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Thermal Properties of Injection Moulded Polylactic Acid – Kenaf Fibre Biocomposite

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ABSTRACT: Biocomposite made of polylactic acid (PLA) reinforced with natural kenaf bast fibre (KF) using twin screw extruder and injection molding machine has been developed. The effect of kenaf fibre content on crystallization and melting behavior has been studied by means of differential scanning calorimetry (DSC). The amourphous state of PLA was remain unchanged with kenaf fibre content. Although there were increment in melting enthalpy (ΔH_m) and cold-crystallization enthalpy (ΔH_{cc}), but it was not significant to cause kenaf fibre to act as nucleating agent for PLA. The effect of kenaf fibre content on the stiffness of the PLA-KF biocomposite at elevated temperature has been investigated by using dynamic mechanical analyzer (DMA). The storage modulus (E’) of the composites is higher as compared to unreinforced PLA, whereas the mechanical loss factor (tan δ) decreases with kenaf fibre content which can be associated to the compatibility of PLA matrix and kenaf fibre.

Keywords: Thermal properties, differential scanning calorimetry, dynamic mechanical analysis, kenaf fibre, polylactic acid.

1.0 INTRODUCTION

Thermal methods are useful in attaining morphological information for polymers, blends and composites [1]. Differential Scanning Calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperature to be scanned. Dynamic mechanical analysis (DMA) is a sensitive technique that characterizes the mechanical responses of materials by monitoring property changes in a material with regard to the temperature and frequencies. DMA separates the dynamic response of materials into an elastic part, E’ (storage modulus) and viscous or damping component, E” (loss modulus). The elastic process described the energy stored in the system, whereas the viscous component describes the energy dissipated during the process.

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DSC and DMA have been used as a tool to investigate the improvement in phases in studies of PLA-ramie composites [2]. Cheung and coworkers [3] found dropped in crystallization temperature and concluded that the presence of silk fibers increased the viscosity of the biocomposite mixture by hindering the migration and diffusion of PLA molecular chains in the biocomposite. Another studies on PLA-chicken feather fibre (CFF) composite found out that melting and crystallization enthalpies increase with CFF which indicates that CFF act as nucleating agent for PLA [4]. Preceding studies also have shown that the presence of fibres in the polymer creates complexities in the morphology of the system. The surface properties of fibres and the use of coupling agents and other additives can alter morphology of the polymer phase as well as interphase. This sequentially, influences the mechanical and dynamic properties of the composite system [1,5].

This project aims to develop environmentally safe and biodegradable material for low end application such as for packaging. The objective of this paper is to analyze the effect of kenaf fibre content on PLA-KF biocomposite with respect to differential scanning calorimetry and dynamic mechanical analysis.

2.0 EXPERIMENTAL

2.1 Preparation of PLA-KF Biocomposite

Poly(lactic acid), PLA 3051D in the pellet form was manufactured by Nature Works. The kenaf bast fibre was supplied by Kenaf Natural Fiber Industries Sdn. Bhd, Kelantan in the form of long fibre. The kenaf fibre was then cut and ground to shorter length. Then kenaf fibre was sieved to obtain 300-500 μm in size. PLA and kenaf fibre has been dried in a vented oven at 80℃ for 5 hours prior to use. Kenaf fibre content has been varied from 0-20 wt%. Table 1 shows formulation of the composites prepared in this study. Poly(lactic acid) and kenaf fibre have been manually mixed and then extruded using Brabender Plasti-Corder type 814402 twin screw extruder. Temperature was maintained between 180-190 ^{o}C in all four zones.

Table 1 Compositions of PLA-KF biocomposites prepared.

	PLA matrix (wt%)	**Kenaf fibre (wt%)**
PLA	100	0
PLA-10KF	90	10
PLA-20KF	80	20

Note: PLA = polylactic acid, KF = kenaf fibre.

2.2 Mechanical Characterization of PLA-KF Biocomposite

Tensile testing has been evaluated using Z020 Universal Tensile Tester according to EN ISO 527-5:1999. The strain rate used was 50 mm/min. 3-point flexural testing was carried out on the same machine with span length of 64 mm and the compression speed was 5 mm/min. For the mechanical tests, an average has been taken on seven specimens.

2.3 Thermal Characterization of PLA-KF Biocomposite

The melting and crystallization behavior of the unreinforced PLA matrix and the PLA-KF biocomposites were studied using a Perkin Elmer DSC2 equipped with a cooling attachment, under a nitrogen atmosphere. The data were collected by heating the composite specimen from 35 to 200 °C at a constant heating rate of 10 °C/min. Samples in the range of 3-5 mg were used. The samples were sealed in aluminum pans and the sealed samples were placed in the furnace along with an empty reference aluminum pan. The heat flow changes of the samples in the sealed aluminum pans were recorded with reference to an empty aluminum pan. Melting temperature was obtained from the peak in the heating curve.

