A Review on Thermal Performance of Hybrid Natural Fiber/Nanoclay Polymer Composites

M. Norkhairunnisa and D.L. Majid

Abstract This chapter review on the thermal analysis on the performance of hybrid natural fiber/nanoclay in polymer composite. During the last decade, there has been an interest in using natural fiber as an alternative to synthetic fiber such as glass fiber. The major attraction in using natural fiber as part of reinforcing materials in nanocomposite are renewable materials, biodegradable, low material price, and weight saving. Some efforts have been made on improving the thermal properties of natural fiber reinforced polymer (NFRP) composite by inclusion of thermally stable layered silicate of nanoclay. The layered silicate structure of nanoclay can act as a barrier towards heat by forming layer of char residue after burn at high temperature. This characteristic delays the degradation process and further improves the thermal stability of the composite. In addition, the flammability of the hybrid natural fiber/nanoclays polymer composite was found to decrease with presence of exfoliated layered structure of nanoclay.

Keywords Nanoclay · Natural fiber · Thermal stability · Flammability · Crystallization temperature

---

M. Norkhairunnisa (✉)
Institute of Tropical Forestry and Forest Products (INTROP),
Universiti Putra Malaysia, 43400 Serdang,
Selangor Darul Ehsan, Malaysia
e-mail: norkhairunnisa@upm.edu.my

M. Norkhairunnisa · D.L. Majid
Department of Aerospace Engineering, Faculty of Engineering,
Universiti Putra Malaysia, 43400 Serdang,
Selangor Darul Ehsan, Malaysia

D.L. Majid
Aerospace Manufacturing Research Centre (AMRC),
Universiti Putra Malaysia, 43400 Selangor,
Serdang Darul Ehsan, Malaysia

M. Jawaid et al. (eds.), *Nanoclay Reinforced Polymer Composites*,
Engineering Materials, DOI 10.1007/978-981-10-0950-1_7

1 Introduction

Over the past few years, natural fibers have attracted much attention from researcher worldwide due to its unique properties. Common natural fibers used in composite include empty fruit bunch, kenaf, bagasse, bamboo, flax, jute, hemp, pineapple, animal fibers and fibers from wood. The attractive features of natural fibers are green in nature which is eco-friendly, biodegradable, reproducible as the origin comes from renewable resources, processing advantages at low cost. Natural fibers are alternative materials used to replace conventional fibers as reinforcing material in polymer composite especially in producing low weight composite. Processing of composite with natural fiber possess some benefit such as less machine wear and the fiber itself will bend rather than fracture during processing. Unlike synthetic fiber such as glass fiber, it breaks easily when intensively mixed with polymer resin. However, due to poor compatibility of natural fiber with hydrophobic type of polymer matrix, temperature difference of compounding process and flammability characteristics of natural fibers, limit the use of biocomposite in certain applications especially for aerospace and automotive areas.

Clay materials have been used progressively in heat resistant and flame retardant applications. Layered silicate or known as nanoclays are the most common nanofillers which have been used in polymer composite to improve the thermal characteristic of the polymer matrix (Duquesne et al. 2003; Haurie et al. 2007; Olewnik et al. 2010). Common type of nanoclays are montmorillonite, bentonite, mica, saponite and hectorite. Size reduction of macro/-microclay to nanoclay is expected to improve the thermal barrier property of the composite due to the increase in surface area. The improvement of the properties for composite embedded with nanoclays are well beyond than what can generally be achieved from pure polymer or conventional composites. Nanoclays have gained acceptance as possible reinforcing materials due to its unique properties such resistance to fire, excellent heat distortion temperature, and have good permeability towards gas and water. Dispersion of low amount of nanoclay within a polymer matrix tend to enhance the properties of the pure polymer or polymer reinforced with fiber composite (Rajasekar et al. 2009; Alhuthali et al. 2012). Polymer filled with nanoclay also have better toughening properties due to its plate structure, high surface to volume and strength to weight ratio (Liu et al. 2005; Liqun and James 2005; Subramaniyan and Sun 2007).

Recently, development of hybrid nanocomposite consist of polymer, natural fiber and nanoclay, often exhibit remarkable improvement in mechanical, thermal and various other properties compared to conventional composite (Reddy et al. 2010; Rajini et al. 2012; Zahedi et al. 2013; Eng et al. 2014). Inclusion of nanoclay in natural fiber/polymer composite (NFRP) system to overcome the drawback of the natural fiber due to it hydrophilicity in nature, low weathering resistance, and delamination of the composite. Thus, addition of nanoclay tend to improve the fiber/polymer composite strength, improve the thermal stability of the composite, function as a bridge between fiber and resin, and reduce gas and water permeability in the composite (Kumar et al. 2012). Moreover, the layered silicate structure of nanoclay can delay the gasification process through formation of carbonaceous-silicate char by providing a protective layer on the nanocomposite surface. Thus, thermal stability of the fiber nanocomposite can be improve and reduced the flame spread.

Combination of low cost natural fiber with nanoclay as an excellent thermal insulator, can be an ideal alternatives to the available synthetic fiber which is commonly used in composite for insulation applications. In this chapter, a review on thermal analysis of hybrid natural fiber/nanoclay reinforced polymer composite based on recent research findings. Various thermal analysis such as thermal stability, flammability, glass transition temperature, etc. were carried out to investigate the effect of nanoclay and natural fiber the thermal properties of the polymer composite.

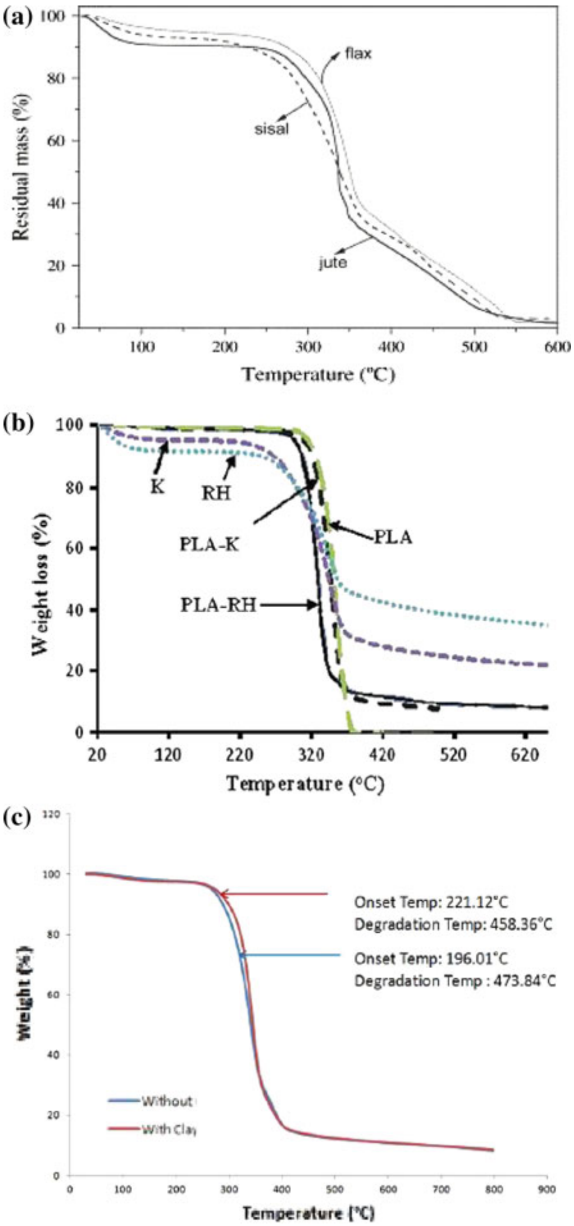
2 Studies on the Thermal Stability of Hybrid Nanocomposite

Determination of thermal stability and weight loss of polymer composite as a function of temperature under controlled atmosphere are generally performed by using thermogravimetric analysis (TGA) instruments. In general, it have been reported that thermal stability of natural fiber reinforced polymer composite are thermally less stable than virgin polymer (Lee and Wang 2006; Lei et al. 2007a; Arrakhiz et al. 2013). Plant fiber primarily consist of cellulose, hemicellulose and lignin. There are four principle steps in degradation of natural fibers which are (i) removal of water uptake by fiber at region between 50–150 °C; (ii) depolymerisation of hemicellulose and cleavage of glycosidic linkage at region between 250–370 °C; (iii) degradation of lignin ranging from 200–500 °C, and (iv) decomposition of cellulose at region more than 430 °C (Dorez et al. 2013; Manfredi et al. 2006). Figure 1a shows the example on the degradation behaviour of natural fibres.

Variation in initial decomposition temperature for different type of natural fibers was due to content of the chemical composition of the fibers (Manfredi et al. 2006). Table 1 shows different chemical composition of some natural fibers which tend to affect the thermal stability of the fibers. Presence of high lignin content tend to increase the thermal decomposition temperature which is due to its aromatics ring structure consist of various branches (Liu et al. 2004).

