 °C with