Hybrid Composite Foams Based on Nanoclays and Natural Fibres

Hajar Yousefian and Denis Rodrigue

Abstract In this chapter, a brief introduction on natural fibers (types, properties and advantages) is presented first to show their application in various industries. Then, nanoclay as one the most widely used fillers is presented. The structures, properties and applications of this filler are described with examples related to the nanocomposite industries. Then, the combination of nanoclay with synthetic and natural fibers to produce hybrid composite systems is reviewed showing recent achievements and activities in this field. Foamed materials are then introduced. The basic concepts of foaming are discussed followed by the effect of adding particles on structures and properties. Finally, composites and hybrid foams based on nanoclay and natural fiber is reviewed followed by a conclusion and openings for future works.

Keywords Nanoclay · Natural fiber · Hybrid composites · Foam

1 Natural Fibers

Interests of replacing synthetic fibers with natural fibers to produce fiber reinforced polymers increased substantially in recent years according to the many advantages provided by these eco-friendly fibers. Natural origin, bio-degradability, low cost, relatively good mechanical properties, and high specific strength make fibers such as jute, flax, hemp, kenaf, cotton, sisal, and ramie good replacements for glass, aramid, and other non-natural fillers (Ku et al. 2011; Koronis et al. 2013; Yousefian and Rodrigue 2014).

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The ultimate challenge while using these natural fibers is their variability and wide range of characteristics and properties depending on their source, type, processing methods, and any modifications affecting the final properties of a composite (Faruk et al. 2012).

One of the most used natural filler is wood (flour and fiber). It can be easily and economically prepared (wood waste of different processing like pulp and paper, building and construction, furniture, etc.) and used after a simple sieving. The main drawback of applying natural fibers in polymer matrices is their poor compatibility, water absorption and thermal stability. Nevertheless, these limitations can be improved by using physical (stretching, calendaring, etc.) or chemical (alkylation, esterification, etc.) modifications. Other natural fillers of potential interest are residues of the food and agriculture industry such as nutshells, oil palm empty fruit bunch fibers, corn plant extracted fibers, etc. Nevertheless, these particles are less studied for polymers reinforcement since they provide limited mechanical properties improvements (La Mantia and Morreale 2011).

2   Nanoclays

Until the late 1970s, minerals (talc, calcium carbonate, mica, etc.) were widely used as fillers in polymers. The main goal was economic as those materials were less expensive than polymers. Nowadays, with the developments associated with nanotechnology, one of the most used mineral fillers are nanoclays (Anadão 2013).

Nanoclays or naturally formed alumina silicate (generally referred to as phyllosilicates) are well-known for their platelet-like shape. These multifunctional materials are environmentally friendly and also cost effective (Majeed et al. 2013). Nanoclays were extensively studied and applied in agriculture and medicine. These minerals are fundamentally made of tetrahedral and octahedral sheets. Depending on the arrangement and/or number of these sheets, they are categorized in three main classes:

a. 1:1 clays containing one tetrahedral and one octahedral sheet.
b. 2:1 clays having one octahedral sheet sandwiched between two tetrahedral sheets per layer.
c. 2:1:1 clays containing one octahedral sheet next to a 2:1 layer.

2.1   Structure

Layered silicates are very small crystalline substances from the 2:1 phyllosilicates group. They could be either natural (montmorillonite, hectorite and saponite) or synthetic (fluorohactorite, laponite, and magatiide) minerals (Majeed et al. 2013). They mainly contain an octahedral sheet of alumina or magnesia and two tetrahedral

Table 1 Formula and characteristics of three natural clay minerals [7]

Name	Formula	CEC (Mequiv/100 g)	Length of particle (nm)
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100–150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200–300
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6	50–60

M monovalent cation; *x* degree of isomorphous substitution (between 0.5 and 1.3), *CEC* cation exchange capacity

