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Physico-thermal properties of kenaf fiber/high-density polyethylene/maleic anhydride compatibilized composites

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Abstract

Kenaf fiber/high-density polyethylene/maleic anhydride (MA)-compatibilized composites were melt mixed in a twin-screw extruder and molded using injection molding machine. Physicothermal properties of the composites were studied at different percentages of compatibilizer contents using various techniques. The addition of 8% compatibilizer into 8.5 and 17.5 wt% fiber content improved the adhesion and tensile strength by 14.5% and 13.6%, respectively. Compatibilized samples exhibited higher peak load and fracture energy on impact testing compared to the samples without maleic anhydride compatibilizer. The effect of the addition of maleic anhydride compatibilizer on peak load and fracture energy was observed to be at its highest at 8%. Differential scanning calorimetric measurements revealed that the melting enthalpy and degree of crystallinity of composites increased with increasing compatibilizer content up to 8% and then decreased at 12% compatibilizer content. Dynamic mechanical analysis showed that the storage modulus of composites was increased, but the loss modulus and tangent delta were decreased after the addition of compatibilizer. This indicates that compatibilized composites produced have improved toughness and reduced stiffness.

Keywords

Maleic anhydride, physical and thermal properties, kenaf fiber, composites

Introduction

Kenaf is a natural fiber source that has gained attention because of the economic and ecological advantages. A major limitation for natural fiber composites is the weak adhesion between the fiber and matrices which arises due to the hydrophilic nature of the fiber and the hydrophobic character of the polymer. This leads to poor compatibility between the fiber and matrices, resulting in undesired properties of composites. The addition of compatibilizer is important to improve the fiber–matrix interaction. Friedrich et al.[1] stated that the effective load transfer throughout the fiber–matrix interface was due to the strong adhesion between fiber and matrix.

Yang et al.[2] conducted research on the effect of different compatibilizing agents on the mechanical properties of lignocellulosic fiber–reinforced polyethylene (PE) biocomposites. It was found that the improvement in the interfacial bonding led to better Izod impact strength and tensile properties. Sanadi et al.[3] reported that the maleic anhydride–polypropylene (MA-PP) showed great efficiency in the kenaf/PP composite. The unnotched impact strength of kenaf fiber (KF)/PP composites increased with small amounts of MA-PP added to the composites. Salleh et al.[4] studied the mechanical performance and interfacial behavior of KF-reinforced high-density polyethylene (HDPE) composites. The authors found that the addition of 8% compatibilizer into the composites improved the adhesion behavior and enhanced the mechanical properties of composites. The effect of maleated poly(butylene

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succinate) (PBS) on the impact properties of kenaf bast fiber–filled biodegradable PBS composites was studied by Ahmad Thirmizir et al.[5] The addition of maleated PBS as a compatibilizer resulted in the enhancement of composite impact properties.

Araujo et al.[6] investigated the thermal stability of curaua fibers/HDPE composites. From their findings, maleic anhydride–polyethylene (MA-PE) was more stable when compared to ethylene vinyl acetate as a coupling agent. Increase in crystallinity provided by the fibers, which acts as a nucleating agent, due to the transcrystallinity effect as a result of the strong interaction between the curaua fiber and the matrix in the presence of MA-PE as a coupling agent. Improved thermal properties of bioflour-filled polyolefin composites with different types of compatibilizing agents and contents have been reported by Kim et al.[7] Thermogravimetric analysis (TGA) studies by Ayswarya et al.[8] on rice husk ash–reinforced HDPE revealed that the addition of compatibilizer into the composites resulted in improved thermal stability.

Mohanty et al.[9] studied the dynamic mechanical properties of MA-PE-treated jute/HDPE composites. From the findings, the T_g of the composites treated with 1% MA-PE showed an additional shift to -98.0°C when relative to the untreated composites with a T_g of -105.0°C. This indicates enhanced interfacial adhesion between the fibers and the matrix, due to the coupling effect of MA-PE. Dynamic mechanical behavior of the unmodified wood flour / HDPE composite and modified composites with various compatibilizers with loading of 10 phr was studied by Wang et al.[10] From their results, the peak amplitude of tan δ was decreased with the addition of compatibilizer, indicating that the number of molecular segments involved has decreased due to the improved adhesion between the fiber and matrix. In this study, the physicothermal properties of KF/HDPE/MA-compatibilized composites were investigated.

Experiment

Materials

Kenaf bast fiber was obtained from the National Kenaf and Tobacco Board, Malaysia. The average density of Kenaf bast fiber was 0.1343 g cm^{-3}. The fiber was chopped to 3 mm length and sieved fibers with a diameter of less than 0.5 mm were collected. A semicrystalline HDPE, (Titanzex HI1100) manufactured by Titan Petchem (M) Sdn. Bhd, Malaysia, was used as the polymer matrix. The density of HDPE was 0.961 g cm^{-3} and the melt flow index was 7 g/10 min at a load of 2.16 kg at 190°C. MA (1%)-grafted HDPE, (NG 1002) manufactured by Shanghai Zeming Plastic Co., Ltd, China, was used as the compatibilizer. The density of MA compatibilizer was 0.88 g cm^{-3} and melt flow index was 1.5 g/10 min.

Processing

Compounding. A corotating twin-screw extruder (Brabender KETSE 20/40 Lab Compounder, Germany) was used to prepare the KF/HDPE/MA-compatibilized composites. Compounding was carried out at a screw speed of 80 r min^{-1} with temperature settings of 165°C to 185°C from the hopper to the die. Pure HDPE and MA compatibilizer were loaded automatically into the feed hopper, while KF was introduced to the barrel at the side feeder between zones 3 and 4. KF/HDPE/MA-compatibilized composites were prepared at two different fiber contents of 8.5% and 17.5% by weight. The amount of MA compatibilizers was varied from 0%, 4%, and 8% to 12% of the total weight of composites.

