Effect of Nanoclay on Natural Fiber/Polymer Composites

Zhou Chen, Tairong Kuang, Zhaogang Yang and Xiaofeng Ren

Abstract Nanoclays play a significant role to improve composite performance by enhancing their properties such as thermal stability, mechanical strength, and barrier properties. Some of the important parameters contribute most to modify the properties of a variety of composites include the content, shape, size, and the affinity towards matrix material. With their enhanced performance, nanoclay filled polymer matrix based nanocomposites have drawn much attention in the materials industry. In this book chapter, the authors provide an overview of the effect of nanoclay on natural fiber/polymer composites, including the rheological properties, mechanical and thermal properties, morphological and structural properties, modeling of mechanical and rheological properties of nanoclay on natural fiber/polymer composites.

Keywords Nanoclay · Natural fiber · Polymer composites · Mechanical properties · Thermal properties

1 Introduction

Nowadays, fiber reinforced polymer (FRP) composites are widely applied in many areas, such as navigation, aviation, aerospace, building construction, medical industries because of their excellent performance (Chen et al. 2012, 2015a).

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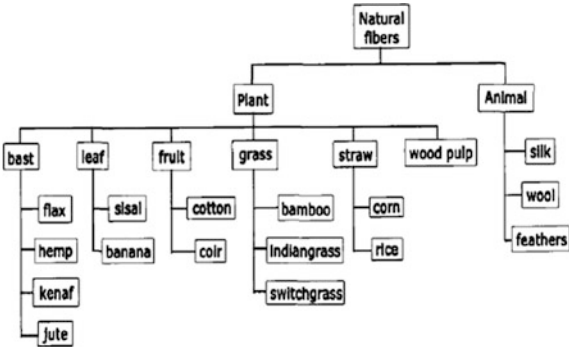


Fig. 1 The classification of natural fibers

However most of synthetic fiber reinforced polymer composites cannot be broken down, thus becomes a burden for the environment nowadays (Bajpai et al. 2013). Natural fiber is a renewable resource, and there are thousands of natural fibers available. Figure 1 shows the classification of natural fibers. Once natural fibers have been added to the biodegradable polymers, it can lead to the production of new biocomposites. Natural fibers have been used as possible alternative to conventional synthetic fibers such as glass fibers, chemical fibers, and carbon fibers (Mohanty et al. 2005). The natural composite structure generally composed of cellulose fibrils and lignin matrix presents high flexural strength. Further, natural fibers possess good electrical resistance as well as thermal and acoustical insulating. Thus it is possible that incorporation of the fibers into low-modulus matrix, e.g. polyester, leads to the wider application due to enhanced properties (Saheb and Jog 1999). Meanwhile, compared to inorganic fibers, they demonstrate many advantages, such as low cost and density (1.25–1.5 g/cm^3), high toughness, good biodegradability, as well as low tool wear. They could be widely used as the potential micro-reinforcements because of the improvement of mechanical properties, thermal, as well as structural properties of biodegradable polymer composites (Leng and Lau 2011).

In many applications, natural fiber reinforced polymer (NFRP) composites are gradually used to replace synthetic fiber reinforced polymer composites due to their being biodegradable and cost effective (Mallick 2008; Bajpai et al. 2012). Research shows that 50,000 MJ of net energy can be saved when 30 % of glass fibers are alternative by hemp fibers, equivalent to cutting 3 tons of carbon dioxide (CO_2) emissions. In addition, the results indicate that, compared to polypropylene (PP) reinforced with glass fiber, 21 % weight was reduced for PP reinforced with hemp. Due to new environmental regulations and depletion of oil resources, attempts have been made to replace the petroleum-based materials by natural fiber reinforced composites. The waste and recycled natural fibers is used to reinforce polymer which is a major step taken in promoting environmental sustainability (Bajpai et al. 2014). However, there are also several limitations of natural fibers, including high moisture absorption, low melting point and relatively narrow incompatibility with the polymer matrix (Taj et al. 2007; Alamri and Low 2012). Because the hydroxyl content of cellulose is very high, natural fibers are prone to absorb water, leading to deduction of the mechanical properties of composite such as flexural strength, flexural modulus and fracture toughness. When the temperature is higher than 200 °C, natural fiber degradation will occur, with hemicellulose degradation first, followed by the degradation of lignin. The degradation will cause odor, discoloration, release of volatiles, and reduction of mechanical properties.

Stress concentration and poor interfacial adhesion between natural fiber and polymer have been considered as a main cause of composites material brittleness. Thus, the technology of fiber surfaces and polymeric matrices modification have been used to improve the interface between natural fibers and polymer matrix (Uma Devi et al. 2004; Cantero et al. 2003; Qiu et al. 2011, 2012; Ren et al. 2012a, b, 2013a, b). Lots of researchers have been working on hygrothermal aging of natural fiber, and those researches have been successfully used in different load-bearing applications. Thermoplastic matrices (polyethylene, polypropylene, polyvinyl alcohol, polystyrene and polylactic acid) have been mixed with natural fibers to fabricate composites to obtain desired attributes (Patel et al. 2005; Rout et al. 2001).

In recent advances in the composites field, nanoparticles (nanoclays, carbon nanotubes or silicates nanoparticles) are added to improve the thermal, mechanical, and electrical properties of composite materials (Chen et al. 2015b). The size of conventional fillers is from 10 μm to 1 cm; however, the size of nanofiller ranges is from 1 to 500 nm. It indicates that the high aspect ratio of the nanoclays leads to a greater interfacial area, enhancing reinforcement properties. Nanoclays are also widely used in different industries (cable coatings, adhesives, inks, pharmaceutical and automotive) (Sattler 2011). Research found that nanoclays in the natural fiber/polymer system can improve the mechanical properties (Nguong et al. 2013). In order to obtain similar results, 3–5 wt% nanoclay is greater than 30 wt% for a conventional filler (Hetzer and De Kee 2008). Since most of the nanoclays are hydrophilic in natural state meanwhile unevenly distributed, they have to be organically improved to avoid agglomeration between the platelets in the dispersion media (Nazare et al. 2006; Bartholmai and Schartel 2004). The degree of exfoliation is increased by this improvement leading to increase the level of surface interaction. This improvement can be done through common dispersion techniques, i.e., exfoliation absorption, in situ polymerization, melt-intercalation or sonication (Wang et al. 2000; Haq et al. 2009). Surface modification of nanoclays have been used extensively in the fields of engineering and technology due to the improvement of properties such as strength (Song et al. 2005), modulus (Hetzer and De Kee 2008), solvent resistance (Mravčáková et al. 2006), biodegradability (Ray et al. 2003), and water vapor transmission resistance (Osman et al. 2004), and all the improvement is based on the uniformity of dispersion of nanoclays in polymer resin.

2 Rheological Properties

Well intellectual of the fluxional phenomenon is compulsive and the liquidity need to be guaranteed so that fibers can be fully processed and prepare composites with a variety of strength and thermal property. Polymer dispersion characteristics and flow characteristics of the resin are influenced by many factors, i.e., molecular morphology, molecular weight, size. The viscosity and flow of the material properties are influenced by the dispersion and deformation characteristics of enhanced nanoparticles. To master the processing performance and organizational structure to the material, it is necessary to know the flow property of polymer materials and nano enhanced phase. The research of liquidity and viscosity of reinforced material also makes analysis of material in melt state easier.

Sepiolite nanoclay has uniform grain size, high specific surface area, porosity, and therefore can be used as reinforced phase to greatly improve the flow performance of the nano reinforced material (Bilotti et al. 2008). Increase of the reinforcing particles can solve the problem of viscosity increase and improve the strength of the materials (Shen et al. 2005).