Fig. 1 Structure of Na-MMT
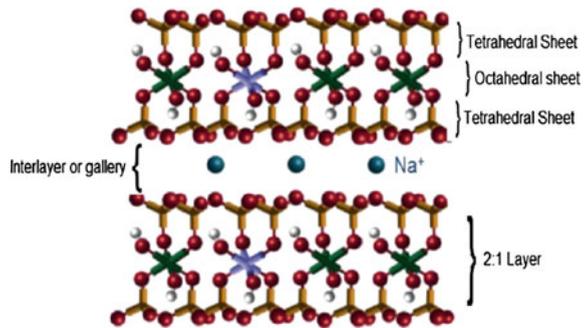
sheets of silica. The side dimensions of these layers range from 3000 nm to several microns with thicknesses of about 1 nm. A weak electrostatic force keep these layers together, so various agents such as water, organic cations or polar organic liquids can penetrate into the space between them. Table 1 summarizes some characteristics of three natural mineral clays.

Among these nanoclays, montmorillonite (MMT) is the most common filler in nanocomposite production due to its large aspect ratio (50–1000). A typical structure of MMT is presented in Fig. 1 where an octahedral layer (thickness = 1 nm) of alumina or magnesia located between two silica tetrahedral layers. Besides, metal cations such as Na^+ and Ca^{+2}, placed between the sheets, usually balance the overall negative charge caused by isomorphic exchange of Al^{3+} in the octahedral layer by Mg^{2+} or Fe^{2+}, and Mg^{2+} by Li^+.

2.2 Polymer Clay Nanocomposite

To date, the use of nanoparticles in composites has been an efficient way to improve the mechanical (toughness, stiffness and heat distortion), thermal, electrical, and barrier properties of composites (Ali and Ahmad 2012). But the effectiveness of nanofillers as reinforcement strongly depends on their concentration, shape, size,

surface nature, dispersion, and interaction with the polymer matrix. As nanotechnology progresses, nano-size becomes of interest as it was reported that these particles, due to their small sizes, high surface areas and high aspect ratios, could bring substantial improvement to the polymer world compared to their micron-size counterparts (Ali and Ahmad 2012).

Among the different mineral fillers, nanoclays attracted much attention, especially for packaging industries who recently concentrated on nanoclays because they are low cost and available (Majeed et al. 2013). Compared to commonly use fine particles such as talc, they are much smaller in size (1400 times smaller).

Nanocomposites based on clay were primarily produced in 1950, but the turning point of their development occurred in late the 1980s (Anadão 2013). In particular, Toyota used organophilic modified clays in polyamide 6 (Nylon) for the timing belt covers of their cars (collaborating with UBE Industries, a Japanese provider of polyamide 6). The nanocomposites produced contained only 5 % wt. clay but this substantially improved the mechanical properties of polyamide 6: 60 % in tensile modulus, 126 % in flexural modulus, 40 % in stress at break and a 65–152 °C improvement in the heat distortion temperature.

Moreover, a major advantage of working with nanoclay is they can be easily used with most polymers via standard processing techniques like extrusion, injection, compression, and solution casting to produce various products such as films, membranes, automotive and electronics parts, packaging materials, etc. (Anadão 2013).

According to their difference in surface energy, interfacial bonding between polymers and clays can be thermodynamically classified as (Ray 2013a):

a. Intercalated nanocomposites (Fig. 2 left) in which the polymer chains regularly penetrate inside clay layers.
b. Flocculated nanocomposites (Fig. 2 middle) are similar to the intercalated state, with the exception for some silicate layers which are flocculated because of hydroxyl group interactions.
c. Exfoliated nanocomposites (Fig. 2 right) are randomly dispersed clay layers in the polymer matrix. Commonly, the clay content is much lower than the other two groups.
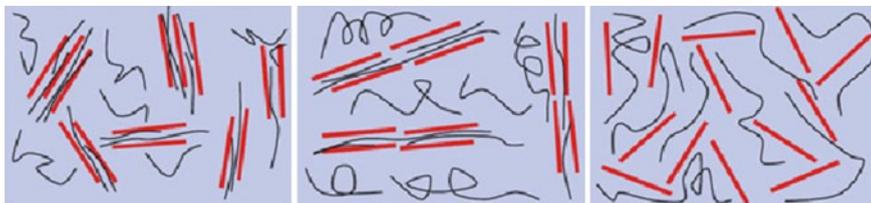

Fig. 2 Three thermodynamically different polymer clay composites: (*left*) intercalated, (*middle*) flocculated, and (*right*) exfoliated

2.3 Properties

Nanoclay filled thermoplastics received a great deal of attention due to the improved performances they bring to nanocomposite industries. In particular, exfoliated nanocomposites have high modulus, enhanced strength and heat resistance, as well as reduced gas permeability and flammability compared to neat polymers, along with increased biodegradability for biodegradable polymers (Majeed et al. 2013). The three most influenced properties in polymer clay nanocomposite are discussed next.

