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**THERMAL ANALYSIS OF KENAF DERIVED CELLULOSE-FILLED
POLY(LACTIC ACID) COMPOSITE FILMS**

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ABSTRACT

Thermal analysis of KDC-filled PLA composite films were carried out using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray diffraction. The composites composed of KDC loading ranging from 0 to 60 % (based on dry weight of PLA) were prepared via melt blending which followed by hot and pressing procedure to produce films with thickness of 0.30 mm (± 0.05 mm). From TGA, incorporating higher loading of KDC in the composites reduced the degradation temperature in comparison to neat PLA, indicating less thermal stable composites. From DSC, with the exception of the slight increment in melting temperature (T_m), other thermal properties namely glass transition temperature (T_g), and crystallization temperature (T_c), remain unaffected by the presence of increasing KDC loading in PLA matrix. The percentage of crystallinity ($\%X_c$) do not show a clear trend with increasing KDC loading in PLA composites. In conclusion, with just a slight increment of approximately 6 °C in T_m , KDC-PLA composites can be processed without changing the novel operating temperature of processing PLA. It is also worth noting that the ability of KDC-PLA composites to degrade at lower temperatures in comparison to PLA is considerably vital during thermal decomposition.

Keywords: *Poly(lactic acid), Kenaf, Cellulose, Composite, Thermal analysis.*

INTRODUCTION

The growing demand for environmental friendly packaging materials has engaged much research works by the academic and industrial communities. Besides for green environment, transiting from non-environmental friendly products to environmental friendly products may offer promising ventures. Poly(lactic acid) (PLA), polycaprolactone (PCL), poly (butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB) are among the biopolymers that are commercially available. Amongst stated, PLA is highly in demand especially as a raw material for packaging, besides applications in biomedical and agricultural sector [1]. PLA, which is a linear aliphatic thermoplastic polyester can be produced by the petrochemical route or derived through fermentation of carbohydrate [2]. When biopolymer is incorporated with fillers such as plant fibers, it is often noted that it demonstrates a unique composite's property. In comparison to synthetic fillers such as glass fibers and carbon fibers, it is supported that natural fibers were in the leading hand in terms of cost, process capability and significant reduction in tool wear [3]. Natural fibers for composites manufacturing are in varied forms such as raw fibers [4], chemically treated fibers [4], nanofibers [5], cellulose [6&7] and microcrystalline (MCC) cellulose [8]. Rather than filling them into polymer matrices as it is, natural fibers were commonly chemically treated or modified to widen their applications. It is supported that the properties such as mechanical, barrier, and morphology were seemingly improved [9–11]. In this study, cellulose from kenaf fibers (KDC) was derived via chemical treatments of chlorination and mercerization prior to them incorporating into PLA matrix. The chemical treatments were executed in accordance to literature to effectively remove lignin and hemicellulose [7]. As established by the FTIR spectrum, Tawakkalet al. [7] has effectively produced alpha-cellulose from kenafbast fibers. From the same study, with optimum mixing time and processing temperature during compounding, the resulted composites have better tensile strength and modulus. It is stated that such an improvement was due to the physical interaction between cellulose as there was no new chemical bonding observed from the FTIR. As stated by Sreekala et al. [12], the more prominent porous surface morphology resulted from alkali treated oil palm empty fruit bunch (OPEFB) is fundamental for mechanical interlocking

between the fibers and the matrix. Sreekala et al. [12] further studied the thermal stability of alkali and silane treated OPEFB. With significantly higher degradation temperature in TGA analysis, it was supported that the chemical treatments improved the thermal stability of oil palm fibers. Apart from studying the thermal properties of chemically treated fibers alone, the thermal properties of the chemically treated fibers incorporated into biopolymer matrices would be an interesting study as well especially in the packaging field. It is noticed that from most of the composite related studies done, majorly are focused on the mechanical properties rather than on thermal properties. Via DSC and TGA analyses, Tajeddinet al. [13] reported that incorporation of cellulose that was derived from kenaf into Low Density Poly(Ethylene) (LDPE) improved thermal resistance as compared to LDPE polymer. Rudnik[14] stated that the changes in glass transition temperature (T_g) of composite with natural fibers incorporated in it is dependent on its' fiber-matrix interaction. When the fiber-matrix interaction is strong, it decreases the chain mobility that consequently reduces the matrix glass transition. Another important factor that influences the thermal stability of a semi-crystalline PLA system is its crystallization behavior. A separate study carried out by Mathew *et al.* [10] reported thermal stability of PLA composites improved due to the occurrence of cold crystallization in the composites reinforced with microcrystalline cellulose (MCC) and wood flour (WF) respectively. Realizing the importance of thermal properties of composites for packaging application in order to determine their end use, this current work intended to further investigate their thermal behaviour. Thus, the composites was performed by TGA to investigate their thermal stability whereas DSC was carried out to provide other thermal properties of the composites. XRD was performed to investigate the crystallinity of composites filled with different KDC loadings.

