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

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A R T I C L E   I N F O

Article history:
Received 29 May 2014
Accepted 10 September 2014
Available online 21 September 2014

Keywords:
Chemical reactions
Thermal analysis
Adhesion
Graft copolymerization
Kenaf

A B S T R A C T

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 Tg 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 break 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...
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 latter approach has been applied to natural fiber plastic biocomposites because of the ease of application, specifically mal- eated 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 copolymeriza- tion 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 industry application. 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 interficial 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 (TBL) (TS-100M) were purchased from Lonov-er Scientific Supplier Ltd., London. Ethylene vinyl acetate, EVA with 15% vinyl acetate content was purchased from Polyolefin Company, Singapore (grade COSMOTHENE EVA 2020). The kenaf fiber, grade V36 (a variety of kenaf species that planted in Malaysia), obtained from National Kenaf and Tobacco Board (Lembaga Tem-bakau 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 (Sleezle, 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 thermostet water bath at desired temperature. 1.000 g of fiber was placed in a 250 mL

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fiber type</th>
<th>Kenaf</th>
<th>Flax</th>
<th>Hemp</th>
<th>Jute</th>
<th>Ramie</th>
<th>Coir</th>
<th>Sisal</th>
<th>Cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($g/cm^3$)</td>
<td></td>
<td>1.5</td>
<td>1.4</td>
<td>1.48</td>
<td>1.46</td>
<td>1.5</td>
<td>1.25</td>
<td>1.33</td>
<td>1.51</td>
</tr>
<tr>
<td>Tensile strength $^*$ <strong>1065</strong> N/m²</td>
<td>350–600</td>
<td>800–1500</td>
<td>550–900</td>
<td>400–800</td>
<td>500</td>
<td>220</td>
<td>600–700</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>E-modulus (GPa)</td>
<td></td>
<td>40</td>
<td>60–80</td>
<td>70</td>
<td>10–30</td>
<td>44</td>
<td>6</td>
<td>38</td>
<td>12</td>
</tr>
<tr>
<td>Specific (E/density)</td>
<td></td>
<td>27</td>
<td>26–46</td>
<td>47</td>
<td>7–21</td>
<td>29</td>
<td>5</td>
<td>29</td>
<td>8</td>
</tr>
<tr>
<td>MOF (moisture absorption %)</td>
<td></td>
<td>2.5–3.5</td>
<td>1.2–1.6</td>
<td>1.6</td>
<td>1.8</td>
<td>2</td>
<td>2</td>
<td>3–10</td>
<td>3–10</td>
</tr>
<tr>
<td>Price/kg ($), raw (mat/fabric)</td>
<td></td>
<td>0.33–0.88</td>
<td>–1.5 (2/4)</td>
<td>0.6–1.8 (2/4)</td>
<td>0.35 1.5</td>
<td>1.5–2.5</td>
<td>0.25–0.5</td>
<td>0.6–0.7</td>
<td>1.5–2.2</td>
</tr>
</tbody>
</table>
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 for 2 h before it is filtered and dried to a constant weight. Finally, 5 mL amount of monomer (MMA) was added into the vessel and the mixture was stirred at chosen reaction period.

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

\[ P_g(\%) = \frac{W_i - W_2}{W_1} \times 100 \]  

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 4 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.

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 \times 6 mm length \times 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]:

\[ X_c = \frac{\Delta H_f}{\Delta H_{f0}} \times 100 \]  

Certificate

where \( \Delta H_f \) is the heat of fusion of the sample measured at mass fraction of EVA, and \( \Delta H_{f0} \) 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 2


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

### Table 1

Comparison of properties of some natural fibers. Source: [12].

<table>
<thead>
<tr>
<th>Material/batch</th>
<th>Formulation (%)</th>
<th>Moisture (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>PVC</td>
<td>50</td>
<td>45</td>
</tr>
<tr>
<td>EVA</td>
<td>50</td>
<td>45</td>
</tr>
<tr>
<td>TLBS</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Kenaf</td>
<td>–</td>
<td>10</td>
</tr>
<tr>
<td>Kenaf-g-PMMA</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 4