2.3.1 Mechanical Properties

Nanoclays, modified or even unmodified, have significant effects on the mechanical properties of polymer matrices. It was observed that nanoscale interactions between the matrix and nanoclay particles lead to new and unique properties in the final nanocomposite which is not like traditional composites (Ray 2013b). It has been shown that nanoclay, compared to conventional fillers such as glass fibers, can increase the elastic modulus of Nylon 6 at very low content (less than 10 % wt.) as shown in Fig. 3.

It can be seen that only 6.5 % of nanoclay will double the modulus, while 20 % of glass fiber is needed to get the same increase. Lower content usually leads to economic and processing advantages (Ray 2013b). With lower filler content, raw material costs can decrease and lighter composites (lower overall density since fillers are usually denser than polymer matrices) with higher performances are produced leading to higher specific properties (property per unit weight) which are highly desirable for packaging and automotive applications.

In another study, the effect of nanoclay on the mechanical properties of high density polyethylene (HDPE) with and without compatibilizer (polyethylene grafted maleic anhydride: MAPE) were evaluated and the results are reported in Table 2

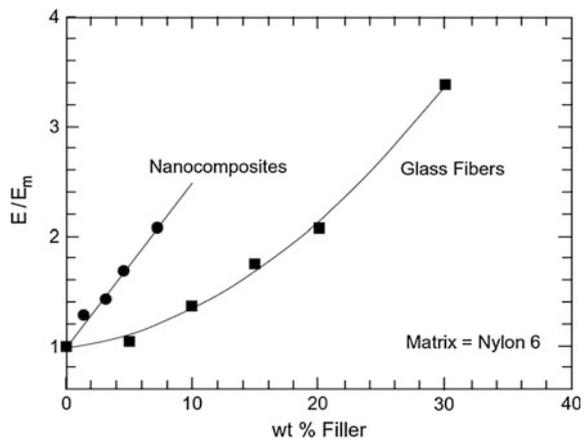**Fig. 3** Comparison between nanoclay and glass fiber on the relative elastic modulus of Nylon 6

Table 2 Tensile properties of HDPE-clay composites (Rezanavaz and Aghjeh 2012)

Sample	Young modulus (MPa)	Strain at yield (%)	Elongation at break (%)
HDPE	512	24.7	1790
HDPE-(15 %) MAPE	545	24.1	1090
HDPE-(3 %) clay	576	17.5	1200
HDPE-(15 %) MAPE-(3 %) clay	651	18.6	1250

All samples contain very small amount of antioxidant ($\sim$0.1 % wt.) and all percentages are based of weight

(Rezanavaz and Aghjeh 2012). It can be seen that with the addition of only 3 % wt. clay, the tensile modulus increased (from 512 to 576 MPa) and this increase was more noticeable when adding MAPE (from 512 to 651 MPa) to enhance the interfacial bonding between HDPE and clay. Elongation at break also changed and significantly decreased with clay addition, but was improved with MAPE (Kumar and Singh 2013). For polypropylene (PP), similar trends were observed for mechanical properties improvement: a 76 % increase in tensile modulus when 7.7 % wt. clay was added to PP-(5 % wt.) MAPP (Tabuani and Camino 2011).

Overall, nanoclays in polymers can alter the mechanical properties of the composites in either of these three possible ways (Ray 2013b):

- Clay particles bring their inherent toughness and strength to the matrix and improve the mechanical properties of the composites.
- Clay sheets can improve composite failure by stopping crack propagation.
- Polymer chains close to the nanoclay surface go through structural variations changing the overall mechanical properties.

