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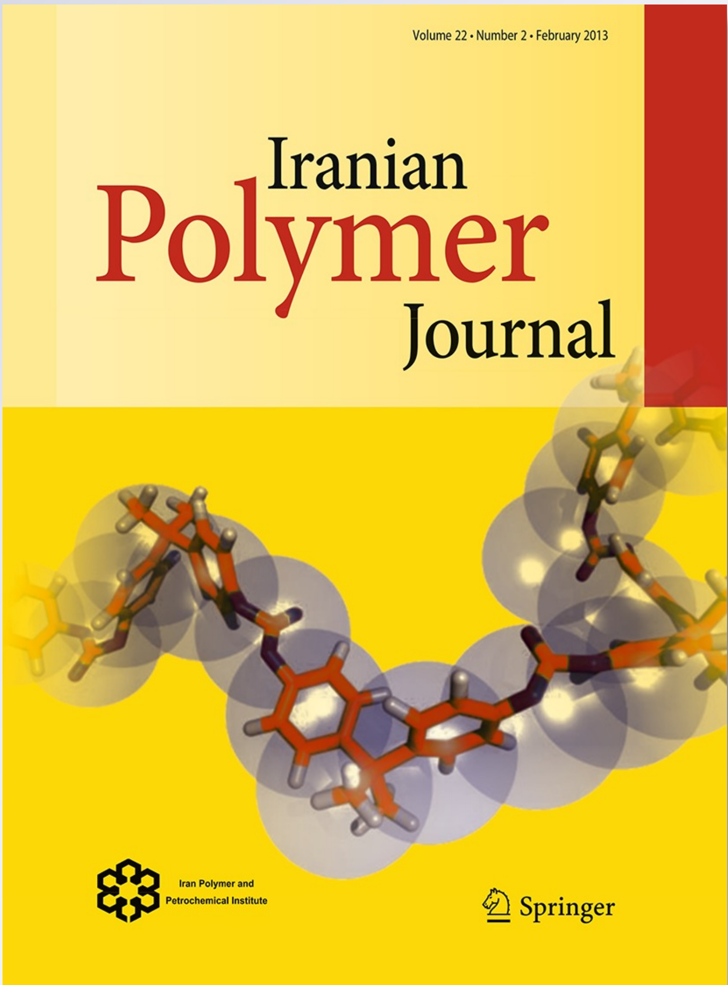

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ORIGINAL PAPER

Effect of processing routes on the mechanical, thermal and morphological properties of PLA-based hybrid biocomposite

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Abstract Due to environmental awareness and depletion of petroleum oil, bioplastics and their composites are one of the most researchable topics throughout the world. Polymers that are produced from renewable sources are expected to be the best alternative to replace conventional polymers. The bottles neck of these bioplastics is its cost which limits its application in certain purposes. Bioplastics filled or reinforced with natural fibers can reduce cost and improve properties, like stiffness, strength and toughness of biocomposites. Impact strength and fracture toughness are the main demerits of short fiber-filled biocomposite. On the other hand, when nanoclay, having a very high aspect ratio, is mixed with bioplastics it may significantly affect the thermal and mechanical properties of the final composites. A composite may also suffer dispersion inefficiency, which is considered the key factor to improve the properties. The aim of this paper was to hybridize nanoclay and short kenaf fiber in polylactic acid (PLA) by double extrusion method and followed by mechanical, thermal and morphological characterizations. Mechanical properties showed improvement with nanoclay, specifically the impact strength increased more than 50 % compared with unreinforced PLA. A double extruded composite showed 3–10 % better tensile and flexural properties than the single extruded composite. Similarly, addition of nanoclay increased decomposition and melting temperatures (T_m) from 198 to 225 °C and 152 to 155 °C, respectively. Crystallization temperature (T_c), however, dropped with nanoclay from 116 to 106 °C and storage modulus (E') increased by about 1 GPa. These findings were also supported by scanning electron micrograph (SEM) and transmission electron micrograph (TEM) where in double extruded composite a better dispersion of nanoclay was observed. By employing X-ray diffraction (XRD) it was found that higher percentage of crystallinity was obtained while Fourier transform infrared (FTIR) displayed new bond formation. The presence of nanoclay enhanced thermal and mechanical properties of the hybrid composite.

Keywords Hybrid biocomposite · Double extrusion · Thermo-mechanical properties · Kenaf fiber

Introduction

Due to higher manufacturing cost, bioplastics and their composites have only been used in medical applications like drug delivery, sutures and orthopedic implant fabrications [1–3]. Among biodegradable polymers, researchers have focused on polylactic acid (PLA) because of its biodegradability, biocompatibility, properties and processability. PLA can be produced from renewable sources, like sugar beets or corn starch by fermentation process which is the most important factor that makes it unique among bioplastics [4–6]. At present, researchers are focusing to extend applications of PLA in packaging and film making, etc. [7–9].