Injection molding. The granulated and pelletized samples with a diameter of 3 mm were then oven-dried at 80°C for 24 h. The dried pelletized composites were injected in the injection molding machine (Boy 55 M, Germany) for tensile and impact specimens. The barrel was set at 100–120 bar of injection pressure. Injection temperatures ranged between 160°C and 190°C and mold temperature of 20°C with a cooling time of 120 s.

Characterization

Tensile test. Tensile tests were examined using a universal testing machine (Instron 5569, Norwood, MA, USA). All injection-molded tensile test specimens were subjected to a load cell of 50 kN with a gauge length of 50 mm and a crosshead speed of 5 mm min^{-1} according to ASTM D-638 standard. An average of at least 7 reproducible results were presented from 10 samples tested. All tests were conducted under ambient conditions.

Impact test. The falling weight impact tester (Instron Dynatup 9210, USA) with a V-shaped impactor tup was run in Charpy mode. The impact test bars of average dimensions of 6 × 12 × 80 mm^3 were notched with a notch-to-depth ratio (*a/D*) of 0.2 at the center of the bars. The impact test was done under ambient conditions with 6.448 kg impactor load weight. For each batch, a minimum of 10 specimens were tested and the results presented were taken from the average of at least 7 reproducible data.

Differential scanning calorimetry. Differential scanning calorimetry (DSC) was done using the Perkin Elmer DSC-6 (Waltham, MA, USA) on 8–13 mg samples in aluminum pans. Each sample was scanned from 35°C to 250°C at a heating rate of 10°C min^{-1}. Results were analyzed with the Pyris software version 11. The melting temperature (T_m), enthalpy (ΔH_m), crystallization temperature (T_c), crystalline enthalpy ($-\Delta H_c$), and crystallinity (X_c) were determined after the melting and crystallization processes. The melting temperature, T_m, was taken as the peak of the endothermic curve and T_c from the exothermic curve.

Thermogravimetric analysis. TGA measurements were carried out using the Perkin Elmer TG 6 on 8–13 mg samples in a ceramic crucible, over a temperature range of 50–900°C, at a heating rate of 10°C min^{-1}. The tests were conducted in nitrogen atmosphere at a flow rate of 20 mL min^{-1}. The weight change was recorded as a function of temperature. Degradation peak temperature, T_p, was taken as the maximum temperature acquired from the derivative of the weight change as a function of time. TGA data were collected and analyzed with the Pyris software.

Dynamic mechanical analysis. A dynamic mechanical analyzer model Q800 (TA Instruments, New Castle, DE, USA) was used to analyze the dynamic mechanical properties of composites in the three-point bending mode. The measurement was conducted at a heating rate of 3°C min^{-1} and a constant frequency of 1.0 Hz, over a temperature range of between –135°C and 100°C with an amplitude of 15 μm. The samples were taken from the middle section of injection-molded tensile test specimens to the dimension of $60.0 \times 13.0 \times 3.3$ mm^3. The storage modulus, loss modulus, and tan δ peaks were obtained by the TA universal analysis software version 5.

Fractured surfaces behavior. The field-emission scanning electron microscope (FESEM, Auriga-39-22, Jena, Germany) was used to observe the fractured surfaces of the impact specimens. A FESEM study was carried out in order to investigate the interfacial adhesion between the KF and HDPE matrix of composites after the addition of compatibilizer. The samples were mounted on an aluminum sample holder and placed in the specimen chamber, in a vacuum condition of 0.06 mbar at room temperature under an accelerating voltage of 1 kV. Digital images were taken from the fracture surfaces of the samples at 1000× magnification.

Results and discussion

Physical properties

Tensile test. The effect of MA compatibilizer on the tensile strength of composites, at 8.5 and 17.5 wt% fiber contents, is shown in Figure 1. Composites with lower fiber content (8.5 wt%) presented a lower tensile strength when compared to composites with higher fiber content (17.5 wt%). Li and Matuana[11] reported that beyond the critical fiber content, the tensile strength of composites increased with an increase in fiber fraction. Increase in tensile strength is due to the efficient stress transfer from the matrix to the fiber, attributing to the increase in the weight percentage of the fiber within the matrix.[12]

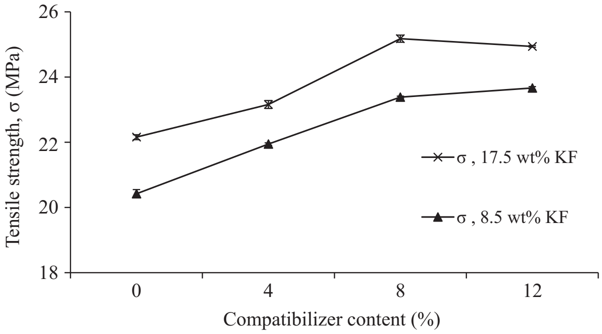

Figure 1. The tensile strength of KF/HDPE/MA-compatibilized composites. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

The addition of compatibilizer into the composites resulted in higher tensile strength when compared to the one without the compatibilizer. At 8.5 and 17.5 wt% fiber content, the tensile strength increased by 14.5% and 13.6%, respectively, after the addition of 8% compatibilizer when compared to the composite without compatibilizer. The low tensile strength of composites without the compatibilizer is due to the poor wettability of the hydrophilic fiber by the hydrophobic polymer matrix[4,12,13] which is an indication of weak interfacial adhesion between the fiber and the matrix.[4,11–16] The enhancement in the tensile strength occurred after the addition of the compatibilizer into the composites, which improved the interfacial bonding between the fiber and the matrix, resulting in better stress transfer from the matrix to the fiber.[2–3,17–19] A slight reduction in the tensile strength was observed after the addition of 12% compatibilizer into the 17.5 wt% fiber content. Sathe et al.[20] reported that most of the compatibilizers are located at the interphase between the matrix and the dispersed phase, up to a saturation level of the compatibilizer. However, when the compatibilizer concentration exceeds the saturation level, only a part of the molecules remains in the interfacial area and the excess is dispersed in the matrix, affecting its homogeneity and consequently the mechanical properties of the blends. The excess compatibilizers will agglomerate and hinder crystallization, thus altering the matrix properties.