Generally, it is believed that both degree of dispersion and interfacial bonding have important effects on the mechanical properties of final nanocomposites as described next.

2.3.2 Barrier Properties

In each material, barrier properties determine how substances such as gases and liquids permeate from a high concentration side to a low concentration side (Ray 2013c). This process consist of four steps:

- Adsorption
- Dissolution
- Diffusion
- Desorption

Gases or liquids enter the substance on the high concentration side, then diffuse into the material and finally desorb on the other side.

Clay particles, according to their specific shape, are assumed to provide a tortuous pathway in the polymer composite consequently improving the barrier properties as depicted in Fig. 4. Another important advantage of this longer diffusion path is higher thermal insulation. Nanoclay based composites, even at low contents, were shown to be highly impermeable to small size molecules such as O_2, H_2O, CO_2, etc. For instance, 2 % wt. of nanoclay decreases the permeability of polyamide by a factor of around 10. Comparing different nanoclays according to their shapes, it was observed that clays having higher length to diameter ratio (aspect ratio) produced highly impermeable composites (Ray 2013c).

A study on polyethylene terephthalate (PET) showed that incorporation of nanoclay significantly increased the oxygen barrier properties of virgin PET. Composites containing 1–4 % wt. of clay were shown, through TEM and XRD, to be intercalated composites and the oxygen barrier results are presented in Fig. 5. It is clear that even low nanoclay content can substantially reduce the oxygen permeability of PET-nanoclay; 3 % wt. decreased the permeability of the neat matrix by 50 %. This information is important for applications like packaging.

As dispersion is a key factor in polymer nanocomposites, an interesting study on using CO_2 in polystyrene (PS) was presented to improve clay dispersion

Fig. 4 Schematic representation of the origin of improved barrier properties (higher tortuosity) of polymers filled with nanoclays
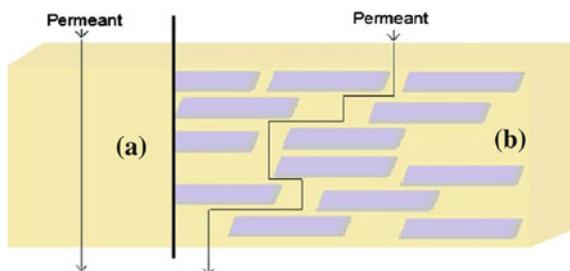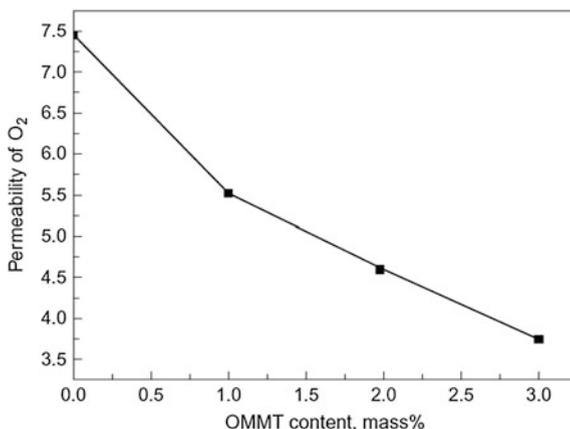

Fig. 5 Effect of clay content on PET oxygen permeability

(Yang et al. 2014). Morphological results showed that this methodology help clay particles to lose their layered structure and produce an intercalated/exfoliated structure. In this case, O_2 permeability was substantially reduced (around 49 %) using only 1.09 % wt. of clay.

Barrier properties of polylactic acid (PLA)/nanoclays were also studied (Picard et al. 2011). Organo-modified MMT was shown to have a significant effect on PLA crystallisation and oxygen permeability of annealed PLA samples was reduced (13 %) while using 4 % wt. of MMT.

The effect of chain extenders (multifunctional epoxy based: Joncryl®) was also studied on PET-organo-modified clay systems (Ghanbari et al. 2013). It was found that the chain extender react with PET end groups and consequently increased the viscoelastic properties of the matrix, leading also to improved clay exfoliation level. This is why the samples with chain extenders exhibited higher barrier properties. In particular, the O_2 permeability of PET decreased by 46 % for a composite containing 4 % wt. clay and 1 % wt. Joncryl.