Several attempts have been made to make PLA as a household product and for packaging purposes by different

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techniques, methods and appliances [7, 9]. However, low impact strength, toughness and high modulus have limited its application in only rigid thermoformed packaging industry while for flexible packaging new grades of PLA with specific end-use performances are required. To overcome these problems several attempts have been made such as, addition of plasticizer, filler, fiber and nanoparticles [10, 11]. However, some researchers [12, 13] have also tried to overcome this problem through hybridization processes or adding natural fibers, fillers in conventional polymers to achieve the desired properties.

Ray et al. [14] have reported on the effect of hybridization of glass fiber in thermoset biocomposites. Bakar et al. [15] have studied the tensile and impact properties of oil palm fiber-glass reinforced epoxy resin and Burgueno et al. [16] have employed cellular biocomposite cores, fabricated from industrial hemp or flax fibers with unsaturated polyester hybridized with woven jute, chopped glass, and unidirectional carbon fabrics. Mishra et al. [17] studied the moisture uptake characteristics of hybrid systems whereas Reis et al. [18] have reported on the flexural behavior of hybrid laminated composites (LC) with a hemp fiber/polypropylene core and two glass fibers/polypropylene surface layers at each side of the specimen. Morye et al. [19] focused on the mechanical properties of glass/flax hybrid composites based on a novel modified soybean oil matrix material. Panthapulakkal et al. [20] investigated the mechanical, water absorption, and thermal properties of injection-molded short hemp fiber/glass fiber-reinforced polypropylene hybrid composites. Wambua et al. [21] concentrated on the ballistic properties of flax, hemp, and jute fabric-steel hybrid polypropylene composites processed by hot compression molding. All these investigations have tried to find suitable hybrid composites for their desired properties. However, so far no one has tried to combine nanoclay and natural short fibers. As far authors knowledge only Amin et al. [22] investigated the mechanical and thermal properties of hybrid biocomposites from oil palm empty fruit bunch (EFB) fibers and kaolinite in polyurethane. There is no paper reported on montmorillonite nanoclay (MMT) and short kenaf fiber (KF) hybrid biocomposite in PLA matrix.

The word "hybrid" is originated from Greek–Latin and used in different scientific fields. For polymer matrix composites, hybrid composites refer to one kind of reinforcing material which is incorporated into a mixture of different matrices (blends) [23], or two or more reinforcing and filling materials which are incorporated into a single matrix [24, 25] or a combination of both approaches may be utilized. The incorporation of two or more lignocellulosic fibers into a single matrix has led to the development of hybrid composites. The behavior of hybrid composites is a sum of the individual components in which there is more favorable balance between the inherent advantages and disadvantages. While using a hybrid composite that contains two or more types of fibers, the advantages of one type of fiber could complement what are lacking in the other fiber. As a consequence, a balance in cost and performance could be achieved through proper material design [26].

The properties of a hybrid composite depend on the fiber content, fibers length, orientation of fibers, extent of intermingling of fibers, fiber to matrix interface, layering pattern of both fibers and also depending on the failure strain of individual fibers. Maximum hybrid results are obtained when the fibers are highly strain compatible [27]. The properties of the hybrid system consisting of two components can be predicted by the rule of mixtures.

$$P_H = P_1V_1 + P_2V_2 \tag{1}$$

Property of hybrid system = property of 1st system × volume fraction of 1st reinforcement + property of 2nd system × volume fraction of 2nd reinforcement.

Here, P is the property, H is hybrid system and 1 and 2 refer to the corresponding property of the first and second systems. V_1 and V_2 are the relative hybrid volume fractions of the first and second systems and $V_1 + V_2 = 1$.

To date, no study has reported on the combination of PLA, KF and MMT for fabrication of hybrid biocomposites. The objectives of the present work were to fabricate hybrid biocomposite through single and double extrusion methods by PLA, KF and MMT. The newly developed composite was mechanically, thermally and morphologically characterized to evaluate its performance.

Experimental

Materials

PLA, 3051D graded PLA was obtained from Nature-Works®, China. Its specific gravity was measured 0.998 g/cm^3, crystalline melt temperature and glass transition temperature were 145–155 °C and 55–65 °C, respectively. Nanoclay (MMT) from Nanomers® I.31PS was used as filler which was manufactured by Nanocor, USA. It was in powder form with a mean mesh size of 15–25 μm. It is an onium ion modified montmorillonite, designed for maximum compatibility and dispersion in a polyolefin matrix. In addition to the typical onium treatment, Nanomer I.31PS contained a silane-coupling agent to promote higher tensile properties. It contained 0.5–5 wt % aminopropyltriethoxysilane and 15–35 wt % octadecylamine. Its density was about 0.89 g/cm^3. MMT had the chemical formula of $R^+_{0.33}(Al, Mg)_2Si_4O_{10}(OH)_2.nH_2O$ where, R^+ in natural mineral is composed of one or more Na^+, K^+, Ca^{2+}

cations. KF was obtained from Kenaf Natural Fiber Industries Sdn. Bhd., Kelantan, Malaysia. The density of KF was about 1.13 g/cm^3. The size of KF was in the range of 150–250 µm.