Figure 2 shows the tensile modulus increased up to 8% with increasing compatibilizer content, both at 8.5 and 17.5 wt% fiber contents. These trends were decreased after the addition of 12% compatibilizer into the composites. The reduction in the modulus can be attributed to the matrix-altering effect of excess compatibilizers in the system which leads to the matrix being more ductile. Wong et al.[21] state that an enhancement in the tensile modulus is achieved only on particular coupling agents at specific loading.

The tensile strain curves of composites at 8.5 and 17.5 wt% KFs with different percentages of compatibilizer content are shown in Figure 3. Composites at higher fiber content of 17.5 wt% showed a lower tensile strain relative to composites at 8.5 wt% fiber content. Increasing the

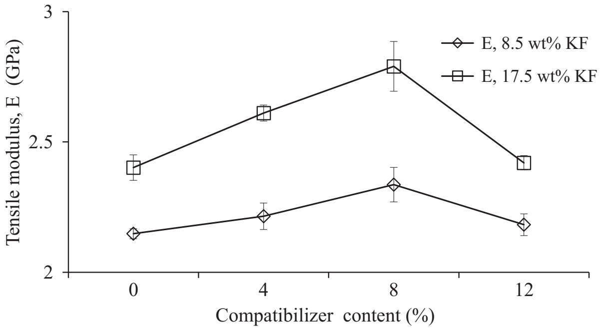

Figure 2. The tensile modulus of KF/HDPE/MA-compatibilized composites. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

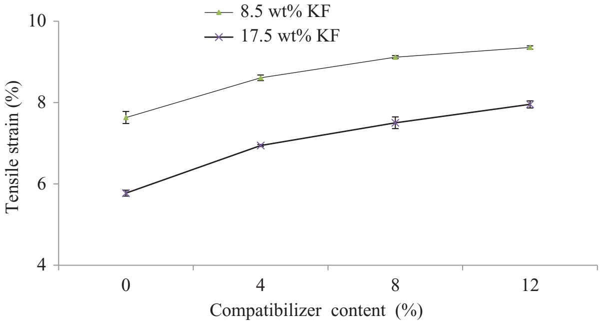

Figure 3. The tensile strain of KF/HDPE/MA-compatibilized composites. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

amount of fiber decreased the amount of polymer available for elongation.[22] Composites without compatibilizer at 8.5 and 17.5 wt% fiber contents present a lower tensile strain when compared to the composites containing compatibilizer. The addition of wood to the PE matrix without coupling agents significantly reduced the elongation at break of the composites[11,23] due to the incorporation of a brittle filler into the polymer matrix. The addition of a less-stiff material, such as compatibilizer, into composites shows a significant increment in elongation at break.[10]

Impact test. The effects of the different percentages of compatibilizer contents on the peak loads, P and fracture energy, W at 8.5 and 17.5 wt% fiber contents are presented in Figure 4. All samples were tested at 0.2 notches. Hassan et al.[24] reported that G_c and K_c values were closest to the calculated values at a/D ratio of 0.2. Composites without compatibilizer exhibited lower P and W values when compared to the composites with compatibilizer. In comparison with the different KF contents for composites without compatibilizer, 8.5 wt% fiber content showed higher P and W values when compared to the 17.5 wt% fiber content. The P and W values were found to decrease from 304.3 N (8.5 wt%) to 287.4 N (17.5 wt%) and 144.2 mJ (8.5 wt%) to 124.1 mJ (17.5 wt%), respectively. Higher fiber content leads to an increase in the probability of agglomeration of the fiber in the matrix which, in addition to the already created notches, could act as a stress concentration area that requires lower energy to failure.[19] As the fiber loading increased, more traces of void and cavities were observable in the uncompatibilized composites.[4] The existence of void in the composites decreased the mechanical strength[25,26] due to the increase in fiber agglomeration which creates regions of stress concentrations that require less energy to initiate cracks.[19]

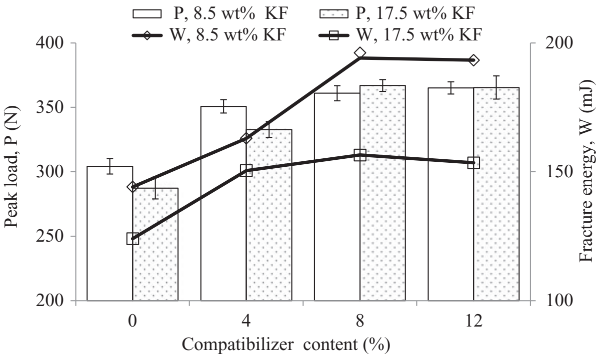

Figure 4. The peak load and fracture energy of KF/HDPE/MA-compatibilized composites. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

Generally, P and W increased with MA compatibilizer content in all the categories of composites studied. At 8.5 wt% fiber content, the effect of the addition of compatibilizer on P and W was observed to be at its highest at 8% and levels up at 12%. It has been reported that better wettability between MA-PE and PE matrix polymer improved the stiffness of the composites.[2] The improved interfacial bonding between the KF and the HDPE matrix resulted in a higher energy requirement for fracture.

The addition of compatibilizer to the 17.5 wt% fiber loading showed that the highest P occurred at 8% compatibilizer loading, beyond which the reduction in P value was observed. Reduction in P value is attributed to the excess MA compatibilizer, which migrates to the surface of the KF, leading to self-entanglement rather than interact with the polymer matrix, thus resulting in slippage.[3,27] At 17.5 wt% fiber loading, as the MA compatibilizer content increased from 0% to 8%, a significant increase in W was observed. Nevertheless, as the compatibilizer content increased to 12%, W remained relatively unchanged. For cases where no deterioration was observed beyond certain level of compatibilizer, this might probably be due to the migration of compatibilizer around the fibers, acting as a damper to the shock wave imparted during the impact testing that was transmitted onto the fibers evenly.[3]

Figure 5 shows the effects of the different percentages of compatibilizer content on the critical strain energy release rate, G_c and critical stress intensity factor, K_c at 8.5 and