2.3.3 Thermal Stability

Generally, the presence of nanoclay improves the thermal stability of polymers which can be associated to various effects like silicate content, platelet-like geometry and high aspect ratio, low permeability, reduction in the rate of development of volatile substances, as well as the formation of carbonaceous silicate chars on the surface of the nanoclays covering the materials and reducing the discharge of volatile substances created during the decomposition process (oxidation/combustion) and absorption of the generated gas on the nanoclay platelets (Ray 2013d). Well-dispersed nanoclays can significantly change the decomposition mechanism of the polymer to from a thermally different material than the virgin matrix.

During the past years, several works were done on the effect of nanoclays on the thermal stability of polymers such as polystyrene (PS) and ethylene-vinyl acetate (EVA) (Ray 2013d). In the case of PS, thermal stability of clay containing nanocomposites showed a significant improvement with clay content. Like most of the nanocomposites, degree of dispersion has a direct influence on the thermal stability of PS/nanoclay composite systems. Different kinds of modified clays have been used in PS to study their effect on the thermal stability of the composite and in most samples, the thermal stability was reasonably improved compared to virgin PS (up to 50 °C improvement) (Ray 2013d). Similar trends were observed for low density polyethylene (LDPE). Addition of nanoclay, improved the thermal stability of LDPE and in most cases, 4 % wt. is the optimum value (see Fig. 6) (Ray 2013d).

PP clay composites were also shown to behave like LDPE. High improvement in thermal stability level were related to polymer chains entrapped between clay platelets. It is also possible that the production of carbonaceous silicate char lead to a surface barrier (Ray 2013d).

The thermal stability of PLA also was investigated whit different clay (N. Najafi et al. 2012). The rheological results also showed that PLA degraded faster with the

Fig. 6 Effect of clay content on LDPE thermal stability
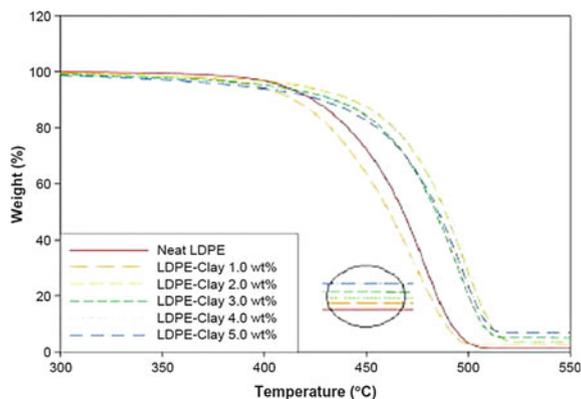
addition of organo-modified clays. However, using a chain extender such as polycarbodiimidein (PCDI) at its optimum value (2 % wt.) could help controlling the rate of polymer degradation and viscosity change.

3 Hybrid Composites

The idea of reducing synthetic fibers use along with minimizing production costs and environmental issues led to the development of new composite systems called hybrid composites. With hybridization, the weaknesses of one component will be balanced by the strengths of another. In these systems, a combination of synthetic and natural fibers is generally used to achieve the goals of hybrid systems. Nanoclay-natural fiber system is one of the most interesting hybrid systems in which the strength and rigidity of the nanoclay balance the flexibility and specific stiffness of natural fibers (Ali and Ahmad 2012). Natural fiber/nanofiller hybridization in polymers lead to lower water uptake and improved mechanical properties. Several investigations were devoted to hybrid systems producing improved mechanical and thermal properties. For example, rice husk flour/HDPE composite with the addition of small amount of nanoclay were produced (Kord 2011). Different polymers, such as polypropylene (PP), epoxy, polyester and polyurethane (PU), have been used to produce hybrid systems (Saba et al. 2014).