Preparation and processing

The composition of the fabricated composite is presented in Table 1. Anuar et al. [28] investigated the suitable combination of PLA-kenaf and PLA-nanoclay in terms of thermal and mechanical properties. This paper also concentrates on thermal and mechanical properties of similar composition reported by Anuar et al. [28]. Prior fabrication of PLA specimen, KF and MMT were dehumidified in a dry oven at 110 °C for a period of 1 h. Then PLA, KF and MMT were manually mixed followed by extrusion in a twin-screw counter rotating extruder for the first round extrusion process.

There were two different approaches applied in producing double extruded hybrid composite. The extruded PLA-KF composite was manually mixed with nanoclay followed by second extrusion. The second approach was exactly similar like the first one, however, in this approach, PLA and nanoclay were extruded first and KF was introduced during second extrusion process. It should be mentioned here that the same percentage of PLA, KF and nanoclay is maintained for all single and double extrusion processes. For extrusion process, Thermo Hakke twin-screw extruder was used where the temperature was 180–190 °C and screw speed was 100 rpm which was also used by Anuar et al. [28]. After compounding the composites were pelletized before being sent to a Battenfeld HM 600/850 injection molding machine. The temperature was 185–210 °C for all the four zones of injection molding machine.

Mechanical characterizations

Tensile test was carried out by Lloyd (Ametec) universal testing machine. The stain rate was 50 mm/min. Flexural test was also performed on the same universal testing machine according to ASTM D790. The load cell was 10 kN and the span length was 100 mm. Impact test was then conducted according to ASTM D6110 using Dynisco polymer test, Simatic OP7 machine to estimate sample's fracture toughness. For impact test, the maximum applied energy was 7.5 J. To measure the density of the fabricated composite according to ASTM D792, a Rillins Sains, Malaysia densometer machine was used. This machine uses Archimedes principle for density measurement.

Thermal characterization

Differential scanning calorimetry (DSC) analysis was carried out using a Perkin Elmer instrument. The temperature range was 30–200 °C with a heating rate of 10 °C/min. Thermogravimetry analysis (TGA) was conducted by using Perkin Elmer instrument to investigate the thermal stability of the nanocomposite. The samples were heated from 30 to 1,000 °C with a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was carried out using a Perkin Elmer DMA at temperature range from −80 to 100 °C with a heating rate of 5 °C/min and frequency of 1 Hz.

Morphological characterization

X-Ray diffractometer (XRD) was used to determine crystallinity of the hybrid biocomposite using XRD-6000, Shimadzu. During XRD, the target metal was copper, axis range was 10–80°, rotation was 2 °/min, voltage and current were 40 kV and 30 mA, respectively.

Fourier transform infrared (FTIR) spectroscopy was carried out by a Perkin Elmer, Spectrum-100 machine to find the bond formation.

FEI Quanta 200 scanning electron microscope (SEM), The Netherlands, was used to observe the fracture surface of tensile fracture specimen.

Transmission electron microscope (TEM) was used to observe the dispersion of nanoclay in the PLA matrix. A CM 12 Philips TEM, with different magnification analyses, was used to assess nano to microscale dispersion.

Table 1 Compositions, process and names of composite

Sample	Denotation	Matrix		Kenaf fiber		Nanoclay		Process
		wt %	V %	wt %	V %	wt %	V %	
PLA	S1	100	100.2	0	0	0	0	Single extrusion
PLA-20KF	S2	80	80.16	20	17.7	0	0	Single extrusion
PLA-20KF-3MMT	S3	77	77.15	20	17.7	3	3.38	Single extrusion
*(PLA-20KF)-3MMT	S4	77	77.15	20	17.7	3	3.38	Double extrusion
*(PLA-3MMT)-20KF	S5	77	77.15	20	17.7	3	3.38	Double extrusion

* Bracket indicates first extruded product

Results and discussion

Mechanical characterization

Rule of mixture (Eq. 2) is widely accepted formula to determine the physical properties of materials. This formula is widely used to determine the stress, force and density.

$$\rho_{\text{Hybrid}} = \rho_{\text{PLA}} V_{\text{PLA}} + \rho_{\text{KF}} V_{\text{KF}} + \rho_{\text{Nanoclay}} V_{\text{Nanoclay}} = 1.019\, g/cm^3 \quad (2)$$

Based on this equation, the theoretical density is 1.019 g/cm^3. Table 2 shows the experimental density of the hybrid composite. In general, none of the experimental densities has a similar value compared with the theoretical densities. However, it is noted that the experimental density of S4 and S5 which are 1.015 and 1.022, respectively, is closer to the calculated density. This could be due to efficient dispersion of fibers and fillers in these composites (S4 and S5) which resulted from the double extruded process. The effect of processing route on the mechanical properties of hybrid composites is presented in Fig. 1.