2.1 Effect on Viscosity

Bensadoun et al. (2011) prepared nanoclays modified flax fiber/unsaturated polyester resin (UPR) composites (FF/UPRs) with different forming methods and nanoclays (Tables 1 and 2). Nanoclays and styrene were used as the modified

Table 1 Properties of nanoclays (Bensadoun et al. 2011)

	Cloisite 11B	Cloisite 15A	Cloisite 30B
D-spacing (Å)	18.4	31.5	18.5
Density (g/cm^3)	1.9–2.1	1.66	1.98
Surface treatment	Dimethyl, salts with bentonite	Dimethyl, salt with bentonite	Alkyl quaternary ammonium bentonite

Table 2 Different forming methods of FF/SUPRs

No.	Dispersion method			Add	Remove (stirring + heat)
	Raw material	Modified material	Dispersion method		
0	Resin	/	Ultrasonication	Styrene	Styrene
1	/	Nanoclays + styrene	Ultrasonication	Resin	Styrene
2	Resin	Nanoclays + styrene	Ultrasonication	/	Styrene
3	Resin	Nanoclays	Ultrasonication	/	/
4	Resin	Nanoclays	Ultrasonication	Styrene	Styrene

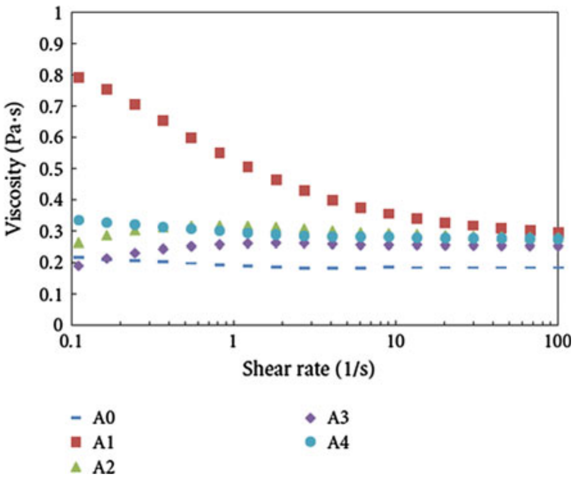


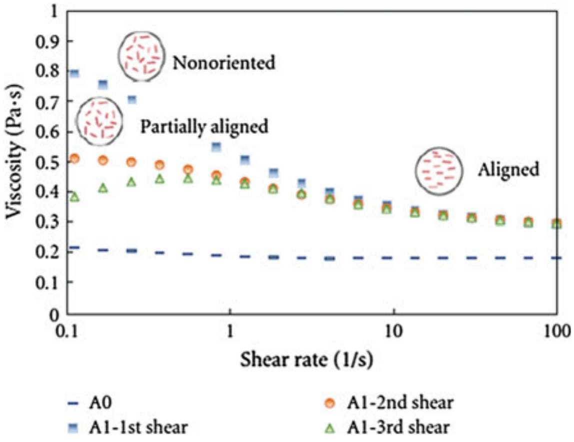
Fig. 2 Shear viscosity sweep at 23 °C for 3 %wt C30B nanoclay dispersed in R937 resin by different methods (Bensadoun et al. 2011)

material and dispersion media for resin, respectively. Styrene was either deleted or increased after ultrasonication to assure the same proportion.

As shown in Fig. 2, the viscosity of UPR with 3 wt% nanoclay has greatly improved compared to the UPR without nanoclay (No. 0). However, a non-Newtonian shear-thinning behavior appears in the No. 1 mixture, while No. 0 to the neat resin is similar to mixtures No. 2 to No. 4 in Newtonian behavior. The resin and the nanoparticles are able to a direct result of the connection in the non-Newtonian behavior of mix No. 1. These results show that the exfoliated and well-dispersed structure was able to produce in the only dispersion technique of No. 1. Due to the physical properties and intercalation in the polymer diffusion of MMT nanoclay, an exfoliated structure could lead to a higher interaction of surface (Carreau et al. 1997; Morrison 2001). Continuous shear measurements were conducted in No.1 dispersion method to study the change of orientation structure of MMT nanoclay. In the Fig. 3, during the rotation, the prepreg viscosity of 0.8 Pa s under the 0.1 (1/s) can be turned into 0.3 Pa s under the 100 (1/s). In the rotational axis, this shear force reduction trend is closely related to the orientation structure of strengthening nanoclay. When the test is started for about 1 min in first stage, the nanoclays have the tendency to recombine with the original stochastic construction. Consequently, the shear measurements show that the viscosity with low shearing rate in the first rotation has higher number than the second. It also applies to the third shearing stage, as was neatly demonstrated in Fig. 3. The numerical value of viscosity in three shear measurements is the same in 100 (1/s), which means the same reorganization of nanoclays for the three sweeps.

Duran et al. (2000) showed the similar discipline of MMT suspension in different shearing force testing, and Sinha (Ray and Okamoto 2003) observed that the composition with the addition of the nanoparticles altered for a performance of the linear viscoelastic polymer chains. The dispersant of styrene can facilitate uniform distribution of the nanoclays in polymer solution. The nanoparticles can accomplish

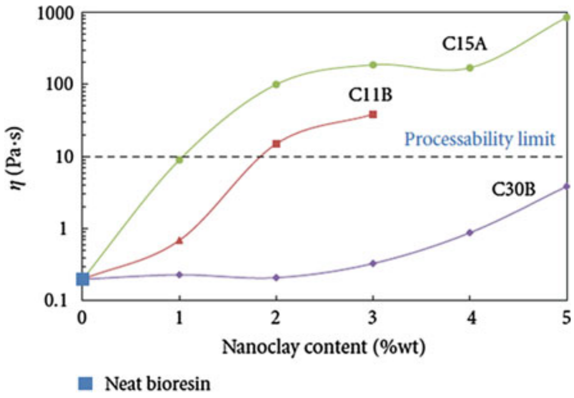
Fig. 3 Successive shear viscosity sweeps at 23 °C for 3 %wt C30B nanoclay dispersed in R937 resin by No. 1 method (Bensadoun et al. 2011)



the super-duper movement because of the low viscosity of styrene (0.762 mPa s). And the special intercalated-exfoliated structure can be kept by appending the polymer.

As shown in Fig. 4, the initial viscosities of UPR with three different nanoclays at 0.1 s^{-1} both increase with the content of nanoclays. However different nanoclays have different viscosity at the same content of nanoclays, the viscosity of C11B and C30B is lower than C15A. Nanoclays and the UPS have a higher surface interaction showing this phenomenon that it can lead to a possible high dispersion about C15A. The chemical d-spacing and the treatment of nanoclay platelets explained this difference. To wipe out sonication energy, the latter can also have an influence on the capacity of the particles. As is showed in Table 1, even though the particles of C15A and C11B have the same chemical treatment, a higher d-spacing belongs to C15A. Higher viscosity and the platelets that have a higher surface interaction improve the diffusion of the polymer macromolecules with a higher d-spacing. Although the chemical treatment of C30B and C11B was very distinct, their

Fig. 4 Viscosity at 23 °C for various types of nanoclays and percentage (Bensadoun et al. 2011)



d-spacing is similar. Therefore, the initial viscosity value will be affected due to the difference, for C30B is 0.28 Pa s and for C11B0.8 Pa s.

2.2 *Modified Nanoclays*

Veronica et al. (Morote-Martínez et al. 2011) improved the performance of UPR-coated natural stone by adding the natural sodium montmorillonite nanoclay (MMT) for modifying the rheology of the prepolymer solution. The changes of viscosity of the different MMT-modified UPR according to the shear rate of polymer solutions were shown in Fig. 5. The viscosity properties of all MMT-modified UPR polymer solutions showed Newtonian behavior, they will not be changed no matter if the shear rate increases. As shown in Fig. 6, the viscosity can be increased by more than three times by adding MMT. And it stabilized with

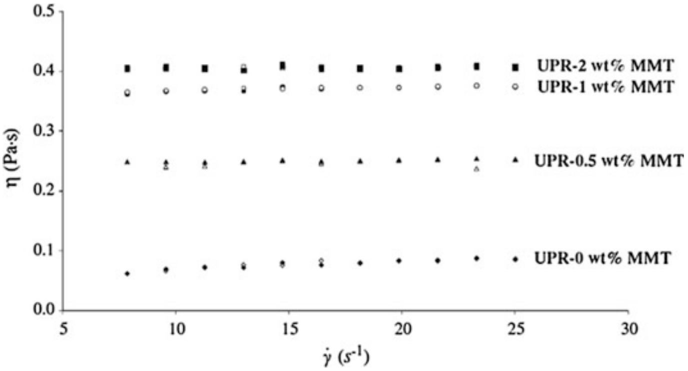


Fig. 5 Variation of the viscosity of the UPR-MMT as a function of the shearing rate (Morote-Martínez et al. 2011)

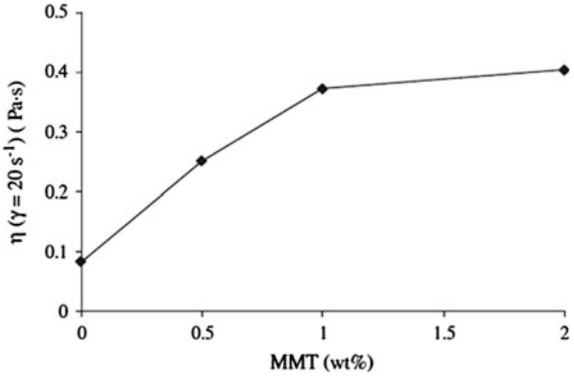


Fig. 6 Variation of the viscosity of the UPR-MMT as a function of the MMT content (Morote-Martínez et al. 2011)

the increase of the addition when the addition of MMT exceeding the 1 wt% limit. The reason of this phenomenon can be described as the unevenness of MMT nanoclay particles in the UPR.