MATERIALS AND METHODS

Material

Polylactic acid resin 2002D grade was purchased from NatureWorks LLC (U.S.A) and kenafbast fiber was kindly provided by the Institute of Tropical Forestry and Forest Products (INTROP, Malaysia). The basic properties of this PLA are tabulated in Table 1 below.

Table 1: Properties of PLA resin from PLA D2002 Datasheet.

Properties	PLA polymer 2002D	ASTM
Melting Point, °C	150-160	-
Melt Index, g/10 min	5.0-7.0	-
Tensile Strength at Break, MPA	53	D882
Tensile Modulus, GPa	3.5	D882
Tensile Elongation, %	6	D882

Cellulose extraction was carried out according to the previous study. The procedure for extracting cellulose from the kenafbast fiber is described in the next section below. Reagent grade sodium hydroxide (NaOH), acetic acid (CH_3COOH) and technical grade sodium chloride (NaClO_2 , 80% purity) were purchased from Fisher Chemicals Sdn. Bhd. (Malaysia).

Kenaf Derived Cellulose Preparation

KDC preparation involves two main steps namely chlorination and mercerization. Chlorination is the process to produce holocellulose via bleaching according to ASTM D1104. In this step, lignin is removed (delignification) from kenafbast fiber. Initially 2.5g of kenafbast fiber were rinsed up with tap water to remove dust and foreign materials. After that the fibers were soaked in 250 ml beaker containing 80 ml of hot distilled water. The beaker was transferred to a 70 °C water bath. Next, 0.5 ml of acetic acid and 1g of sodium chlorite were consecutively added to the beaker every hour for 5 hours. Delignification occurred when the color of kenafbast fiber changed from light brown to white. The holocellulose produced then washed and rinsed with tap water. The second step involves conversion of holocellulose to cellulose by mercerization process.

The α -cellulose was prepared according to ASTM D1103. The holocellulose was added to beaker with 10 ml of 17.5 % NaOH solution and was heated at 20 °C in a water bath. After 5 min, 5 ml of 17.5 % NaOH was added to the mixture 3 time at 5 min intervals and was incubated for a final 30 min at the end of the process. Next, 30 ml of distilled water was added to the mixture for 1 hour for filtration and rinsing with tap water. 100 ml of 8.3 % NaOH was added to the cellulose for 5 min. the alkalized cellulose was neutralized by adding 10 % acetic acid for 5 min. finally the xcellulose was filtered, washed and rinsed with distilled water, until the

cellulose residue was free form acid, as indicated by pH meter. The cellulose was dried overnight in a vacuum oven at 100 to 105 °C.

Preparation of Composite Films

The 500 µm sieve size was used with a Grinder (Huang Chuan Machinery, China) to obtain uniform diameter of KDC. KDC and PLA resins were dried at 60 °C for 12 h before the mixing process. Cellulose loading ranging from 0-60 % (dry weight basis) was melt blended using an internal mixer (Brabenderplastograph, Germany). The loading of KDC stops at 60 % as the mixer cannot compound 70 wt % loading of KDC-PLA. This is due to very low volume of PLA polymer that cannot wet all the KDC. The mixing was performed at screw speed of 50 rpm with operating temperature at 170 °C. This mixing parameter was used as the optimization for this process has been carried out by [15] in her previous study. The neat PLA (0 % KDC loading) acts as control in this study. Composite pellets produced from mixing process were dried at 60 °C for 24 hours. KDC-PLA composite film then prepared by hot and cold press machine (Hot and Cold Press Machine LP-50, Thailand) in rectangular mailer sheet mold having dimension of 15 mm x 15 mm x 0.35mm with pressing condition shown in Table 3.1.

Table 2: Pressing condition for hot and cold press machine.

Parameter	Value
Melting temperature (°C)	160
Pre heating time (min)	5
Venting time (s)	10
Max Pressure (psi)	1550
Full press cycle (min)	3
Cooling cycle (s)	60

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed using thermogravimetric analyzer (TGA HT 441.1 Mettler Toledo) under nitrogen gas atmosphere. The kenaffiber, KDC and composites were heated from 30-600 °C and 5 °C/min of heating rate. Nitrogen gas flow rate is 0.2 l/min.