It is clear that the addition of MMT enhanced the tensile strength and modulus of the hybrid biocomposite. For instance, both values of tensile strength and modulus of S3, S4 and S5 increased from 8 to 13 MPa and from 0.1 to 1 GPa, respectively as compared to S2. Interestingly, the tensile strength and modulus of double extruded hybrid biocomposites (S4 and S5) were further increased than a single extruded hybrid biocomposite (S3). A similar trend was also obtained for flexural properties as shown in Fig. 2. From Figs. 1 and 2, it is also noted that, although both S5 and S4 were produced by double extrusion, the mechanical properties of S5 are higher than S4. The differences of mechanical properties in S5 and S4 could be due to different processing routes used during the fabrication process. Question may arise why S5 shows better properties than S4, even though both were produced via double extrusion method? The probable answer may be, for S4 composite, PLA and KF were extruded first and mixed with MMT before pelletization. It was then followed by second extrusion. In addition, pelletization after first extrusion may also contribute to fiber breakage which reduces the size of fibers below the critical length leading to deterioration of the properties of hybrid biocomposite. On the other hand, for S5 composite, PLA and MMT were extruded first followed by KF which suggested KF experienced only single time heating and was not pelletized.

Table 2 Measured density of hybrid biocomposite

	Wt. in air (g)	Wt. in water (g)	Density (g/cm^3)
S1	2.85	0.57	0.998
S2	1.79	0.37	1.008
S3	1.88	0.42	1.026
S4	1.63	0.35	1.015
S5	1.64	0.36	1.022

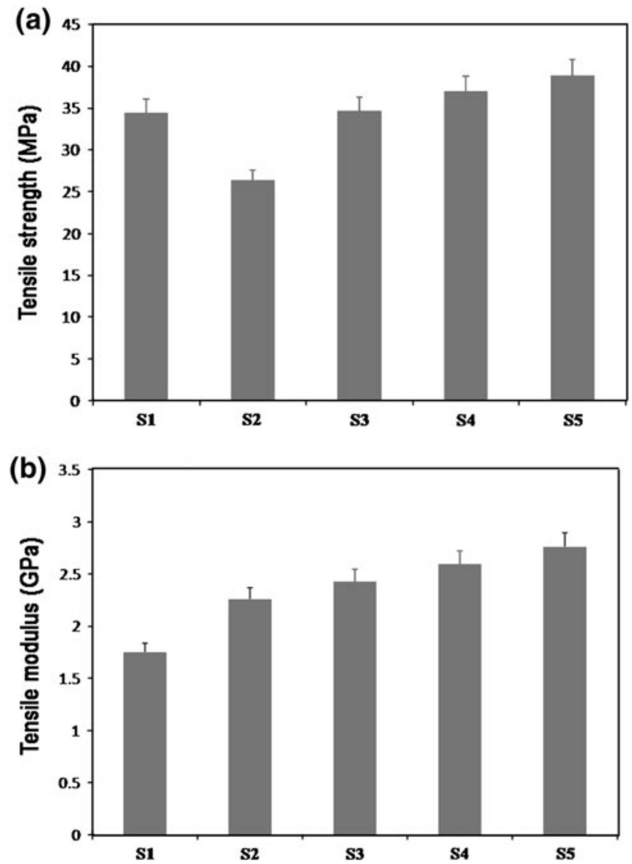

Fig. 1 Tensile modulus (**a**) and strength modulus (**b**) of PLA composites

Hence, from the mechanical properties it can be suggested that the key factor for this hybrid biocomposite was the incorporation of MMT for enhancement of its properties. The nanoclays enhance properties of composite only if it is followed by intercalation or exfoliation [29]. It is well known that the smaller particle has higher tendency to adhere to other particles due to its larger surface area, and vice versa. As for S5, MMT particles experience extrusion processes twice which help MMT particles to disperse homogeneously.

Studies by Anuar et al. [28] on the impact properties of PLA-KF biocomposite have shown decrements in impact strength with addition of KF in PLA matrix. Figure 3 shows the effect of KF and MMT on the impact properties of PLA composites and it is apparently found that the incorporation of MMT has increased impact strength of hybrid biocomposite almost 6–8 times higher than that of