Zhong et al. (2007) incorporated a modified MMT (Cloisite 20A) into wood reinforced polyethylene (PE) composites (MMT-W/PEs) with maleic anhydride grafted polyethylenes (MAPEs). The thermal expansion coefficient and the flexural strength of MMT-W/PEs are reduced by 60 and 24 % for 3 wt% nanoclay loading, respectively. Meanwhile the thermal deformation temperature and the flexural modulus increased by 10 °C and 10 %, respectively. However, the incorporation of the modified MMT had no significant effect on the viscosity of the MMT-W/PEs (Hetzer et al. 2009). Kumar et al. (Pratheep Kumar and Pal Singh 2007) prepared the nanoclay-modificated cellulose fibers/ethylene-propylene (EP) composites (N-M CF/EPs). The elastic modulus of EPs can be significantly improved by adding nanoclays and cellulose fibers from 773 to 1622 MPa, and the water absorption rate of CF/EPs can be reduced by 15 % as the nanoclays are added. The melt temperature of EPs can be increased up to 170 °C with the reinforcement of nanoclays and cellulose fibers. However, the breaking yielding stress, fracture length and elongation at break point are nothing breathtakingly different.

Two sorts of WF/HDPEs composites which comprise intercalated and exfoliated nanoclay were prepared by Lee et al. (2011), WF and HDPE here are the abbreviation of wood fiber and high density polyethylene, respectively. When the contents of wood fiber and nanoclay were different in the foamed WPCs, the die pressure would change with the die temperature differently; the functions between them were shown in Fig. 7. The varying degrees of nanoclay dispersion reflected on the die resistance, when the amounts of clay and wood fiber increased or the exfoliated clay incorporated, the die pressures increased.

Gu et al. (2010) systematically analyzed the effects of different modified nanoclays on wood fiber/linear low density polyethylene (LLDPE) composites (WF/LLDPEs). As shown in Table 3, modified MMT nanoclays can be categorized

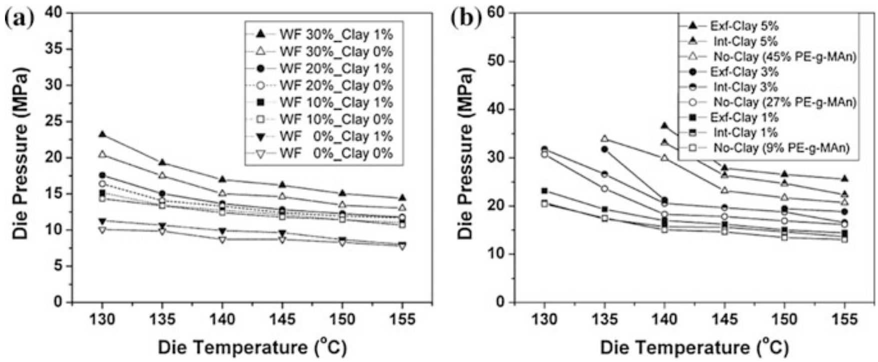


Fig. 7 Die pressure as a function of die temperature **a** with different wood fiber content and **b** with different clay content (30 % wood fiber) (Lee et al. 2011)

Table 3 Different modified nanoclays (Gu et al. 2010)

Type	Physical properties			
	Surfactant[a]	Tails	Particla size (μm)	Density (kg/m^3)
Cloisite® Na$^+$	None	–	2–13	336
Cloisite® 10A	125 meq/100g dimethyl benzyl hydrogenated tallow quaternary ammonium chloride	1	2–13	265
1.28 E	25–30 wt% trimethyl stearyl ammonium	1	8–10	420
1.34 TCN	25–30 % methyl dihydroxyethyl hydrogenated tallow ammonium chloride	2	16–22	300–360
1.44 P	35–45 wt% dimethyl dialkyl (C14–C18) amine	2	≤20	200–500
1.30 E	25–30 wt% octadecyl amine	1	8–10	410
1.31 ps	15–35 wt% octadecyl amine and 0.5–5 wt% aminopropyltriethoxysilane	1	≤20	200–500

[a] Tallow (alkyl) consists of 65 % C18, 30 % C16, and 55 % C14

into five families based on the varying structures of the surfactants except the Cloisite Na$^+$. The first one is the ammonium salts-altered nanoclay with one alkyl tail, such as the Cloisite 10 A and I.28 E. I.34 TCN is a typical example of the second one, the surfactant used here is a kind of amines with double tails. The third one like I.44P is the amines-modified nanoclay with double tails. I. 30E and I.31 PS are the representatives of the fourth family, which is changed by primary amine with one tail. There are hydroxyl groups attaching to either the tallow tail or the ammonium head in the surfactants of the last one like I.34TCN, which can exert an influence on the properties and structure of the composites.

PE nanocomposites can be prepared by a versatile process named melt compounding. At the same time, if the polymer was compatible with the clays, the nanoclays with lamellar structure can be combined with the polymer solution by melt intercalation. However in reality, hydrophilous nanoclays and hydrophobe polymeric resin are incompatible with each other at the virgin states. In order to improve the compatibility between clays and polymers, surface modification of the clay was commonly adopted (Hetzer and De Kee 2008; Fornes et al. 2002), alkyl groups with low molecular mass was introduced to convert the surface of nanoclay from hydrophile to organophile, which also results in the rise of interlaminar d-spacing (Tjong 2006). Figure 8 shows the FTIR spectra of the organo-nanoclays. The typical bands for oxides were found around 1050 cm^{-1}, which belong to the characteristic bands of Si–O–Si or Si=O, and the broad bands at 3600 cm^{-1} are associated with the hydrates including Al–OH and Si–OH (Wu et al. 2002). The bands of the bound H_2O appeared at 1640 cm^{-1} (Frankowski et al. 2007). At 523 and 466 cm^{-1}, two characteristic bands that elastic vibration by Si–O and flexural vibration by Al–O and Si–O of MMT could be found (Wang et al. 2009).

As the symmetrical and asymmetrical chains of CH_2 and CH_3 stretched, two apparent peak values of modified-nanoclays at 2924 and 2846 cm^{-1} can be found

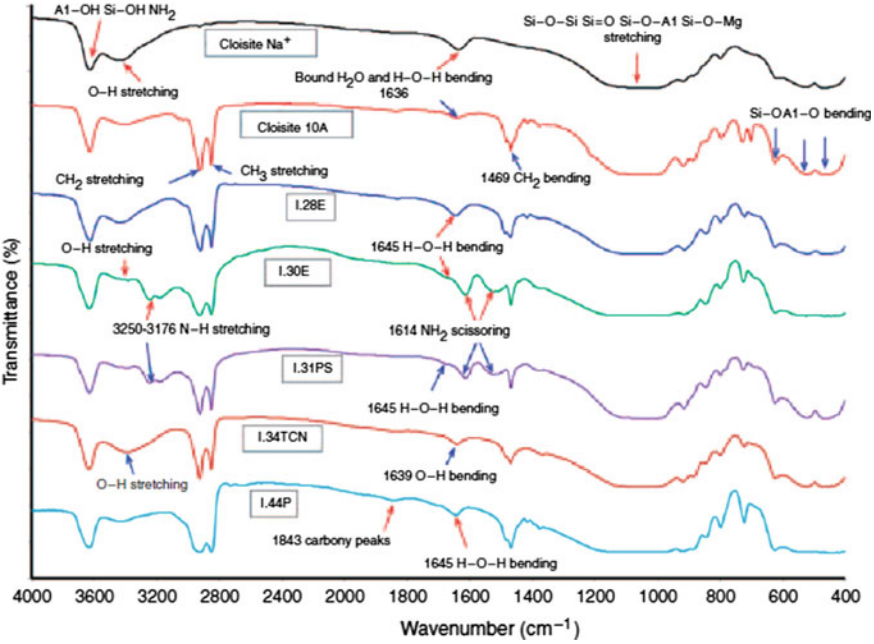
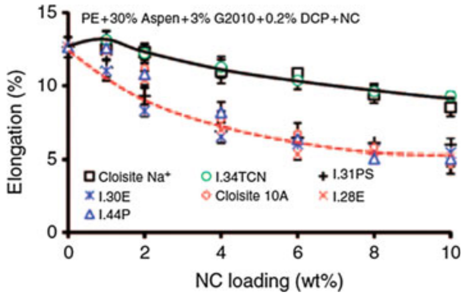


Fig. 8 FTIR spectra of organo-nanoclays with different surfactants (Gu et al. 2010)

(Park et al. 2005). The CH_2 bending corresponds to the band was at 1469 cm^{-1} (Park et al. 2005). The N–H stretching vibrations reflect two bands in the spectra of I.30 E and I.31 PS near 3200 cm^{-1}, which means that the surfactant in the modified nanoclay has amine groups (Wang et al. 2009). The band at 1639 cm^{-1} was further strengthened as indicated in Fig. 8.