3.1 Clay Based Hybrid Composites

One of the most traditional and widely used fillers in automotive and aerospace industries is glass fiber (GF). Due to its inherent high strength, GF has been used to improve the mechanical properties of polymers such as PP (Rahman et al. 2012). However, because of high stress concentration and week GF-matrix bonding, it was

observed that in PP-GF composites the tensile modulus increases while tensile strength and impact strength decrease. On the other hand, nanoparticles were believed to significantly improve the physical and mechanical properties of the composites. The most important effect, while being used in semi-crystalline thermoplastics, is their nucleating agent role. As crystallinity of a polymer such as PP increases, this modifies the mechanical properties of the composites: increased modulus while decreasing strength and deformability. So in such systems (PP-GF), adding nanoclays as a third component to produce hybrid systems leads to a balance of the overall properties. In a work on PP-GF-nanoclay systems, the morphological and mechanical analyses showed that the presence of nanoclay in PP-GF composites improved the overall properties of composite system (Rahman et al. 2012). DSC results showed that the melting temperature of the system shifted to higher temperature when nanoclay was added to PP-GF system (from 161.6 to 165.5 °C while adding 6 % wt. of clay) and the degree of crystallinity was strongly affected by both nanoclay and GF in the system (14 % increase when 15 % wt. GF and 6 % wt. nanoclay were added to neat PP). As seen in Fig. 7, the authors reported some evidence of ductile deformation in Fig. 7a due to fiber debonding and pull-out. As nanoclay was added (Fig. 7b–d), ductility decreased which is clear with smaller deformation pattern. These observations were also in agreement with impact results.
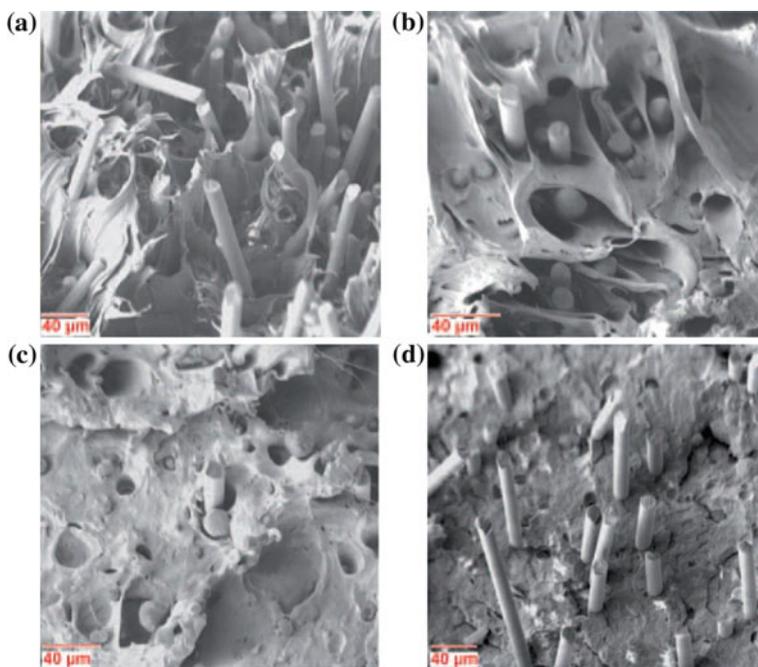

Fig. 7 SEM images of **a** PP-GF (15 % wt.), **b** PP-GF (15 % wt.)-nanoclay (3 % wt.), **c** PP-GF (15 % wt.)-nanoclay (6 % wt.), and **d** PP-GF (15 % wt.)-nanoclay (9 % wt.)
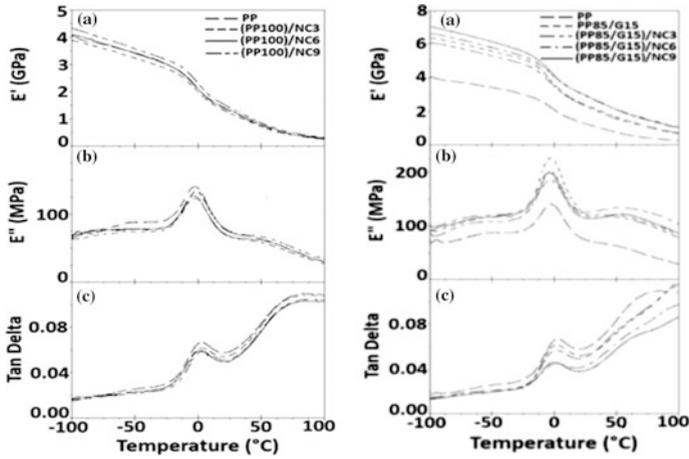
Fig. 8 DMA results of PP-nanoclay (*left*) and PP-GF-nanoclay hybrid system (*right*)

