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FTIR and TGA Analysis of Biodegradable Poly(Lactic Acid)/ Treated Kenaf Bast Fibre: Effect of Plasticizers

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ABSTRACT

A biodegradable composite (PLA/KBF blends) was prepared using melt blending technique in a brabender mixer and characterized with FTIR and TGA analyzer. Five percent of triacetin and glycerol contents were used as plasticizers to plasticise PLA matrix. KBF was treated with 4% NaOH solution, while 30 wt% of fibre loading was used constantly for all the composite samples. From the FTIR analysis, the additions of triacetin and glycerol to PLA composites did not produce any significant difference, and there were no chemical changes in both the plasticized PLA with the treated and untreated KBF, respectively. Observation done on the TGA analysis revealed that both plasticizers did improve the thermal stability of the composites, and this might be due to the modification on the fibre surfaces, which further led to the delay in the degradation of the PLA matrix and to significant stabilization effect.

Keywords: Polylactic acid, kenaf bast fibre, triacetin, glycerol, TGA, FTIR analysis

INTRODUCTION

In the recent years, attention has been focused on the development of technologies that utilise composite materials. However, combining biofibers with a biodegradable and renewable resource-based polymer offers additional sustainability benefits. Kenaf bast fibre (KBF) (Nina *et al.*, 2009) has received considerable interest as an environmental-friendly alternative to glass fibre in polymer

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composites for excellent mechanical properties, especially when low density and price are taken into account. Undeniably, it has high strength and modulus to weight ratio, as well as fatigue and corrosion resistance (Islam *et al.,* 2010). Hence, great attention has been given to KBF composites, such as KBF reinforced poly(lactic acid) (PLA) composites, in which the effects of triacetin (Mingkang *et al.,* 2010; Yijun *et al.,* 2007) and glycerol (Caroline *et al.,* 2009) were studied.

Triacetin is a renewable resource-based plasticizer compared to glycerol which is a multiple plasticizer. These plasticizers are extensively used in the polymer industry and research has shown that they have the potential to improve the properties of PLA (Caroline *et al.,* 2010; Lima *et al.,* 2008; Oksman *et al.,* 2003). The use of triacetine to plasticize PLA has successfully been found to lower the melting point (Tm) and glass transition (Tg) temperature by 10°C at 25 wt%, after which phase separation occurred and the melting temperature increased. In this phenomenon, triacetine-plasticized PLA films underwent crystallization, and plasticizer molecules migrated towards the surface with storage time due to their low molecular weight resulting in improvement of the elastic properties at the cost of tensile strength (Rahul *et al.,* 2010) and high percentage of nominal strain at break (Marius *et al.,* 2008).

In contrast, glycerol is nearly and systematically incorporated in most of the hydrocolloid films because it lowers Tg and Tm and increases elongation at break (Maharana *et al.,* 2009). It is indeed a highly hygroscopic molecule that is generally added to film-forming solutions to prevent film brittleness. However, as a compromise between film mechanical resistance and flexibility to maintain low solubility and swelling in water, the use of 5–10% glycerol in the finishing cross-linking step was recommended. Concentrations lower than 3% glycerol produced brittle films, while phase separation was observed on the film surface when concentrations higher than 12% glycerol were used (Melissa *et al.,* 2011).

In this study, treated KBF was combined with PLA and impact modifier (plasticizers), a bio-based plastic which is commercially available. These renewable materials can be referred to as biocomposites due to their superior sustainability profile from the perspective of Industrial Ecology, such as calculated using the tools of life cycle analysis (Harding *et al.,* 2007; Martin *et al.,* 2007). Thus, the objective of this study was to determine the effects of triacetin and glycerol on treated KBF reinforced poly(lactic acid) composites.

MATERIALS AND METHODS

Long KBF, with the V36 variety, was obtained from Lembaga Kenaf - Tembakau Negara (LTN) in Kelantan. Meanwhile, the Kenaf stem was chipped before flaking to reduce the size of the kenaf fibre. The KBF used in this study was ground to 75-150µm. After that, the KBF was dried in an oven at 60ºC to a constant weight. This lignocellulosic fibre consists of 65% cellulose and 19% lignin. Triacetin and glycerol (1.158g/cm^3 and 1.262g/cm^3, respectively) were purchased from Sigma Aldrich Chemie GmbH, Steinheim, Germany. Meanwhile, sodium hydroxide pellet grade UN 1823 Pro Analysis consisting of 40g/mol was obtained from MERCK, Germany.