Figure 9 shows the impacts of different nanoclays on the tensile property of WF/LLDPEs. The elongation of WF/LLDPEs decreases with the incorporation of nanoclays, and the growth process can be divided into two stages: the growth rate is dramatic changing under 10 wt% of nanoclays, and then the elongation of Cloisite Na^+, I.34 TCN and I.44 P decreases up to 33, 33 and 63 %, respectively

Fig. 9 Effects of nanoclays on elongation of WF/LLDPEs (Gu et al. 2010)



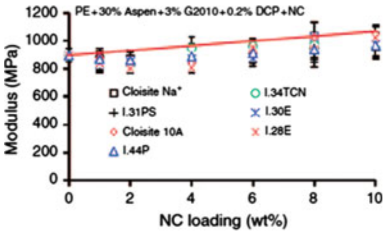


Fig. 10 Effects of nanoclays on modulus of WF/LLDPEs (Gu et al. 2010)

(Lee et al. 2005). This indicates that the surfactants of nanoclays have a critical impact on the interactions between nanoclays and composites. For the WF/LLDPEs including Cloisite 10 A and I.28 E, the elongation at maximum load is about 5 and 9 %, while for the WF/LLDPEs with I.34TCN, (Cloisite Na^+) or without nanoclays, the elongation is up to 12.6 %. The modulus as a function of nanoclays loading is shown in Fig. 10. It is easily to find that the addition of nanoclays make WF/LLDPEs more brittle, corresponding to the increase of modulus in Fig. 10. The stretch modulus show a gradual increase by adding nanoclays, and it peaked at 1000 MPa with 10 wt% nanoclays. This was because the torque and viscosity would be strengthened by the addition of nanoclays, and an increase of the contribution of crystallinity may be caused by the nanoparticles.

2.3 Storage Modulus and Loss Modulus

Rajini et al. (2013a) utilized dynamic mechanical analysis to test the dynamic rheological properties of different contents of nanoclay (0–5 wt% MMT) modified coconut sheath/polyester composite (CS/Ps), such as storage modulus (E′) and loss modulus (E″).

When the temperature is above T_g in the rubbery plateau region, the E′ value of the nanoclay incorporated composites is higher than unfilled composites. It illustrates that the dynamic storage modulus of CS/Ps increased with the addition of nanoclay. The dispersed nanoclay in the state of exfoliated or intercalated would produce efficient stress transition between the fiber and polymer resin at the nanoscale level, resulting in an effect of secondary reinforcement with CS/Ps. It can be observed that the modulus was enhanced because of the large surface-to-contact ratio of nanoclay with polymer in the hybrid nanocomposites, and it can also find the intercalation of nano-multilayers in the chains of PE (Rajini et al. 2012). Due to the strengthening of nano-scale second phase, the thermal stability of nanocomposites would be enhanced with the temperature increasing. At about 100 °C, the E′ of pure CS/Ps is 812 MPa, and the E′ value of CS/Ps with 2 and 3 wt% nanoclay keeps on increasing until more than 1580 MPa. However, evident improvement in E′ was not found with further addition of nanoclay, and it will even decrease the E′ when adding 5 wt% nanoclay. This can be interpreted as the reduction of the efficient stress transition caused by the formation of agglomeration and clustering of nanoclay.

3 Mechanical and Thermal Properties

In this section, the mechanical and thermal properties of composites were comprehensively studied and introduced. Such natural fibers/nanoclay materials are summarized in Table 4.

3.1 Mechanical Properties

Nano-clay reinforced polymer/natural fiber nanocomposites have received much attention due to their excellent characteristics which include improved physical, thermal, and mechanical properties. The addition of nano-clay to the polymer/natural fiber composites resulted in the change of mechanical properties, which providing an effectively way to board the application of polymers in industry area (Table 5).

Table 4 Representative work on nanoclay based natural fiber reinforced polymer composites

Matrix	Filler	Reference
Polypropylene (PP)	Hemp fiber/nanoclay	Kord (2012)
Polypropylene (PP)	Pineapple leaf fiber/nanoclay	Biswal et al. (2009)
Polypropylene (PP)	Banana fiber/nanoclay	Biswal et al. (2011, 2012)
Polypropylene (PP)	Bamboo fiber/nanoclay	Rahman et al. (2014)
Polypropylene (PP)	bagasse fiber/nanoclay	Nourbakhsh and Ashori (2009)
Polyethylene (PE)	Wood fiber/nanoclay	Lei et al. (2007), Lee et al. (2010)
High density polyethylene	Bamboo fiber/nanoclay	Han et al. (2008)
Poly (lactic acid HDPE)	Banana fiber/nanoclay	Kumar et al. (2013)
Polyester	Soybean oil/natural fiber/nanoclay	Haq et al. (2008)
Polyester	Wild cane grass fiber/nanoclay	Prasad et al. (2015)

Table 5 Tensile, flexural and impact properties of biocomposite and its bionanocomposites (Sajna et al. 2014)

Sample	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (J/m)
PLA + SiB(70/30)	66 ± 3	102 ± 1	150 ± 1.45
PLA + SiB + C30B	67 ± 1	180 ± 3	120 ± 3.45
PLA + NSiB (70/30)	65 ± 5	96 ± 4	143 ± 1.37
PLA + NSiB + C30B	67 ± 5	105 ± 4	119 ± 2.89

NSiB silane-treated fibre; *PLA* poly(lactic acid); *SiB* silane-treated fibre

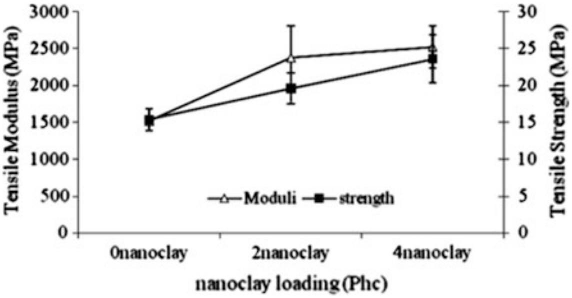


Fig. 11 Effect of nanoclay content on tensile strength and modulus (Najafi et al. 2012)

3.1.1 Tensile Properties

Najafi et al. (2012) found that the incorporation of nanoclay with MAPP as compatibilizer to PP/reed flour fiber composites significantly improved the tensile strength and Young's modulus from 14.6 and 1390 MPa to 28.7 and 2630 MPa, respectively (Fig. 11).

Nayak et al. (Biswal et al. 2009) also reported that the addition of modified nano-clay improves the mechanical strength of PP/pineapple leaf fiber. Also, the presence of MA-g-PP could also contribute to improvement in tensile strength. Similar improvement in the tensile strength was reported by many other works (Faruk and Matuana 2008; Kord and Kiakojouri 2011; Han et al. 2008; Chen and Yan 2013; Alamri et al. 2012). However, Davis D.C. et al. (Withers et al. 2015) reported that at higher nanoclay loadings large aggregates could be formed in the matrix that causes a reduction in mechanical strength. Therefore, the improvement of the tensile strength and modulus is dependent on the dispersion and morphology of nanoclay in the polymer/fiber composites (Fig. 12).

3.1.2 Flexural Properties

Great flexural strength can be achieved in the hybrid composites when nanoclay reinforced polymer/natural fiber was acted as the matrix. The dispersions of nanoclay on the composites are still important for improving the flexural properties. Also, it was found that composites with MAPP treated nanoclay provided significantly higher flexural strength and moduli, compared with untreated nanoclay composites. Ashori et al. (Tabari et al. 2011) indicated that PP/Wood flour fiber composites made with 3 % nanoclay and 5 % MAPP could achieve highest flexural strength and modulus than pure PP and PP/3 % nanoclay with 2.5 % MAPP treated. The enhancement in flexural properties was mainly ascribed to the improved adhesion between polymer composites matrix and nanoclay itself.