Differential Scanning Calorimetry (DSC)

DSC thermograms of neat PLA and KDC-PLA composites were acquired using Perkin Elmer DSC 7 by employing ~ 7 mg of testing material. The DSC equipment was calibrated using indium as a standard. The heating was performed from 30 to 200 °C at a rate of 10 °C/min. Glass transition onset temperature (T_g), crystallization onset temperature (T_c), melting onset temperature (T_m) and melting enthalpy (ΔH_m) were obtained from the temperature versus enthalpy curves. The sample percentage of crystallinity ($\%X_c$) was calculated by comparing the ΔH_m value of the sample with ΔH_m of 93.7 J/g for fully crystalline PLA [16]. The measurement of kenaffastfiber and cellulose (KDC) thermal properties was carried out at extended heating range from 30 to 500°C while the other parameter were kept the same.

X-Ray Diffraction (XRD)

X-Ray diffraction measurement was carried out using X-Ray Diffractometer (X-Ray Diffractometer X'pert Pro PW3040) on kenaffiber, KDC and composites. All data acquisition was performed using CuK α radiation at a scan speed 0.02s⁻¹ from 5 to 70 ° of angle of incidence. From this intensity value, the crystallinity index for both kenaffast fiber and KDC were calculated using the equation as follows[17]:

$$CI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (1)$$

Where CI = crystallinity index; I_{002} = is the maximum intensity (in arbitrary units) of the 002 lattice diffraction and I_{am} is the intensity of diffraction in the same units at $2\theta = 18^\circ$.

RESULTS AND DISCUSSIONS

Thermogravimetric Analysis

Thermal treatment that involved in the manufacturing of cellulose reinforced composite leads to variety of physical and chemical changes. The degradation of natural fibers leads to poor organoleptic properties such as odor and color and also deterioration of their mechanical properties [18]. Thus, it is important to study the thermal degradation of KDC as it will influence the thermal properties of resulted composite produced. Thermal degradation of KDC, neat PLA and KDC-PLA composite were studied using TGA. Fig. 2 and 3 show the loss of wt% with increasing temperature of KDC, neat PLA and KDC-PLA composite. In this study, the initial weight loss of the KDC, neat PLA and composites were considered when the sample lost 3 % of its weight from the baseline of the TG curve ($T_{3\%}$). The value of $T_{3\%}$ for KDC was at 298.3°C. The TG curve shows first mass loss step between room temperature and 298.33°C and second mass loss step between 298.3°C and 356.7 °C with 78.3% of mass loss.

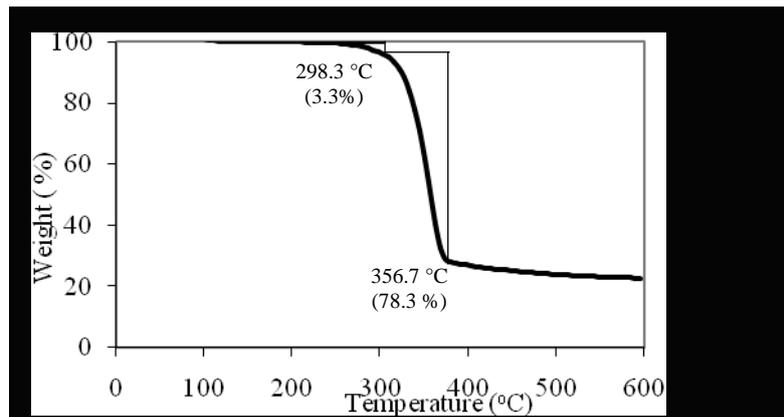


Fig. 1: TGA curve of KDC.

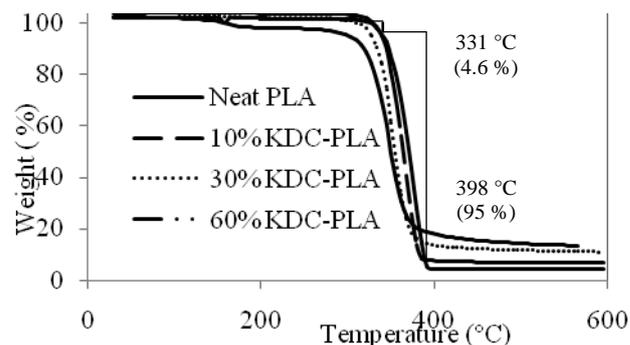


Fig.2: TGA curves for neat PLA and KDC-PLA composite.