Figure 1b, c shows the thermogravimetric curves of natural fiber reinforced polymer and hybrid natural fiber/nanoclay reinforced polymer composite, respectively. Incompatible surface nature between natural fiber and polymer matrix, tend to reduce the thermal stability of the natural fiber/polymer composite as shown in Fig. 1b. Work done by Eng et al. (2014), shows improvement of thermal stability of the OPMF/blend polymer composite with inclusion of nanoclay (Fig. 1c). Therefore, from Fig. 1, it can be concluded that the degradation trends of natural fiber reinforced polymer nanocomposite change with presence of different phases which are natural fiber, nanoclays and the polymer matrix itself. Inclusion of clay into polymer system promote flame retardancy of the pure polymer. Formation of carbonaceous residue over the molten polymer at high temperature acts as

Fig. 1 Trend on the thermogravimetric curves of **a** natural fibers (Manfredi et al. 2006); **b** kenaf, rice husk, PLA/kenaf and PLA/rice husk (Yussuf et al. 2010); and **c** hybrid oil palm mesocarp fiber (OPMF)/nanoclay in polymer blend of PLA/PCL (Eng et al. 2014)



protective barrier to hinder transfer of volatile products and heat transfer between flame and polymer (Zanetti et al. 2000; Sánchez-Jiménez et al. 2012). The carbonaceous residue consist of high concentration of silicate layers from nanoclay which function as an excellent insulator (Manias et al. 2001). On top of that, increase in thermal decomposition temperature was attributed to the hindered

Table 1 Chemical composition of some natural fibers (% of total)

Type of fiber	Extractive	Holocellulose	α-cellulose	Lignin	Ash	Reference
Oil palm frond	4.5	83.5	49.8	20.5	2.4	Abdul Khalil et al. (2007)
Coconut	6.4	56.3	44.2	32.8	2.2	
Pineapple leaf	5.5	80.5	73.4	10.5	2.0	
Banana stem	0.2–8.5	60–80	30–60	21–37	<1	
Kenaf core	4.7	87.2	49	19.2	1.9	Abdul Khalil et al. (2010)
Kenaf bast	5.5	86.8	55.0	14.7	5.4	

diffusion of volatile decomposition products in the composite, together with physic-chemical adsorption of volatile degradation products on the silicate surface of nanoclay (Iman and Maji 2012). Presence of acidic sites on the clay layered structure can increase the thermal-oxidative degradation too (Qin et al. 2005). Moreover, tortuous path created by silicates layer, delay the volatilization of carbon-carbon scission to produce degradation products (Qin et al. 2004; Deka and Maji 2011).

Reinforcing of nanoclay in fiber/polymer composite tend to increase the decomposition temperature. Work done by Shuvo et al. (2015), observed increment of maximum thermal decomposition temperature of jute/polyester composite with inclusion of 1 wt% of nanoclay for about 3 %. The authors suggested that heat distribution between fibres and nanoclay are uniform and more energy required to thermally degrade the composite structure. Similar finding by Kumar and Kumar (2012), in which they observed increased in thermal stability after adding 1 wt% of nanoclay in bamboo/epoxy composite. Good dispersion of nanoclay combined with good interfacial adhesion of nanoclay in polymer matrix restrict the thermal motion on epoxy molecules which subsequently improve the thermal stability of the composite. Thus, less surface area of nanoclay being contact with polymer and further reduce the interfacial adhesion between agglomerate nanoclay and polymer resin. However, adding nanoclay content up to 10 wt%, does not improve the thermal stability of the bamboo/epoxy composite. High content of nanoclay may lead to the formation of agglomerates, in which high particle to particle interactions than particle to polymer interactions in the nanocomposite (Zainuddin et al. 2010). Compare to hemp/PLA nanocomposite, 10 wt% of nanoclay is needed to increase the thermal decomposition temperature. Low content of nanoclay does not contribute significant thermal performance due to less amount of clay platelet function as barrier towards heat (Hapuarachchi and Peijs 2010).

Figure 2 shows the micrographs on the composite upon TGA test conducted by Kovacevic et al. (2015). Composite contain nanoclay (MMT) showed the firm and intact structure of the composite surface (Fig. 2b), while for composite without nanoclay was found to be totally damaged (Fig. 2a). Authors suggested that movement of nanofiller from the inner part of the composite to the surface, form char residue thus prevent degradation on the composite structure. It was observed that

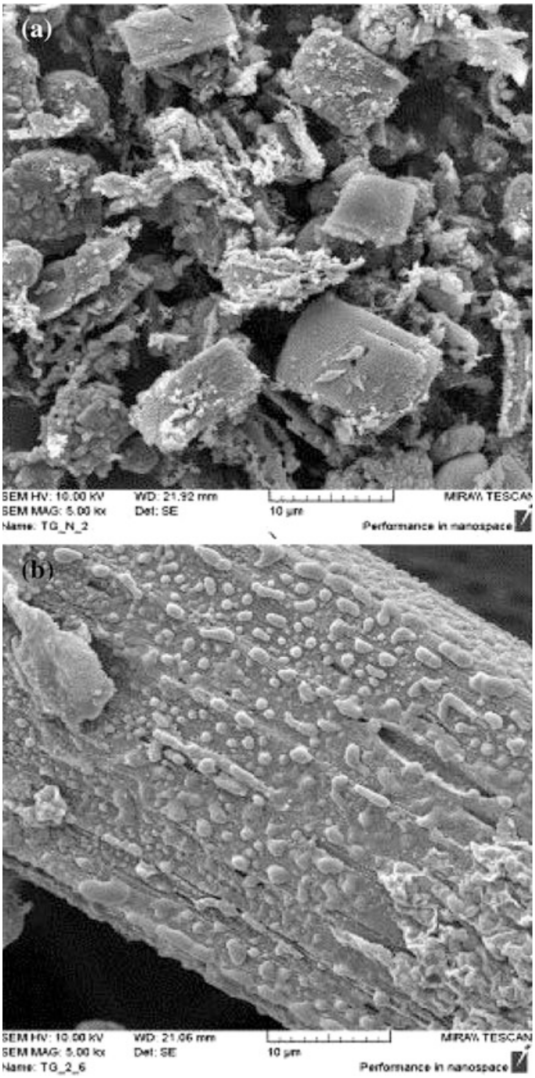


Fig. 2 Scanning electron micrograph of chars after TGA for: **a** *Spartium junceum* L. fiber/PLA composite and, **b** *Spartium junceum* L. fiber/PLA/MMT nanocomposite (adapted from Kovacevic et al. 2015)

char residue increased for about 12 % as the clay content increase to 5 wt% for 0.75 MDF/UF nanocomposite (Zahedsheijani et al. 2012). It was said that increasing amount of nanoclay as flame retardant materials will subsequently increase the char residue of composite at relatively low temperatures and thus, improved the thermal insulation property.

One of the issue addressing the stability and flammability of clay composite is the behaviour of the layered silicate structure in polymer. Morgan (2006) reviewed that both intercalate and exfoliate of nanoclay structures shown reductions in heat release. He highlighted that the most important is the dispersion of nanoclays in the polymer matrix. Poor dispersibility or agglomerations of nanoclays will reduced the heat transfer efficiency. If poor interfacial adhesion between clay and polymer matrix, clay will no longer function as insulator and tend to increase the flammability property of the composite (Biswal et al. 2012). The dispersibility of the nanoclays can be enhance by modified the nanoclay surface. The initial onset degradation temperature for composite filled with modified nanoclay shows low decomposition temperature compared to unfilled polymer at earlier stage of degradation. The early stage of degradation temperature was attributed to the loss of water and solvent from the fiber, and due to the hydrophobicity nature of the plant fiber (da Silva Santos et al. 2010). In addition, this scenario occurred due to the Hofmann elimination reaction, in which clay function as catalyst to promote the degradation of the matrix (Madaleno et al. 2010; Hapuarachchi and Peijs 2010). However, when reached to the second stage of decomposition, composite filled with nanoclay shows higher thermal decomposition temperature than unfilled polymer. Similar case can be observed from polymer nanocomposite reinforced with natural fibers (Alamri et al. 2012). High temperature of thermal decomposition was due to the properties of the nanoclay which hinder the diffusion of volatile products from the nanocomposite.

Use of modified or unmodified nanoclay give an effect to the thermal properties of the composite as well. Unmodified nanoclay have high tendency to clump together and form large agglomerations of layered structure. Alongside that, no intercalation or exfoliation of the clay structure appear in the polymer composite and the composite can be classified as microcomposite. Modified nanoclay provide good contact or adhesion with polymer resin. In addition, surface modified nanoclay showed high tendency to change the organized layered structure into exfoliate during mixing with polymer resin.

Effects of different type of nanoclay on the thermal properties of natural fiber reinforced polymer nanocomposite was studied by Delhom et al. (2010). They prepared cotton fiber nanocomposite with different type of nanoclay which are montmorillonite and cloisite. Generally, can be observed that adding nanoclay increase the degradation temperature of the cotton fiber nanocomposite. However, different type of nanoclay produce different degradation temperature peak. The cotton fiber nanocomposite filled with montmorillonite demonstrated the high thermal degradation temperature peak value. This is because different intercalant chemistry can effects the degradation property of the polymer (Lei et al. 2006; Rahimi-Razin et al. 2012; Molinaro et al. 2013).

