THERMAL CHARACTERIZATION OF INDIUM DOPED ZINC OXIDE COATED KENAF/POLYANILINE/POLYLACTIC ACID HYBRID COMPOSITE

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ABSTRACT: The unique properties of conductive polymer composites such as electrical conductivity, biodegradability and mechanical strength enable them to be applied in various novel applications such as chemical sensors, fuel cell and shielding material. A combination of polylactic acid (PLA) with indium doped zinc oxide (IZO) coated kenaf fiber and polyaniline (PANI) appears as a potential approach for green-conductive composite development. However, a lower thermal stability of natural fiber reinforced polymer composite (NFRPC) is always the main issue despite its biodegradability and renewability. Thus, this study aims to analyze the effects of hybridization of PLA/IZO-Kenaf/PANI to the resulted thermal properties. In this study, hybrid composites were developed by melt-mixing followed with hot-pressing to form composite samples. The samples of each composition were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) for the decomposition temperature and transition temperature, respectively. Besides, the materials were also analyzed by X-ray diffraction (XRD) and Fourier-transform infrared (FTIR). The results from TGA has revealed an increase of 20.43% in thermal stability of PLA/IZO-Kenaf/PANI hybrid composite as compared than PLA-IZO-Kenaf composite. Meanwhile, the DSC results demonstrate an increase of melting temperature, T_m and melting enthalpy, ΔH_m which signifies higher heat resistance of hybrid composite as compared to PLA-Kenaf composite. Besides, changes on crystallinity and peaks of functional group of PLA and PLA polymers prove the interaction between the elements which leads to the variation of thermal properties.

KEYWORDS: *Polylactic Acid; Indium Doped Zinc Oxide Coated Kenaf; Polyaniline; Thermal Properties*

1.0 INTRODUCTION

Kenaf fiber and polylactic acid (PLA) are usually known as non-conductive materials. Due to that, combination of these materials is seen to be less interesting for electrical and electronic applications. The higher resistance of electric current in natural fiber reinforced polymer composite (NFRPC) hinders the electrons or the charge carriers to be transferred along the body. Based on this argument, researchers have gradually come up with various approaches in realizing the possibilities of producing conductive NFRPC. One of the approaches is by hybridization of the NFRPC via adding conductive fillers such as carbon, metals and intrinsic conductive polymers to develop electrically conductive polymer composites [1-2]. Another approach is via conductive coating of the natural fiber filled in NFRPC [3].

Intrinsic conductive polymer (ICP) is one of the potential fillers for polymer composite. Its infusibility and dispersibility in the polymer at elevated temperature have been the biggest advantage. ICP can be known as polyacetylene, polypyrrole, polythiophene, polyaniline, poly (3,4-ethylene dioxythiophene), and polyphenyl vinylene. Polyaniline (PANI) is one of the intrinsic conductive polymers that are widely used in polymer composite due to its excellent electrical properties, environmental stability, simple and low cost of the synthesis process. In some studies, PANI is significantly altered according to specific chemical modification, functionalization, compositions and applications [4]. On the other hand, conductive material impregnation on natural fiber is another approach for conductive NFRPC. Based on previous successful study of indium zinc oxide (IZO) coating on kenaf fiber, it showed an improvement in conductivity of kenaf fiber [5].

Despite all the merits of NFRPC, its thermal performance has been the main concern of all. Kenaf fiber is normally burnt at above 220 °C due to its hemicellulose and cellulose content [6]. Thus, the hybridization of NFRPC with PANI and IZO coating to produce a conductive material is expected to improve its thermal stability. Therefore, this study intends to evaluate the synergistic effects on the thermal stability in the hybrid composite consists of polylactic acid (PLA), IZO-kenaf and polyaniline (PANI). The thermal characterization will include thermogravimetric analysis (TGA), and differential scanning calorimeter (DSC). X-Ray Diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy will also be performed to support the findings.

2.0 MATERIALS AND METHODS

2.1 Materials

The materials in this study consist of kenaf fibers, PLA polymer and chemicals. The non-woven kenaf mats were supplied by Innovative Pultrusion Sdn Bhd. Meanwhile, semicrystalline polylactic acid (PLA) 3052D polymer in pallet form with a specific gravity of 1.24 g/cm^3 was provided by Biztap Resources. The chemicals including sodium hydroxide (NaOH) pallets, zinc acetate dihydrate, indium chloride, absolute ethanol, ammonium peroxydisulfate, hydrochloric acid (HCl) and anilinium chloride were purchased from Polyscientific Sdn Bhd and only analytic grades chemicals were used.