DSC data for the composites.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>( T_r ) (°C)</th>
<th>( \Delta H_f ) (J/g)</th>
<th>( T_m, \text{max} ) (°C)</th>
<th>( X_c ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC/EVA</td>
<td>65.82</td>
<td>18.28</td>
<td>88.05</td>
<td>44.53</td>
</tr>
<tr>
<td>PVC/EVA/KNF10u</td>
<td>66.82</td>
<td>22.95</td>
<td>87.25</td>
<td>55.91</td>
</tr>
<tr>
<td>PVC/EVA/KNF30u</td>
<td>66.28</td>
<td>14.15</td>
<td>87.42</td>
<td>34.47</td>
</tr>
<tr>
<td>PVC/EVA/KNF10g</td>
<td>68.00</td>
<td>20.53</td>
<td>85.89</td>
<td>50.01</td>
</tr>
<tr>
<td>PVC/EVA/KNF30g</td>
<td>67.95</td>
<td>14.15</td>
<td>85.92</td>
<td>34.47</td>
</tr>
</tbody>
</table>

* Parts per hundred of PVC.
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 \(-100^\circ C\) to \(150^\circ C\). The frequency used was 1 Hz and the heating rate was 5 \(^\circ C/min\).

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 \(100^\circ C\), although the transitions are somewhat ambiguous. A much clearer indication of \(T_g\) in PVC/EVA/kenaf composites was observed via a strong tan \(\delta\) maxima in the DMA measurements reported subsequently.

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 crystallinity 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 crystallinity. 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 \(-\text{CO}\) and \(-\text{C–C}\) bonds [12]. The second decomposition occurred in a range of 400–500 °C with
the main peak at around 480 °C with the weight loss about 84.1%. This two step degradation process demonstrated that the incorporation of kenaf fiber did not affect the decomposition behavior of PVC/EVA blend matrix. On the other hand, the grafted kenaf composites displayed the temperature range of about 200–370 °C with the initial peak at around 276 °C which is due to the decomposition of hemicellulose and cellulose while the second peak around 290 °C due to the decomposition of lignin. The third decomposition temperature as revealed from the thermogram (Fig. 2(b)) was detected at approximately between 370 °C and 430 °C with a main peak of around 414 °C which is mainly due to decomposition of PMMA. The fourth mass loss step is approximately between 430 °C and 510 °C with a main peak at around 475 °C.

DTG curves of PVC/EVA blend and the ungrafted and grafted kenaf composites at 30% fiber loading are illustrated in Fig. 2(b). It can be seen that the main peaks of grafted kenaf composites have lower value compared to ungrafted kenaf composites. From these results, it is clear that the thermal stability and decomposition temperature of the composites can be affected by the presence of PMMA on the surface of kenaf fiber. Good interfacial adhesion between the grafted kenaf fiber and the PVC/EVA blend matrix would result in good compatibility between fiber and matrix where it shows the increasing in degradation temperature of grafted composites compared to grafted kenaf fiber. The decreasing in degradation temperature of ungrafted composites compared to ungrafted kenaf fiber also indicated that poor compatibility between the fiber and matrix. However, a slight decreased seen in the TG of grafted composites compared to ungrafted composites is due to the addition of amorphous content (PMMA) in the composites which decreased the thermal stability of the grafted composites. Therefore, in this study, the thermal stability of the composites was not influenced by a good interaction between fiber and matrix but it was influenced by the amorphous content in the composites. Summary of the DTG$_{\text{max}}$ degradation temperature of both the ungrafted and grafted kenaf composites was shown in Table 5.

### 3.3. Dynamic mechanical analysis (DMA)

#### 3.3.1. Storage modulus

The storage modulus, (elastic behavior) describes the energy stored in the system where it is a measure of the reversible elasticity of the samples. Fig. 3 shows the storage modulus ($E'$) of PVC/EVA blend, grafted and ungrafted composites at 30% fiber loading. It can be noticed that there is an increase in the modulus of PVC/EVA matrix with the presence of kenaf fibers. This observation attributed to the reinforcement imparted by the fibers to the PVC/EVA matrix which allowed a greater stress transfer at the interface and lead to an increase in the stiffness. A similar observation was noted by Mohanty et al. [20] in their studies on the surface modification of jute and its influence on the performance of biodegradable jute-fabric/Biopol composites. The storage modulus curves presented three distinct regions which are the glass region, transition region and rubbery region. In the glassy region, the chain in amorphous regions begins to coordinate large scale motions [21]. As the heating continues, the materials reach a plateau state. During this region, the amorphous part has been deformed whereas the crystalline region remains a crystalline solid until it reaches the melting temperature [15]. At the end of the plateau state, a dramatic increase of storage modulus has occurred. This might because the chains (crystalline chains) have gained enough mobility to rearrange into crystallite [21]. This crystallization behavior can be observed in the DSC in the previous figure (Fig. 1(a)). As the temperature continued to increase, the materials reached the melt stage where the chain slippage occurred.