The storage modulus, loss modulus and loss factor were measured as a function of temperature (from 25 to 75 °C). In this paper only storage modulus and tangent delta are presented. A Perkin Elmer 7e with TAC 7/DX dynamic mechanical analyser (DMA) with a three-point bending fixture in frequency-strain modes was used. The frequency of 1 Hz at the amplitude of 10 μm and the heating rate of 3 °C/min were used. The dimensions of the sample were 3×20×5 mm. The span length was 15 mm.

3.0 RESULTS AND DISCUSSION

3.1 Crystallization and Melting Behavior of PLA-KF Biocomposites

The thermal properties such as glass transition temperature (T_g), cold-crystallization temperature (T_{cc}), melting temperature (T_m), cold-crystallization enthalpy (ΔH_{cc}) and melting enthalpy (ΔH_m) obtained from the differential scanning calorimetry (DSC) studies are summarized in Table 2. The unreinforced PLA and PLA-KF biocomposite are assumed as amorphous since cold crystallization enthalpy and melting enthalpy values are almost the same.

PLA-KF biocomposite has undergone two stages of heating process. However, result of second heating which is related to materials behavior only is discussed in this paper. In general, cold-crystallization temperature (T_{cc}) decreases with kenaf fibre content from 0, 10 and 20 wt.% for both heating process. This signifies that kenaf fibers hinder the migration and diffusion of PLA molecular chains to the surface of the nucleus in the composites [3, 6]. This result in no effect on the crystallization of polymer as shown in Table 2, where differences in enthalpies value were very small which is less than 10 J/g. This may suggest that PLA-KF system is remained amourphous. This finding is contradicted with studies by Lee et. al [7] on kenaf fibre reinforced polylactide with the present of coupling agent. Reduction in T_c is also associated to the increased in viscosity of the biocomposite mixture, which hindered the migration and diffusion of PLA molecular chains in the biocomposite [3]. It is noted also in Table 2, that glass transition temperature, T_g increases by about 4.8% from 60 °C to 63 °C for unreinforced PLA and PLA-20KF biocomposite, respectively. The values of ΔH_m and ΔH_{cc} however increased in the presence of kenaf fibre. The enhancement in melting and cold crystallization enthalpies are opposed to several studies reported on PLA composites [3, 8]. In future, study will be carried out with the use of plasticizer to stabilize the PLA-KF system.

Table 2 Thermal properties of unreinforced PLA and PLA-KF biocomposites.

	T_g (°C)	T_c (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	X%
PLA	60	125	5.8	150	7	Amorphous
10KF	60	123	29.3	150	29.5	Amorphous
20KF	63	121	31	149	31	Amorphous

3.2 Dynamic Mechanical Analysis

3.2.1 Storage Modulus

The DMA investigation was performed to study the effect of incorporation of kenaf fibre on the dynamic-mechanical performance of unreinforced PLA and PLA-KF biocomposites. The range of temperature investigated was within 25 – 75 °C. Figure 1 shows the dynamic storage modulus curves of unreinforced PLA, PLA-KF biocomposites as a function of temperature. Variation in storage modulus occurs due to the effect of different fibre content incorporated in the biocomposite system. At low temperature, the storage modulus (E’) for PLA-10KF was lower than unreinforced PLA. This shows that kenaf fibre contributed less stiffness to the biocomposite in the glassy state and just acted as a filler. However, with higher kenaf fibre content up to 20 wt.% has increased the E’ value at low temperature region. The sharp drop can be seen in the area of 50 to 60 °C, which is associated with the glass transition temperature (T_g) of poly(lactic acid) biopolymer. The E’ continues to drop after glass transition region.

The high storage modulus obtained for PLA with 20 wt.% kenaf fibre is consistent with the result obtained from tensile test and 3-point bending test. As shown in Table 3, the tensile modulus and bending modulus increase with kenaf fibre content and the highest was at PLA-20KF. It is generally known, that the kenaf fibre is a kind of natural fibre and is very stiff, hence leading to higher modulus of PLA-KF biocomposite.

