Effect of montmorillonite clay on flax fabric reinforced poly lactic acid composites with amphiphilic additives

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ABSTRACT

Bio-composites (PF) were successfully prepared by reinforcing poly lactic acid (PLA) with woven flax fibers (F) in the presence of mandelic acid, benzilic acid, dicumyl peroxide (DCP) and zein as additives. To improve the mechanical properties of the bio-composites, montmorillonite clay (MMT) was also added. Characterizations of the bio-composites in presence and absence of MMT were performed by FTIR, DSC, TGA and DMTA. The interfacial adhesion between the fibers and the matrix was qualitatively assessed from SEM micrographs of fractured specimens. Intercalation of MMT with 1.4 nm basal spacing was observed in the PLA matrix leading to the increased modulus and water resistance of the bio-composites. Results indicated that mandelic acid and dicumyl peroxide acted as efficient additives for this system. This work provided us the exploratory idea of using MMT in presence of amphiphilic compounds as additives in bio-composites for possible applications.

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1. Introduction

Synthetic fiber reinforced polymer composites have been used for aerospace, defense, marine, automotive, civil infrastructure, sporting goods, etc. for over a quarter century offering high strength and stiffness, dimensional stability, and thermal properties [1]. But finite nature of the synthetic polymers and fibers and due to new imperatives on environmental pollution the focus of the researchers is shifted to bio-composites with the application areas remaining the same [2,3]. Furthermore, the advent and application of nanotechnology have generated renewed interest in composites which show promising potential as next generation material for structural applications [4–6].

Polylactic acids (PLA) are expensive in comparison to conventional thermoplastics and they are sometimes too weak for some applications. The important thing is that it is considered as "green polymer" being available from renewable agricultural resources by the combination of fermentation and polymerization; thus, its production consumes less fossil resources than comparable petroleum-based plastics. With PLA, carbon dioxide is removed from the atmosphere when growing the feedstock crop, and returned to the earth when the polymer is degraded [7]. To reduce the cost and improve the material properties without interfering its "green polymer" image, researchers are trying to prepare natural fiber reinforced bio-composites. Short fiber, nonwoven mat or woven fabrics have been used to prepare bio-composites [8–12]. Several papers have reported the preparation of natural fiber reinforced PLA composites but the low compatibility of hydrophobic PLA with hydrophilic natural fibers leads to a composite with poor mechanical properties [13]. To improve the interfacial adhesion between natural fibers and the matrix, chemical modifications, such as silanization of natural fibers [14–19] have been studied and found to improve the mechanical properties of the composites. Zein has been used as a coupling agent for preparing natural fiber based polypropylene composites [20]. The preparation of bamboo fiber-filled poly(lactic acid) (PLA) eco-composites in the presence of dicumyl peroxide as a radical initiator has also been reported [21]. In this paper, we have used woven flax fabric treated with amphiphilic additives to prepare the bio-composites. In this work, montmorillonite clay (MMT) has been added to the bio-composites and the properties of the composites with and without the addition of MMT have been evaluated and discussed.

2. Experimental

2.1. Materials

PLA resin (CP-INJ-1001EZC) was obtained from Cereplast, Inc., Hawthorne, USA. To improve the biodegradability of the PLA resin, supplier has incorporated cereal starch (wheat, potato and tapioca) in this grade of resin. Flax woven fabric: 180 g/m^2 was purchased

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from Libeco, Belgium with warp (19 threads/cm) and weft (21 threads/cm). The tensile strengths of the fabric in warp and weft, as provided by the supplier, are 835.4 N and 1181 N, respectively. Benzilic acid, mandelic acid and dicumyl peroxide (DCP) were procured from Sigma–Aldrich, Germany. Montmorillonite clay (MMT) surface modified with 0.5–5 wt.% aminopropyl triethoxy silicone and 15–35 wt.% octadecylamine (Nanomer$^{(R)}$) was purchased from Sigma–Aldrich, Germany. Zein protein was obtained from Scientific Polymer Products, New York, USA and chloroform was purchased from Minema Chemicals, South Africa. Laboratory grade chemicals were used without further purification.

2.2. Preparation of the woven fabric PLA bio-composites

In a process described below, a square woven fabric of 15 cm × 15 cm in dimensions and the average mass of this was 4.0 g was cut and dried in an oven at 60 °C for 24 h to remove moisture. PLA pellets equivalent to 0.9, 0.8 and 0.7 weight fractions of the woven fabric were dissolved in chloroform. The dried woven fabric was then placed inside a square metal frame mold of 15 cm × 15 cm in dimensions and the PLA solution was poured over the woven fabric. It was observed that 5–6 g of PLA in 100 ml of chloroform gave homogeneous suspension for wetting the fibers in the woven fabric. The assembly was kept at a room temperature for 24 h to evaporate the solvent. The solution cast samples of one layer woven fabric and PLA were subsequently hot pressed in compression molding machine fabricated in-house at CSIR Port Elizabeth, South Africa, at 190 °C under 50 bar pressure for 15 min to get the bio-composite samples. The samples were taken out from hot press after cooling the upper and lower platens by circulating water through them. The thickness of the bio-composites with one layer of woven fibers, prepared by compression molding at 50 bar, was found to be 0.50 ± 0.05 mm. At 0.3 weight fraction (W_f) of the fibers, the observed wetting (by homogeneous flow of PLA suspension) of the woven fabric with PLA was better with high mechanical properties than with 0.2 (W_f) of the fibers; hence the solution-cast composites with different additives (1% w/w in PLA) were prepared at 0.3 W_f of the fibers by adding the additives to the PLA chloroform suspensions before pouring over the woven fabric. The composites, thus prepared, were designated as PF-B, PF-M, PF-Z, PF-D, where B, M, Z and D represent benzilic acid, mandelic acid, zein and DCP, respectively. Bio-composites were also prepared by adding MMT (2.5% w/w in PLA) with all the additives [22]. The composites, thus prepared by adding MMT in presence of additives were designated as PFN-B, PFN-M, PFN-Z, PFN-D, where N represents MMT nanoclay and all other designations remain the same. PF and PFN represent the PLA-fiber and PLA-fiber-MMT bio-composites, respectively.