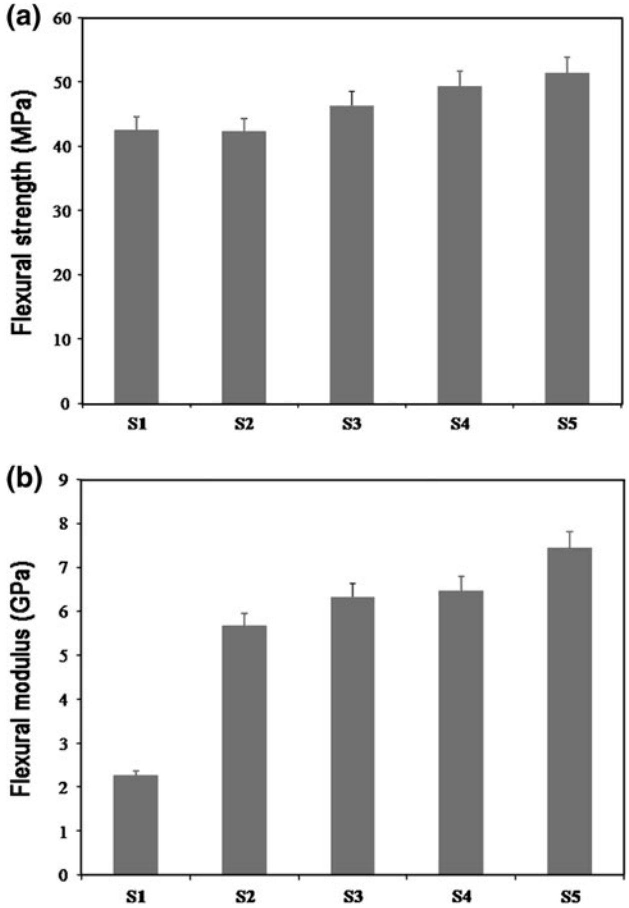

Fig. 2 Flexural modulus (**a**) and strength modulus (**b**) of PLA composites

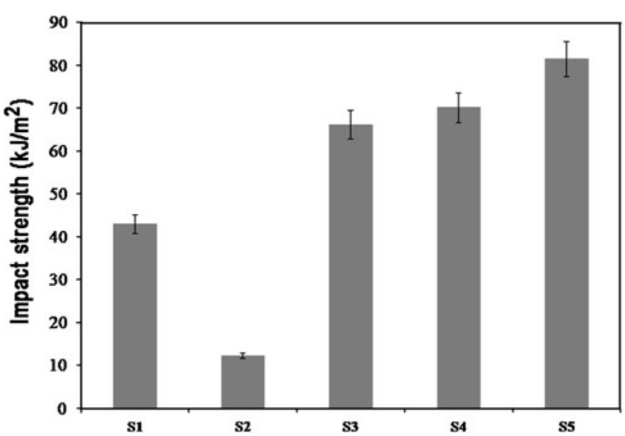

Fig. 3 Impact properties of PLA composites

pristine PLA and PLA-KF biocomposite. The same goes to a double extruded composite where it exhibits higher impact property than single extrusion. Similar to tensile and flexural strength, the impact strength of S5 is better than S4. Despite of different processing routes, the reason behind the drastic improvement of the impact property could be related to the impediment of polymer chain by MMT and better dispersion of MMT in S5 than S4 and S3.

From fractography analysis (Fig. 4), it can be seen that, the fibers in S4 and S5 are randomly oriented compared with S2 and S3. Furthermore, higher number of fiber pull out and fiber debonding in double extruded specimens (S4 and S5) could be the key factors for higher impact strength. TEM was employed to observe the dispersion of MMT. Double extruded composites (S4 and S5) show better dispersion than the single extruded composite (S3) as shown in Fig. 5. Thus, this may suggest that S4 and S5 show intercalated and partially exfoliated structure. Again S5 shows more intercalation and exfoliation than S4 which has led to better mechanical properties.

Thermal characterization

From the results of mechanical characterization tests it can be said that double extruded product shows higher properties than the single extruded product, where S5 has the highest properties. Thermal characterization is also significant for polymers and composites. Table 3 represents the DSC results for all five composites and there were no significant changes of glass transition temperature (T_g) and melting temperature (T_m) with MMT. Crystallization temperature (T_c), however, shows a sharp decrease with addition of MMT, suggesting that MMT acts as a nucleation point during crystallization. Therefore, higher percentage of crystallization occurs in S3, S4 and S5. Again it is well known [30] that the higher value of supercooling (T_m-T_c) is an indication of higher percentage of crystallization. Thus, S3, S4 and S5 show higher percentage of crystallinity compared with S2 and S1 and in agreement with the X-ray diffractogram in Fig. 6.

XRD in Fig. 6 shows higher percentage of crystallinity (%X) with addition of MMT and double extruded shows higher %X than single extrusion which is one of the reasons of higher mechanical and thermal properties.

Another important thermal analysis is TGA which determines the thermal decomposition. Table 4 presents the data obtained on initial decomposition temperature (T_i) and final decomposition temperature (T_f) for all five compositions. It is noted from Table 4 that addition of MMT has decreased T_i. The T_f is, however, increased with MMT. The reduction of T_i is due to addition of KF which helps to decompose quickly and the increment of T_f is due to addition of nanoclay which has a higher flame retardant tendency. There has been no significant difference observed in TGA analysis between the double extrusion and single extrusion.

The most effective and important thermal characterization is DMA, which represents the behavior of materials in terms of molecular structure, product properties and