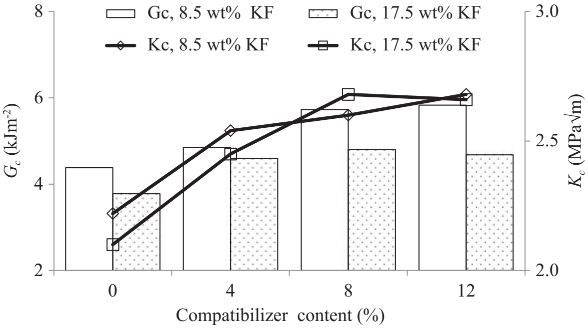

Figure 5. The G_c and K_c of KF/HDPE/MA-compatibilized composites. G_c: critical strain energy release rate; K_c: critical stress intensity factor. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

17.5 wt% fiber content. The 8.5 wt% fiber loading showed a higher G_c value compared to the 17.5 wt% fiber loading. G_c, at 8.5 wt% of KF composites without compatibilizer, is 4.38 kJ m^{-2} and decreased to 3.78 kJ m^{-2} with increasing KF content of the same system. At higher fiber content, fiber-to-fiber contacts were increased, thus reducing the effectiveness of stress transfer between the fiber and the matrix, contributing to the deterioration of the impact strength.[12,16]

G_c and K_c of the compatibilized composites were significantly greater than those of the composites without compatibilizer due to the enhanced interfacial adhesion of composites by MA compatibilizer. The compatibilized composites at 8.5 wt% fiber content showed a marked improvement in G_c and K_c with increasing compatibilizer content. According to Samal et al.,[16] the addition of MA-PP to natural fiber composites and natural fiber hybrid composites improved the impact strength due to the flexibility of the interface molecular chain, resulting in comparatively greater energy absorption of the compatibilized composites.

There are evidences that broken fiber ends have been embedded in the polymer matrix and the cross section between embedded KF and HDPE matrix can be clearly seen (Figure 6). This means that the interfacial adhesion is very strong even after the specimen was subjected to an impact force. This characteristic of the compatibilized system shows the toughness of the composite when the impact force is applied. Improved interfacial bonding leads to improved impact property, which is reflected in increased G_c and toughness of the composite. At 17.5 wt% fiber loading, G_c and K_c values increased up to 8% MA compatibilizer content. Further addition of compatibilizer up to 12% did not show any further improvement, instead a decrement was observed. A reduction of G_c and K_c at higher compatibilizer content may indicate an excess of MA compatibilizer on the surface of the KF which tends to soften the material, thereby plasticizing the system.

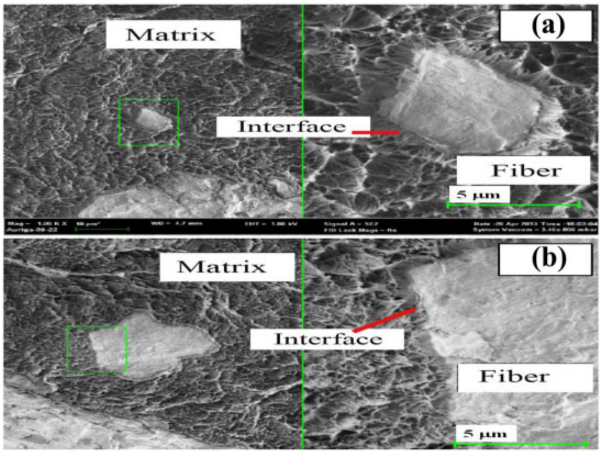

Figure 6. FESEM micrographs of impact fractured composite specimen of 8.5 wt% fiber content with 8% MA-compatibilized composites at 1000× magnification. Right side: Enlarged micrographs. FESEM: field-emission scanning electron microscope; MA: maleic anhydride.

Thermal properties

Differential scanning calorimetry

Figure 7 presents the second heating thermograms of compatibilized composites and composites without the compatibilizer at 8.5 and 17.5 wt% fiber content. Data extracted from these thermograms are summarized in Table 1. Overall melting temperature, T_m, of the composites was not significantly changed by the addition of the fiber and MA compatibilizer. This suggests that there were no significant changes in the microstructure of the matrix with the addition of KF and compatibilizer. No correlation of the T_m results with the fiber and compatibilizer content can be established. Melting enthalpy, ΔH_m, of pure HDPE was 163 J g^{-1}; the addition of KF and compatibilizer reduced the ΔH_m of composites (Table 1) when compared to pure HDPE. Compatibilized composites at lower fiber content of 8.5 wt% showed a higher ΔH_m value when compared to those at higher fiber content. From Table 1, the value of ΔH_m increased with increasing compatibilizer content up to 8% and then dropped at 12%. These trends were observed both at 8.5 and 17.5 wt% fiber content.

The incorporation of MA compatibilizer increases the degree of crystallinity, X_c, of the composites (Table 1). A slight increment in the X_c of composites with increasing MA compatibilizer can also be observed up to 8% for the 8.5 and 17.5 wt% fiber content. The improvement in the X_c value of composites is due to the effect of MA compatibilizer, which extended the predominance of the crystallization process.[7] Higher X_c values of the compatibilized composites at 17.5 wt% fiber content suggest that an enhanced interfacial adhesion in the composites had occurred at higher fiber content following the addition of MA compatibilizer. On the other hand, as the

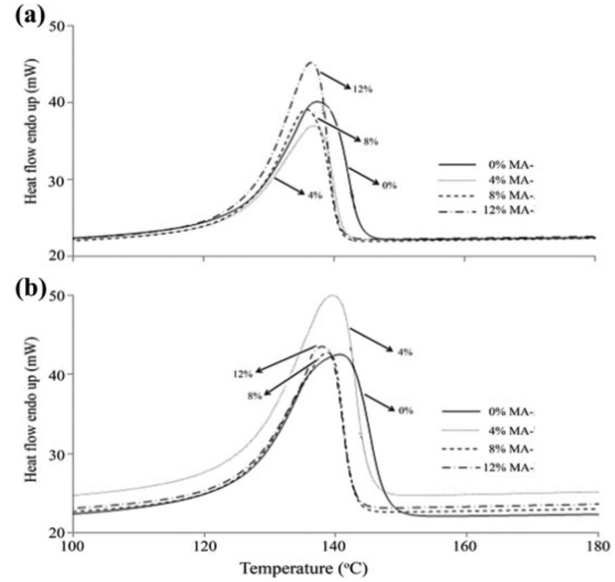

Figure 7. Heating DSC thermograms of KF/HDPE/MA-compatibilized composites: (a) 8.5 and (b) 17.5 wt% fiber contents. DSC: differential scanning calorimetry; KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

Table 1. DSC parameters of 8.5 and 17.5 wt% fiber contents of KF/HDPE/MA-compatibilized composites.