2.3. Characterizations

Fourier transform infrared spectra (FTIR) of the composites were obtained on a Spectrum 100 FT-IR (Perkin Elmer, Buckinghamshire, UK) in the range from 4000 to 600 cm^{-1} using 8–10 mg of composite powder. The composite powder were prepared manually in pestle and mortar. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical analyzer (DMA8000, Perkin Elmer, Buckinghamshire, UK) with dual cantilever at a frequency of 1 Hz. The films tested were 50 mm × 10 mm (length × width) in dimensions, and the test temperature ranged from 25 to 150 °C, with a heating rate of 2 °C per min. The thickness of the specimens was 0.50 ± 0.05 mm. The α-relaxation temperature, α_r, was determined as the peak value of the loss angle tangent (tan δ). Scanning electron microscopy (SEM) images of the cross-sections of the composites were taken on FEI Quanta 200 (Eindhoven, The Netherlands) electron microscope at an accel-

erating voltage of 20 kV. The samples for SEM characterization were prepared by freezing them in liquid nitrogen before fracturing. Gold sputtering was not required for the preparation of the sample in this instrument.

Differential scanning calorimetry (DSC) of the 8–10 mg powder composites was carried out on a Diamond DSC (Perkin Elmer, Buckinghamshire, UK) in the temperature range of 25–220 °C at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) of approximately 5 mg dried films was carried out at a heating rate of 10 °C min^{-1} between room temperature and 700 °C in nitrogen atmosphere on a TG–IR interface (Perkin Elmer, Buckinghamshire, UK). Wide angle X-ray diffraction (WAXD) patterns were obtained using an Anton Paar SAXS (Österreich, Austria) with line collimation equipped with Cu Kα radiation at a wavelength of 0.1542 nm, accelerating voltage of 45 kV, and electric flow of 40 mA. The scanning range was from 2° to 79° with a rate of 0.01 °C s^{-1}. From the position of a peak, the corresponding d spacing was computed from the Bragg's diffraction equation:

$$2d \sin \theta = n\lambda$$

In the above equation, n is the order of reflection, λ is the wavelength of radiation, θ is the angle of reflection and d is the interlamellar spacing.

The tensile strength, elongation at break, and the Young's modulus (E) of the composites were measured on an Instron 3369 testing machine at a strain rate of 10 mm min^{-1} according to ASTM D882 (E). The films tested were 110 mm × 15 mm (length × width) in dimensions and the thickness of the specimens were 0.50 ± 0.05 mm. The clamping length for each specimen on each jaw was 15 mm and no extensometer has been used for tensile tests. An average value from five replicates of each sample was taken for each of the tests mentioned above.

The water uptake of the composites was evaluated according to ASTM D570-81. The composites were preconditioned at 50 °C for 24 h and weighed (W_0). After immersing in distilled water for 24 h, the films were dried with paper towels to remove the excess water on the surface and weighed (W_1). The total weight gain of the composites was used to calculate the absorbed water. An average value from three measurements was reported.

3. Results and discussion

3.1. Properties of the composites

Table 1 shows the mechanical properties of PLA based composites with different additives at 0.3 W_f of the fibers. We have investigated the characteristics of the neat PLA prepared by same method as we have prepared the bio-composites. In our study, neat PLA showed tensile strength of 5.9 MPa which is very low compared to 37.9 MPa that has been provided in the property guide of CP-INJ-1001EZC resin as well as the value of 60–90 MPa reported in the literature [8,9]. The reasons for low mechanical properties of neat PLA used in our study are attributed to cereal starch added to PLA as supplied by Cereplast, USA as well as the solution casting cum compression molding methods which we have employed to prepare the bio-composites. However, introduction of fibers resulted in significant increase in the mechanical properties. The method employed to prepare the bio-composites was basically aimed to study the comparative effect of the additives on the properties in the presence of nanoclay.

PF showed tensile strength of 21 MPa followed by PF-D (18.4 MPa). Additionally, PF-M showed the lowest tensile strength of 11.9 MPa. Interestingly, the addition of MMT increased the tensile strength of PFN-D and PFN-Z while PFN and PFN-B showed a decrease in the tensile strength. Tensile test results indicate that

Table 1
Tensile strength, modulus and elongation of the bio-composites. The fiber content in all the bio-composites is 0.3 W_f. The suffix M, B, Z and D in PF and PFN represent mandelic acid, benzilic acid, zein protein and dicumyl peroxide, respectively.