Dynamic mechanical analysis of both composites and hybrid systems also showed that the storage modulus (E′) increased with the addition of nanoclay to PP-GF and PP resulting in higher stiffness. Tan δ obtained via dynamic mechanical analysis (DMA) was also shown to be significantly influenced from clay and GF content in the composites as presented in Fig. 8.

3.2 Clay-Natural Fiber Based Hybrid Composites

Recently, the combination of nanoclay/natural fibers became of high interest to produce hybrid systems. This is related to reduced water absorption and dimensional swelling with improvement in tensile properties of PP-reed flour composites with the addition of nanoclay (Figs. 9 and 10). The effect of coupling agent on the

Fig. 9 Effect of nanoclay content on water absorption of PP-reed flour composites
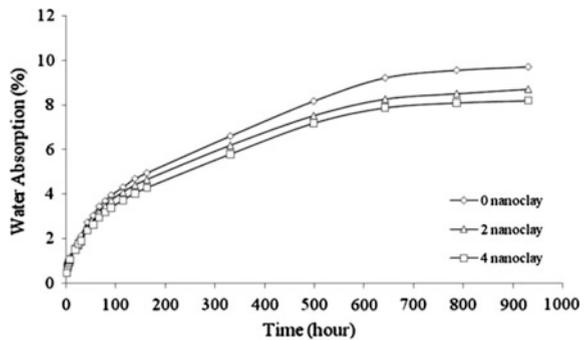
Fig. 10 Effect of nanoclay content on thickness swelling of PP-reed flour composites
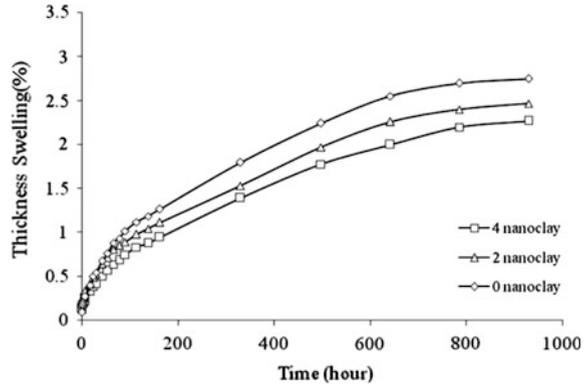
mechanical and physical properties of this system was also studied (A. Najafi et al. 2012). It was observed that the addition of 4 phc (parts per hundred contents) nanoclay with polypropylene grafted with maleic anhydride (MAPP) increased the tensile strength and modulus by around 96 and 89 %, respectively.

In another work, the positive effect of adding nanoclay and rice husk on the mechanical properties of HDPE was reported (Kord 2011). It was observed that the composite having the best structure (intercalated) contained 2 phc of nanoclay. Moreover, nanoclay had an effect on the crystallization behavior of rice husk filled HDPE by increasing the crystallization temperature, enthalpy, and crystallinity. To obtain an exfoliated structure, the authors suggested to increase the compatibilizer (MAPE) content (2 phc).

A combination of nanoclay and hemp was also found to have synergistic effects on the flexibility and stiffness of PP as reported in Fig. 11 (Kord 2012). A noticeable reduction in water absorption and thickness swelling (Fig. 12) was also observed with increasing nanoparticles content for the range studied (0–5 % wt.). Dynamic mechanical behavior as well as fire retardancy and dimensional stability were also improved with the presence of nanoparticles (Figs. 13 and 14).