Poly(lactic acid) (PLA) (NatureWorks^{TM} PLA 4060D) in the pellet form was obtained from Natureworks$^{®}$ LLC, Minnetonka, Minnesota. It is important to note that PLA has a specific gravity of 1.25 and a melt flow index of around 15 g/10 min (190°C/2.16 Kg). Its Tg is 52°C and the melting temperature is 135°C, while its density is 1.24g/cm^3.

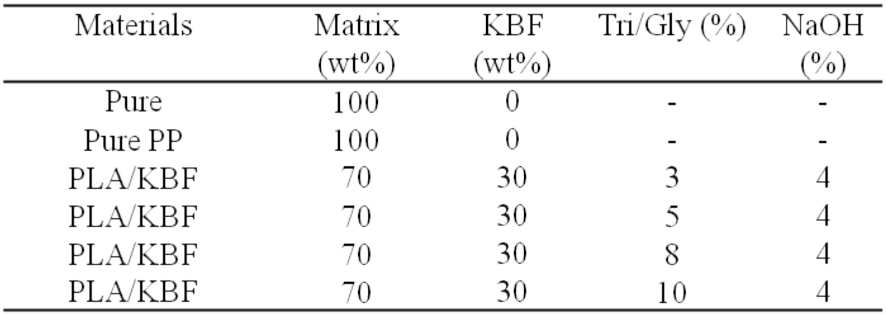
Preparation of the Kenaf Treatment

The concentrations of NaOH used were 2, 4, 6 and 8%, respectively. All the solutions of sodium hydroxide (NaOH) were prepared using the pellets of NaOH in deionised water and a stirrer. The fibres were then placed in these solutions for 3 hours at 25ºC. Later, the fibres were washed with distilled water until all the alkali was removed from their surface. After that, the fibres were tested for neutralisation using pH paper to confirm that there was no more alkalinity occurrence. The filter paper was placed under a sieve to avoid the fibres from leaking and being flushed out. After washing, the KBF was dried in air (ambient temperature) for two days. Next, the treated fibres were left to dry in an oven at 60°C for 24 hours.

Preparation of the PLA/Treated KBF with Triacetin and Glycerol

Prior to blending, the polymer and fibres were kept in an oven at 60˚C for 24h. PLA was premixed with several percentages of triacetin and glycerol, respectively, before they were mixed with 30 wt% of the treated KBF content. These mixtures were prepared using the Brabender internal mixer at 170˚C for 10 min at 50rpm. Pure PP was also processed in the same way to obtain a reference material. The blended materials were processed using a hot press to produce sheets of about 1mm thickness. The moulding process was carried out at the moulding temperature of 150˚C, with a 15 minute-preheat time and a pressing at full pressure for 5 minutes, followed by 8 minutes of cooling time at 827.37 kPa.

TABLE 1: The compositions at different triacetin and glycerol contents



Materials	Matrix (wt%)	KBF (wt%)	Tri/Gly (%)	NaOH (%)
Pure	100	0	-	-
Pure PP	100	0	-	-
PLA/KBF	70	30	3	4
PLA/KBF	70	30	5	4
PLA/KBF	70	30	8	4
PLA/KBF	70	30	10	4

Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier Transform Infra Red (FTIR) spectroscopy was carried out using the Perkin Elmer Model 1750x FT-IR spectrometer and KBr method. The transmission of the infrared spectra was obtained in the range between 400 cm^{-1} to 4000 cm^{-1} at room temperature. The difference between the FTIR spectra was studied to find any new form of bond or interaction.

Thermogravimetric Analysis (TGA)

The thermo-stability property of the composite prepared was analysed using the Mettler Toledo TGA/SDTA 851º thermogravimetry analyser. About 10mg of the sample was used for the analysis and was heated from -50ºC to 500ºC at the rate of 10ºC/min, using about 20-25mg of the samples with a nitrogen gas flow rate of 50mL/min. The weight and percentage of the residue were recorded to determine the weight losses of the sample after heating.