Saw (2015) prepared nanocomposite made from modified nanoclay (organo modified montmorillonite, OMMT) with coir fiber in blend of epoxy novolac resin (ENR) and diglicidyl ether of bisphenol A (DGEBA) based epoxy resin. TGA analysis shows that incorporation of 30 wt% of coir fiber and 2 wt% OMMT in blend epoxy (ENR:DGEBA) have better thermal stability than in nanocomposite with single epoxy component. The polymer chains of blend epoxy is interact well with the OMMT and coir fiber surfaces through hydrogen bonds. In addition, the catalytic effect of OMMT enhance the curing rate of the epoxy blends. Therefore, the crosslink density of the epoxy blends increase and high temperature need to break the polymer chain. On top of that, the char residue was found high at 800 °C which is 28.19 % which support good adhesion and ordered structure of the nanocomposite. However, increase the ENR loading to 65 %, a decrease in thermal degradation temperature of the nanocomposite was observed. This attributes to the high intensity of polymer chains, thus form less ordered structure and lower the dispersibility of the coir fiber and OMMT in the epoxy blend.

Mohan and Kanny (2015) fabricate short banana fiber/nanoclay reinforced epoxy composites by resin casting method. Banana fibers and nanoclay were initially treated in alkaline solution. High shear force was applied in the solution mixture in order to ease the infusion of nanoclay particles into the fibers. From tensile analysis, it shows improvement in modulus and strength of treated fiber/nanoclay in epoxy matrix. Strengthening mechanism of nanoclay in fiber greatly retard the deformation process of the fiber/epoxy composite. In addition, fiber infused with nanoclay can effectively bear load applied on it due to good interfacial adhesion with epoxy matrix. As shown in Fig. 3a, untreated fiber easily being pull out from epoxy matrix. While for treated fiber, the pull out process is difficult due to high resistance from the nanoclay inside of the fiber (Fig. 3b). Authors add that the thermal stability of treated fiber/nanoclay/epoxy composite was higher than epoxy filled with untreated fiber. Interestingly, the mass loss of treated fiber/nanoclay/epoxy composite was low due to reinforcing ability of nanoclay and it delays the degradation process by form a protective layer on the composite surface. A summary of the decomposition temperature of some natural fiber reinforced polymer is given in Table 2.

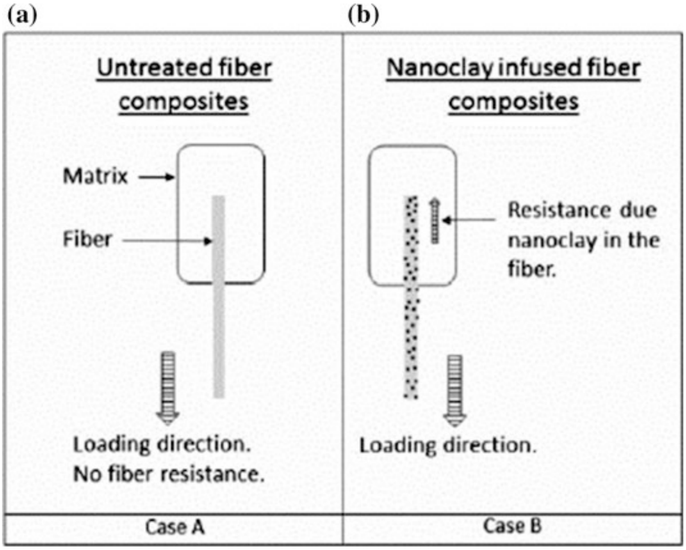


Fig. 3 Schematic illustration on the fiber matrix interface: **a** untreated fiber composite, and **b** nanoclay infused fiber composite (adapted from Mohan and Kanny 2015)

Table 2 Decomposition temperature of some natural fiber reinforced polymer nanocomposites

Sample	Initial decomposition temperature (°C)	Maximum degradation temperature (°C)	Final decomposition temperature	References
Polymer blend/5phr PE–co–GMA/40 phr wood	255	451	At 600 °C = 7.2 %	Deka and Maji (2011)
Polymer blend/5 phr PE–co–GMA/40 phr wood/3 phr nanoclay/1 phr ZnO	277	503	At 600 °C = 10.8 %	
Polymer blend/5 phr PE–co–GMA/40 phr wood/3 phr nanoclay/3 phr ZnO	289	517	At 600 °C = 14.5 %	
Polymer blend/5 phr PE–co–GMA/40 phr wood/3 phr nanoclay/3 phr ZnO	281	510	At 600 °C = 12.7 %	
Wood/polymetylmethacrylate (PMMA)/glycidyl methacrylate (GMA)	215	411	At 600 °C = 10.6	Hazarika et al. (2012)
Wood/PMMA/GMA/0.5 % nanoclay	229	418	At 600 °C = 13.5	
Wood/PMMA/GMA/1.0 % nanoclay	245	425	At 600 °C = 16.4	
Wood/PMMA/GMA/1.5 % nanoclay	272	439	At 600 °C = 23.1	
Polymer blends (PB)	251	407	At 600 °C = 6.1	Deka et al. (2011)
40 wt% Nals (W40)/ PB/5 wt% PE–co–GMA (G5)	257	455	At 600 °C = 7.2	
W40/ PB/G5/1 wt% nanoclay (N1)	260	466	At 600 °C = 8.4	
W40/ PB/G5/N3	270	496	At 600 °C = 11.7	
W40/ PB/G5/N5	263	480	At 600 °C = 10.2	
Spartium junceum L. fiber/PLA/MMT	328	364.8	At 800 °C = 4.9	Kovacevic et al. (2015)
Jute/polyester	–	385.30	At 700 °C = 1.591 %	Shuvo et al. (2015)
Jute/polyester/1 wt% graded nanoclay (GNC)	–	396.97	At 700 °C = 1.746 %	
Arboform$^{®}$/lignin	–	343	–	Guigo et al. (2009)
Arboform$^{®}$/lignin/2 % sepiolite	–	344	–	
Arboform$^{®}$/lignin/5 % sepiolite	–	348	–	
Arboform$^{®}$/lignin/2 % OMMT	–	341	–	
Arboform$^{®}$/lignin/5 % OMMT	–	353	–	

(continued)

Table 2 (continued)

Sample	Initial decomposition temperature (°C)	Maximum degradation temperature (°C)	Final decomposition temperature	References
PP	–	398	–	Biswal et al. (2011b)
PP/nanoclay (OPP)	–	452	–	
Mercerized banana fiber (MBF)/OPP	–	475	–	
PLA	–	364	At 800 °C = 1 %	Hapuarachchi and Peijs (2010)
Hemp/PLA/1 wt% sepiolite	–	359	At 800 °C = 2 %	
Hemp/PLA/10 wt% sepiolite	–	364	At 800 °C = 7 %	
0.65 medium density fiberboard (MDF)/urea-formaldehyde (UF)/2.5 % NaMMT	–	332	At 500 °C = 14.77	Zahedsheijani et al. (2012)
0.65 MDF/UF/5 % NaMMT	–	339	At 500 °C = 15	
0.75 MDF/UF/2.5 % NaMMT	–	339	At 500 °C = 12.98	
0.75 MDF/UF/5 % NaMMT	–	336	At 500 °C = 14.8	
Cotton	–	282	–	Delhom et al. (2010)
Cotton/montmorillonite	–	327	–	
Cotton/cloisite	–	311	–	
Ramie	–	290	–	
Ramie/montmorillonite	–	335	–	
Ramie/cloisite	–	313	–	
Kenaf	–	283	–	
Kenaf/montmorillonite	–	321	–	
Kenaf/cloisite	–	305	–	
Coir/DGEBA/nanoclay	223.4	371.9	At 800 °C = 0	Saw (2015)
Coir/ENR/nanoclay	235.9	393.8	At 800 °C = 0	
Coir/ENR:DGEBA(50:50)/nanoclay	294.7	485.7	At 800 °C = 28.19	
Coir/ENR:DGEBA(65:35)/nanoclay	274.4	461.6	At 800 °C = 22.78	

3 Studies on the Flammability of Hybrid Nanocomposite

Flammability is one of the crucial parameters that limit the properties of the composite for certain area of applications. It described the reactions of particles in producing fire and can be classified into four different phases such as ignitability, flame spread, heat release and the resulting products from the fire process (Walters and Lyon 2008).

Thermal conductivity of natural fiber was 0.29–0.32 W/mK, which is very low and make it suitable for thermal barrier application. However, due to lack of oxidation resistance from the aromatic rings of lignin, the thermal stability of the fiber would be low. In addition, poor fire resistance of natural fiber, limit its application especially in aerospace and automotive industries.