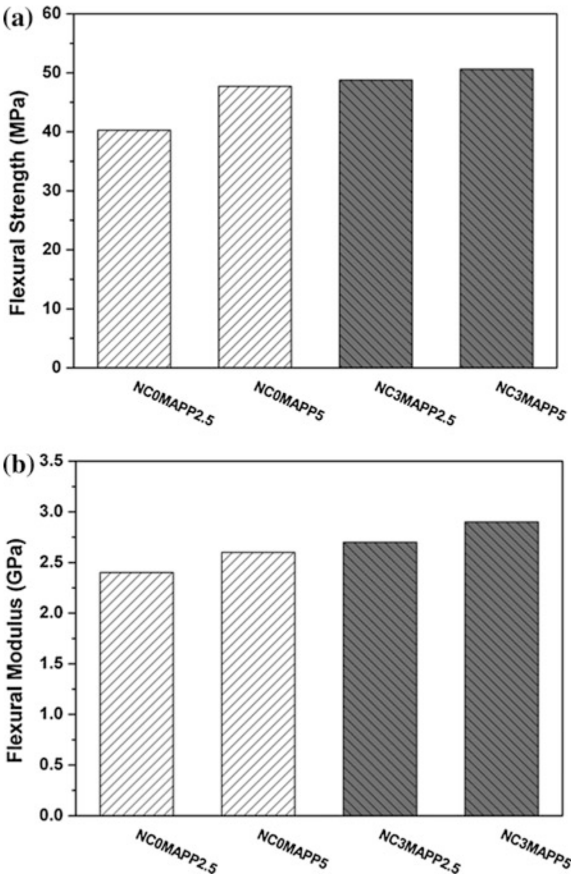


Fig. 12 Comparison of flexural properties of composites as function of the nanoclay and coupling agent loading (Tabari et al. 2011)

3.1.3 Impact Properties

In the presence of nanoclay in the polymer/natural fiber composites, the impact strength would be reduced because the nanocomposites become more brittle, thereby resulted in lower resistance for fracturing. Nayak S.K. et al. (Sajna et al. 2014) studied the addition of nanoclay on the poly (lactic acid) (PLA) with banana fiber composites. They found that the bio-nanocomposites presented maximum tensile and flexural properties than that of pure PLA, whereas the impact strength of composites was reduced due to the inherent brittle of matrix.

3.2 Thermal Properties

In the study of polymers and their practical applications, it is important to understand the thermal properties, which including thermal stability, thermal expansion, glass transition temperature, melting temperature etc., of polymer nanocomposites. In general, the incorporation of nano-clay into polymer matrix could efficiently improve the thermal properties of nanocomposites. Thus, adding nanoclay into polymer/natural fiber composites has attracted more attentions in the past decades.

3.2.1 Thermal Stability

Thermogravimetry was as a way for investigating the thermal stability of polymer composites. The thermal stability is a very important parameter which should be taken into account when choosing polymers for engineering use. Thermal stability of nanocomposites can be investigated using a thermogravimetric analyzer. The test sample was heated from air temperature (room temperature) to desired temperature (above melting temperature) at a speed of desired heating rate (5, 10, 20 °C/min) under nitrogen atmosphere. For polymer/fiber composites, the relatively low thermal stability of these fibers limited the composites application in industry. Thus, it is urgent to find an efficiently method to improve the thermal stability of polymer/natural fiber composites, thereby boarding its application value. Hezer et al. (Xu and Van Hoa 2008) found that the incorporation of nanoclay to the polymer/wood fiber systems increased their thermal degradation onset temperature, which means the thermal stability of polymer/wood fiber composites was improved. Also, Nayak et al. (Biswal et al. 2011) investigated the thermal degradation behavior of PP/banana fiber/nano-clay, indicated that adding banana fiber into PP/nanoclay nanocomposites occurred a two-stage decomposition behavior (Fig. 13), which mainly due to the dehydration and thermal cleavage at first stage and aromatization involving the dehydration reaction at second stage. Moreover, the addition of nanoclay has been shown to reduce the thermal expansion coefficient of polymer/natural composites.

3.2.2 Thermal Properties

Thermal properties, which including glass transition temperature, melting temperature and crystallization behavior etc., are very important issue when we select which polymer to process and which polymer to use. The thermal properties of nanocomposites were studied by differential scanning calorimetry (DSC). DSC tests were performed at a heating and cooling rate of 5, 10 or 20 °C/min under nitrogen atmosphere protection environment to study the thermal properties of composites. The test samples were first heated to desired temperature (above melting temperature) and kept isothermal at this temperature for 3–5 min to eliminate thermal history of the sample, then cooled to room temperature and subsequently scanned to desired temperature at a heating rate of desired heating rate (5, 10, 20 °C/min).

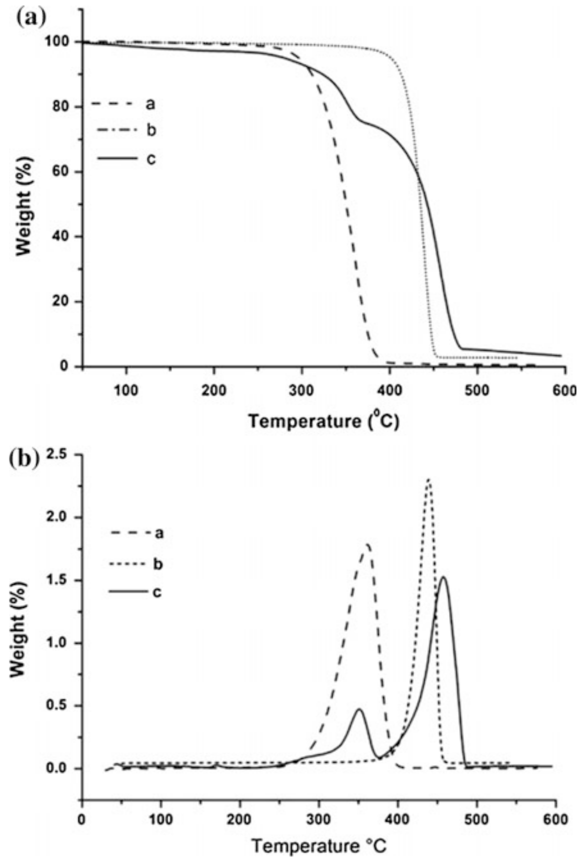


Fig. 13 TGA and DTG curve of PP, OPP, and OPP/MBF nanocomposites (OPP PP/nanoclay composites; OPP/MBF PP/nanoclay/mercerized banana fiber) (Biswal et al. 2011)

The degree of crystallinity (χ_c) of polymer was determined by Eq. (1) (Benhamou et al. 2015)

$$\chi_c = \frac{\Delta H_m - \Delta H_c}{\varphi \times \Delta H_m^0} \times 100\,\% \tag{1}$$

where, ΔH_m^0 is the melting enthalpy and ΔH_c is the crystallization enthalpy obtained by the DSC curves. ΔH_m^0 is the enthalpy of 100 % crystalline polymer sample. Moreover, it is well known that Avarami equation was normally used to analyze the rate of crystallization. The Avarami equation was presented as below (Guo et al. 2015):

$$X_t(t) = 1 - e^{-Kt^n} \tag{2}$$

where, K and n are important parameters for understanding the crystallization mechanism. In general, the addition of fiber into polymer matrix could be reduced the crystallization rate, whereas the addition of nano-clay into polymer/natural fiber composites would be shorten the crystallization time and reached the peak quickly. Also, to investigate the nucleation effect of nano-clay on PP/natural fiber composites, many researchers also studied it by Avarami equation. The values of K and n were calculated by plotting log $[-\ln(1 - X_t)]$ versus log(t); n and log (K) are the slope and the intercept values, respectively. They found that there was a remarkable decrease in n, increase in K and the rate of crystallization, which indicates that the nanoclay functions as the nuclearing agent in the composites and thus enhances the degree of crystallinity and rate (Di Maio et al. 2004; Fornes and Paul 2003; Yuan et al. 2006).

The aim of this section was to investigate the benefits of reinforcing polymer/natural fiber composites with nanoclay filler. In most cases, the addition of nanoclay into polymer/natural fiber composites led to a significantly increase in both the mechanical and thermal properties. It will lead to expand the application area of polymer itself due to the most promising and encouraging mechanical and thermal properties. Further research on polymer/natural fiber/nanofiller composites not only used in automotive and industry applications, but also it should be explored further applications on biomedical areas.

4 Morphological and Structural Properties

4.1 Nanoclay-Modified Polymer Matrix

The best way for analyzing morphology of nano composites is transmission electron microscopy (TEM). It can show the size and integrity of nanoparticles from only a few nanometers to hundreds of nanometers. It can describe the decomposition and reduction of agglomerated, non-agglomerated and overlapped structures of nanoclays. Meanwhile it can reflect the discrete degree of the nanoclays in different states in polymer matrix. Figure 14 shows the three different kinds of dispersion of nanoclay in polymer matrix. Referring to immiscibility in Fig. 14, the nanoclay platelets exist in particles which composes of, to some extent, tactoids or aggregates of tactoids, just as they are in the organoclay powder, there is no separation of platelets.

Ali et al. (Ali and Ahmad 2012) focused on the mechanical property and microstructure of MMT-modified empty fruit bunch/polyurethane foam composite (EFB/PUFs). As shown in Fig. 15a, b, the aluminum and silica elements from the MMT distributed uniformly in the composite. MMT is placed at the strut of the cell structures, and with partially exfoliated and intercalated morphologies, MMT platelets were well distributed (Fig. 15c, d). This nanoclay reinforced structure leads to the high compressive modulus and strength of EFB/PUFs.