RESULTS AND DISCUSSIONS

Characterization Analysis

The infrared spectra for the treated KBF, untreated KBF, plasticized PLA (triacetin), with treated and untreated KBF, are presented in Fig.1, while the results for the treated KBF reinforced plasticized PLA with triacetin (tri) and glycerol (gly) obtained using an FTIR spectrometer are shown in Fig.2.

In the alkali treatment process, the presence of Na^+ in fibre changes the hydrophilic to the hydrophobic fibre properties. Fig.1 shows peak at 3350 cm^{-1} for the untreated and treated KBF, indicating the presence of hydroxyl group. A large band at 3500-3000 cm^{-1} and a small absorption at 2950 cm^{-1} are mainly related to the hydroxyl groups and the bonded O-H stretching vibration present in carbohydrate (Bilba *et al.,* 2007). Meanwhile, the decreased intensity of the OH peak at 3350 cm^{-1} on the treated KBF compared to the untreated KBF could be clearly seen, which was assigned to the hydroxyl group and reduced due to the removal of the hemicellulose component (Ghazanfari *et al.,* 2008). However, there were no chemical changes in both the plasticized PLA with the treated and untreated KBF, respectively.

As depicted in Fig.2, both the plasticized PLA with the treated KBF samples showed that the characteristics of asorption of hydroxyl group around 3500-3200 cm^{-1} were reduced due to the removal of the hemicellulose component. Due to the alcohol group of cellulose OH deformation, another peak appeared at 1310 cm^{-1}, and this was also observed to have been decreased by the alkaline treatment.

The peaks located at 3000-2800 cm^{-1} were attributed to the CH group and this band had a higher absorption of the plasticized PLA composites with the treatment as compared to the untreated spectrum, which was rather expected since the PLA led to $-CH_2-$ and –CH group formation (Ogata *et al.,* 1997). As for the plasticized PLA composites with the untreated and treated samples, all the samples showed the absorption band of carbonyl stretching at 1700cm^{-1}, which corresponded to the hemicelluloses, and this absorption seemed to be smaller for the treated KBF composite samples as compared to the untreated KBF composite samples. The asorption band in the range of 1600-1400 cm^{-1} region in all the composite spectra might be attributed to the presence of aromatic or benzene ring in lignin, whereas the aliphatic or aromatic (C-H) in plane deformation vibration of methyl and methoxy groups in fibres could be seen near 1400-1300 cm^{-1}. The research by Mubarak *et al.* (1993) suggested that the band in the region of 1300-1000 cm^{-1} represented the C-O stretching vibration of aliphatic primary and secondary alcohols in cellulose, hemicelluloses, lignin and primary and secondary aromatic alcohols in lignin. It was observed that there was no absorption peak at 1245 cm^{-1} for the treated

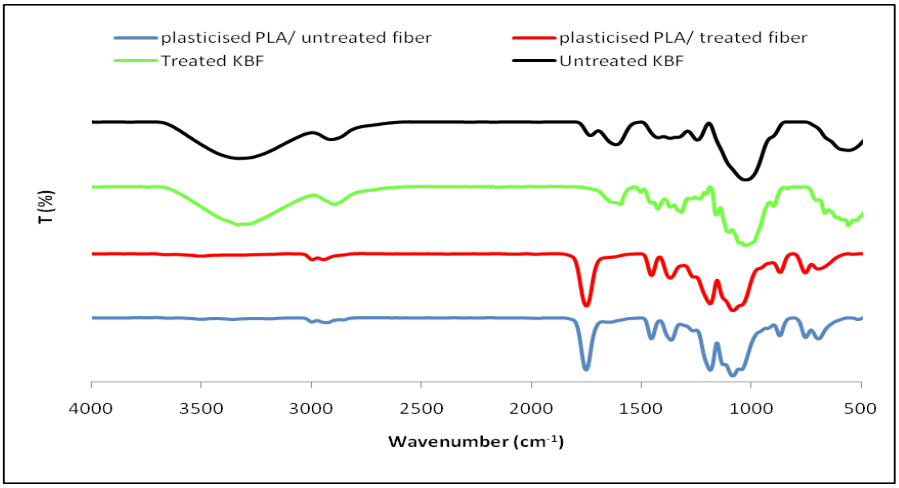


Fig.1: IR spectra for the treated KBF, untreated KBF, and plasticized PLA (tri), with treated and untreated KBF

