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Thermal properties of coir and pineapple leaf fibre reinforced polylactic acid hybrid composites

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Abstract. This study examined the thermal behaviour of raw coir fibre (CF) and pineapple leaf fibre (PALF) reinforced Poly lactic acid (PLA) composites. Coir fibres were hybridized with PALF in order to achieved better thermal stability. The biocomposites contained 30% (vol.) fibres in the form of short fibres (1-2 mm), and the composite samples were made up by different fibre ratios. In this research, the composites were fabricated by hot press at 180 ^{0} C for 10 minutes pre-heat and 3 minutes press after melt compounding the fibres and polymer in Internal Mixer Brabender. The aim of this work is to investigate the effect of different fibre ratio on the thermal properties of CF/PALF/PLA hybrid composites by using thermogravimetric analysis (TGA). The effect of different fibre ratios in hybridization and thermal degradation of CF/PALF hybrid composites was analyzed and C1P1 hybrid composite showed highest thermal stability in all composites samples. Thermal properties of CF/PALF/PLA hybrid composites vary with fibre ratio probably due to difference in chemical composition of the two fibres. C1P1 hybrid composites (1CF: 1PALF) showed highest thermal stability all composites which could be due to optimum hybridisation of both fibres. The thermal degradation analysis showed that both CF and PALF slightly affected the thermal stability of PLA composites. Consequently, surface treatments of CF and PALF will be effective to further improve composite's thermal stability.

1. Introduction

Natural fibres (NFs) have been used for reinforcement for diverse polymer matrixes due to their various beneficial properties like low density and cost, biodegradability, high-specific strength and renewability[1, 2]. Environmental sustainability concern also drives researchers on utilizing NFs for reinforcement purpose in manufacturing composites to get comparable or even better composites with synthetic fibres such as glass, carbon, and aramid [3, 4]. Many NFs like jute, kenaf, hemp etc. are used in composite as these are cultivated with the main purpose of fibre production[5, 6]. In addition to these fibre plants there are other plants in which the fibre has secondary value such as banana, coconut and pineapple as these are cultivated for their fruits[6, 7]. However, these fibres are seldom used since they are discarded as agro-wastes [8].

Agro-waste fibres such as coconut coir and pineapple leaf fibres (PALF) draws great attention due to their low density and thermal conductivity to yield cost-effective and lightweight composite products[9]. Coir fibres have lower cellulose (36–43%) and hemicellulose (15.7 %) contents, higher lignin content (35.25 %) and microfibrillar angle (30–45) than other natural fibres which results in their relatively low mechanical strength[10]as well as highest elongation at break among popular NFs [11]. PALF is a smooth glossy fibre with high cellulosic content (70-82 %), hemicelluloses (18.8 %) and lignin (5-12.7 %) with high tensile strength and it has a softer surface than other NFs [12]. Selection of polymer depends on the requirements for specific applications and performances. A bio-based polymer that is used today, is poly lactic acid (PLA) [13]. It is made from polymerisation of lactic acid monomers which is derived from renewable sources such as corn starch; potato starch, sugarcane etc.[14].

Extensive research literature has covered the studies of natural fibre reinforced biodegradable composites. Coir fibres are one of the most used natural fibres as reinforcement in polymer composites due to their high structural and wear properties combined with availability [15].Jang et al. [16] studied the thermal stability and flammability of PLA/coir fibre composites and found that plasma treatment enhance the thermal properties of composites in addition to their decreased shrinkage with increasing the fibre content. Mir et al.[17] reported that coir fibres have high failure strain, providing better strain compatibility between the fibre and the matrix in short fibre reinforced polypropylene composites. Rosa et al. [18] investigated the mechanical, thermal and structural properties of biocomposites based on starch/ethylene vinyl alcohol/glycerol blends matrix and coir fibres in relation to the fibre content. The increase of fibre content resulted in decreased tensile strengths but considerably improved tensile moduli. Additionally, the fibre content slightly influenced the thermal stability of biocomposites without affecting its biodegradability.

Kaewpirom et al. [19] evaluated the tensile and thermal properties of PALF reinforced PLA green composites. Tensile modulus of the composites depends on PALF content in the composite and slightly affects the thermal stability. In addition, elongation at break was dramatically increased by incorporation of maleic anhydride coupling agent. Liu et al. [20] performed multiple properties evaluation on green composites from soy based plastic and PALF. The mechanical properties including tensile and, flexural properties and impact strength of the green composites increased with increasing fibre content and the presence of the compatibilizer (PEA-*g*-GMA). The addition of the compatibilizer also helps in fibre dispersion but decreased the moisture absorption. Many researchers have studied PLA composites reinforced with various NFs. The effect in PLA of various NFs such as jute [21], kenaf [22], coconut fibre [23-24], and PALF [19-20] has been extensively studied and is well understood.

Incorporating NFs into PLA composites enables the composites to overcome the high brittleness and improved thermal stability [25]. However, no report of PLA composites reinforced with coir fibre and PALF hybrid has been found. This work evaluated the influence of coir and PALF alone or together on the thermal properties of Coir fibre/PALF/PLA composites and hybrid composites. In this study, 30 vol.% untreated coir fibre and PALF were used as reinforcements in the PLA biocomposites.