The first degradation peak at 65 °C for KDC is highly associated with the presence of water in the specimen samples [19], [20] while the second endothermic peak (main decomposition temperature) at 355.7 °C. Enthalpy (ΔH) value for main decomposition temperature of KDC is 196.06 J/g. The thermal degradation of the neat PLA started at 331 °C and completed at 398 °C with a mass loss of 95%. In this case the neat PLA exhibit the first mass loss step between room temperature and 331 °C while the second mass loss step occurred at 331 °C to 398 °C. The mass loss of neat PLA was 93.3%. The decomposition temperature can vary depending on the experimental conditions of a material which is the loading of the KDC. As shown in Fig. 2, thermal degradation of KDC-PLA composite occurred at different stages. Incorporation of 10% KDC has producing composite with $T_{3\%}$ of 333 °C and main degradation temperature of 368.3 °C. Composite with 30% of KDC loading has the $T_{3\%}$ at 322 °C and main degradation temperature of 356.7°C and for 60% of KDC loading the composite has $T_{3\%}$ at 275 °C and main degradation temperature of 350.8 °C. The TGA curve also shows the mass loss of 93.2 %, 89% and 86.6 % for 10, 30 and 60% KDC loadings respectively. The additional loadings of KDC show that

degradation temperature of the bicomposite has been rushed. The TGA curves of the composites demonstrate that the thermal degradation of KDC-PLA composites is likely to be intermediate between neat KDC and PLA. A clear indication therefore is that the incorporation of KDC has rushed the degradation temperature of neat PLA in the composite system. The explanation lies in the fact that the thermal stability of KDC is much lower than the thermal stability of neat PLA matrix.

Differential Scanning Calorimetry (DSC) Analysis

The DSC thermograms (Fig. 3) reveal the thermal behavior of neat PLA in the KDC-PLA composite system. Using the literature reference value for the PLA melting enthalpy (assuming PLA is fully crystalline) of 93.7 J/g [16], the percentage of crystallinity of neat PLA and KDC-PLA composites was also calculated. Fig. 3 shows typical DSC thermograms for semi crystalline materials with an endothermic peak of T_g , T_c and T_m . All the results reported are based on the onset value. Dual melting endothermic peaks appear in the KDC-PLA composite as shown in Fig. 3. Neat PLA is characterized as T_g at 56.0 °C, T_c at 96.4 °C and T_m at 138.8 °C. A weak endothermic peak was exhibited at around 138 °C for 10 % KDC-PLA composites. This peak shifted to higher temperature for higher loading of KDC in the composites. The same phenomenon has been observed in a few other composites [16], [21]. The occurrence in this weak endothermic peak is possibly associated with impure polymeric materials or imperfections in the KDC. The slow heating ramps (10 °C/min) subjected to the material when performing the experiment can also cause melt crystallization to the PLA which could also contribute to this phenomenon. DSC results in Table 3 shows that thermal properties of PLA in the composites remain unaffected by the presence of KDC in term of T_g and T_c values. The almost unmodified T_c suggests that KDC does not significantly affect the crystallization behaviour of PLA matrix in the KDC-PLA composites system. An appreciable difference has been observed in the T_m value between neat PLA and KDC-PLA composites. The T_m value slightly increases from 138.8 °C for neat PLA to 145 °C with only a 10 % incorporation of KDC into the PLA. The additional loadings of KDC also shift the T_m value to the higher temperature as compared to the neat PLA. It means that by incorporating KDC into the PLA matrix the melting point of the composites increases. Table 3 also reveals that the percentage of crystallinity (% X_c) of the composite was improved by 20 % with incorporation of 10 % KDC. Neat PLA contains 45.6 % crystallinity whereas the 10 % KDC-PLA composite has 56.7 % crystallinity. However the higher loading of KDC (20-60 %) in the composite does not appear to have any certain trend in terms of percentage of crystallinity for composites. This results is in accordance with the findings by [22] where based on studies of isothermal crystallization, they have confirmed that neither standard sized cellulose fiber nor nanosized fibers had a considerable influence on the crystallization of PLA.