Therefore, in order to improve flammability of the fiber reinforced polymer composite (NFRP), a flame retardant additives such as nanoclay is suitable to be embedded into the composite system. Another point of view is, during combustion process, nanoclay particle inhibit formation of vigorous bubbling by develop a large lateral surface crack layer (Pandey et al. 2011). Recently, there are few number of researchers looking into the flammability performance of nanoclay in NFRP (Zhao et al. 2006). The flammability analysis can be carried out using cone calorimeter according to ASTM E1354-92 and ISO/DIS 13927 standards (Zanetti et al. 2000). From this instrument, a number of parameters such as char residue (CR), total time to ignite (TTI), time to peak heat release rate (TPHRR), smoke production rate (SPR) and total smoke production (TSP) data can be evaluated. Another way to measure the flammability of the nanocomposite is by limiting oxygen index (LOI) test. This test can be done in accordance to ASTM D-2863 method. LOI test is conduct to measure the tendency of material to sustain flame by applying oxygen and nitrogen gaseous mixture over the burning specimen.

Chigwada et al. (2005) carried out research on the effect of fire behavior on ABS, PE and epoxy with incorporation of nanoclays through cone calorimeter. This research works proves that addition of nanoclays into polymer matrix decreases maximum heat release rate and increases the ignition time. Similar findings by Zhao et al. (2006), based on a study on flammability of wood flour/polyvinyl chloride (PVC) nanocomposite with varying loading of organo modified montmorillonite (OMMT). From cone calorimeter analysis, it was observed that at OMMR loading of 4.5 %, the TPHRR was approximately 63 % higher than composite without OMMT. The TTI of the fiber nanocomposite also improve from 25 s for wood flour/PVC composite to 78 s for wood flour/PVC nanocomposite filled with 4.5 % OMMT. Improvement in TPHRR and TTI indicate that presence of OMMT delayed the formation of ignition and heat release process in the fiber nanocomposite. There is a small peak (peak A) at 25 s shows in Fig. 4 indicates decomposition of some PVC and wood flour molecules. While the following peaks correspond to the latter ignition of the fiber nanocomposite samples. According to the study, homogeneously distribution of OMMT in the PVC matrix tend to form an inorganic shell-like structure until the ignition start to occur by heating.

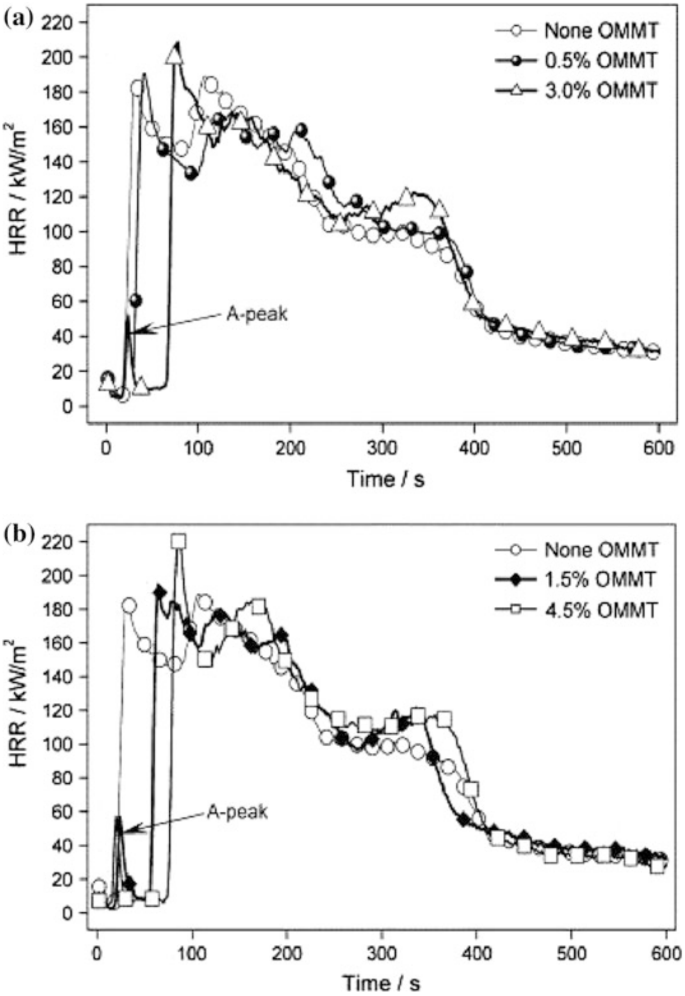


Fig. 4 Heat release rate (HRR) versus time relations for different loading of OMMT in wood flour/PVC nanocomposites (adapted from Zhao et al. 2006)

Moreover, high degree of nanoclay exfoliation have high oxidation protection against heat (Camino et al. 2005). On top of that, good interfacial adhesion between PVC, wood flour and OMMT delay the time for fire to start.

The burning behaviour of the fiber nanocomposite is largely determined by the synergistic effect on the adhesion between matrix and surface of the fiber or nanoclay according to Guo et al. (2007), in a study on the flammability of wood fiber/HDPE/nanoclay composites with and without coupling agent. Different concentration of maleic anhydride (MAH) was added into the composite to improve the interfacial adhesion between wood flour and HDPE. As reported by Zhang et al. (2004), blending of coupling agent with polymer system tend to improve the interfacial adhesion between polymer resin and fillers. As reported by Guo et al. (2007), they added 0–50 % of MAH coupling agent in wood fiber/HDPE nanocomposites. As shown in Fig. 5a, it is observed under TEM view that for wood fiber/nanocomposite without MAH, the layered silicate structure did not expand and distribute well in the HDPE resin. With addition of 5 % of MAH, the size of the nanoclay agglomeration decrease and orientation of the layered silicate change to intercalate structure (Fig. 5b). Thus, by increasing the MAH content up to 50 %, the layered silicate structure of nanoclay have been fully exfoliated in the HDPE matrix (Fig. 5c). Therefore, owing to the good dispersion of exfoliated nanoclay in fiber nanocomposite with 50 % of MAH, the flammability analysis shows low burning rate of the nanocomposite which is 18 % less than fiber nanocomposite without nanoclay (Fig. 6). Thus, sufficient amount of coupling agent to be blend with polymer resin is important to facilitate the diffusion of polymer chains into the silicate layers of nanoclay (Mittal 2013). Lee et al. (2010) reported that in order to

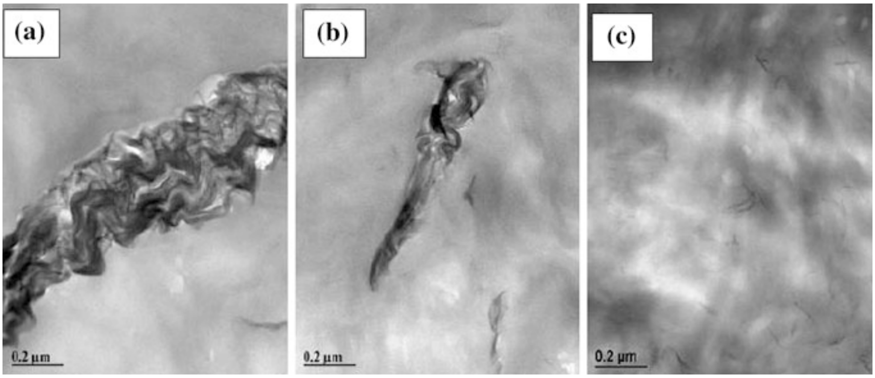
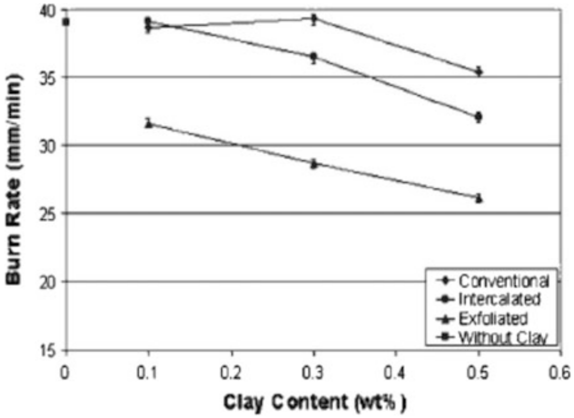


Fig. 5 Transmission electron micrographs (TEM) for different nanoclay orientation in fiber/HDPE nanocomposites; **a** Conventional, **b** intercalated, and **c** exfoliated (adapted from Guo et al. 2007)

Fig. 6 Burning rate versus clay content for fiber nanocomposites with different type of structural orientation layered of nanoclays (adapted from Guo et al. 2007)



improve the flame retardant properties of the fiber/polymer nanocomposite with low loading of nanoclay, it is crucial to have a higher degree of exfoliation of nanoclay.