Sample	Tensile strength (MPa)	Modulus (MPa)	% Elongation at break
Without MMT			
PF	21	137	14.8
	(2.6)	(22.8)	(6.3)
PF-B	14.7	101	12.9
	(2.8)	(17.8)	(7.5)
PF-D	18.4	1369	2.6
	(4.9)	(7.5)	(20.4)
PF-M	11.9	100	6.7
	(7.4)	(16.1)	(23.0)
PF-Z	16.5	111	13.4
	(4.1)	(12.1)	(9.8)
With MMT			
PFN	19	1280	6.9
	(3.6)	(29.8)	(13.6)
PFN-B	9.4	400	10.6
	(13.3)	(10.5)	(19.8)
PFN-D	21.2	1794	1.6
	(8.4)	(3.1)	(15.0)
PFN-M	12	716	2.7
	(3.6)	(20.8)	(20.9)
PFN-Z	19.5	1615	9.2
	(3.8)	(9.4)	(12.9)

Data in the bracket represent coefficient of variation (%).

the individual nature of the additives determines the tensile strength of the bio-composites. Except for PF-D (1369 MPa), the moduli for all the composites without MMT were in the range of 100–140 MPa, which is very low for any meaningful structural applications of the bio-composites [1]. The addition of MMT showed an increase in tensile modulus for all the bio-composites. For PFN, the modulus increased from 137 to 1280 MPa while for PFN-Z it increased from 111 MPa to 1615 MPa. There was seven and four times increase in modulus for PFN-M and PFN-B, respectively. PFN-D showed less increase in modulus, i.e., from 1369 to 1794 MPa as compared to all other bio-composites. It can be concluded that the moduli of the bio-composite films can be tuned through proper choice of novel additives. Among the additives tested, DCP was the most effective in maintaining high values of tensile strength and modulus in presence and absence of MMT. The addition of MMT decreased the elongation at break (%) of all the bio-composites with the highest decrease in elongation at break (%) for PFN-M followed by PFN. In the case of PFN-B the decrease in elongation at break (%) was the lowest. It is also to be
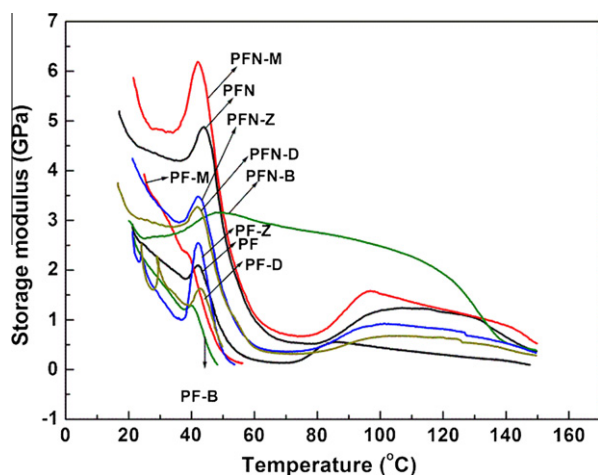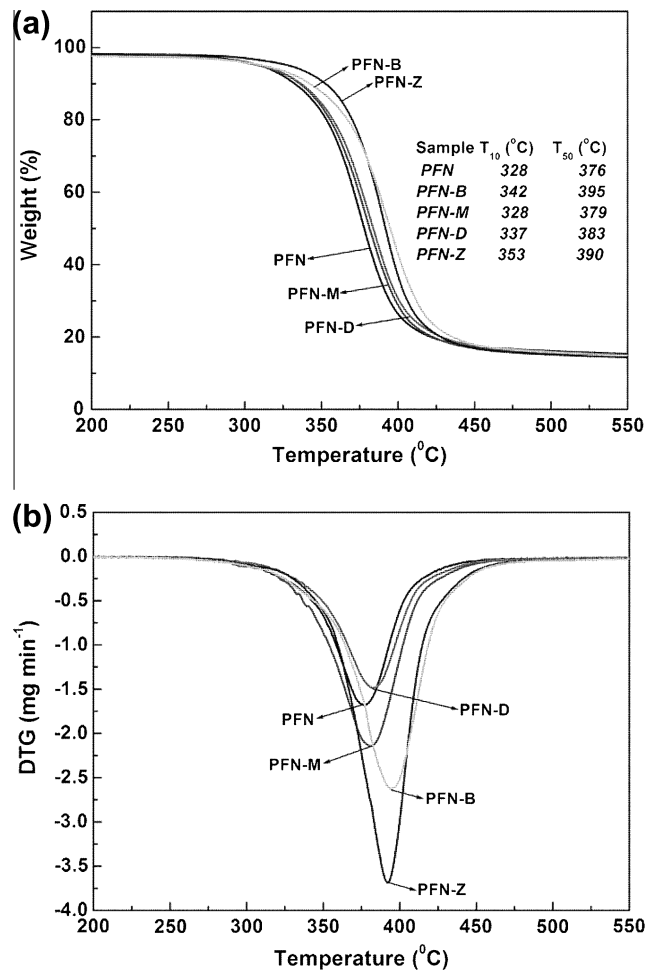
Fig. 2. TGA (a) and DTG (b) curves for the bio-composites.

noted that for PF-D the elongation at break (%) was the lowest and it further decreased for PFN-D. The relatively high decrease in percentage elongation at break for the bio-composites upon the addition of MMT signified the magnitude of the interaction between PLA-fiber in presence of MMT and additives.

Fig. 1 shows the storage moduli of the composites. PF series composites without MMT show low storage modulus from 1.4 to
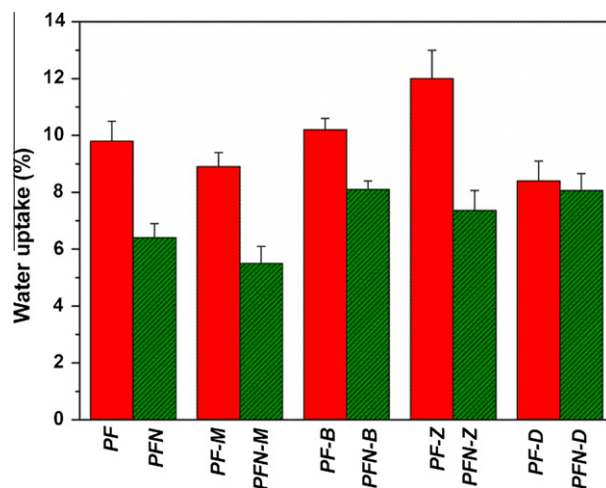
Fig. 1. Storage modulus for the bio-composites.