#### 3.3.2. Loss modulus

The imaginary part (loss modulus) describes the component of the response that is phase shifted by 90° where it is a measure of mechanical energy that has been converted to heat. Fig. 4 presents the loss modulus of grafted and ungrafted kenaf composites at 30% fiber loading. It can be seen that two relaxation peaks are observed in all the investigated samples. The loss modulus peaks for EVA and PVC are observed at –32 °C ($\beta$) and 77 °C ($\alpha$) respectively. The $\alpha$ relaxation is the $T_g$ of PVC and also related with crystalline relaxations occurring below the melting point which is due to reorientation of defect areas in the crystals as reported by Mohanty et al. [20]. It is noticed that the $\alpha$ relaxation peak shifts to a higher temperature as the fiber loading increases where it can be seen between 73 °C and 77 °C for both composites. As reported by Khallid et al. [22], this situation occurred due to the prevention of molecular mobility between the matrix and fiber surface. The $\beta$ relaxation corresponds to the motion of the amorphous region side chains from the polymer backbone and due to the glass transition of EVA. This figure also showed at the $\beta$ relaxation, the loss modulus peak of ungrafted kenaf composite is lower than the grafted kenaf composite which is related to the amount of amorphous PVC chains involved in the transition. The higher $\beta$ peak amplitude of grafted kenaf composite indicates that their composite has a higher amorphous content than the ungrafted kenaf composites. This observation is associated with the additivity effect of PMMA which is an amorphous polymer.

#### 3.3.3. Loss tangent

The effect of grafted and ungrafted kenaf fiber composites on the mechanical loss factor is represented in Fig. 5. The $\tan \delta$ curve exhibited two transition peaks ($\alpha$ and $\beta$) corresponding to the glass transition temperature ($T_g$) of individual component which can be observed in all the blends indicating the incompatibility and immiscibility between the phase [23–24]. The $\beta$ transition corresponds to the glass transition temperature of EVA copolymer and is related to the relaxation of unrestricted amorphous chains of PVC while the $\alpha$ transition corresponds to the glass transition...
temperature of PVC which is related to the relaxation of restricted crystalline phase of EVA as discussed in the above section. In the $\beta$ transition, the damping peak in the grafted composites showed a slightly decreased magnitude of $\tan \delta$ in comparison to PVC/EVA blend and ungrafted composites. This could be attributed to the greater extent of stress, which is carried by the fibers where it only allows a small part to strain the interface. Hence, the deformation energy is dissipated mainly in the matrix and at the interface with a stronger interface characterized by less energy dissipation [20,25]. The $\tan \delta$ peak of ungrafted composites exhibited a lower magnitude compared to the PVC/EVA blend, but it showed a higher magnitude when compared with the grafted composites. Damping is one of the indicators that show any changes through the incorporation of fibers in the composites. Several factors need to be considered to explain the variation in $\tan \delta$ including the interfacial bonding between fiber and matrix. According to Pothan et al. [26], a transition with a higher damping at the interfaces implies poor interfacial adhesion.

The $\alpha$ transition also shows the damping peak of 30% loading fiber of grafted and ungrafted composites. It is also clearly seen from the Fig. 5 that the $T_g$ of PVC for the composite containing kenaf-g-PMMA has shifted to a higher temperature compared to the composite incorporated with ungrafted kenaf fiber. This increase in $T_g$ suggests that interfacial bonding between the fiber and PVC/EVA matrix is improved upon grafting. SEM micrographs of the fractured surface of ungrafted and grafted PVC/EVA/kenaf composites are shown in Fig. 6(a) and (b) respectively. A closer gap observed at the boundary between the fiber and PVC/EVA matrix in Fig. 6(b) compared with Fig. 6(a) indicates that the grafted fiber has a better interfacial bonding with the matrix. Therefore, it is evident that improved adhesion between fiber and the polymer matrix is achieved upon grafting. Fig. 6(c) shows the SEM micrographs on the kenaf fibers by the PVC/EVA matrix at lower magnification.