MA content (%)	KF fraction (wt %)	T_m (°C)	T_c (°C)	ΔH_m (J g^{-1})	$-\Delta H_c$ (J g^{-1})	X_c (%)
0	8.5	141	112	139	146	52
	17.5	141	113	139	148	58
4	8.5	137	118	159	178	59
	17.5	140	116	150	164	62
8	8.5	136	118	161	167	60
	17.5	139	117	150	164	62
12	8.5	137	118	160	165	60
	17.5	138	117	148	163	61

DSC: differential scanning calorimetry; KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride; T_m: melting temperature; T_c: crystallization temperature; ΔH_m: enthalpy, $-\Delta H_c$: crystalline enthalpy; X_c: degree of crystallinity.

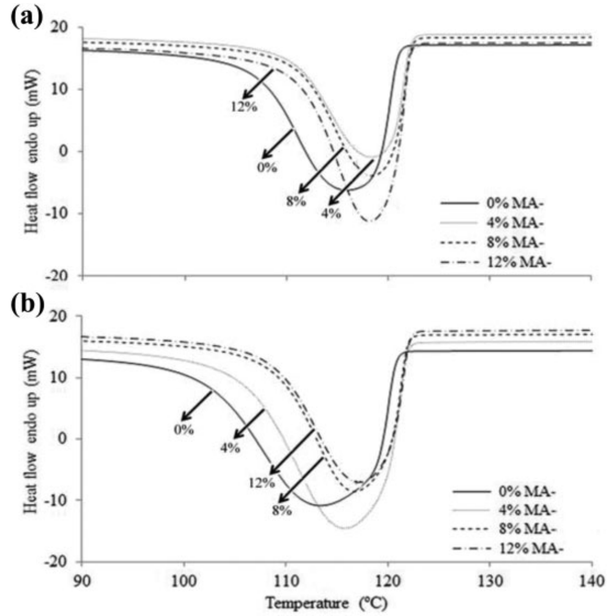

Figure 8. Cooling DSC thermograms of KF/HDPE/MA-compatibilized composites: (a) 8.5 and (b) 17.5 wt% fiber contents. DSC: differential scanning calorimetry; KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

compatibilizer content was further increased to 12%, X_c decreased at 17.5 wt% fiber content. The excess compatibilizer dispersed in the system tends to agglomerate. The agglomeration hinders crystallization of the matrix, thus reducing its X_c.

Figure 8 shows the DSC cooling thermograms of compatibilized composites and composites without compatibilizer at different fiber contents. Crystalline temperature, T_c, of pure HDPE was recorded as 116°C. The addition of 8.5 and 17.5 wt% KF to the matrix without compatibilizer slightly reduced the T_c of composites to 112°C and 113°C, respectively. It seemed that without compatibilizer, the addition of fibers to the composites led to poor wettability between polymer matrix and fiber which interrupted the nucleation process in the polymer matrix.[18] However, T_c of the compatibilized composites was found to be higher, relative to the composites without compatibilizer, which indicates a further enhancement in the nucleation process in the presence of compatibilizer, due to the formation of ester linkage between the polymer matrix and the fiber. This finding agrees with that reported by Nayak and Mohanty.[12] At 8.5 wt% fiber content, composites without compatibilizer showed a lower ΔH_c and X_c when compared to those at 17.5 wt%. The increment in ΔH_c and X_c for composites without compatibilizer at higher fiber content is due to the presence of higher cellulose content in the composites. The fiber surface could act as a nucleating agent, thereby promoting crystalline growth and the formation of transcrystalline regions around the fibers' surface, thus leading to higher X_c.[28]

Thermogravimetric analysis

Figure 9 shows the TGA/derivative thermogravimetric (DTG) thermograms of compatibilized composites and composites without compatibilizer at 8.5 and 17.5 wt% fiber contents. Generally, a two-stage weight loss of composites was observed from the DTG thermograms. The first stage occurred at around 400°C, corresponding to the degradation of the fiber and the second stage occurred at around 480°C, corresponding to the degradation of the polymer matrix. Generally, the thermal stability of compatibilized composites was lower when compared to the composites without compatibilizer. In order to verify the