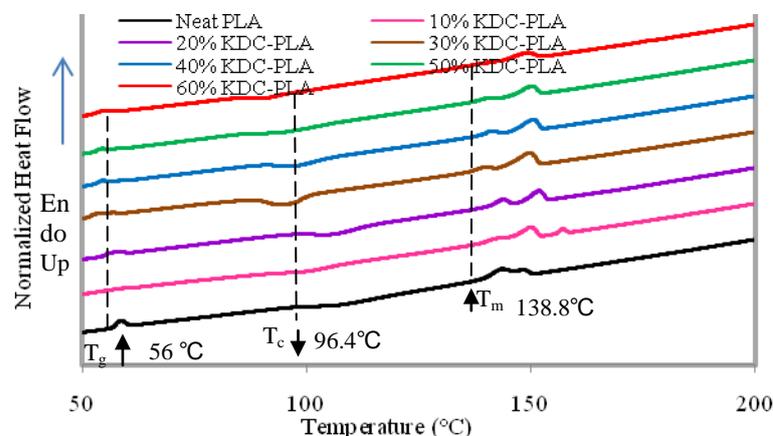


Fig. 3: Effect of KDC loadings on DSC thermograms of KDC-PLA composites.

Table 3: DSC results for neat PLA and KDC-PLA composites from the heating run.

Composition	T _g (°C)	T _c (°C)	T _m (°C)	%X _c (DSC)
Neat PLA	54.4	96.4	141.2	45.6
10 % KDC-PLA	53.5	98.8	145.9	56.7
20 % KDC-PLA	53.7	98.1	147.6	48.0
30 % KDC-PLA	54.7	89.1	146.6	42.8
40 % KDC-PLA	53.6	96.1	146.0	49.6
50 % KDC-PLA	53.4	94.6	146.0	48.2
60 % KDC-PLA	53.2	86.8	145.3	43.2

X-Ray Diffraction Analysis

The KDC, neat PLA and KDC-PLA composites were characterized by X-Ray diffraction to study the effect of various KDC loadings on the crystallinity of PLA. The KDC showed peaks at $2\theta = 22.1^\circ$ and $2\theta = 33.7^\circ$ and a shoulder-like hump at around $2\theta = 14^\circ$ to 17° (Fig. 4). This observation was almost identical with the XRD pattern for PLA and microcrystalline cellulose found in previous research [23]. For the case of Neat PLA there is not any clear peak pattern shown with the observation of a simple broad hump (Fig. 4) as compared to the KDC. Thus, the PLA exhibited an amorphous nature and it can be considered to be in a semicrystalline phase [8]. Fig. 4 presented the effect of the KDC loading on the crystallinity of the resultant composite. In the KDC-PLA composite, the peaks are observed at $2\theta = 14.5^\circ$ and $2\theta = 22.1^\circ$ which is indicative of PLA and KDC crystallinity, respectively. These peaks become more prominent with additional KDC loading. With the incorporation of KDC, it is apparent that the hump at $2\theta = 14.6^\circ$ has gradually decreased, showing that the amorphous chain has rearranged to form crystalline regions. In all the composites, the peaks appeared at $2\theta = 14.6^\circ$ and 22.1° . The peak observed at $2\theta = 22.1^\circ$ is from the KDC. There are no particular trends observed in the percentage of crystallinity with additional KDC loading. A possible explanation for this is most likely due to the crystallization behaviour (for example the crystallization rate) that varies with various cellulose loading [24]. Thus, even with the same heating rate, the formation of crystals in composites could be different and affect the value of the percentage of crystallinity, %X_c.

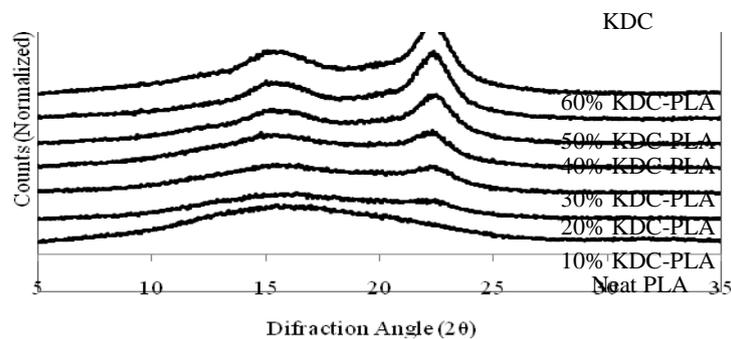


Fig. 4: X-Ray diffraction patterns of neat PLA and KDC-PLA composites.

CONCLUSIONS

The thermal analysis of 0 -60% KDC-filled PLA composites has been successfully studied and compared to neat PLA. Thermal stability of KDC-filled PLA composites reduced with the increase of KDC loading. Melting temperature of the composites showed a slight increase than the neat PLA, while glass transition temperature (T_g), and crystallization temperature (T_c), remain unaffected by the presence of increasing KDC loading in the composites. As conclusion, some thermal properties of the composites are

unchanged as the neat PLA but these composites are more readily decomposed by thermal treatment for composting and disposing purposes.

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