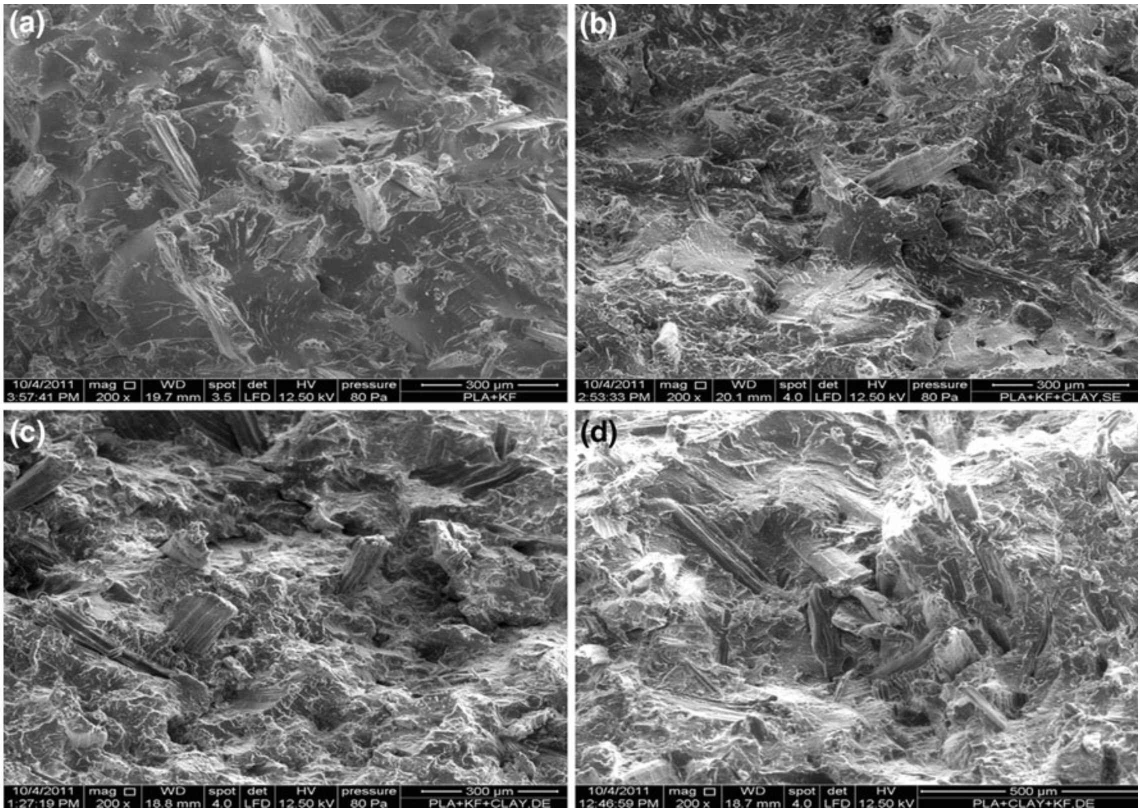

Fig. 4 Scanning electron micrographs of **a** S2, **b** S3, **c** S4 and **d** S5 at 200× magnifications

processing conditions. This is because polymer does not follow Hookean behavior and they are non-Newtonian fluids which make them different in terms of mechanical and thermal properties as compared to metals and ceramics. In DMA analysis, time–temperature scan at a fixed frequency is recommended as DMA is sensitive to determine T_g and other transitions in materials and to probe relaxation of polymer as a function of temperature. Moreover, toughness of polymers, impact strength and operating range are possible to be detected by DMA.

Figure 7a, b shows the storage modulus and loss modulus curves obtained from DMA. The addition of MMT has increased the storage modulus by about 0.5–1.0 GPa and no change is observed in loss modulus of S2, S3, S4 and S5. There is also no significant change between S4 and S5.

Table 3 Thermal properties obtained from DSC

	T_g	T_c	T_m	$T_m - T_c$
S1	58.24	115.9	152	36.1
S2	59.33	119.46	153.06	33.6
S3	58.78	105.48	153.91	48.43
S4	59.34	108.4	155.13	46.73
S5	59.44	106.42	155.03	48.61

The increment of storage modulus could be due to the formation of new bond that helps to absorb higher energy that resulted in higher storage modulus as in Fig. 7a.

FTIR curves in terms of percentage of infrared transmission (%T) for all the five samples are demonstrated in Fig. 8. The circle indicator shows the difference of peak among five samples. However, other important peaks at 1,079, 1,453 and 1,747 cm^{-1} indicate C–O, C–H and C = O, respectively. In S1, the transmission percentage (%T) is higher on the particular frequency $\sim$800 cm^{-1} for the absence of a bond to absorb the infrared energy. The curve S2 is almost similar to S1, however, S3, S4 and S5 show lower transmission, where they absorb higher energy which is used to vibrate the atomic bonding in that particular frequency (shown in circle), specifically in double extruded product, which indicate formation of new bonds that absorb or prevent infrared transmission. By referring to Fig. 8, the wavelength of this new bond is about 798 cm^{-1} which falls under alkenes (=C–H, 675–1,000 cm^{-1}) functional group with strong bending type vibration. It is predicted that this bond is formed with MMT that contains OH group and H_2O shown in Fig. 9. Therefore, it can be hypothesized that this new bond is responsible for better thermal properties as well as mechanical properties.