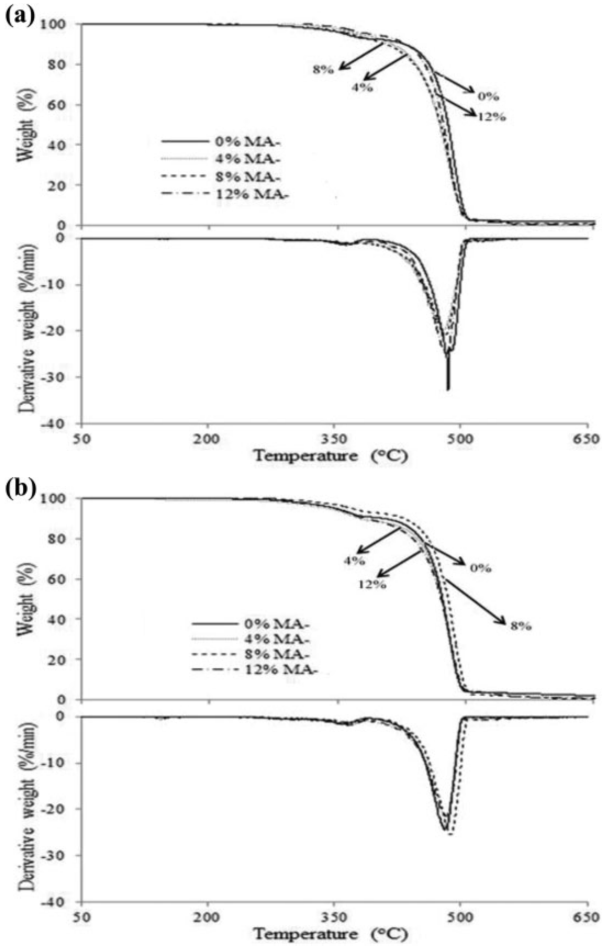

Figure 9. TGA/DTG thermograms of KF/HDPE/MA-compatibilized composites: (a) 8.5 and (b) 17.5 wt% fiber contents. TGA: thermogravimetric analysis; DTG: derivative thermogravimetric; KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

Table 2. TGA/DTG parameters of 8.5 and 17.5 wt% fiber contents of KF/HDPE/MA-compatibilized composites.

MA content (%)	KF fraction (wt%)	T_p (°C)	T_{onset} (°C)	$T_{50\%}$ (°C)	Degradation temperature range (°C)
0	8.5	485	272	480	250–600
	17.5	481	268	473	240–670
4	8.5	478	314	470	260–585
	17.5	479	280	472	250–630
8	8.5	482	322	471	260–585
	17.5	487	296	479	250–650
12	8.5	483	325	474	260–580
	17.5	483	282	471	245–600

TGA: thermogravimetric analysis; DTG: derivative thermogravimetric; KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride; T_p: degradation peak temperature; T_{onset}: decomposition temperature; T50%: degradation temperature at 50% decomposition.

Table 3. TGA/DTG parameters of KF/HDPE/MA-compatibilized composites at different fiber loadings.

KF fraction (wt%)	T_p (°C)	T_{onset} (°C)	$T_{50\%}$ (°C)	Degradation temperature range (°C)
0	467	380	466	320–515
3.4	474	313	467	265–640
8.5	485	272	480	250–600
17.5	481	268	473	240–670

TGA: thermogravimetric analysis; DTG: derivative thermogravimetric; KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride; T_p: degradation peak temperature; T_{onset}: decomposition temperature.

interactions between the degradation mechanisms affecting the char residues, weight loss from derivative thermograms was measured.

TGA/DTG parameters of 8.5 and 17.5 wt% fiber contents at different MA compatibilizer contents are enumerated in Table 2. The thermal degradation patterns of pure HDPE and the resultant composites reveal that the pure matrix was less thermally stable than the composites, as reported in Table 3. The degradation temperature at 50% decomposition $T_{50\%}$ of pure HDPE was 460°C, while $T_{50\%}$ of 8.5 and 17.5 wt% was 480°C and 473°C, respectively.

T_p and $T_{50\%}$ of pure HDPE were reduced between 13°C and 18°C and 8°C and 14°C, respectively, when compared to the composites. Furthermore, the degradation profiles of composites, from Table 2, also indicate an improvement over the fiber and the pure matrix before compounding, which degraded earlier over a wider range. From Table 2, it was observed that the decomposition temperature, T_{onset}, and $T_{50\%}$ of the composites without compatibilizer at higher fiber content were lower when compared to the composites at lower fiber contents. Incorporation of fibers at higher loadings decreased the thermal stability of the composite without compatibilizer systems. This is as a result of the lower thermal stability of the natural fiber when compared to the matrix.

The areas under the derivative thermograms were calculated and the results of the calculated char residue are presented in Table 4. Composites without compatibilizer showed less char residue when compared to the compatibilized composites at 8.5 and 17.5 wt% fiber loadings. This behavior occurred due to the increase in the degradation processes, contributing to char residue formation. One explanation for this fact is that the compatibilized composites show a better interfacial interaction due to the reaction between the acid groups of the MA groups and the hydrophilic groups on the fiber surfaces. This larger interface promotes more interaction between the degradation processes of the two components, that is, the degradation of one component may be accelerating the degradation of the other component or it could be due to the presence of residues of the peroxide used to graft MA to PE.[6]

Table 4. Area of derivative thermograms related to the weight loss for KF/HDPE/MA-compatibilized composites.

Samples	KF fraction (wt%)	1st weight loss (%)	2nd weight loss (%)	Total weight loss (%)	Char residues (%)
Pure HDPE	—	—	97.8	97.8	2.2
Composite + 0% MA	8.5	4.5	88.2	92.7	7.3
	17.5	5.5	83.9	89.4	10.6
Composite + 4% MA	8.5	1.4	84.5	85.9	14.1
	17.5	5.3	81.0	86.3	13.7
Composite + 8% MA	8.5	1.6	87.3	88.9	11.1
	17.5	5.0	85.5	90.5	9.5
Composite + 12% MA	8.5	1.9	87.6	89.5	10.5
	17.5	5.0	82.5	87.5	12.5

KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

Only compatibilized composites at 8% MA compatibilizer at higher fiber loading showed an improvement in thermal stability when compared to the composites without compatibilizer. At higher fiber loading (17.5 wt%), more fiber is available to adhere with the polymer, 8% MA compatibilizer content seems to provide good compatibility, wetting, and adhesion, leading to a more uniformly dispersed fiber within the matrix.[15] This may be responsible for the highest thermal stability achieved at this MA compatibilizer content. The improvement in the thermal stability of composites with the addition of compatibilizer was due to the enhanced interfacial adhesion and additional intermolecular bonding, which produced an esterification reaction between hydroxyl groups of rice husk fiber (RHF) and the anhydride functional group of MA-PP and MA-PE.[7]