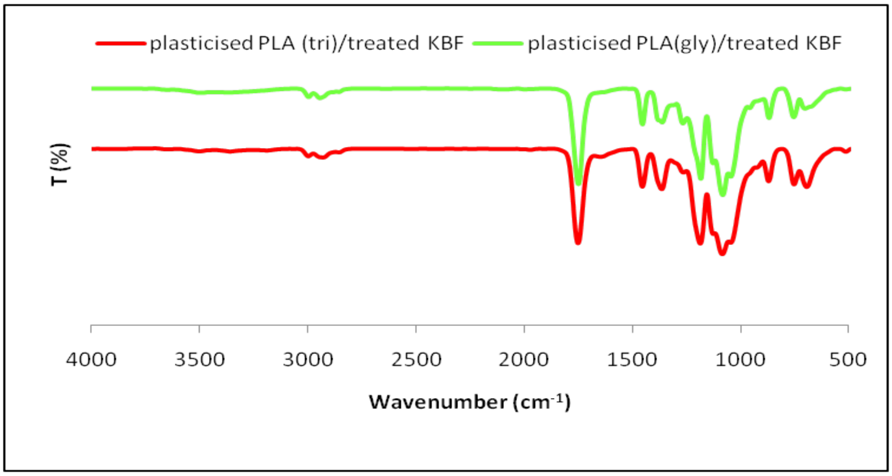


Fig.2: IR spectra of treated KBF reinforced plasticized PLA with Triacetin (tri) and glycerol (gly)

KBF for both types of plasticized PLA composite samples. This happened in the process of the surface modification as the alkaline removed the waxy epidermis tissue, adhesive pectins and hemicelluloses, which bound the fibre bundles together. The C-O-C symmetry glycocidic, stretched at 1100 cm^{-1}, arose from the polysaccharide components that were largely cellulose, and the asorption band widely appeared for the untreated and treated fibre composite systems as compared to the PLA single system.

Thermal Stability Analysis

One of the advantages of the surface modification treatment of KBF is that it makes KBF hydrophobic instead of hydrophilic. Polypropylene (PP) acts as reference to the modified composites. The thermograms depicted in Fig.3 and Fig.4 show only about 2% weight loss at the temperature below 100°C, indicating that there was less water absorbed in the plasticized PLA (tri)/ treated KBF and plasticized PLA (gly)/treated KBF composite samples as compared to the plasticized PLA/untreated KBF composite sample and pure PLA. Meanwhile, Fig.3 shows the degradation of plasticized PLA with the untreated KBF that occurred between 250°C and 300°C, whereas the degradation of plasticized PLA (tri) with the treated KBF occurred between 350°C and 450°C, leading to a weight loss of 85.5%. The PP sample was used as a reference to the modified composites. The degradation temperature of PP was about at 360ºC.

The plasticized PLA, with the treated KBF, provided a higher decomposition temperature as the addition of the plasticizer had improved the adhesion between the PLA and fibres and prevented the migration and leaching of the plasticizer molecules from the PLA matrix at the same time. This finding is similar to that of Murariu *et al.* (2007), who also found that the decomposition temperature was increased by adding plasticizer to PLA.

The differential gravimetric analysis (DTG curve) indicated that there were decomposition peaks for the plasticized PLA treated KBF with triacetin and glycerol. The first decomposition peak, i.e. at about 300°C to 430°C, is due to thermal depolymerisation of hemicelluloses and the glycosidic linkages of cellulose, as well as α-cellulose decomposition. Lignin degraded first and at a slower rate than other constituents. The second peak occurred at about 450°C, it might also be due to the late degradation of the plasticized PLA with glycerol.

The area under the peak at 270°C for the plasticized PLA with the untreated KBF was found to be greater than both types of the plasticized PLA with the treated KBF. A possible explanation for this is that because of the treatment, which is, part of the lignin was removed from the fibre (Claudia *et al.,* 2004). Hence, this caused a better adhesion between PLA and the treated KBF, and thus influenced the decomposition temperature.

As shown in Fig.4, the thermal stability of the plasticized PLA/ treated KBF with triacetin and glycerol also improved as compared to that of the pure PLA. The increase in the thermal stability in the plasticized PLA with the treated KBF might be due to the modification done on the fibre surfaces, which delayed the degradation of the PLA matrix and to significant stabilization effect.