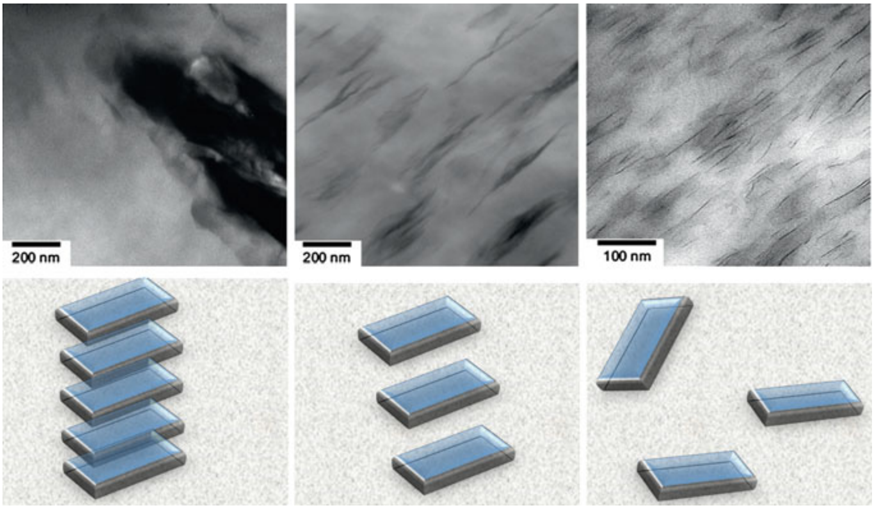


Fig. 14 Three different kinds of dispersion of nanoclay in polymer matrix **a** immiscible dispersion, **b** intercalated dispersion, **c** exfoliated dispersion

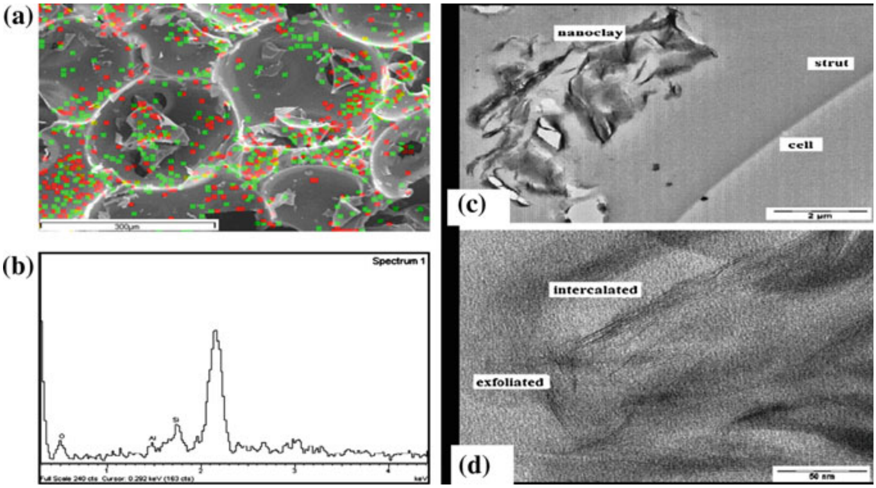


Fig. 15 The micrographs of EFB/PUFs **a** SEM and mapping elements, **b** EDX curves of traced elements, **c** and **d** TEM of EFB/PUFs and nanoclay (Ali and Ahmad 2012)

Islam et al. (2015) studied the tensile fractures morphology of wood fiber and coir reinforced PP composites with MMT nanoclay. As shown in Fig. 16, the wood fiber/PPs, coir fiber/PPs and wood fiber/coir/PP hybrid composite all had rough surface. It demonstrates the interfacial binding force between the natural

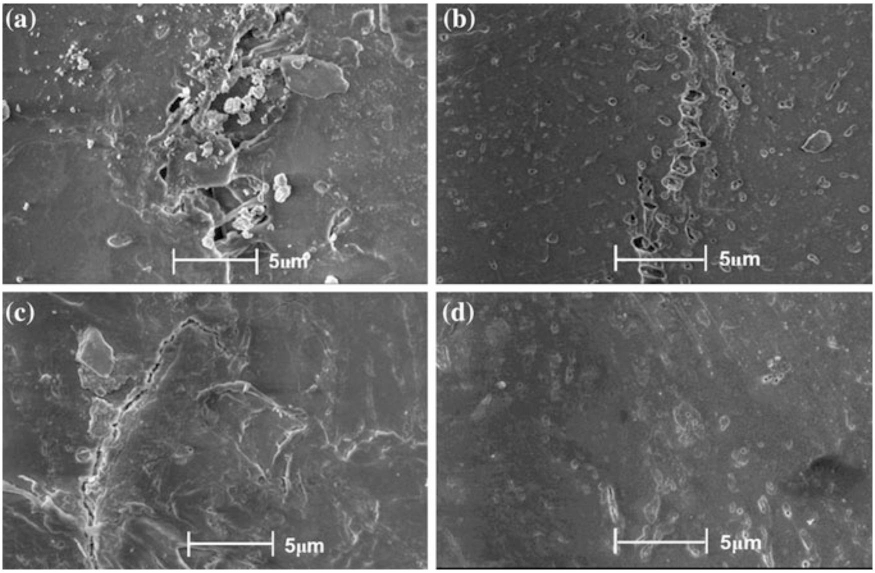


Fig. 16 SEM of the tensile fracture surfaces of the **a** wood fiber/PP composite, **b** coir/PP composite, **c** wood fiber/coir/PP hybrid composite, and **d** MMT-modified wood fiber/coir/PP hybrid composite (Islam et al. 2015)

fibers and during impact, polymeric matrix was weak to resist fiber pull-out, as the energy consumption was small. The MMT-modified wood fiber/coir/PP hybrid composite exhibited a smoother surface than the single fiber composite. As a result, high interfacial adhesion and surface smoothness is obtained by the addition of nanoclay in the hybrid composite, it also increased the mechanical properties of the hybrid composite (Smart et al. 2008).

4.2 Natural Fiber

Kovacevic et al. (2015) researched on the influence of MMT nanoclay modified Spartium junceum L. fiber (SJLF) on thermal properties of SJLF/ PLA composites. Figure 17 shows the SEM picture of pure SJLF, NaOH-treated SJLF, MMT-treated SJLF, and MMT-citric acid (CA)-treated SJLF reinforced PLA composites. The surface of pure SJLF/PLAs was smooth and regular compared with other composites. With the additional treatment of the SJLF, there is increasing roughness on the surface of composites from Fig. 17a to d. With the crosslinker (CA) introduced into the MMT-treated SJLF/PLAs, the size range of clusters of nanoclay became larger.

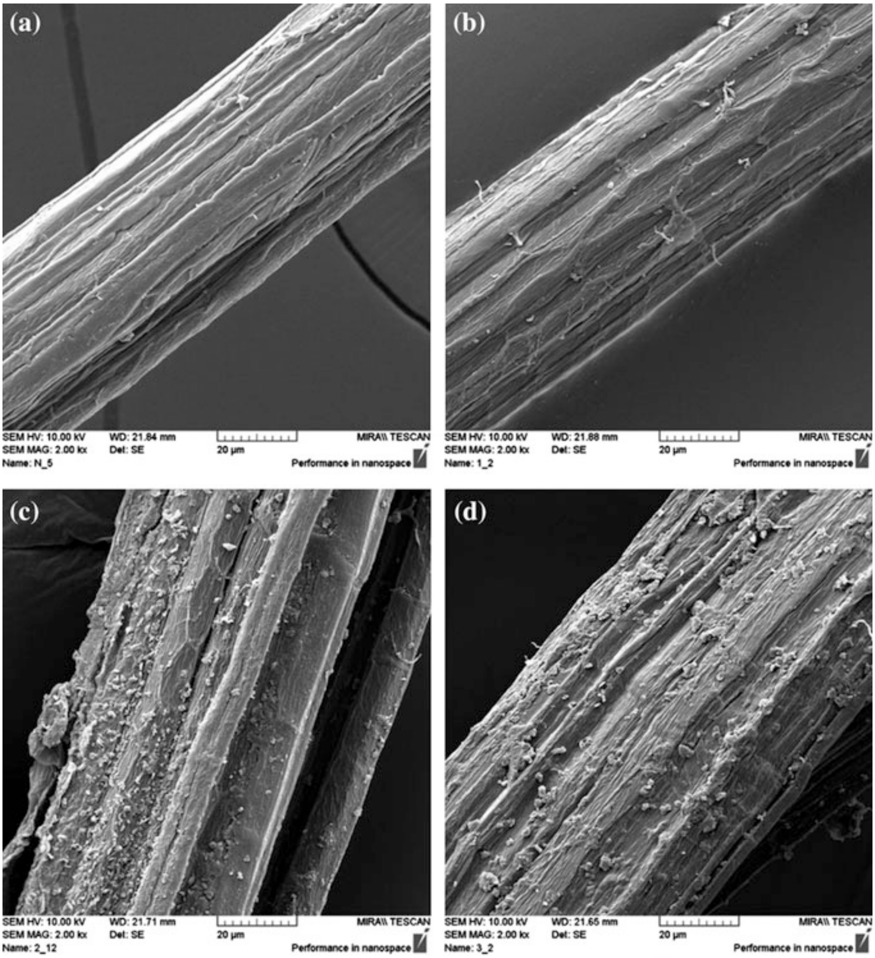


Fig. 17 SEM of **a** pure SJLF, **b** NaOH-treated SJLF, **c** MMT-treated SJLF, and **d** MMT-CA-treated SJLF reinforced PLA composites (Kovacevic et al. 2015)