2. Materials and method

2.1. Materials

Polylactic acid (PLA) pellets from Natureworks® with a molecular weight (M_w) of approximately 74,000 g/mol, density of 1.25 g/mol, glass transition temperature (T_g) of 55 to 60 °C and melting point (T_m) of 160 to 180 °C was purchased from TT Biotechnologies Sdn. Bhd., Malaysia.

Coir fibres (*Cocus nucifera*) were obtained from Innovative Pultrusion Sdn Bhd. Malaysia with an average density of 1.20 g/cm3. Pineapple leaf fibres (*Ananas comosus*) were procured from Tamil Nadu state of South India with an average density of 1.07 g/cm3. All fibres were used in as-received condition without any surface treatment.

2.2. Composite fabrication

Coir and PALF used as reinforcements in fabrication of composites were chopped into short fibres (1-2 mm) by using ring flakers machine; fibres were maintained at 6-8% moisture content. The composites were prepared by melt mixing in an internal mixer (Brabender-Plasticizer machine) All the five types of composites/hybrid composites were prepared through the following procedures. Composites were obtained by mixing 70% (35 g) of PLA at 180 °C for 3 min. Then, 30 % (15 g) of CF or PALF, previously dried at 80 °C for 24 h under vacuum, were added, and the mixture was blended at 180 °C for further 7 min, at a speed of 50rpm. Corresponding sample is coded as C30 and P30. Hybrid composites were obtained by mixing 70 % (35 g) of PLA at 180 °C for 3 min. Then, 30 % (15 g) of mixed coir and PALF in a specific proportion such as 1:1, 3:7 and 7:3 were added, and the mixture was blended at 180 °C for further 7 min, at a speed of 50 rpm. Composites were fabricated by using 15 x 15 x 3 mm stainless metal plate mould. The mould was placed into hydraulic pressure hot press at 180 °C temperature and was removed from the press after 15 minutes pre-heat and 5 minutes press kept for cooling in cold press for 3 minutes, and then samples were prepared for testing according to ASTM standard. The formulations of hybrid composites are described in Table 1.

Table 1. Formulation of Coir/ PALF/PLA hybrid composites

Designation	**PLA (Weight %)**	**Coir (Weight %)**	**PALF (Weight %)**
Pure PLA	100	_	_
C-30	70	30	_
P-30	70	_	30
C1P1	70	15	15
C7P3	70	21	9
C3P7	70	9	21

2.3. Thermogravimetric Analysis (TGA)

Thermal properties were characterized on the CF and PALF reinforced PLA composites by TGA machine Model (TGA Q 500 TA Instrument, USA). For each type of composites, 1 gram of powdered samples was used for all composites testing according to ASTM E- 03 (2003) [26]. The entire samples testing were carried out at the rate of 20 ^{0} C/ minutes in nitrogen gas flow under room temperature ranging from 30 ^{0}C to 600 ^{0} C. TGA helps to understand the thermal stability of the samples.

3. Results and discussion

Thermal stability of pure PLA as well as CF and PALF reinforced PLA composites and hybrid composites were investigated with thermogravimetric (TGA) analysis. Figure 1 and 2 shows the TGA and DTG curves for pure PLA, C 30 P 30, C1P1, C7P3 and C3P7 composites. Generally speaking, NFs degrade through two steps process and a pre- degradation stage which is the evaporation of absorbed moisture from the NFs at 50 to 100 ^{0}C. Since natural fibres are quite hydrophilic, they are subject to a dehydration process in which absorbed water is released. The first transition which occurs from 200 to 300 °C where the NFs undergoes hemicellulose degradation; finally at 400 to 500 °C, the NFs starts to decompose due to cellulose and lignin degradation [27].

Table 2.TGA characterization of neat PLA and Coir/PALF/ PLA composites

Designation	Maximum Degradation Temperature (ºC) T_m	Char Residue (%) at 600 ^{0}C
Pure PLA	277.81	1.05
C30	252.73	11.17
P30	287.23	5.53
C1P1	290.07	7.56
C7P3	288.64	1.14
C3P7	284.59	3.84

The temperature (T_m) corresponding to the maximum depomposition rate was used as the indicator of the PLA and composites thermal stability. Table 2 shows the T_m and final char residue of the composites against pure PLA. According to Fig. 1 and 2, the results of pure PLA and Coir/PALF/PLA composites do not show much difference, as the curves are relatively close to each other. It is seen from the TGA graph in fig 1 that for PLA and Coir/PALF/PLA composites and hybrid composites, the weight percentage drops significantly starting from 250 ^{0}C, which is mainly due to hemicellulose degradation.