2.2 Development of IZO Coated Kenaf

The IZO solution was prepared by diluting 0.1 M zinc acetate dihydrate in ethanol and stirred using a magnetic stirrer for 1 hour. Then, 5.0 wt% of indium (III) chloride was added into the solution and stirred at 75 °C for another hour while deionized water was dripped into the solution until it turned into a clear solution. Meanwhile, the non-woven kenaf mat was chemically treated with 6 wt% of sodium hydroxide (NaOH) for 3 hours and dried for 24 hours at 60 °C. After that, the fiber was soak in the IZO solution and pad-dried under constant load to obtain 30-40% uptake of excessive solution. Finally, it was cured at 150 °C for 4 hours.

2.3 Synthesis of Polyaniline

Polyaniline was synthesized via chemical oxidative polymerization. In this process, 0.2 M anilinium chloride and 0.25 M of ammonium peroxydisulfate were dissolved in separate beakers of 100 ml of 1.0 M hydrochloric acid, before both solutions were left at room temperature for 1 hour. After that, both solutions were mixed together and mildly stirred for 2 hours and then left for 24 hours at room temperature for the polymerization process. After a day, the resulted precipitate was filtered and washed thoroughly with 0.2 M hydrochloric acid and acetone. Then, it was dried at 60 °C for 24 hours in a vacuum oven to remove the residual solvent. The resulted powder of emerald green PANI was ground to obtain a fine powder.

2.4 Fabrication of Composites

The hybrid composites were produced by laminating IZO-kenaf fiber mat, PANI and PLA under a hot press machine. Prior to that, PLA pallets and PANI powder were mixed in HAAKE Rheomix 600 mixer at 170 °C for 10 minutes to get a homogenous polymer mixture. After that, the polymer sheets were laminated together with the IZO-kenaf fiber mat and pressed again using the hot press at a constant pressure of 95 kg/cm^2 and temperature of 170 °C for 15 minutes followed with 10 minutes of cooling equipped by water coolant. The amounts of each constituent were set according to Table 1 which are represented as S1 (PLA), S2 (PLA/PANI), S3 (PLA/IZO-Kenaf) and S4 (PLA/IZO-Kenaf/PANI).

Table 1: Compositions of PLA hybrid composites

Sample	IZO-Kenaf (wt %)	Polylactic acid (wt %)	Polyaniline (phr)
S1	-	100	-
S2	-	100	10
S3	30	70	-
S4	30	70	10

2.5 Characterization of Hybrid Polymer Composite

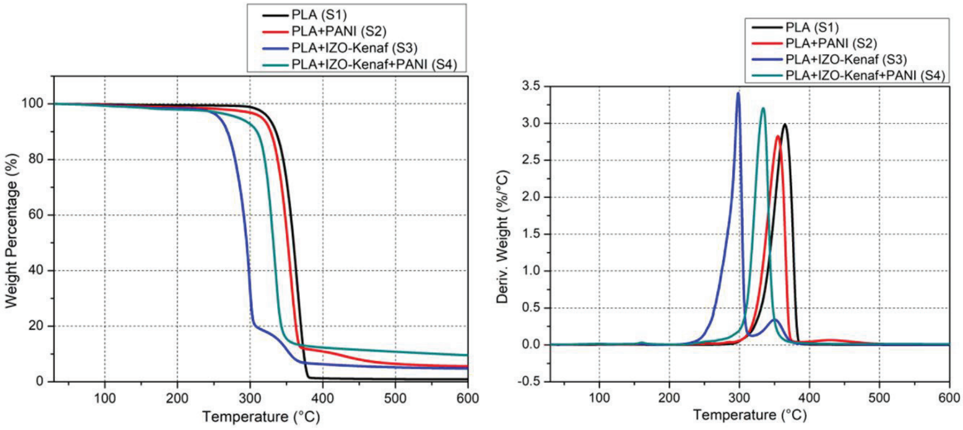
There are two difference thermal characterization method were performed, which are the Thermogravimetric Analysis (TGA) and the Differential Scanning Calorimeter (DSC). For TGA, it was examined by using a TA Instrument: Model Q50 to investigate the decomposition temperature of the polymer and its hybrid composite samples. The analysis samples were weighed for 10-15 mg range prior of the test. Then, the samples were heated up to 600 °C at a constant rate of 10 °C/min in nitrogen gas. While, DSC analysis was carried out by using Perkin Elmer Model Jade DSC apparatus to measure glass transition temperature, T_g, cold crystallization temperature, T_{cc}, melting temperature, T_m and melting enthalpy, ΔH_m of each sample of polymer composites. The samples used were in range of 5-15 mg, and tested between cooling temperature of 5 °C to heating temperature of 210 °C at a constant rate of 10 °C/min.