Figure 18 shows the SEM picture of tensile fracture surface of the four composites above. Interface debonding and fiber pull-out were shown in (a) and (b). The interfacial adhesion between the pure SJLF and matrix was lower (strength of composite is 41.87 MPa) than NaOH-treated SJLF (strength of composite is 42.65 MPa). The MMT-treated SJLF/PLAs had a low strength (19.81 MPa) and fiber-matrix interface separation of the composite was observed (Fig. 18c). The MMT-CA-treated SJLF/PLAs showed smooth fractured surface (Fig. 18d) and good mechanical property (46.67 MPa). It illustrates that the combination of nanoclay and modifier may increase the interaction between polymer and matrix natural fiber.

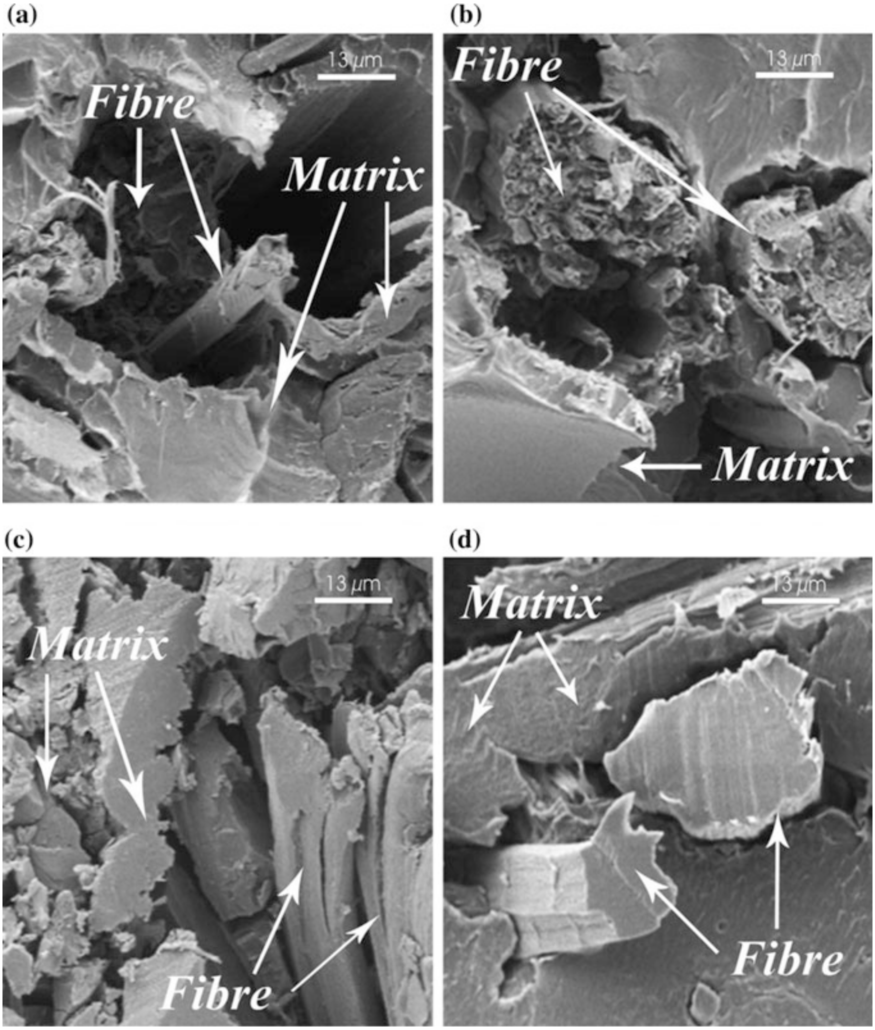


Fig. 18 SEM of tensile fracture surface of **a** pure SJLF, **b** NaOH-treated SJLF, **c** MMT-treated SJLF, and **d** MMT-CA-treated SJLF reinforced PLA composites (Kovacevic et al. 2015)

5 Modeling of Mechanical and Rheological Properties

5.1 Computation Model for Theoretical Modulus

To estimate the composite properties P^*, we can use the micromechanical analysis by the properties of each components according to the rule of mixtures:

$$\mathrm{P^* = P_f \times V_f + P_m \times V_m} \tag{3}$$

In Eq. (1), the properties of the fibers ($\mathrm{P_f}$) and matrix ($\mathrm{P_m}$) have influence on the homogenized property P through their volume fractions $\mathrm{V_f}$ and $\mathrm{V_m}$. The rule of mixture regards to the interface between phases as perfect condition, which means ignoring the effects of fibers and matrix on each other. Two new coefficients n and g relying on the individual phases and the effective property evaluated by rule of mixture model were put forward by Halpin and Tsai (Halpin and Kardos 1976), which can compensate the effect of the interface condition on the composite effective properties:

$$\xi = \frac{P_f(P^* - P_m) - V_f \times P^*(P_f - P_m)}{P_m(P_f - P^*) - V_m(P_f - P_m)} \tag{4}$$

$$\eta = \frac{P_f - P_m}{P_f + \xi \times P_m} \tag{5}$$

To be suitable for non-perfect interface conditions, the Halpin-Tsai model which estimates the effective properties of unidirectional composite materials could be demonstrated by the following equation:

$$P^* = \frac{P_m(1 + \xi \times \eta \times V_f)}{1 - \eta \times V_f} \tag{6}$$

The composites of flax fiber/soy protein resin (FF/SPRs) modified with nanoclay (Cloisite $\mathrm{Na^+}$) were prepared by Huang et al. (Huang and Netravali 2007). Moreover, they provided the theoretical modulus through the calculation of mixture:

$$\mathrm{E_c = E_y V_y + E_m\left(1 - V_y\right)} \tag{7}$$

When the fiber volume percentage ($\mathrm{V_y}$) is 48 %, modulus $\mathrm{E_y}$ is 12.1 GPa and modulus of resin $\mathrm{E_m}$ is 969 MPa, the composite modulus $\mathrm{E_c}$ calculated was about 6.3 GPa. Meanwhile, the experimental Young's moduli of FF/SPRs with and without nanoclay were 4.3 and 3.8 GPa, respectively. In the process of fabrication, both the loss of alignment caused by resin shrinking and voids generated in the composites resulted from water vaporization can lead to the difference between the calculated and experimental values. The process can be slower or divided to two or three stages in order to solve these problems.

Yeh et al. (2005) modified the wood fiber/polypropylene (PP) composites (WF/PPs) with layered silicates. MAPEs also used as a compatibilizer. It is demonstrated that the Young's modulus of WF/PPs was increased from 4.2 to 4.58 GPa with a 10 wt% clay loading by the addition of layered silicates. Besides, the adhesion between polymer matrix and wood fibers became poor due to the incorporation of layered silicates to the wood/PP matrix. So it was guessed that the adhesion between the polymer matrix and wood fibers could be improved by the addition of more compatibilizer. The following relation is a modified mixing rule which the modulus of layered silicates reinforced WF/PPs could be expressed:

$$E_c = E_f \xi_1 \xi_0 V_f + E_m(1 - V_f) \tag{8}$$

In the equation, E_c, E_f, and E_m represent the moduli of the composite, fiber and matrix, respectively, V_f means the volume fraction of fiber, $\xi_1\xi_0$ are length and orientation correction factors, respectively.

5.2 *Dynamic Mechanical Model*

Rajini et al. (2013b) examined the effect of MMT addition and surface treatment of coconut sheath on CS/Ps. To research the impact of nanoclay addition on free shaking characteristic, they have tested the natural frequency and modal loss factor associated with some low frequency bending modes in all cases. Modal damping factor ($\zeta = \Delta\omega/2\omega_n$) of first three modes are gained by the half power bandwidth method for each case.

The analytical and numerical model is mainly based on the assumption that the CS/HPs are quasi-isotropic. The following equation is to express the angular natural frequencies of first three modes of a cantilever isotropic beam:

$$\omega_n = \beta_n^2 \sqrt{EI/\rho A L^4} \tag{9}$$

where E represents the Young's modulus, I means the area moment of inertia, A is the cross-sectional area, L is the length of the beam, ρ means the density of the beam, and β represents the first n lowest frequency bending modes.