Fig. 3. Water uptake of the bio-composites with and without MMT.

3.2 GPa at 30 °C. The addition of MMT increased the storage moduli of the composites significantly. PFN-M showed the increase in storage modulus from 3.2 GPa to 4.8 GPa at 30 °C. The intercalation of clay layer in PLA may be responsible for high storage modulus. Importantly, PF-M and PFN-M gave higher storage modulus than PF and PFN. It has been established that as the material becomes cross-linked or highly crystalline in nature there is a rise in storage modulus. But from the % crystallinity data and WAXD pattern (discussed in Section 3.2), it is observed that neither of the factors is responsible for this perceptible increase in storage modulus. We anticipate that the less bulky structure of mandelic acid as well as reduction in crystallinity (from WAXD pattern of PFN-M biocomposites as discussed in Section 3.2) has reduced the inter gallery interaction and thus the affinity between hydrophilic MMT plus fabric and hydrophobic PLA has been maximized.

The thermal stability of the PLA composites, in presence of MMT, determined by thermogravimetric analysis in nitrogen is shown in Fig. 2. The thermal degradation of all the samples expe-
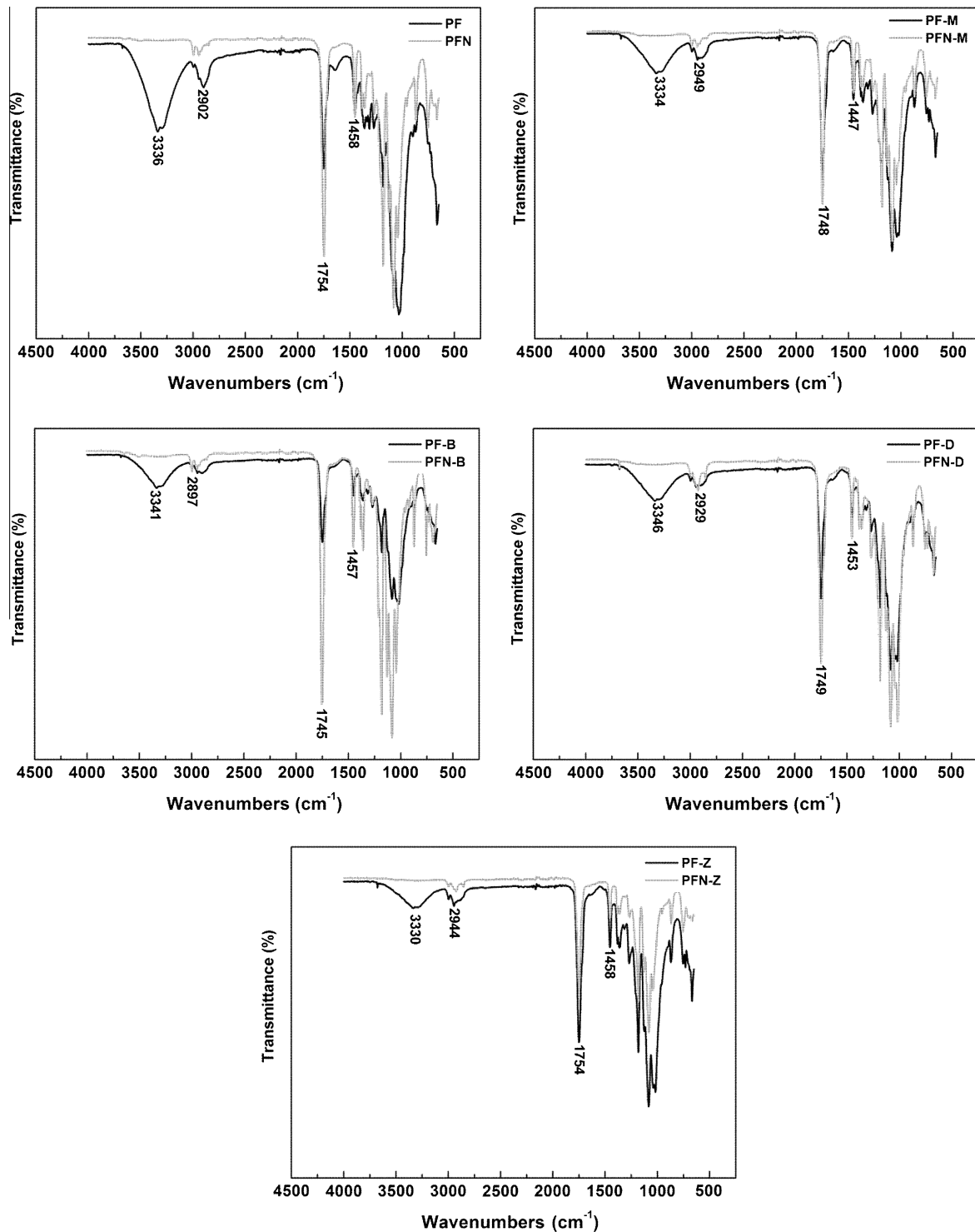

Fig. 4. FTIR spectra of the bio-composites with and without MMT.