Another characterization of X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy were performed to support the thermal analysis findings. For XRD testing, the samples were cut into 10 cm × 10 cm and characterized by Panalytical X'pert Pro X-Ray Diffraction (XRD) varying from 10° to 60° of 2-theta. For FTIR spectroscopy, the samples were characterized by Jasco FTIR-6100 to identify the functional groups in the polymer composites. The samples were analysed for the wave number in the range of 400-4000 cm^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Thermal Stability Analysis by TGA

Figure 1 illustrates the thermogravimetric curves for all four samples (S1, S2, S3 and S4) from 30 to 600 °C. The samples exhibit various thermal stabilities, in the range of 220-300 °C before they start to degrade. The degradation points indicate the temperature of kenaf fiber, PANI or PLA starts to decompose. Prior to these temperatures, the composites are able to sustain an average mass of 98% of its original mass, which clarifies that the 2% of mass loss from initial moisture vaporization in the materials before its rapid decomposition. It is shown that the composite of PLA/IZO-Kenaf (S3) starts degrading at the lowest temperature and exhibits two-step degradation at 200-210 °C and 310-320 °C which represents kenaf fiber and PLA decomposition, respectively. Meanwhile, the PLA (S1) gives the highest thermal stability among the composite samples.



(a) (b)

Figure 1: Graphs of (a) thermogravimetric and (b) derivative thermogravimetric curves of the hybrid composites

Detailed data from Table 1 illustrate decomposition temperature of 332.4 °C and 312.7 °C for the PLA (S1) and PLA/PANI composite (S2), respectively. The addition of PANI in PLA causes the least decrease of thermal stability. In comparison, composites containing kenaf show relatively low decomposition temperatures at 253.2 °C and 305.0 °C, for PLA/IZO-Kenaf (S3) and PLA/IZO-Kenaf/PANI (S4), respectively. These samples decompose more rapidly with the addition of kenaf fiber. This finding explains that the existence of kenaf fiber reduces the thermal stability of the composite due to its hemicellulose and cellulose content which usually degrades around 220 °C.

Table 2: Results of derivative thermogravimetric (DTG) analysis

Sample	Onset decomposition temperature (°C)	Temperature at maximum mass loss (°C)	Residual weight at 600 °C (%)
PLA (S1)	332.4	364.8	0.91
PLA/PANI (S2)	312.7	354.9	5.40
PLA/IZO-Kenaf (S3)	253.2	298.3	4.36
PLA/IZO-Kenaf/PANI (S4)	305.0	334.0	8.54

However, as the polyaniline is added into the PLA/IZO-Kenaf/PANI composite (S4), the resulted hybrid shows improved thermal resistance by 20.43% compared to the sample without polyaniline. The reason for this is that thermal stability is increased due to more thermal energy needed to break the crosslinking and large molecular weight of oxidized PANI in the hybrid composites [7-8]. The results of the thermogravimetric also show that hybrid composite of PLA/IZO-Kenaf/PANI yields the highest residue at 600 °C. This phenomenon is associated with the undecomposed carbon or char yielded from the polymer with crosslinking and aromatic rings structure such as polyaniline in the composite.

3.2 Transition Temperature Analysis by DSC

The transition temperatures of PLA and its composites are plotted in Figure 2 to show the endothermal glass transition temperature (T_g), melting temperature (T_m) and exothermal cold crystallization temperature (T_{cc}). The results indicate that there is a significant influence of PANI and IZO-Kenaf addition to PLA as demonstrated by the changes in the values of T_g, T_m and T_{cc}. The first peak in the graph (Figure 2) specifies the glass transition temperature, T_g of PLA and its composites. The results show slight decrease in T_g value of PLA from 60.8 °C to 57.5 °C in PLA hybrid composite (Table 3) which explains greater molecular/chain mobility and flexibility resulting from the addition of PANI and IZO-kenaf filler. In this case, less thermal energy is required for the transition hence leads to early glass transition occurrence of PLA composites [9].

Meanwhile, the observation on cold crystallization temperature, T_{cc} shows a shift towards lower temperature as the PLA combined with PANI and IZO-Kenaf. The lowest T_{cc} is represented by PLA/IZO-Kenaf composite (S3) at 113.5 °C. As highlighted by Obgomo et al. [10], the decrease of crystallization temperature signifies the improvement of crystallinity which possibly could contributed by transcrystalline between kenaf fiber and PLA. Besides, the changes of the crystallization temperature are strongly believed due to the nucleating effect by the fillers which could accelerate the crystallization of PLA composite [11].