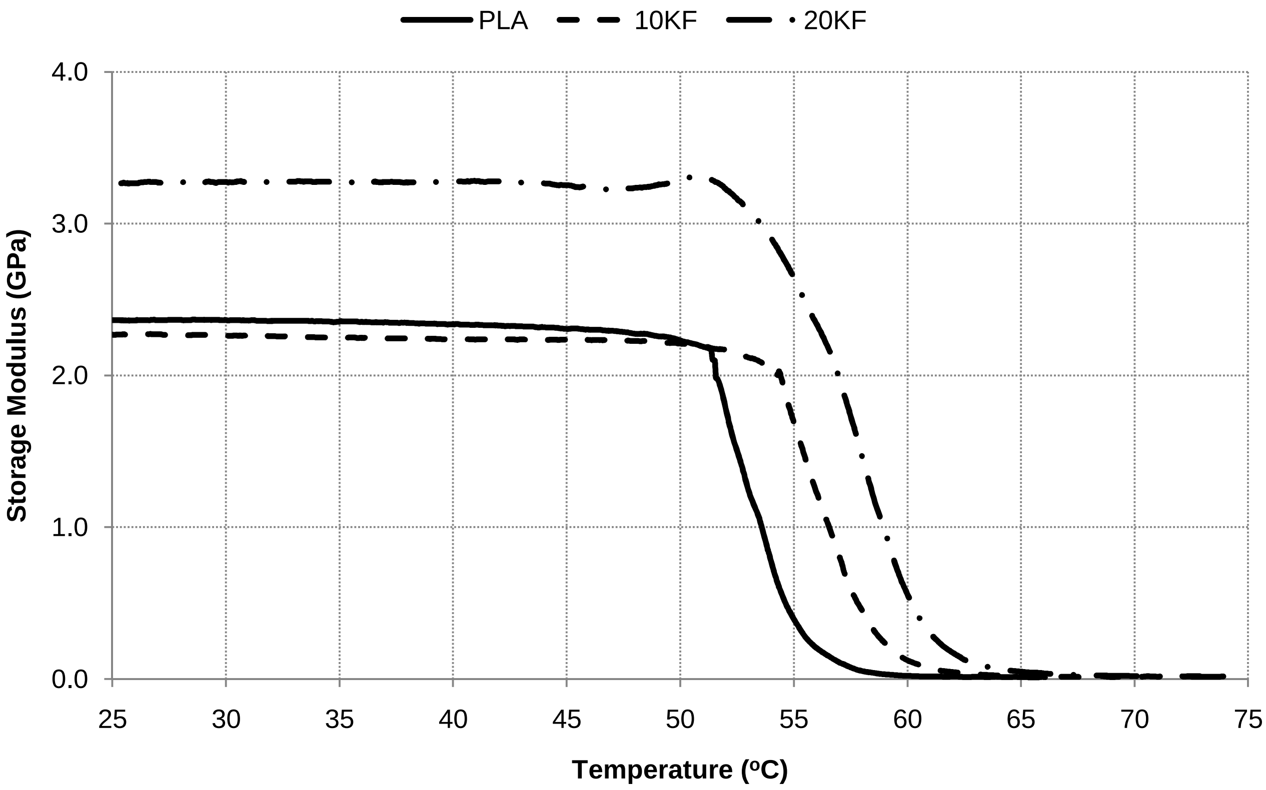

Figure 1 The effect of fibre content (wt%) on storage modulus of PLA-KF biocomposites.

Table 3 Comparison of bending modulus and storage modulus of PLA-KF biocomposites.

	Storage Modulus		**Damping Parameters**		**Tensile Modulus (GPa)**	**Bending Modulus (GPa)**
	°C	**GPa**	**°C**	**tan δ_{max}**		
PLA	50.7	2.2	64.9	2.9166	2.7	3.7
PLA-10KF	53.8	2.1	63.4	2.2921	3.8	5.1
PLA-20KF	51.4	3.3	63.9	1.8256	5.3	7.0