riences a one-stage weight loss as shown in Fig. 2a. The introduction of MMT has no clear effect on the thermal stability of the composites. This is attributed to low content of MMT (in our case 2.5%), at which intercalation dominates (discussed in Section 3.2) but the amount of intercalated silicate layers is not sufficient to promote any significant improvement in thermal stability [5]. Temperature at which weight loss is maximum (T_{max}) for PFN-Z (392 °C), PFN-D (384 °C) and PFN-B (394 °C) is higher than that of PFN (377 °C) as shown in Fig. 2b. However, PFN-M showed almost similar values as observed for PFN. The characteristic thermal degradation temperatures, including T_{10} and T_{50}, defined as the temperatures at which 10% and 50% mass loss occur, respectively are summarized in Fig. 2a. It can be easily seen that T_{10} and T_{50} increased for biocomposites with MMT, except for PFN-M which is the same as that for PFN. Hence, depending on the nature of the additives, this effect is more or less pronounced. We have not presented the thermal stability of the composites without MMT due to less pronounced changes.

Fig. 3 shows the water uptake of PLA based bio-composites. With the introduction of low amount of MMT, the water uptake of the bio-composites decreased considerably resulting in improved moisture resistance properties. The water uptake for composites containing MMT was the highest in the case of PFN-D (8.1%) sample while it was the lowest for PFN-M (5.5%).

3.2. Structural characterization

Fig. 4 shows the FTIR spectra of PLA based bio-composites with and without addition of MMT. It is interesting to note that the hydroxyl (—OH of alcoholic and carboxylic) peaks represented between 3330 and 3346 cm^{-1} decreased significantly with the introduction of MMT in the bio-composites. At the same time there is an increase in the intensity of the —C=O bands at 1745–1755 cm^{-1} for all the bio-composites except that for PFN-Z. The changes of —C=O band are connected with the increase of the number of unbounded/free carboxylic end groups in the polymer chain with the incorporation of the additives. Mandelic and benzilic acid have one carboxylic acid per molecule. Interestingly, the carbonyl peak of very high intensity for PFN-B compared to PF-B was observed. This indicates that in the case of benzilic acid, the composite shows higher number of unbounded/free carboxylic end groups. Due to the presence of two phenyl rings in benzilic acid there is also steric hindrance which prevents the interaction of carboxyl groups with PLA, which in turn leads to the presence of a large number of unbounded/free carboxylic end groups. Inefficiency of benzilic acid as an amphiphilic additive is well justified by the lowest mechanical properties (Table 1) and lowest storage modulus (Fig. 1) for PF-B and PFN-B bio-composites in addition to high water uptake (Fig. 3).

The DSC results on percentage crystallinity of PLA based biocomposites with and without the addition of MMT are shown in Fig. 5. The melting enthalpy of 100% crystalline PLA was taken as 93 J/g [23]. The cold crystallization and melting can be clearly observed in the curves. Crystallization in polymers is known to be influenced by a number of factors such as chain linearity, absence of bulky substituent and presence of strong intermolecular attractions. There was no effect on the percentage crystallinity ($\%\chi_c$) of PLA with the introduction of MMT. DSC analyses have also shown that the presence of the MMT does not affect the melting temperatures of the PLA based bio-composites [5].

Fig. 6 shows WAXD patterns of bio-composites in presence of MMT and additives. PLA, procured from Cereplast and used in this research paper, shows several peaks at a 2θ angle of 6.0°, 9.5°, 12.4°, 16.5°, 18.8°, 25.1°, 28.5° unlike what has been reported in the literature for neat PLA [24]. It has been reported by several authors that PLA shows strong crystalline peak at 2θ angle of
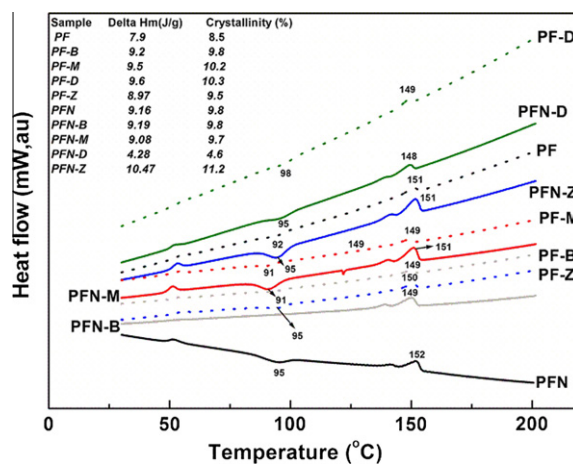

Fig. 5. DSC curves of the bio-composites with and without MMT.
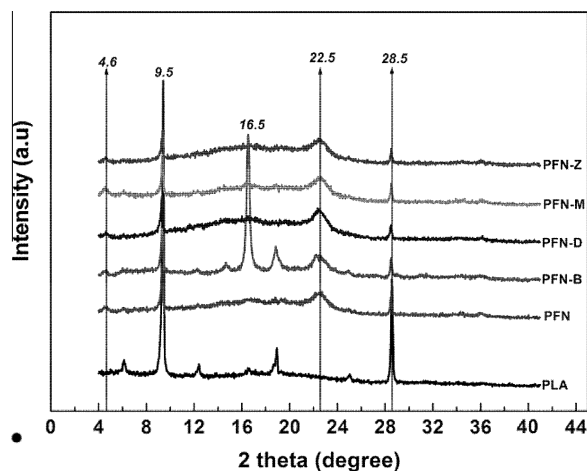

Fig. 6. WAXD patterns of the bio-composites with MMT.