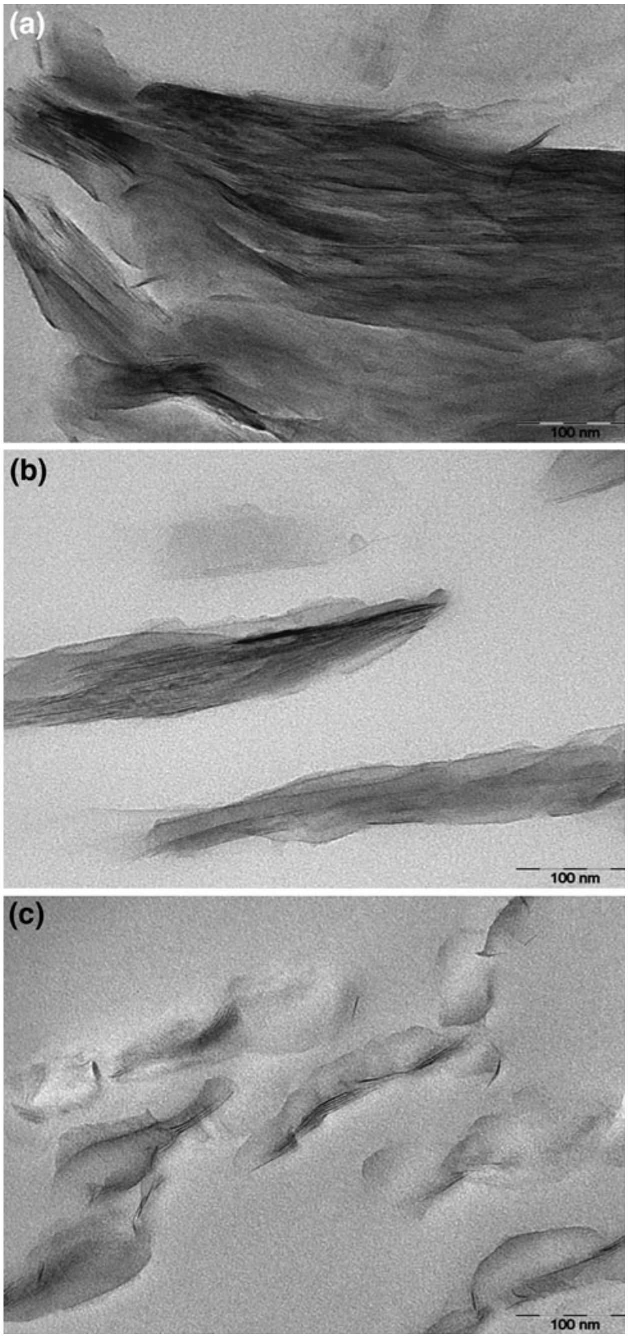

Fig. 5 Transmission electron micrographs of **a** S3, **b** S4 and **c** S5 at 175,000× magnification

Table 4 TGA analysis

	T_i	T_f	Procedural decomposition temperature (T_f−T_i)
S1	291	416.7	125.7
S2	251.64	450.07	198.43
S3	249.47	478.98	229.51
S4	251.82	474.77	222.95
S5	245.4	470.23	224.83

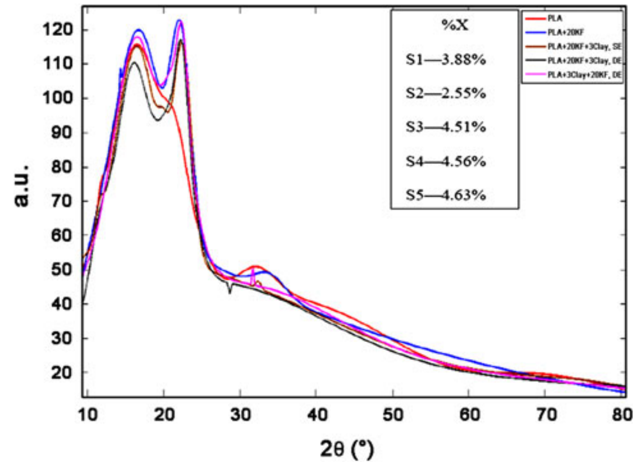

Fig. 6 XRD of S1, S2, S3, S4 and S5

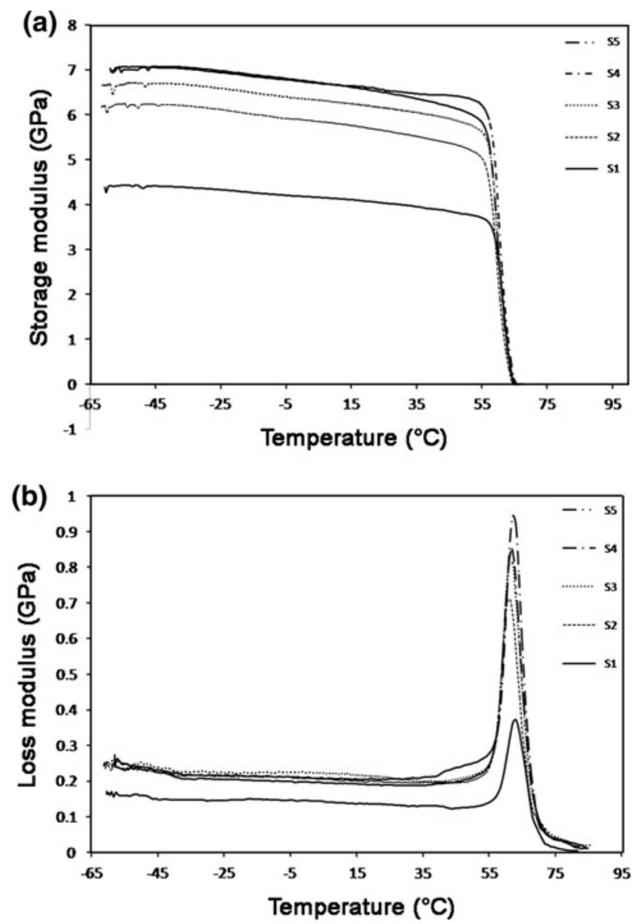

Fig. 7 **a** Storage modulus and **b** loss modulus of PLA composites

Conclusion

PLA-KF-MMT hybrid biocomposite is a new material with enhanced mechanical, thermal and morphological properties as compared to other natural fiber biocomposites.