Paluvai et al. (2015), investigated on the LOI of unsaturated polyester (UP) toughened epoxy nanocomposites filled with alkaline silane treated sisal fiber (ASTF) and cloisite 30B type nanoclays (C30B). The high pressure mixing (HPM) method was used to disperse the C30B into epoxy/UP blend matrix. Good exfoliation of silicate layer nanoclay structure have been obtained due to the interactions between carboxylic ester group from polymer and OH group from the nanoclay. The LOI analysis increase to 27 % with addition of C30B into the ASTF/UP/epoxy composite system. Reason to the improvement in LOI analysis is due to the strong covalent bonding between Si–O–Si linkages of the ASTF surface with alkyl ammonium ion on C30B.

Biswal et al. (2012) prepared mercerized banana fiber (MBF) reinforced polypropylene nanocomposites (OPP). The banana fiber was soaked into 5 % NaOH solution to remove the presence of impurities before being compound with organically modified nanoclay in PP/MA-g-PP matrix. Different loading of banana fiber in the composite system was prepared to investigate effects of fiber loading. By applying 50 kW/m^2 radiant heat flux from cone calorimeter analysis, it was observed a decreasing of TTI value from 30 s for blank PP to 36 s for PP filled with nanoclay (OPP). Then, the trend shows reduction of TTI value to 26 for OPP filled with 30 wt% of MBF. The inconsistent TTI value was due to the addition of MBF into the nanocomposite system. Authors mentioned during pyrolysis process, the levoglucosan from lignin and hemicellulose was found increase. Thus, lead to the formation of flammable fluid tar which subsequently reduced the TTI value as shown in Table 3. On the other hand, the HRR value was found to be increased with addition of MBF. With addition of 10 wt% of MBF in OPP, the HRR value increase approximately 26 % over the OPP. Poor interfacial interaction between

Table 3 Cone calorimeter information of some natural fiber reinforced polymer nanocomposite

Sample	Total time to ignite (TTI) (s)	Peak heat release rate (HRR), kW/m^2	References
Epoxy/UP	61	829.2	Paluvai et al. (2015)
Epoxy/UP/1 wt% C30B	66	647.2	
Epoxy/UP/ASTF	65	610.9	
Epoxy/UP/1 wt% C30B/ASTF	64	583.3	
PP	30	2498.2	Biswal et al. (2012)
OPP	36	1164.5	
OPP/10 wt% MBF	28	1581.9	
OPP/20 wt% MBF	27	1746.5	
OPP/30 wt% MBF	26	1612.7	

MBF and OPP, explained the increment in HRR. It was suggested by author that in this case, probably PP, MBF and nanoclay does not compliment with each other. PP matrix burn vigorously due to poor adhesion with fillers, lignocellulosic characteristic of banana fiber which is highly flammable and nanoclay does not act as insulator to protect the composite against heat. However, the HRR value for fiber reinforced nanocomposite for OPP/MBF was still lower than blank PP. This indicate that presence of banana fiber and nanoclay gives variation in reaction to fire parameters for the fiber reinforced nanocomposite.

In summary, the addition of nanoclay can improve the flammability of natural fiber reinforced polymer composites through various flame retardant mechanisms which are (i) formation of barrier against heat and volatiles due to the migration of nanoclay towards the surface, formation of char between the surface and the flame, and inhibit formation of bubbles during combustion process.

4 Studies on the Melting and Crystallization Behaviour of Hybrid Nanocomposite

Dynamic Scanning Calorimetry (DSC) is one of thermoanalytical technique to measure the isothermal crystallization behaviour of the composite. Some reactions may occur without any weight loss, therefore in this instance differential scanning calorimetry (DSC) can detect these reactions. The crystallization and melting curves of the nanocomposite can be obtained from cooling and heating process of non-isothermal in DSC measurements.

Two phases of crystallization process of semicrystalline polymer which are the macroscopic expansion of the degree of crystallinity and, crystallization of lateral and interfibrillar chains (Bouafif et al. 2009). Degree of crystallinity depends on several processing parameters such as crystallization temperature, nucleation density, cooling rate type of fiber and annealing time (Wang and Liu 1999). Contact between solid surface and semicrystalline polymers during crystallization process of the polymer matrix induces heterogeneous nucleation. Buoafif et al. (2009) reviewed that presence of high heterogeneous nucleation activity, lead to the formation of transcrystalline layer on the fiber matrix interface as to improve bonding between fiber and matrix. However, presence of nanoclay tend to alter the crystalline structure of the fiber too. This was observed by Delhom et al. (2010) in which the melting temperature of cotton fibre composite drop from 186 to 172 °C after adding with nanoclay.

Crystallization temperature of composite filled with nanoclay was found to be higher than unfilled composite. As shown in Fig. 7a, crystallization temperature for composite contained treated kraft fiber (high density polyethylene-maleic anhydride polyethylene, HDPE-MAPE) and nanoclay was higher than composite without presence of nanoclay. However, comparing with Fig. 7b, presence of clay in treated

Fig. 7 DSC curves of crystallization temperature of **a** 20 wt% treated nanoclay or untreated kraft fiber-HDPE and HDPE-MAPE composites including blank HDPE (adapted from Chen and Yan 2013a) and, **b** pine, HDPE, and HDPE blend with pine and/or clay (adapted from Lei et al. 2007b)

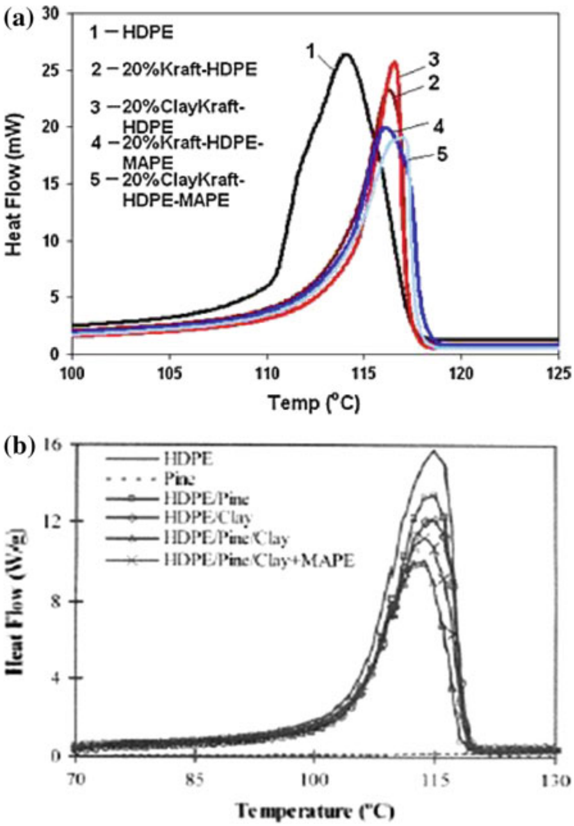
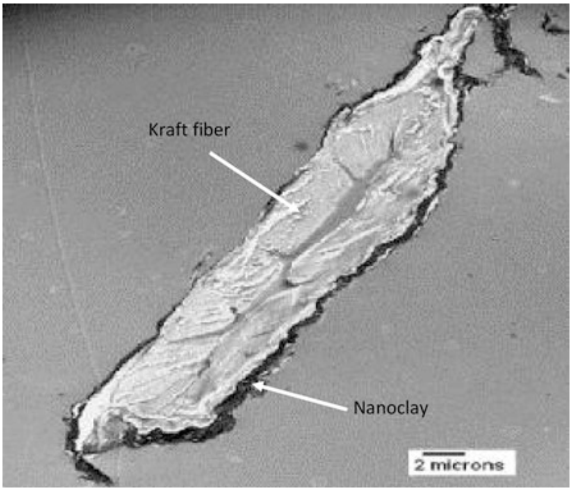


Fig. 8 TEM image of cross section on nanoclay treated kraft fiber (adapted from Chen and Yan 2013b)



pine fiber/HDPE/MAPE nanocomposite does not give significant effect on the crystallization temperature. Basically there are two reasons explaining on this phenomenon. First is the adhesion between nanoclay and fiber. By looking at Fig. 8, kenaf fiber has been coated with nanoclay. According to Chen and Yan (2013b) in their experiment, the exfoliated nanoclay was adsorbed onto the kraft fiber surface to change the surface nature to hydrophobic. It is expected that surface modification of kraft fiber with nanoclay is important to well blend with HDPE. However, it turns out that there is poor distribution of treated nanoclay-kraft in HDPE matrix. Thus, kraft/HDPE nanocomposite have low crystallinity temperature than kraft/HDPE composite. This occurred due to the low interfacial interaction between kraft fiber surface, nanoclay and HDPE matrix. It was explained that presence of nanoclay reduce the chain mobility of the HDPE polymer matrix. Addition of MAPE as compatibilizer improved the adhesion property between kraft fiber, nanoclay and HDPE. Therefore, MAPE was added to improve chain mobility of HDPE matrix with presence of nanoclay. Moreover, the nucleating site at the fiber surface was found to be increase and good adhesion was observed between HDPE-nanoclay-kraft fibers which subsequently increased the crystallinity temperature. Presence of nanoclay treated kraft with addition of MAPE act as an efficient nucleation agent and facilitate the crystallization of HDPE in which the crystallization peak is shift to high temperature. Another factor effects the crystallinity temperature of fiber/nanoclay composite was the particle size of the fiber itself. Nucleating ability of natural fibers depends on the fiber surface topography, wettability, fiber chemistry, surface energy and fiber length. Lei et al. (2007b) explained in their work that addition of nanoclay in pine/HDPE does not give significant effect to the crystalline temperature (Fig. 7b). In fact, addition of 2 % of nanoclay and 30 % of pine fiber flour drop the crystalline temperature and crystallization rate due to reductions of HDPE chain mobility. Thus, adding of nanoclay does not improve the chain mobility of HDPE matrix. This situation can be seen clearly as shown in Fig. 7a, crystallization temperature of blank HDPE is lower than HDPE composites while in Fig. 6b shows the crystallization temperature of blank HDPE is higher than HDPE composites. Therefore, Chen and Yan (2013a) concluded that fiber length is one of the factor that affect the nucleating activity in the polymer matrix. Table 4 summarizes the crystalline peak temperature, crystalline enthalpy and crystalline level of some natural fiber reinforced polymer nanocomposites.