16.5° which is attributed to (1 1 0) and (2 0 0) planes of PLA crystallites [25]. In our case, this peak is very weak. Instead a very strong peak at 9.5° in PLA has been observed which is attributed to the cereal starch that has been added by the supplier to make PLA quickly biodegradable. It has been reported that native starch
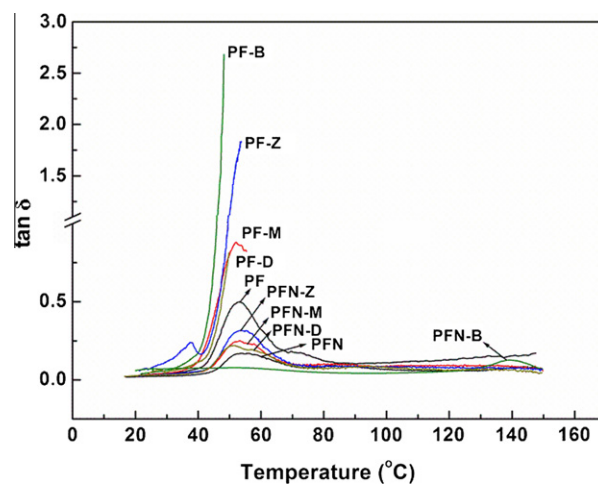

Fig. 7. tan δ curves of the bio-composites with and without MMT.

granules exhibit two main types of X-ray diffraction patterns, the A type for cereal starches and the B type for tuber and amylose-rich starches [26]. The crystalline peaks, observed at 2θ of 9.5° and 28.5° in Fig. 6, are due to A type of cereal starch such as wheat, potato and tapioca. All WAXD patterns of bio-composites with MMT showed similar X-ray crystalline peaks compared to PLA, but the intensities of crystalline peaks were decreased.

The basal spacing of 1.4 nm (using Bragg's function) has been reported for pristine MMT in the literature [27]. With the introduction of MMT, in our bio-composites, a peak at 2θ of 4.6° has been observed which reveals an intercalated structure with d spacing of 1.9 nm. The presence of crystalline peak at 22.5°, in Fig. 6, is related to the (0 0 2) plane of cellulose I. Benzilic acid gives very strong and distinct crystal peaks at 2θ of 7.4°, 10.7°, 13.0°, 14.5°, 16.5°, 18.9°, 20.5°, 21.9° and 24.0° at room temperature [28]. However, the diffraction patterns of PFN-B bio-composite showed only two dominant crystalline peaks at 14.5°, 16.5° which suggests the partial destruction of crystallinity in PFN-B. In literature, it has been reported that mandelic acid also shows several distinct crystalline peaks at 2θ of 24°, 26.7°, 30° and 30.8° [29]. The crystallinity of the mandelic acid in PFN-M has been reduced which is well confirmed by the absence of designated peaks of mandelic acid reported above. Reduction in crystallinity in the case of mandelic acid will only be possible if it interacts efficiently with PLA in the bio-composites.

3.3. Surface morphology and interaction between fibers and matrix

Plots of dynamic loss ($\tan \delta$) as a function of temperature for the PLA based bio-composites are shown in Fig. 7. The damping factor for all the bio-composites without the addition of MMT was very high indicating the low compatibility of the fibers with the matrix in absence of MMT. The stiffness of all the samples without the addition of MMT was so low that it cannot measure the damping factor till the programmed temperature of 150 °C and the experiment had to be discontinued near the glass transition temperature of the PLA (38.2 °C). However, with the introduction of MMT, the stiffness of the bio-composites increased to very high extent thus indirectly increasing the compatibility with further decrease in damping values. We have stated mandelic acid as an efficient additive due to low water uptake, high mechanical properties and high storage modulus of PFN-M than that of PFN-B. Damping factor for PF-D, with DCP as an additive, was similar to that of PF-M. This statement also holds true for all the additives in presence of MMT. To confirm the interfacial adhesion between PLA, fibers and additives, morphology studies of the bio-composites were conducted.
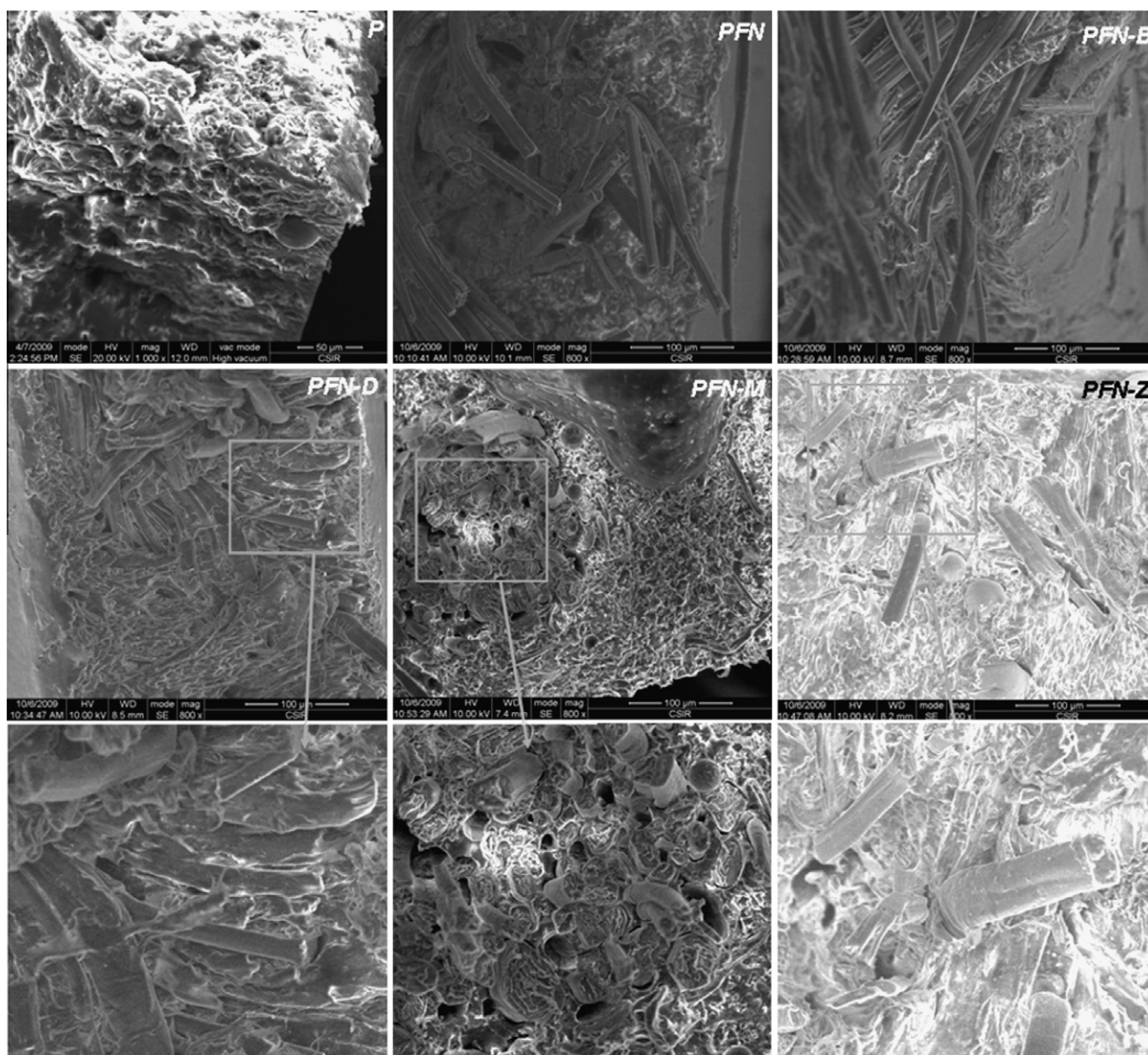