The natural frequencies estimated experimentally are in accordance with analytical and numerical results. As a result of the increased surface area exposed by the nanoclay leading to high internal damping, the fiber and matrix interface will be improved and the frictional resistance and mechanical interlock can be supplied by the incorporation of nanoclay with fiber surface (Ávila et al. 2008). Because the interface between fiber and matrix is weak as a result of the agglomeration and void formation of clay platelets, the damping ratio value becomes reduced as the increase of nanoclay percentage (>3 %).

5.3 *Rheological Properties of Composites*

The amount of the particles in the mixture has great influence on the rheological properties. To explain the effect of filler concentration on the viscosity of suspensions, there are a lot of equations have been put forward. The following relation is one of the equations which describe the effect of volume fraction of the particles φ on the zero-shear viscosity η_0 (Marcovich et al. 2004):

$$\eta_0 = \eta_{0s}(1 - \frac{\varphi}{\varphi_m})^{-b} \tag{10}$$

where η_0 is the zero-shear rate viscosity of the solvent, φ is the volume fraction of the particles, φ_m is the volume fraction at maximum packing and b is an exponent, which is equal to 2 for spherical particles. The Carreau-Yasuda model (Carreau et al. 1997) shown on Eq. (7) is the most common model used for non-Newtonian flows.

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda\gamma)^\alpha]^{(n-1)/a} \tag{11}$$

where η is the shear viscosity, η_0 is the zero-shear rate viscosity, η_∞ is the limiting viscosity at large shear rates, γ is the shear rate, λ is a relaxation time, n is the pseudoplastic parameter (power-law), and a is a parameter which is associated with the curvature in the transition zone between η_0 and the power-law region. Generally, setting $a = 2$ and $\eta_\infty = 0$ can have a good fit which lead to the Carreau model. At last, a simple power for the complex viscosity law expression can represent observed behavior for highly concentrated materials (Marcovich et al. 2004):

$$\eta^* = h(\omega)^{n-1} \tag{12}$$

where $\eta*$ represents the complex viscosity, h is a constant, ω is the frequency (rad/s) and n is a power-law index.

The storage modulus (E′), loss modulus (E″) and complex viscosity (η*) are the most important characteristic parameter in dynamic rheological properties studies (Ying-Chen et al. 2010). The storage modulus (E′) takes as a measure of the energy stored in the materials and recovers from its per capita. It depend on what rearrangements can happen during the period of oscillation, which uses to evaluate the elastic behaviors of the materials. In addition, the energy squandered or lost per capita of sinusoidal deformation is measured by the loss modulus (E″), and it is representative of the viscous behaviors. The viscosity parameter is a measure of the resistance to flow, and the complex viscosity defined as below especially (Shroff and Mavridis 1999):

$$\eta^* = (E'^2 + E''^2)^{1/2}/\omega \tag{13}$$

5.4 Crystallization Kinetics Model

Among the natural fiber plastic composite polymers, there are around 80 % of them semicrystalline polymers. It contains four kinds of crystallization behavior of the polymer matrix. Such behaviors are imperative in determining the final mechanical and thermal properties of the composites (Lenes and Gregersen 2006; Zafeiropoulos et al. 2001).

The relative crystallinity X(t) is the proportion value (crystallized volume/total crystallizable volume) at time t and it was described as following (Zhang et al. 2006):

$$X(t) = \frac{\int_0^t H(t)dt}{\int_0^{t_\infty} H(t)dt} \tag{14}$$

The Avrami equation (Avrami 1939) was defined as following:

$$X(t) = 1 - \exp(-Kt^n) \tag{15}$$

where K denotes crystallization rate constant, and n denotes Avrami exponent related to the form of crystal growth and the mechanism of nucleation (Avrami 1940, 1941).

5.5 Thermal Degradation Kinetics Model

There used to be a variety of kinetic studies been carried out with TGA at different heating rate to determine the rate constants (k), activation energy (E_a), reaction order (n) and Arrhenius pre-exponential factor (A) (Feng et al. 2014). The reaction rate of solid-state reaction $\left(\frac{d\alpha}{dt}\right)$ can be expressed with the following equation regarding the rate constant k and reaction model f(α):

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{16}$$

The conversion rate α, is derived by weight loss:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \tag{17}$$

where W_0, W_t and W_f are the weight of the samples at different times, respectively represent at initial degradation, the time (t) and final degradation.

Depending on the Arrhenius formula, k can be described as:

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \tag{18}$$

Equation 1 becomes:

$$\frac{d\alpha}{dt} = Ae^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \tag{19}$$

where A stands for the pre-exponential factor (1/s), E_a stands for the activation energy (kJ/mol), R the gas constant (J/mol K) and T the temperature.

Equation 6 shows the relationship between the reaction rate, transformation efficiency and the experimental recording temperature. The heating rate β (°C/min) and change in temperature with time (dT/dt) are adopted to kinetically investigate the TGA, so Eq. 6 can be expressed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \tag{20}$$

Isoconversional methods are widely used for determining the E_a of polymers. The two main isoconversional methods, Friedman method (Friedman 1964) and Doyle's linear approximation (Doyle 1962) applied Flynn-Wall-Ozawa (FWO) method (Ozawa 1965; Flynn 1983; Flynn and Wall 1966), are used to evaluate the accurate value of the E_a at an exact conversion rate. The Friedman method and the Flynn-Wall-Ozawa method follow different procedure (Carrasco et al. 2013).

Friedman equation is as following:

$$\ln \frac{d\alpha}{dt} = A \ln f(\alpha) - \frac{E_a}{RT} \tag{21}$$

The E_a is obtained from the slope of ln $\frac{d\alpha}{dt}$ against 1/T from TGA curves at different heating rates.

Flynn-Wall-Ozawa equation:

$$\log \beta = [\log \frac{AE_a}{R} - \log f(\alpha) - 2.315] - 0.4567 \frac{E_a}{RT} \tag{22}$$

The E_a by FWO method is the slope of log β against 1/T for a variety of degrees of conversion.

Kissinger et al. made use of an equation to describe the E_a. The equation is expressed as follows:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{RA}{E_a} - \frac{E_a}{RT_p} \tag{23}$$

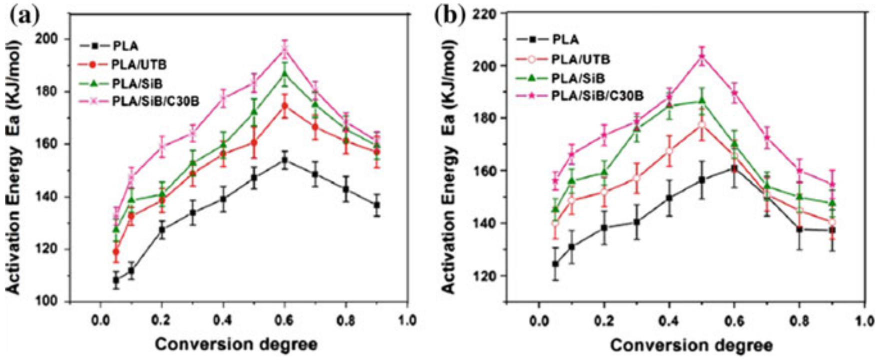


Fig. 19 Activation energy at various conversion rates for PLA, PLA/UTB, PLA/SiB and PLA/SiB/C30B obtained by **a** Friedman method; **b** FWO method (VP et al. 2015)

where T_p is the peak temperature from the corresponding DTG curve. E_a is obtained from the slope of $\ln\frac{\beta}{T_p^2}$ against $1/T_p$ at various heating rates.

VP et al. (2015) studied the reinforcing effect of untreated banana fiber (UTB), silane treated-banana fiber (SiB) and nanoclay (Closite 30B (C30B)) on the thermal degradation kinetics of Poly (lactic acid) (PLA). Based on VP's cone calorimetry test results, nanoclay would not volatilize within a short time, therefore, it delays the ignition of nanocomposites. The result is consistent with Fig. 19.

6 Conclusions and Future Prospective

Nanoclays play an important role to enhance composite performance through the way of enhancing their properties such as thermal stability, mechanical strength, and barrier properties. The content, shape, size, and the affinity towards matrix material are some of the characteristic factors contribute most to modify the properties of the composites. With their enhanced performance, nanoclay filled polymer matrix based nanocomposites have drawn much attention in the materials industry. A common recognition in this area is that exfoliated clays perform superior strength, modulus and higher barrier properties compared to pure polymer matrix. As nanotechnology developed very fast, great interest has been drawn in the correlation of material properties with filler size. Nanoclays have attracted a great deal of interest due to the fact that they have demonstrated cutting-edge properties that cannot be achieved with their traditional micro-scale counter parts.

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