Table 5
Summary of DTG$_{\text{max}}$ of degradation temperature of the 30% fiber loading of ungrafted and grafted kenaf composites.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>First peak (°C)</th>
<th>Second peak (°C)</th>
<th>Third peak (°C)</th>
<th>Fourth peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC/EVA</td>
<td>No peak</td>
<td>302.05</td>
<td>No peak</td>
<td>478.13</td>
</tr>
<tr>
<td>Ungrafted kenaf</td>
<td>273.58</td>
<td>332.41</td>
<td>No peak</td>
<td>No peak</td>
</tr>
<tr>
<td>Grafted kenaf</td>
<td>296.69</td>
<td>367.06</td>
<td>396.58</td>
<td>No peak</td>
</tr>
<tr>
<td>PVC/EVA/Kenaf30u</td>
<td>276.12</td>
<td>296.75</td>
<td>No peak</td>
<td>480.00</td>
</tr>
<tr>
<td>PVC/EVA/Kenaf30g</td>
<td>287.32</td>
<td>290.84</td>
<td>413.48</td>
<td>475.16</td>
</tr>
</tbody>
</table>

Fig. 3. Variation in storage modulus of grafted and ungrafted kenaf composites at 30% fiber loading.

Fig. 4. Effect of 30% fiber loading on loss modulus of PVC/EVA/kenaf and PVC/EVA/kenaf-g-PMMA composites.

Fig. 5. Effect of 30% fiber loading on $\tan \delta$ of grafted and ungrafted kenaf composites.

3.4. FTIR spectra of PVC/EVA composites

FTIR analysis as shown in Fig. 7, was carried out to investigate any chemical reaction between fiber and the PVC/EVA blend matrix. It can be observed that no extra peak appeared to show any chemical interaction between the functional group of kenaf fiber and the matrix. A new functional group will appear when any chemical changes occur between the mixtures. This statement, which was reported by Koeing [27], was also agreed by Ratnam et al. [28]. The presence of sharp peak which represented of PMMA and also assigned to C=O stretching was detected at a peak around 1730 cm$^{-1}$ in the grafted kenaf composite. The presence of grafted kenaf fiber with PMMA has been confirmed by the FTIR spectra as shown in Fig. 8. The IR spectra of ungrafted and grafted yield display absorption band of hydroxyl group around 3400–2900 cm$^{-1}$ due to O—H stretching vibration of cellulose, absorbed water, hemicelluloses and lignin. The IR spectra also found that C=H stretching existed at the peak around 2920–2948 cm$^{-1}$ in both grafted and ungrafted fiber. A peak found near 1730 cm$^{-1}$ on kenaf spectra could be connected with C=O stretching vibration of carboxyl groups in hemicelluloses and lignin in kenaf fiber. However, in the case of kenaf-g-PMMA, a new sharp peak around 1724 cm$^{-1}$ due to the ester group was observed where suggests that MMA has been grafted onto kenaf fiber through covalent linkages (referred to Eq. (3)). The absorption band around 1600–1400 cm$^{-1}$ region in the both spectra may be attributed to the presence of aromatic or benzene rings in lignin. These explanations were agreed by Mohantya et al. [11], Kaith et al. [29] and Raju et al. [30].
Conclusions

The effects of grafted and ungrafted kenaf composites on crystallization, thermal stability, degradation and glass transition temperature of the composites have been investigated. At 30% fiber loading the crystallinity of the PVC/EVA/kenaf composite found to decrease, although the addition of 10% fiber has increased the crystallinity of the composites higher than the neat PVC/EVA blend. The decrease in the crystallinity of the composites upon grafting of the fiber attributed to the improved interaction between the grafted fiber and the PVC/EVA blend matrix, thus, decreases the free volume and molecular mobility and provides more reinforcement.

TGA and DTG curves revealed that although the decomposition of cellulose and hemicelluloses from occurring approximately between 200 to 400 each, the thermal stability of the PVC/EVA/kenaf composites improved upon grafting of the fiber. DMA curves indicate that the $T_g$s of the PVC and EVA in the PVC/EVA/kenaf composites shift to a higher temperature with the addition of the kenaf
fiber. Based on this study, it was found that grafting of PMMA onto the kenaf fiber has improved the interaction between the kenaf fiber and PVC/EVA matrix.

Acknowledgements

The authors acknowledge financial support from UM.C/HIR/MOHE/ENG/52, RP024C-13AET, RU022A-2014 and FP030-2013A.

References