3.2.2 Loss Factor

Material will change from rigid to the elastic state with the movement of small groups and the chains of molecules within the polymer structure. In fibre reinforced composite, damping is affected by the presence of fibres. Figure 2 shows thermogram of tan delta of PLA-KF biocomposites. In general, there were slight decreasing trend of T_g with the presence of kenaf fibre. The lower T_g obtained could be due to the inconsistency of aspect ratio of kenaf fibre and agglomeration of kenaf fibre. However, it is interesting to note that, at higher kenaf fibre content, at 20 wt.%, T_g has shifted to a slight higher temperature than at 10 wt.%. This stressed on the effectiveness of kenaf fibre as reinforcing agent. This is in agreement with the tensile and flexural modulus where the stiffness increased with kenaf fibre content as shown in Table 3. The magnitude of tan delta for unreinforced PLA is higher and sharper as compared to PLA-KF biocomposites. Again, this stressed on the restricted mobility of PLA molecular chain with the present of kenaf fibre as observed in DSC measurement. As can be seen in Table 3, the higher fibre content has lowered the magnitude of tan δ. It is observed also in Figure 2 that the sharpness of the tan δ peak is reduced with kenaf fibre content. It was reported by previous studies [9-10] that damping in the transition region is actually measurement of imperfection in elasticity and energy used to deform the material was dissipated into heat. Hence, this led to the reduction in friction of intermolecular chain with the present of reinforcement. On the other hand, it was claimed by Pothan [9] on banana fibre reinforced polyester that an improvement in interfacial bonding may be achieved by lowering the tan δ values.

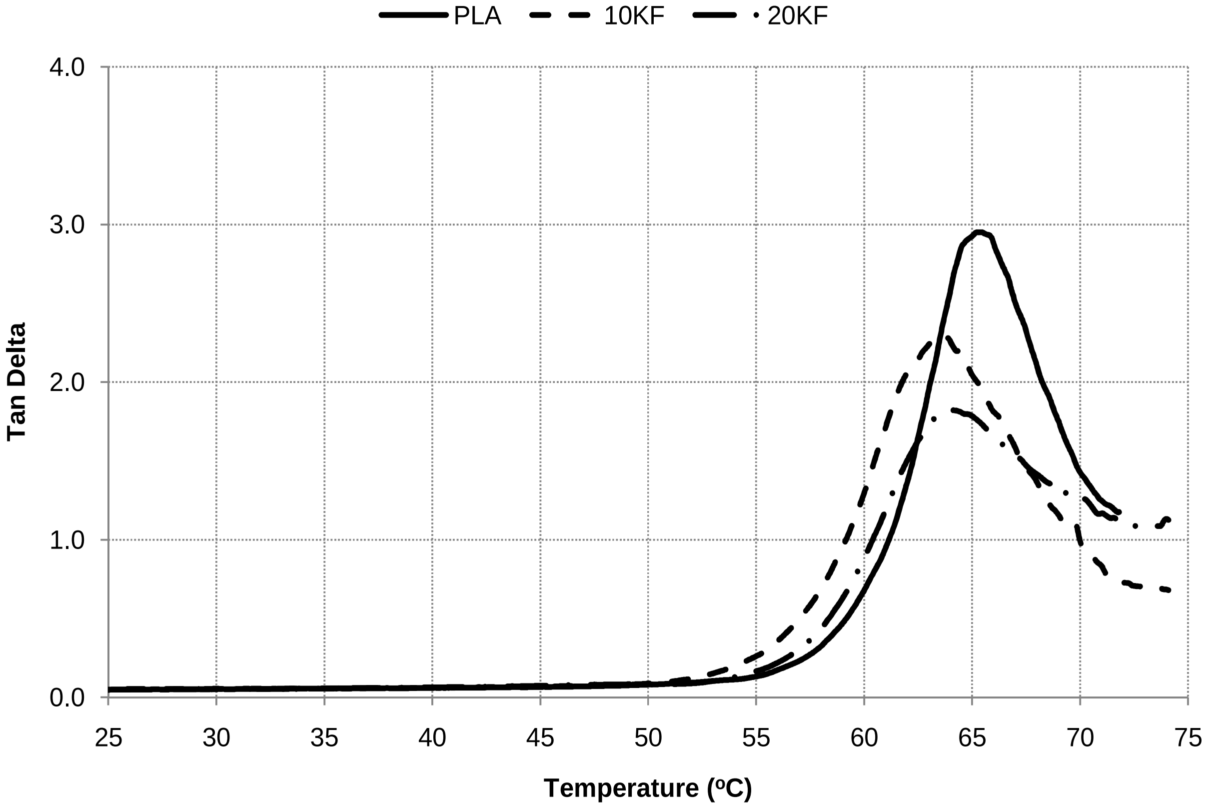

Figure 2 The effect of fibre content (wt%) on tan delta of PLA-KF biocomposites.

4.0 CONCLUSION

Our studies have found that from the differential scanning calorimetry, the glass crystallization temperature and cold-crystallization enthalpy increases with fibre content. However cold-crystallization and melting temperature slightly decreased with fibre content. PLA-KF biocomposite remains amourphous with the fibre content. From dynamic mechanical analysis, storage modulus increases at higher kenaf fibre content. Damping parameter tan δ reduced with kenaf fibre content which could suggest an improvement in interfacial bonding has occurred.

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