Incorporation of pineapple leaf fiber (PALF) and nanoclay in polypropylene (PP)/maleic anhydride grafted polypropylene (MA–g–PP) shows increased in crystallization temperature from 104.43 °C for blank PP to 110.67 °C for PP/PALF/MA–g–PP/organoclay nanocomposite. MA–g–PP was added into the composite mixture to function as a compatibilizer between nanoclay surface, banana fiber and PP matrix. Observation under optical microscope as shown in Fig. 9 revealed that addition of PALF and nanoclay can act as nucleation agents in PP matrix due to the strong bonding between PALF, nanoclay and PP matrix. Biswal et al. (2009) explained that a number of nucleus were produce in limited

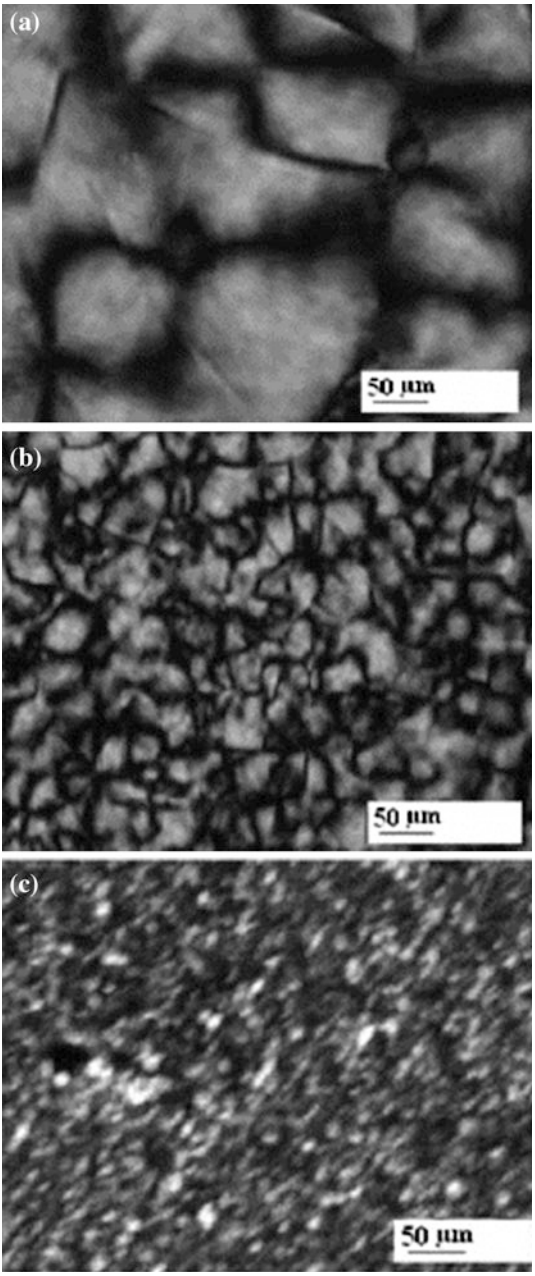
Table 4 Crystallization peak temperature and crystalline level of some natural fiber reinforced polymer nanocomposite

Sample	Crystalline peaks (°C)	Crystalline enthalpy, ΔH (J/g)	Crystalline level (%)	References
10 wt% bamboo/PP	165.3	227.2	55.0	Rahman et al. (2015)
10 wt% bamboo/PP/5 % nanoclay	161.4	220.3	50.2	
10 wt% bamboo/PP/5 % treated nanoclay	162.2	215.4	48.1	
Pine/HDPE/clay	113.1	158.3	54	Lei et al. (2007b)
Pine/HDPE/MAPE/clay	113.6	146.4	50	
PP/PALF/MA–g–PP/C20A	110.67	108.65	45.17	Biswal et al. (2009)
OPP	116.72	65.38	26.68	Biswal et al. (2012)
OPP/10 wt% MBF	118.08	147.41	60.16	
OPP/20 wt% MBF	118.81	189.36	77.28	
OPP/30 wt% MBF	120.99	172.96	70.59	
HDPE	113	192	66	Lee et al. (2010)
Wood polymer composite (WPC)	117.5	112.6	54.9	
5 % intercalated filled WPC	118.2	98.9	51.9	
5 % exfoliated filled WPC	118.6	100.9	52.97	

space with addition of PALF/MA–g–PP/PP, which lead to the evolution of small size crystal of spherulite (Fig. 9b). The crystal growth initially start from fiber itself. However, every neighboring fiber growth together in perpendicular direction and they are competing each other in order to act as a nucleation sites. While, inclusion of nanoclay in PP/PALF/MA–g–PP composite diminish the spherulite crystal with increasing the crystallinity level from 40.60 % for PP/PALF/MA–g–PP composite to 45.17 % for PP/PALF/MA–g–PP/nanoclay nanocomposite (Fig. 8c).

From DSC analysis observed by Biswal et al. (2012), increasing the banana weight fraction up to 30 wt%, does increase the crystallization temperature peak (Table 4). The interaction between anhydride group from MA–g–PP was found to form ester linkage with—OH group from banana fibers. Thus, MA–g–PP are able to diffuse into the PP polymeric network and lead to the formation of interchain entanglements, resulting in improved of interfacial adhesion between fiber, nanoclay and matrix (Bikiaris et al. 2001). The highest crystalline level was observed on the nanocomposite with loading of 20 wt% banana fiber. Presence of banana fibers and nanoclay act as nucleating sites in PP matrix which subsequently accelerated the crystallization rate and increase the crystalline level.

Fig. 9 Optical microscopy of (a) PP, (b) PP/PALF/MA-g-PP, and (c) PP/PALF/MA-g-PP/C20A (adapted from Biswal et al., 2009)



5 Glass Transition Temperature, T_g

The glass transition temperature, T_g of polymer information provide understanding of the polymer properties and this characteristic can be altered by addition of fibers and fillers into the polymer system. Increased or reduction on the T_g were attributed to surface chemistry of the nanoclay, nanoclay/fiber content or loading, dispersibility of nanoclay/fiber and presence of compatibilizer agent. Paluvai et al. (2015) blend surface modified nanoclay with alkaline-silane treated sisal fiber in epoxy/unsaturated polyester (UP) blend matrix. The T_g of the epoxy/UP filled with 1 % modified nanoclay and alkaline silane treated sisal increased for about 41 °C over the epoxy/UP polymer blend. Three factors lead to the improvement in T_g which are: (1) presence of alkyl ammonium on the surface of modified clay functioned as catalyst for amine cured epoxy monomer; (2) modification on the fiber surface via alkaline treatment to increase the surface roughness and amount of polar groups to interact with polymer matrix and (3) presence of silane as compatibilizer agent improve the mobility chain in the epoxy/PU polymer blend.

Significant effect to the shift of T_g, due to the interfacial adhesion effects between fibers and nanosize fillers. The T_g effect of adding nanoclay in treated banana fiber/PP has been investigated by Biswal et al. (2011a). They revealed that the T_g peak shift about 5 °C for the hybrid banana fiber/clay in PP matrix. Addition of treated banana fiber in PP nanocomposite was found to decrease the mobility chains in the PP matrix. Similar observation have been obtained for natural fibers/nanoclays/lignin nanocomposite (Guigo et al. 2009). Inclusion of 5 wt% of nanoclay increase the T_g the due to good layered silicate dispersibility in lignin medium and presence of organophilic cations on the nanoclay surface improve the interfacial adhesion with lignin matrix. Besides that, presence of fibers can alters the response on the polymer chain as well. This effect was investigated by Lin and Renneckar (2011) for wood fiber/nanoclay in PP nanocomposite. Besides nanoclay, fiber can act as nucleating agent which then can accelerate the crystallization process of PP by alter the mobility chain inhomogeneously to amorphous zone. However, fast crystallization rate resulted in lower the T_g value (Nuńez et al. 2004).