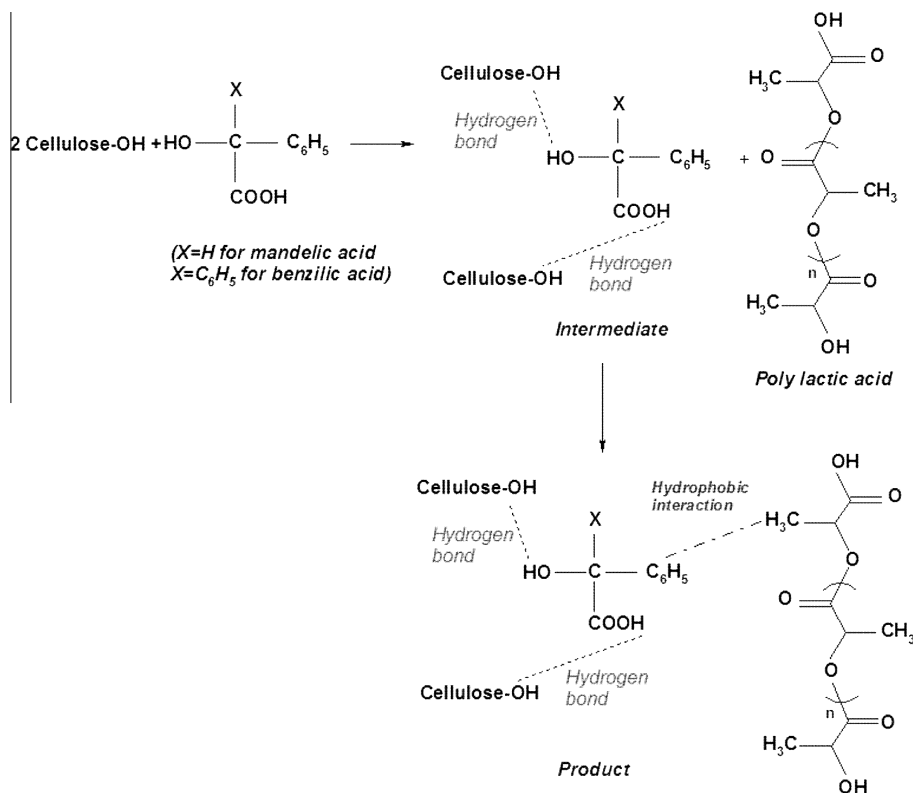**Fig. 8.** SEM micrographs (cross-section) of the bio-composites with MMT. The scale bar is 100 μm.