As the temperature increases up to 145 °C, the polymer composite starts to melt which is represented by T_m. Two peaks of melting temperature (T_{m1}, T_{m2}) are observed in the PLA composites, while only one peak in neat PLA. This is explained in the literature that lower melting temperature (T_{m1}) is attributed by the melting of imperfect PLA crystalline phase, while higher melting temperature (T_{m2}) is assigned to the stable crystalline phase and denser lamellae [12]. The results also prove that the melting temperature of PLA decreases with the addition of fillers especially with the addition of kenaf fiber.

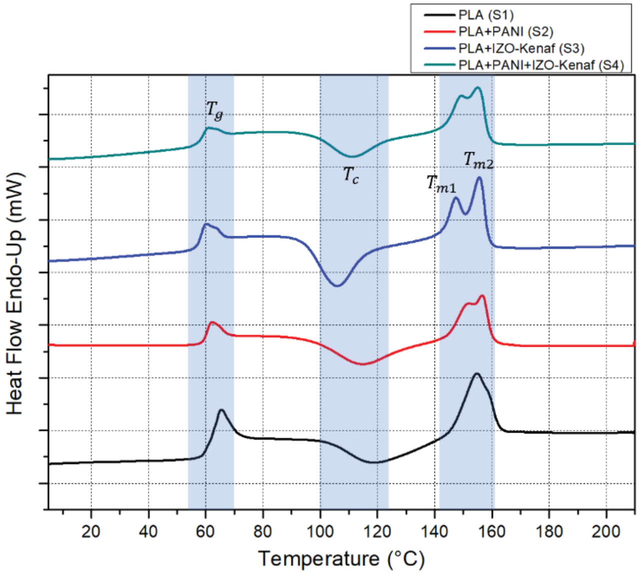


Figure 2: Thermogravimetric and derivative thermogravimetric curves of the hybrid composites

Moreover, the melting enthalpy, ΔH_m shows an increasing value as PANI and IZO-Kenaf are added to the PLA. This explains that PLA composite requires more energy to melt as compared to the neat PLA. Furthermore, the degree of crystallinity, X_c of PLA shows an increase upon the addition of IZO-Kenaf and PANI with the highest value of 8.06 % in the hybrid PLA/IZO-Kenaf/PANI composite.

Table 3: Transition temperatures of the PLA and its composites

Sample	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PLA (S1)	60.8	118.3	11.60	154.6	13.28	1.81
PLA/PANI (S2)	59.7	114.8	20.68	152.5	15.35	5.73
PLA/IZO-Kenaf (S3)	57.2	105.9	25.60	145.5	22.98	2.82
PLA/IZO-Kenaf/PANI (S4)	57.5	111.0	13.25	148.8	20.75	8.06

3.3 XRD Analysis of Hybrid Composites

The effects of PANI and IZO-Kenaf addition in PLA have been studied by XRD as shown in Figure 3. The broad peak from neat PLA and PLA/PANI composite defines their amorphous characteristic. It has been discovered that the peak of PLA polymer with preferred orientation along the (110) and (200) plane at 2θ: 16.58° is apparently unaffected upon the addition of PANI and IZO-Kenaf [10].

However, a stronger peak is obtained in PLA/IZO-Kenaf composite (S3) compared to the neat PLA (S1) [13]. The intensity of the peaks increases as it is hybridized with PANI and IZO-Kenaf. These results correlate with the findings of enhanced degree of crystallinity, X_c of PLA hybrid composite which is attributed by the transcrystalline of the polymer and fibers and also the addition of PANI. This condition is strongly supported the improved thermal resistance of hybrid composite which is proven by its higher crystallinity and denser lamellae upon the hybridization.