6 Conclusions

Inclusion of nanoclay in natural fiber reinforced polymer composite was found to improve the thermal performance of the composite. From thermal stability analysis, layered silicate structure of nanoclay delay the degradation temperature of the natural fiber and polymer in the composite system. During degradation process, the nanoclay move to the surface of the composite and created tortuous to hinder the diffusion of volatiles matter in the composite. In addition, strong interfacial adhesion between nanoclay and natural fiber surfaces with polymer matrix, improve the thermal barrier property of the natural fiber nanocomposite. Moreover, addition of compatibilizer to improve the interfacial adhesion between nanoclay and polymer matrix, help in accelerate the crystallization rate and increase the crystallization temperature peak of the polymer composite. Combination with nanoclay particles and short natural fibers can act as nucleating agent in polymer matrix. Interestingly, T_g characteristics of polymer matrix tend to increase with strong adhesion of nanoclay in fiber reinforced polymer composite.

Acknowledgments Authors would like to thank Universiti Putra Malaysia for funding this research study under Research Universiti (RUGS) Grant (9415401 & 9405400).

References

Abdul Khalil, H.P.S., Siti Alwani, M., Mohd Omar, A.K.: Chemical composition, anatomy, lignin distribution, and cell wall structure of Malaysian plant waste fibers. BioResources **1**(2), 220–232 (2007)

Abdul Khalil, H.P.S., Ireana Yusra, A.F., Jawaid, B.M.: Cell wall ultrastructure, anatomy, lignin distribution, and chemical composition of Malaysian cultivated kenaf fiber. Ind. Crops Prod. **31** (1), 113–121 (2010)

Alamri, H., Low, I.M., Alothman, Z.: Mechanical, thermal and microstructural characteristics of cellulose fibre reinforced epoxy/organoclay nanocomposites. Compos. Part B **43**(7), 2762–2771 (2012)

Alhuthali, A., Low, I.M., Dong, C.: Characterisation of the water absorption, mechanical and thermal properties of recycled cellulose fibre reinforced vinyl-ester eco-nanocomposites. Compos. Part B **43**(7), 2772–2781 (2012)

Arrakhiz, F.Z., El, Achaby M., Malha, M., Bensalah, M.O., Fassi-Fehri, O., Bouhfid, R., Benmoussa, K., Qaiss, A.: Mechanical and thermal properties of natural fibers reinforced polymer composites: doum/low density polyethylene. Mater. Design **43**, 200–205 (2013)

Bikiaris, D., Matzinos, P., Prinos, J., Flaris, V., Larena, A., Panayiotou, C.: Use of silanes and copolymers as adhesion promoters in glass fiber/polyethylene composites. J. Appl. Polym. Sci. **80**(14), 2877–2888 (2001)

Biswal, M., Mohanty, S., Nayak, K.: Influence of organically modified nanoclay on the performance leaf fiber-reinforced polypropylene nanocomposites. J. Appl. Polym. Sci. **114**(6), 4091–4103 (2009)

Biswal, M., Mohanty, S., Nayak, S.K.: Mechanical, thermal and dynamic-mechanical behavior of banana fiber reinforced polypropylene nanocomposites. Polym. Compos. **32**(8), 1190–1201 (2011a)

Biswal, M., Mohanty, S., Nayak, S.K.: Banana fiber-reinforced polypropylene nanocomposites. Effect of fiber treatment on mechanical, thermal and dynamic-mechanical properties. J. Thermoplast. Compos. Mater. **25**(6), 765–790 (2011b)

Biswal, M., Mohanty, S., Nayak, S.K.: Thermal stability and flammability of banana-fiber-reinforced polypropylene nanocomposites. J. Appl. Polym. Sci. **125**(S2), E432–443 (2012)

Buoafif, H., Koubaa, A., Perré, P., Cloutier, A., Rield, B.: Wood particle/high density polyethylene composites: thermal sensitivity and nucleating ability of wood particles. J. Appl. Polym. Sci. **113**(1), 593–600 (2009)

Camino, G., Tartaglione, G., Frache, A., Manferti, C., Costa, G.: Thermal and combustion behaviour of layered silicate-epoxy nanocomposites. Polym. Degrad. Stab. **90**(2), 354–362 (2005)

Chen, J., Yan, N.: Crystallization behavior of organo-nanoclay treated and untreated kraft fiber-HDPE composites. Compos. Part B **54**, 180–187 (2013a)

Chen, J., Yan, N.: Mechanical properties and dimensional stability of organo-nanoclay modified biofiber polymer composites. Compos. Part B **47**, 248–254 (2013b)

Chigwada, G., Jash, P., Jiang, D., Wilkie, C.: Fire retardancy of vinyl ester nanocomposites: synergy with phosphorus-based fire retardants. Polym. Degrad. Stab. **89**(1), 85–100 (2005)

da Silva, Santos R., de Souza, A.A., De Paoli, M.A., de Souza, C.M.L.: Cardonal-formaldehyde thermoset composites reinforced with buriti fibers: preparation and characterization. Compos. Part A **41**(9), 1123–1129 (2010)

Deka, B.K., Maji, T.K.: Effect of nanoclay and ZnO on the physical and chemical properties of wood polymer nanocomposite. J. Appl. Polym. Sci. **124**(4), 2919–2929 (2011)

Deka, B.K., Maji, T.K., Mandal, M.: Study on properties of nanocomposites based on HDPE, LDPE, PP, PVC, wood and clay. Polym. Bull. **67**(9), 1875–1892 (2011)

Delhom, C.D., White-Ghoorahoo, L.A., Pang, S.S.: Development and characterization of cellulose/clay nanocomposites. Compos. Part B **41**(6), 475–481 (2010)

Dorez, G., Taguet, A., Ferry, L., Lopez-Cuesta, J.M.: Thermal and fire behavior of natural fiber/PBS nanocomposite. Polym. Degrad. Stab. **98**(1), 87–95 (2013)

Duquesne, S., Jama, C., Blas, M.L., Delobel, R., Recourt, P., Gloaguen, J.M.: Elaboration of EVA-nanoclay systems-characterization, thermal behaviour and fire performance. Compos. Sci. Technol. **63**(8), 1141–1148 (2003)

Eng, C.C., Ibrahim, N.A., Zainuddin, N., Ariffin, H., Yunus, W.M.Z.W., Then, Y.Y.: Effect of hydrophilic nanoclay on morphology, thermal and mechanical properties of polylactic acid/polycaprolactone/oil palm mesocarp fiber biocomposites. Int. J. Inst. Mater. Malays. **1**(1), 51–70 (2014)

Guigo, N., Vincent, L., Mija, A., Naegele, H., Sbirrazzuoli, N.: Innovative green nanocomposites based on silicate clays/lignin/natural fibres. Compos. Sci. Technol. **69**(11), 1979–1984 (2009)

Guo, G., Park, C.B., Lee, Y.H., Kim, Y.S., Sain, M.: Flame retarding effects of nanoclay on wood-fiber composites. Polym. Eng. Sci. **47**(3), 330–336 (2007)

Hapuarachchi, T.D., Peijs, T.: Multiwalled carbon nanotubes and sepiolite nanoclays as flame retardants for polylactide and its natural fibre reinforced composites. Compos. Part A **41**(8), 954–963 (2010)

Haurie, L., Fernández, A.I., Velasco, J.I., Chimenos, J.M., Cuesta, J.-M.L., Espiell, F.: Thermal stability and flame retardancy of LDPE/PVA blends filled with synthetic hydromagnesite/aluminium hydroxide/montmorillonite and magnesium hydroxide/aluminium hydroxide/montmorillonite mixtures. Polym. Degrad. Stab. **92**(6), 1082–1087 (2007)

Hazarika, A., Devi, R.R., Maji, T.K.: Studies on properties of softwood (Ficus hispida)/PMMA nanocomposites reinforced with polymerizable surfactant-modified nanoclay. Polym. Bull. **68** (7), 1989–2008 (2012)

Iman, M., Maji, T.K.: Effect of crosslinker and nanoclay on starch and jute fabric based green nanocomposites. Carbohydr. Polym. **89**(1), 290–297 (2012)

Kovacevic, Z., Bischof, S., Fan, M.: The influence of Spartium junceum L. fibres modified with montmorillonite nanoclay on the thermal properties of PLA biocomposites. Compos. Part B **78**, 122–130 (2015)

Kumar, V., Kumar, R.: Improved mechanical and thermal properties of bamboo-epoxy nanocomposites. Polym. Compos. **33**(3), 362–370 (2012)

Kumar, V., Sharma, N.K., Kumar, R.: Dielectric, mechanical, and thermal properties of bamboo-polylactic acid bionanocomposites. J. Rein. Plast. Comp. (2012). doi:10.177/07316844124611290

Lee, S.-H., Wang, S.: Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. Compos. Part A **37**(1), 80–91 (2006)