This can be quite well-distinguished in the interval of temperature 340-420°C in Fig.4. The thermogravimetry analysis (TGA) in Fig.4 showed that the weight loss was due to the volatilization of the plasticizers, and the degradation of the materials monitored as a function of temperature. As compared to pure PP, the thermal stability of both types of plasticized PLA/ treated KBF increased dramatically. The additions of 5% glycerol and triacetin to PLA and the treated KBF were found to have shifted the thermal stability of the composites.

CONCLUSION

The FTIR analysis of the plasticized PLA composites with the untreated and treated samples showed the absorption band of carbonyl stretching at 1700cm^{-1}, which corresponded to the hemicelluloses, and this absorption seemed to be smaller for the treated KBF composite samples as compared to the untreated KBF composite samples. Meanwhile, the additions of triacetin and glycerol to the PLA composites did not produce any significant different, and there were no chemical changes in both the plasticized PLA with the treated and untreated KBF, respectively

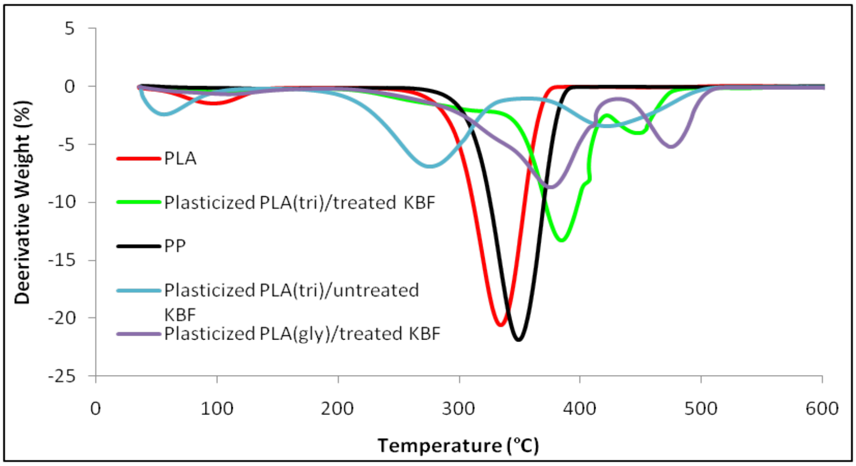


Fig.3: The DTG curves of PP, PLA, plasticized PLA/untreated KBF, and plasticized PLA/treated KBF with triacetin and glycerol

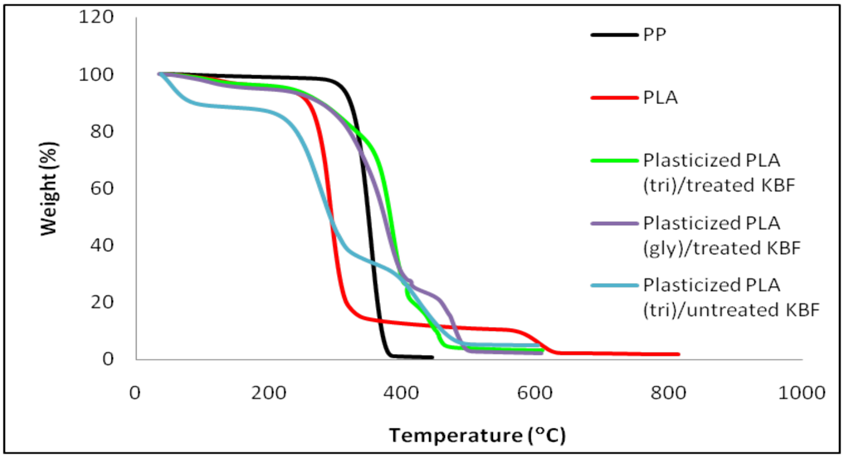


Fig.4: The TGA curves of PP, PLA, plasticized PLA/untreated KBF, and plasticized PLA/treated KBF with triacetin (tri) and glycerol (gly)

Based on the thermogravimetry analysis, an increment was observed in the thermal stability for both the samples of plasticized PLA composites and this was due to the fibre treatment, which further led to the delay in the degradation of the PLA matrix and to significant stabilization effect of the composites.

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