Dynamic mechanical properties

The variations of storage modulus as a function of temperature for pure HDPE and composites with different MA compatibilizer contents and at different fiber contents are graphically illustrated in Figure 10. Pure HDPE showed the lowest E' curves when compared to the composites, at 8.5 and 17.5 wt% fiber contents. Figure 8(a) shows that, at 8.5 wt%, composites without compatibilizer presented the highest E' when compared to the compatibilized composites at all percentages of compatibilizer content. Kim et al.[7] reported that the stiffness of compatibilized composites was not significantly affected by the addition of MA-PE compatibilizer. Only 12% MA compatibilizer content at 17.5 wt% fiber content shows a slightly higher E' at the glassy, leathery, and rubbery plateau regions when compared to the composites without compatibilizer. This behavior was attributed to the improved stiffness of composites at higher fiber content (17.5 wt%) with the highest compatibilizer content (12%). However, the addition of compatibilizer at 8.5 wt% fiber content shows an improvement of E' with the increase in compatibilizer content from 4% to 8% before E' reduced at 12% MA compatibilizer content. In the case of the 17.5 wt% fiber content, the addition of MA compatibilizer increased with the increasing compatibilizer content from 4% to 12%. A comparative account of E' of the compatibilized composites and composites without compatibilizer at 8.5 and 17.5 wt% fiber contents, evaluated at −130°C, −100°C, −75°C, and 25°C, are represented in Table 5. It is also evident from the table that there was a notable increase in the stiffness of composites with the incorporation of KFs. Composites at higher fiber content of 17.5 wt% show a higher E' when compared to the composites at 8.5 wt% fiber content, in all over the range of temperatures evaluated. This is due to the increase in the stiffness of the matrix with increasing fiber loading resulting from the reinforcing effect imparted by the fiber, which allowed a greater degree of stress transfer at the interface.[9]

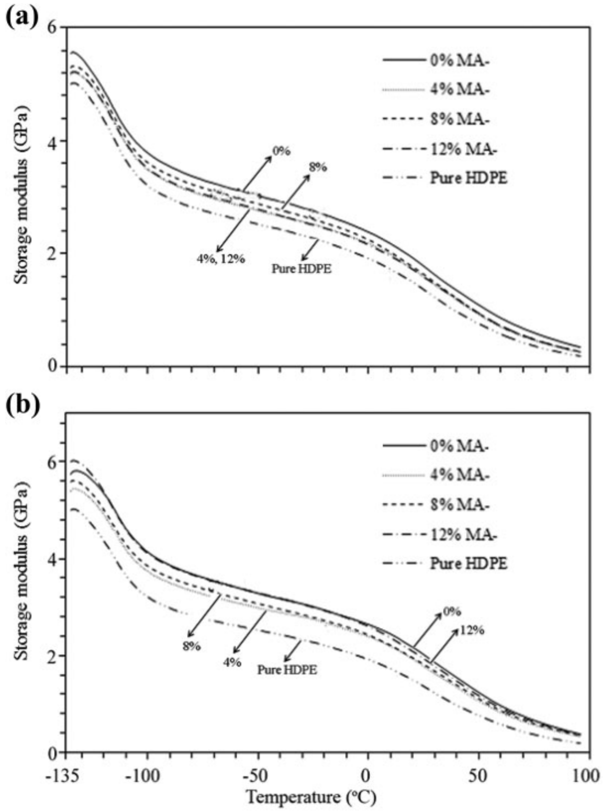

Figure 10. Storage modulus curves of pure HDPE and KF/HDPE/MA-compatibilized composites at: (a) 8.5 and (b) 17.5 wt% fiber contents. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

Variations of loss modulus as a function of temperature for pure HDPE and composites with different MA compatibilizer contents at 8.5 and 17.5 wt% fiber are graphically illustrated in Figure 11. From the figure, pure HDPE and all the composites exhibit two transition peaks (α and γ), where the α-transition peaks were observed at temperature between 37°C and 39°C, while the γ-transition peaks

Table 5. DMA storage modulus of KF/HDPE/MA-compatibilized composites at 8.5 and 17.5 wt% fiber contents.

MA content (%)	KF fraction (wt%)	Storage modulus, E' (GPa)			
		$E'_{-130°C}$	$E'_{-100°C}$	$E'_{-75°C}$	$E'_{25°C}$
0	8.5	5.51	3.84	3.34	1.84
	17.5	5.75	4.08	3.59	1.96
4	8.5	5.12	3.46	3.03	1.57
	17.5	5.36	3.71	3.26	1.75
8	8.5	5.27	3.62	3.17	1.64
	17.5	5.54	3.84	3.38	1.81
12	8.5	5.17	3.50	3.06	1.59
	17.5	5.95	4.10	3.60	1.93

DMA: dynamic mechanical analysis; KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

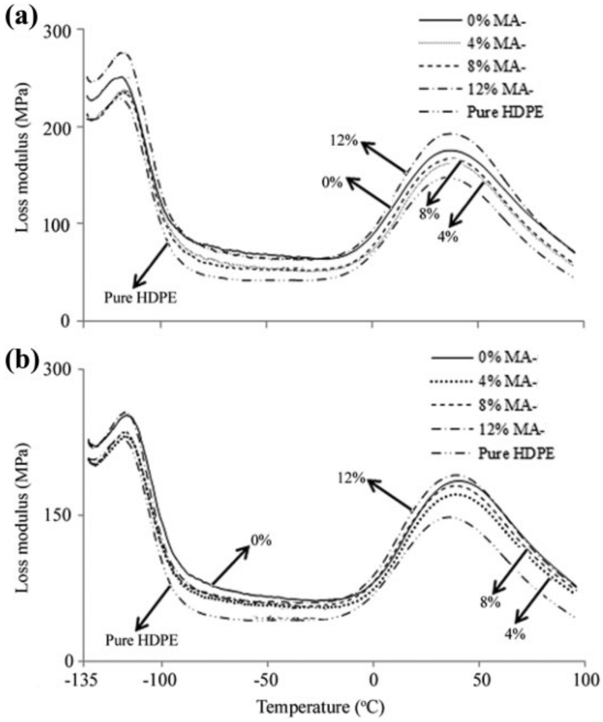

Figure 11. Loss modulus curves of pure HDPE and KF/HDPE/MA-compatibilized composites: (a) 8.5 and (b) 17.5 wt% fiber contents. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