Lee, Y.H., Kuboki, T., Park, C.B., Sain, M., Kontopoulou, M.: The effects of clay dispersion on the mechanical, physical, and flame-retarding properties of wood fiber/polyethylene/clay nanocomposites. J. Appl. Polym. Sci. **118**(1), 452–461 (2010)

Lei, S.G., Hoa, S.V., Ton-That, M.-T.: Effect of clay types on the processing and properties of polypropylene nanocomposites. Compos. Sci. Technol. **66**(10), 1274–1279 (2006)

Lei, Y., Wu, Q., Yao, F., Xu, Y.: Preparation and properties of recycled HDPE/natural fiber composites. Compos. Part A **38**(7), 1664–1674 (2007a)

Lei, Y., Wu, Q., Clemons, C.M., Yao, F., Xu, Y.: Influence of nanoclay on properties of HDPE/wood composites. J. Appl. Sci. **106**(6), 3958–3966 (2007b)

Lin, Z., Renneckar, S.: Nanocomposite-based lignocellulosic fibers 2: layer-by-layer modification of wood fibers for reinforcement in thermoplastic composites. Compos. Part A **42**(1), 84–91 (2011)

Liqun, X., James, L.L.: Kinetic analysis and mechanical properties of nanoclay reinforced unsaturated polyester (UP) resins cured at low temperatures. Polym. Eng. Sci. **45**(4), 496–509 (2005)

Liu, W., Mohanty, A.K., Drzal, L.T., Askel, P., Misra, M.: Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites. J. Mater. Sci. **39**(3), 1051–1054 (2004)

Liu, W., Hoa, S.V., Pugh, M.: Fracture toughness and water uptake of high-performance epoxy/nanoclay nanocomposites. Compos. Sci. Technol. **65**(15), 2364–2373 (2005)

Madaleno, L., Schjødt-Thomsen, J., Pinto, J.C.: Morphology, thermal, and mechanical properties of PVC/MMT nanocomposites prepared by solution blending and solution blending + melt compounding. Compos. Sci. Technol. **70**(5), 804–814 (2010)

Manfredi, L.B., Rodríguez, E.S., Wladyka-Przbylak, M., Vázquez, A.: Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres. Polym. Degrad. Stab. **91**(2), 255–261 (2006)

Manias, E., Touny, A., Wu, L., Strawhecker, K., Lu, B., Chung, T.C. Polypropylene/montmorillonite nanocomposites. Review of the synthetic routes and materials properties. Chem. Mater. **13**(10), 3516–3523 (2001)

Mittal, V.: Polymer Nanocomposite Foams, p. 63. CRC Press (2013)

Mohan, T.P., Kanny, K.: Nanoclay infused banana fiber and its effects on mechanical and thermal properties of composites. J. Compos. Mater. (2015). doi:10.1177/0021998315590265

Molinaro, S., Romero, M.C., Boaro, M., Sensidoni, A., Lagazio, C., Morris, M., Kerry, J.: Effect of nanoclay-type and PLA optical purity on the characteristics of PLA-based nanocomposite films. J. Food Eng. **117**(1), 113–123 (2013)

Morgan, A.B.: Flame retarded polymer layered silicate nanocomposites: A review of commercial and open literature systems. Polym. Advan. Technol. **17**(4), 206–217 (2006)

Nuńez, A.J., Kenny, J.M., Reboredo, M.M., Aranguren, M.I., Marcovich, N.E.: Thermal and dynamic mechanical characterization of polypropylene-woodflour composites. Polym. Eng. Sci. **42**(4), 733–742 (2004)

Olewnik, E., Garman, K., Czerwiński, W.: Thermal properties of new composites based on nanoclay, polyethylene and polypropylene. J. Therm. Anal. Calorim. **101**(1), 323–329 (2010)

Paluvai, N.R., Mohanty, S., Nayak, S.K.: Effect of cloisite 30B clay and sisal fiber on dynamic mechanical and fracture behaviour of unsaturated polyester toughened epoxy network. Polym. Compos. (2015). doi:10.1002/pc.23480

Pandey, P., Dayanidhi, A., Mohanty, S., Nayak, S.K.: Effect of clay loading on flammability of poly(methyl methacrylate)/clay nanocomposites. J. Thermoplast. Compos. **26**(5), 663–679 (2011)

Qin, H., Zhang, S., Zhao, C., Feng, M., Yang, M., Shu, Z., Yang, S.: Thermal stability and flammability of polypropylene/montmorillonite composites. Polym. Degrad. Stab. **85**(2), 807–813 (2004)

Qin, H., Zhang, S., Zhao, C., Hu, G., Yang, M.: Flame retardant mechanism of polymer/clay nanocomposites based on polypropylene. Polymer **46**(19), 8386–8395 (2005)

Rahimi-Razin, S., -Kalajasi, M.S., Asl, V.H., Mamaqani, H.R.: (2012) Effect of different modified nanoclays on the kinetics of preparation and properties of polymer-based nanocomposites. J. Polym. Res. **19**(9), 1–16

Rahman, M., Hamdan, S., Hashim, D.M.A., Islam, M., Takagi, H.: Bamboo fiber polypropylene composites: Effect of fiber treatment and nano clay on mechanical and thermal properties. J. Vinyl Addit. Techn. **21**(4), 253–258 (2015)

Rajasekar, R., Pal, K., Heinrich, G., Das, A., Das, C.K.: Development of nitrole butadiene rubber-nanoclay composites with epoxidized natural rubber as compatibilizer. Mater. Design **30**(9), 3839–3845 (2009)

Rajini, N., Winowlin Jappes, J.T., Rajakarunakaran, S., Jeyaraj, P.: Mechanical and free vibration properties of montmorillonite clay dispersed with naturally woven coconut sheath composite. J. Reinf. Plast. Comp. **31**(20), 1364–1376 (2012)

Reddy, C.R., Sardhasti, A.P., Simon, L.C.: Preparation and characterization of polypropylene-wheat straw-clay composites. Compos. Sci. Technol. **70**(12), 1674–1680 (2010)

Sánchez-Jiménez, P.E., Pérez-Maqueda, L.A., Perejón, A., Criado, J.M.: Nanoclay nucleation effect in the thermal stabilization of a polymer nanocomposite: a kinetic mechanism change. J. Phys. Chem. C **116**(21), 11797–11807 (2012)

Saw, S.K.: Static and dynamic mechanical analysis of coir fiber/montmorillonite nanoclay-filled novolac/epoxy hybrid nanocomposites. In: Book Eco-friendly Polymer Nanocomposites. Advanced Structured Materials, pp. 137–154. Springer, India (2015)

Shuvo, S.N., Shorowordi, K.M., Islam, M.A.: Effect of nanoclay on jute fiber reinforced polyester composites. Int. J. Adv. Eng. Nano Technol. **2**(8), 20–26 (2015)

Subramaniyan, A.K., Sun, C.T.: Toughening polymeric composites using nanoclay: crack tip scale effect on fracture toughness. Compos. Part A **38**(1), 34–43 (2007)

Walters, R.N., Lyon, R.E.: Flammability of polymer composites. Office of aviation research and development. Federal aviation administration (2008)

Wang, C., Liu, C.-R.: Transcrystallization of polypropylene composites: nucleating ability of fibres. Polymer **40**(2), 289–298 (1999)

Yussuf, A.A., Massoumi, I., Hassan, A.: Comparison of polylactic acid/kenaf and polylactic acid/rice husk composites: the influence of the natural fibers on the mechanical, thermal and biodegradability properties. J. Polym. Environ. **18**(3), 422–429 (2010)

Zahedi, M., Tabarsa, T., Ashori, A., Madhoushi, M., Shakeri, A.: A comparative study on some properties of wood plastic composites using canola stalk, Paulownia, and nanoclay. J. Appl. Polym. Sci. **129**(3), 1491–1498 (2013)

Zahedsheijani, R., Faezipour, M., Tarmian, A., Layeghi, M., Yousefi, H.: The effect of Na+ montmorillonite (NaMMT) nanoclay on thermal properties of medium density fibreboard (MDF). Eur. J. Wood Prod. **70**(5), 565–571 (2012)

Zainuddin, S., Hosur, M.V., Zhou, Y., Narteh, A.T., Kumar, A., Jeelani, S.: Experimental and numerical investigations on flexural and thermal properties of nanoclay-epoxy nanocomposites. Mater Sci. Eng. A-Struct. **527**(29), 7920–7926 (2010)

Zanetti, M., Lomakin, S., Camino, G.: Polymer layered silicate nanocomposites. Macromol. Mater. Eng. **279**(1), 1–9 (2000)

Zhang, H., Rizvi, G.M., Park, C.B.: Development of an extrusion system producing fine-celled HDPE/wood fiber composite foams using CO_2 as a blowing agent. Adv. Polym. Tech. **23**(4), 263–276 (2004)

Zhao, Y., Wang, K., Zhu, F., Xue, P., Jia, M.: Properties of poly(vinyl chloride)/wood flour/montmorillonite composites: effects of coupling agents and layered silicate. Polym. Degrad. Stab. **91**(12), 2874–2883 (2006)