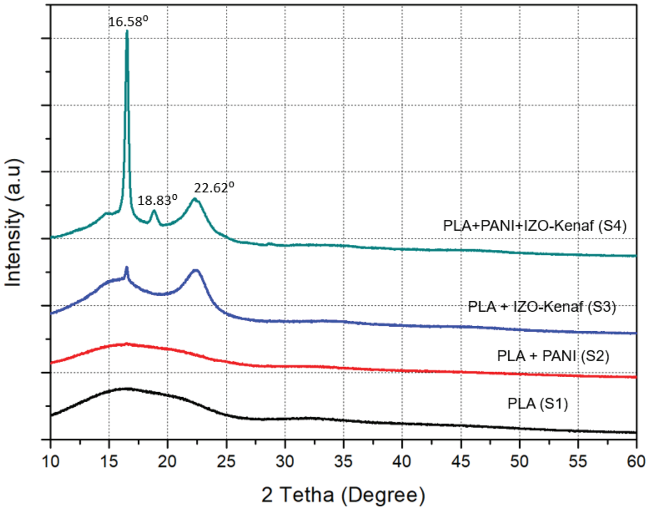
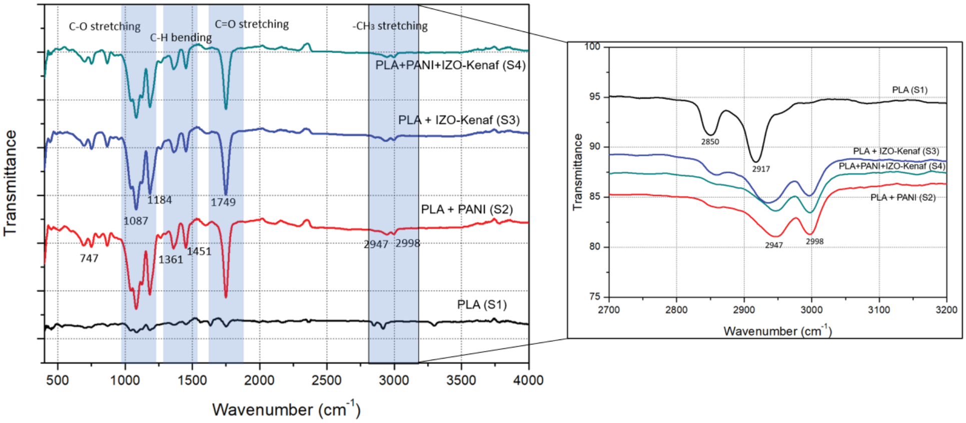


Figure 3: XRD patterns of neat PLA and PLA composites

3.4 Fourier Transform Infrared (FTIR) Spectroscopy

Figure 4 (a) shows the FTIR spectra for neat PLA, PLA/PANI composite, PLA/IZO-Kenaf composite and PLA/IZO-Kenaf/PANI hybrid composite. The recorded peaks are predominant with the functional groups of PLA polymer which are rich with carbon bonds such as C=O, -CH3, C-H and C-O from the lactic acid monomer. The waveband at 701-747 cm^{-1} and 1749 cm^{-1} are associated with the functional group of C=O stretching. The C-O bond can also be seen at 1087-1184 cm^{-1}. Meanwhile, peak at 2850-2998 cm^{-1} and 1361-1451 cm^{-1} signifies the -CH3 stretching and C-H bending, respectively [14]. Upon the addition of PANI, the peak at 1302 cm^{-1} is detected which represents the stretching vibration of benzene in the PANI [15].

All the results specify that the PLA remains its inherent chemical bonding as the core material. However, there is a distinct shifting on the peaks as the PLA polymer combines with PANI and IZO-Kenaf. These peaks intensity also grows with PLA composites compared to neat PLA. For an instant, the -CH3 bond peaks of PLA composite in Figure 4 (b) show a red shift (to the higher wavenumber) at range 2947-2998 cm^{-1} compared to neat PLA. This red shift indicates a successful introduction of filler (PANI and IZO-Kenaf) which is strongly influenced by the chemical interaction occurring within the composite blend [16].



(a) (b)

Figure 4: Graphs of (a) FTIR spectra for PLA with PLA composites and hybrid composite while (b) the close-up graph at 2700-3200 cm^{-1}

4.0 CONCLUSION

The addition of polyaniline (PANI) and IZO-kenaf in PLA composite has given a significant influence to the thermal properties. As expected, the presence of kenaf fiber has lowered the thermal stability of PLA polymer due to its poor thermal resistance. However, the hybridization of PLA/IZO-Kenaf/PANI composite has improved the thermal stability up to 20.43%. The decrease of the transition temperatures T_m, T_c and T_g upon the addition of PANI and IZO-Kenaf has proven the macromolecules interaction between the phases. However, the increase of melting enthalpy, ΔH_m signifies that the more endothermic energy required to overcome their intermolecular force of a solid substance to melt upon the hybridization of PLA with IZO-Kenaf and PANI. Moreover, this hybridization also does influence the XRD and FTIR results. The hybridization of PLA, IZO-Kenaf and PANI is found to be effective in enhancing crystallinity of the material. Meanwhile, the FTIR results have verified the significant existence and shifting of peaks upon the addition IZO-Kenaf and PANI without the alteration of PLA inherent chemical bonding as the core material.

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