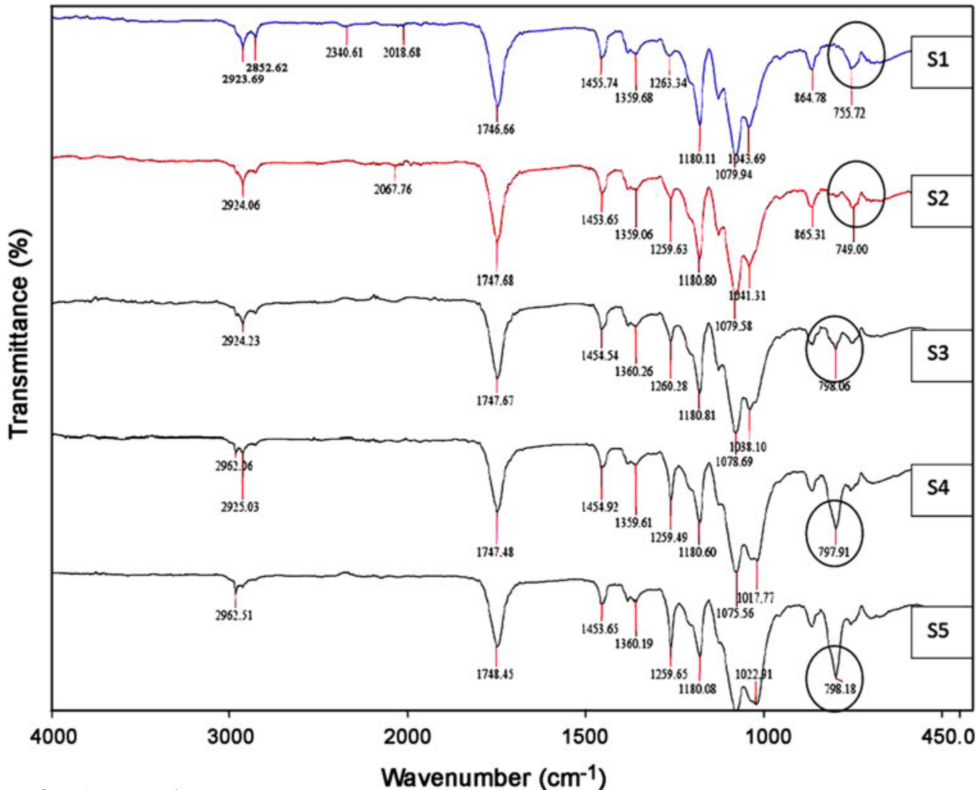

Fig. 8 FTIR curves of PLA composites

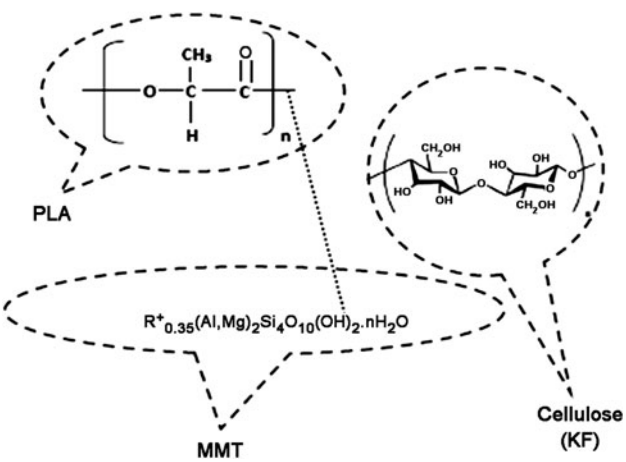

Fig. 9 Possible mechanism for formation of new bond

MMT shows significant effect in improving mechanical properties specifically the impact properties which is the main drawback of PLA and its composites. Storage modulus, decomposition temperature and percentage of crystallinity are significantly improved with MMT and KF. Fabrication processes play a pivotal role in performance. Double extruded composite shows higher mechanical properties than the single extruded composite. S5 (PLA-3MMT-20KF) shows better properties than other composites due to better dispersion of fibers and clays with formation of new bonds between PLA and MMT which have improved all the properties. It should be noted that mechanical, thermal and morphological properties are not the only factors to recommend a material for any specific purposes. Cost and life cycle analysis also plays a vital role to make a material commercially viable. Further research works are necessary to investigate the degradability, production cost and moisture absorption which is very important parameter for natural fiber reinforced composite and specifically hybrid biocomposite.

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