Fig. 9. Reaction schemes of PLA/flax fibers in presence of benzilic/mandelic acids.
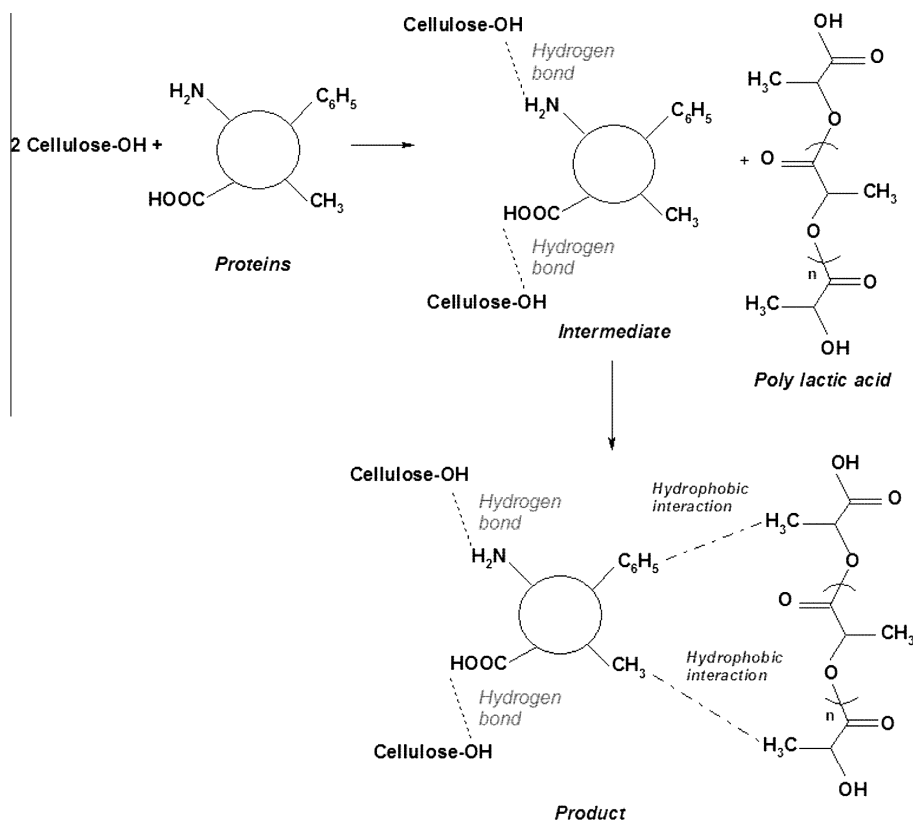

Fig. 10. Reaction schemes of PLA/flax fibers in presence of zein protein.

Fig. 8 shows SEM photographs of freeze-fractured surfaces of PLA based bio-composites in presence of MMT. It is seen that the cross-section of the neat PLA is very clean. However, in the case of PFN-B the fibers are protruding out without the trace of matrix on it, indicating that the interfacial adhesion in the presence of benzilic acid is worse and the fact is supported by low mechanical

properties (Table 1) and high damping factor (Fig. 7) as well as partial destruction of the crystallinity of benzilic acid (Fig. 6). There are no clear differences between the images of PFN-B and PFN samples. This may be due to the method which we have used to prepare the samples. In case of PFN-B, benzilic acid is not working as amphiphilic additive, as we have expected, and that is the reason why the SEM images of both PF and PFN-B look almost the same. Interestingly, in the case of PFN-D the fibers are well coated by PLA during fracture and are supported by high mechanical properties (Table 1) of the bio-composites.

Fig. 9 shows the proposed reaction scheme in case of PLA/flax composites in presence of mandelic or benzilic acid. The hydrophilic units (—COOH, —OH) of the mandelic or benzilic acid will interact through hydrogen bonding with the hydroxyl groups of the fibers to give the intermediate. Aryl groups of the intermediate will interact with alkyl groups of PLA through hydrophobic interactions to give the product. However, the presence of two aromatic rings in benzilic acid causes steric hindrance and thereby prevents the hydrogen bonding or hydrophobic interactions and this is well supported by the lowest mechanical properties (Table 1) and highest water uptake (Fig. 3) as well as highest damping factor (Fig. 7) for the PF-B and PFN-B composites. Fig. 10 shows the proposed reaction scheme in case of PLA/flax composites in presence of zein proteins. Zein protein is high molecular weight amphiphilic additive unlike mandelic and benzilic acid. In zein protein, COOH, —NH$_2$, C$_6$H$_5$ and —CH$_3$ groups are present in abundance. The hydrophilic units (—COOH, —NH$_2$) of the zein protein will interact through hydrogen bonding with the hydroxyl groups of the fibers to give the intermediate. Aryl and alkyl groups of intermediate will interact with alkyl groups of PLA through hydrophobic interactions to give product. In case of PF-D or PFN-D, dicumyl peroxide [C$_6$H$_5$—C(CH$_3$)$_2$—O—O—(CH$_3$)$_2$C—C$_6$H$_5$] at high temperature (80–85 °C) gives free radical [C$_6$H$_5$—C(CH$_3$)$_2$—O$^\cdot$]. Each free radical [C$_6$H$_5$—C(CH$_3$)$_2$—O$^\cdot$] extracts hydrogen from PLA and cellulose to give [C$_6$H$_5$—C(CH$_3$)$_2$—OH] and free radical of PLA and cellulose. Free radical of PLA and cellulose forms a bond to give PLA-cellulose fiber. From the proposed interaction in case of PF-D and PFN-D, it seems that the bond between PLA-cellulose fiber will be strong and this is further confirmed by the highest mechanical properties being observed (Table 1) for the PF-D and PFN-D bio-composites. Further work is in progress to prepare injection molded specimens with DCP and mandelic acid as additives, which will be reported later.

4. Conclusions

The introduction of MMT in the flax woven fabric reinforced PLA based bio-composites increased the mechanical properties and storage modulus of the bio-composites. Water uptake of the bio-composites decreased with the addition of MMT. However, the final properties of the bio-composites were dependent on the nature of the individual amphiphilic additive. The presence of DCP in bio-composites improves the mechanical properties. On the other hand, the presence of mandelic acid gives bio-composites with high storage modulus and low water uptake.

Acknowledgement

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