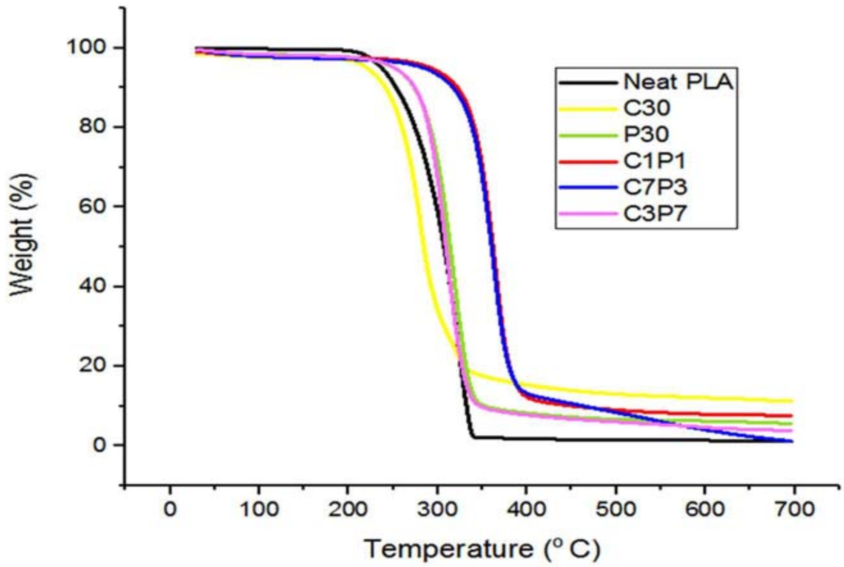

Figure 1. TGA curve of neat PLA and CF/PALF/PLA hybrid composites

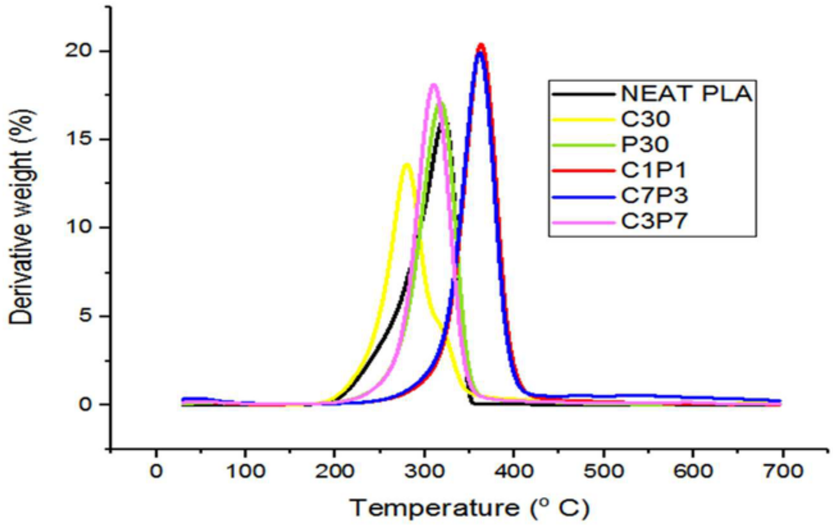

Figure 2. DTG curve of neat PLA and CF/PALF/PLA hybrid composites

Addition of CF to PLA decreases degradation temperature, for instance the maximum weight loss of C30 composite takes place at 252.73 ^{0}C compares to the neat PLA which shows maximum degradation at 277.81 ^{0}C which is in good agreement with the material characteristics of PLA composites reinforced with rice husk and kenaf fibres [28] as well as Phormium fibres [29]. On the other hand, incorporation of PALF into PLA matrix increases the thermal stability of PLA composites slightly as shown in figure 1 and 2, P30 shows T_m of 287.23^0 C . All the hybrid composites also reveals increased thermal stability compares to neat PLA such as 290.07^0 C, 288.64 ^{0}C and 284.59 ^{0}C in C1P1, C7P3 and C3P7 respectively. In all cases, there is more increase in the degradation temperatures when PALF is added. This could probably be explained by the difference in chemical composition of these two natural fibres. PALF has lower content of lignin [12] while coir fibre is rich in lignin [16] which justify highest percent of char residue in case of C30. Furthermore, the cellulose content in coir fibre is much lower than that of PALF. Hence, the thermal stability of PALF is slightly higher than that of coir fibre.

4. Conclusion

Two NFs namely; coir fibre and PALF were utilized to prepare PLA biocomposites and their thermal property were studied and compared. It was found that thermal degradation of pure PLA was faster with the incorporation of CF and slower by PALF reinforcement on the contrary. In particular C1P1 hybrid shows the best thermal stability where as C30 composites reveals fastest thermal degradation. In conclusion, PALF performed much better than CF in terms of improvement in thermal stability when compounded with PLA as a reinforcing fibre. The poor performances of coir fibre compare to PALF could be mainly ascribed the difference in chemical composition between coir fibre and PALF. The lower degradation temperature in CF filled composites as compared to PALF filled composites could be the leading character in the causes of composite's biodegradability. In order to improve the performance of coir and pineapple leaf fibres as reinforcements for PLA composite, chemical modification of coir and pineapple leaf fibres are recommended.

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