appeared between −118°C and −119°C. The α-relaxation is associated with the chain segment mobility in the crystalline phases which can be due to reorientation of defect areas in the crystals. The γ-relaxation corresponds to the glass transition (T_g) of pure HDPE and it is related to the amorphous phase.[9] The loss modulus value corresponding to the T_g in the composites without compatibilizer at 8.5 and 17.5 wt% fiber contents increased by about 8.3% and 8.7%, respectively, when compared with the pure HDPE (229 MPa), as shown in Table 6. There were no significant changes observed in the T_g values between composites without compatibilizer and pure HDPE. From Figure 11, pure HDPE shows the lowest E'' values compared to the E'' values of composites. Compatibilized composites at 4% and 8% MA compatibilizer contents show lower E'' values when compared to the composites without compatibilizer at 8.5 and 17.5 wt% fiber contents. According to Kim et al.,[7] the addition of MA-PE to the composites did not affect the viscous behavior of composites.

The temperature dependence of the tan δ curves of pure HDPE and composites with different MA compatibilizer contents at 8.5 and 17.5 wt% fiber contents is shown in Figure 12. The tan $\delta_{\max}$ peak can also provide information on the T_g and dissipation energy of the composite materials.[7,9] From the tan δ_{max} peak temperature in Table 5, the T_g of composites did not show any significant difference in temperature. At 17.5 wt% fiber content, the tan δ peak of composites without compatibilizer exhibited lower magnitude in comparison to pure HDPE, which in turn showed a higher magnitude when compared with the compatibilized composites. This indicates that energy dissipation of the compatibilized composites was less than that of the composites without compatibilizer and pure HDPE. Composite without compatibilizer produced materials with poor interfacial bonding between the fibers and the matrix and tended to dissipate more energy, thereby showing high magnitude of damping peak in comparison to compatibilized composites with strongly bonded interface.[9] The tan δ values were lowest at 17.5 wt% fiber content with 8% MA compatibilizer content. It seems that the compatibilized composites produced were tough but not stiff materials as shown by the low E', E'', and tan δ values.

Conclusion

The physicothermal properties of KF/HDPE/MA-compatibilized composites were improved by the addition of compatibilizer into the composites. Melting enthalpy (ΔH_m), degree of crystallinity (X_c), tensile properties, critical strain energy release rate (G_c), and critical stress intensity factor (K_c) of the composites increased with increasing compatibilizer content up to 8%. Enhancement in the tensile properties and impact strength of composites was due to the improvement in the wettability and the flexibility of the interface molecular chain in the presence of compatibilizer in the KF/HDPE/MA-compatibilized composites. Increased interfacial adhesion probably increased the intermolecular hydrogen bonding between KF and the anhydride group of compatibilizer and may be responsible for the highest thermal stability achievement. The enhancement in dynamic mechanical properties from the storage modulus and reduction of loss modulus and tangent delta after the addition of compatibilizer indicates that the composites produced were tough and not stiff materials.

Table 6. DMA loss modulus and tan δ of KF/HDPE/MA-compatibilized composites at 8.5 and 17.5 wt% fiber contents.

		Loss modulus, E'' (MPa)						Tan δ	
		α-transition		β-transition		γ-transition			
MA content (%)	KF fraction (wt%)	E''_{max} (MPa)	T_α (°C)	E''_{max} (MPa)	T_β (°C)	E''_{max} (MPa)	T_γ (°C)	Tan δ_{max} ($\times 10^{-2}$)	T_α (°C)
0	8.5	175	39	—	—	248	−118	5.22	−114
	17.5	184	38	—	—	249	−119	4.96	−116
4	8.5	162	37	—	—	234	−118	5.35	−115
	17.5	170	38	—	—	227	−119	4.90	−115
8	8.5	166	38	—	—	231	−118	5.15	−114
	17.5	179	38	—	—	231	−119	4.85	−115
12	8.5	164	37	—	—	239	−119	5.41	−116
	17.5	190	38	—	—	251	−118	4.93	−115

DMA: dynamic mechanical analysis; MA: maleic anhydride; KF: kenaf fiber; HDPE: high-density polyethylene; T_α: temperature of alpha transition peak; T_β: temperature of beta transition peak; T_γ: temperature of gamma transition peak.

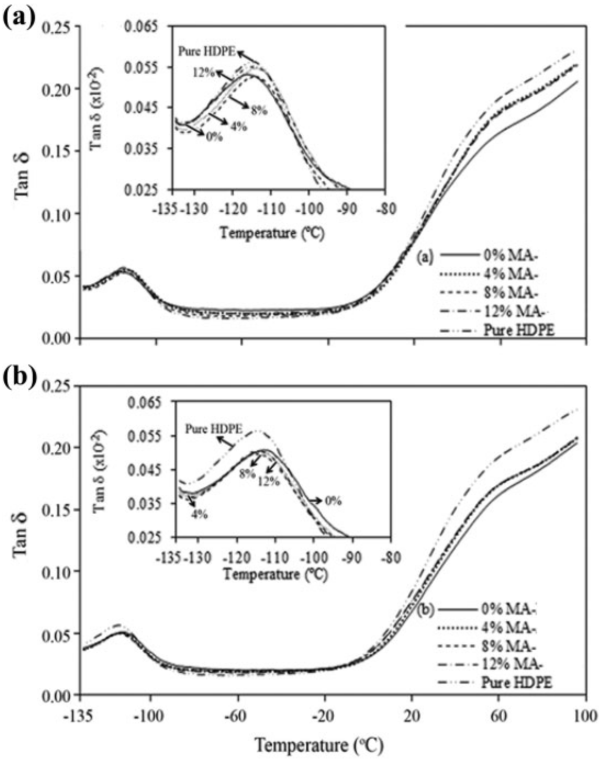

Figure 12. Tan δ curves of pure HDPE and KF/HDPE/MA-compatibilized composites at: (a) 8.5 and (b) 17.5 wt% fiber contents. KF: kenaf fiber; HDPE: high-density polyethylene; MA: maleic anhydride.

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