In another work on microcrystalline cellulose (MCC) filled ethylene-propylene (EP) copolymer, addition of 5 % wt. of nanoclay was found to have a significant

Fig. 11 Effect of nanoclay content on the tensile strength and modulus of PP-hemp composites
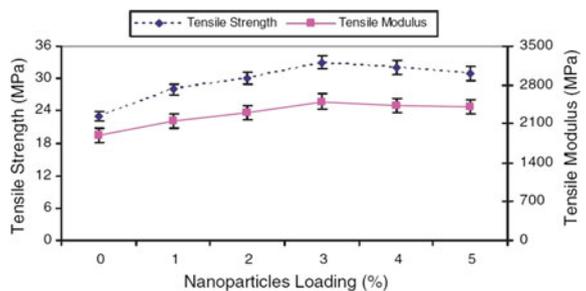
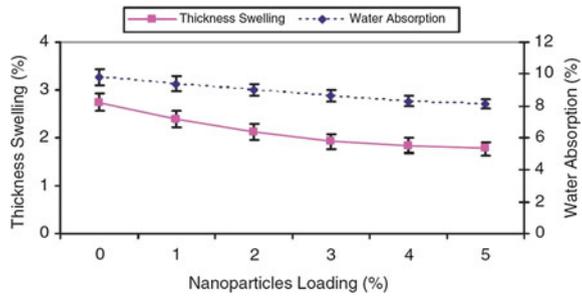**Fig. 12** Effect of nanoclay content on water absorption and thickness swelling of PP-hemp composites

Fig. 13 Effect of nanoclay on the burning rate and time to ignition of PP-hemp composites
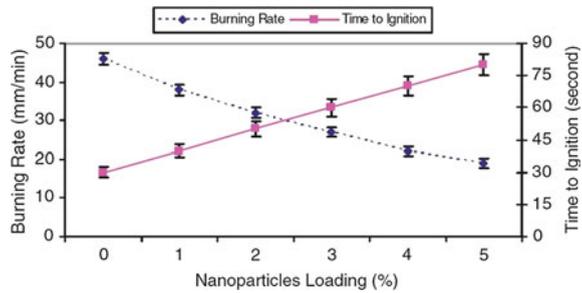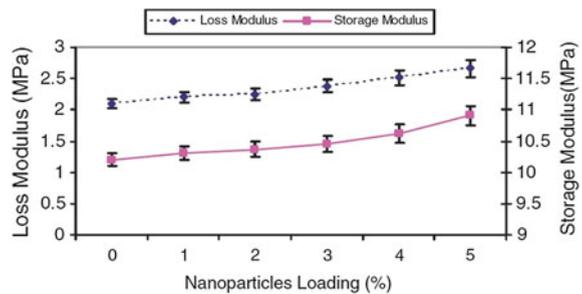

Fig. 14 Effect of nanoclay content on the loss and storage modulus of PP-hemp composites

effect on the elastic modulus of the composites (increase from 1.04 to 1.24 GPa) (Saba et al. 2014).

The effect of nanoclay on the mechanical, thermal and physical properties of hybrid systems such as PP-pine cone fiber (Arrakhiz et al. 2013) and PP-GF-wood flour (Kord and Kiakojouri 2011) was also studied. Nanoclay and MAPP were added to PP-GF-wood flour systems and the tensile properties (modulus and strength) were found to be optimum for a nanoclay content of 4 phc (see Figs. 15 and 16). The positive effect of nanoclay addition on water absorption properties is also presented in Fig. 17.

As all the studies showed, well-dispersed nanoparticles in the polymer matrix can have an effective role as to improve the mechanical, barrier, and fire resistance properties of natural fiber polymer composites (Johansson et al. 2012).

Fig. 15 Tensile modulus as a
function of GF and nanoclay
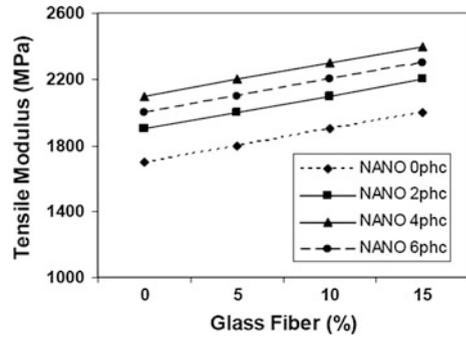contents in PP-wood flour
composites

Fig. 16 Tensile strength as a
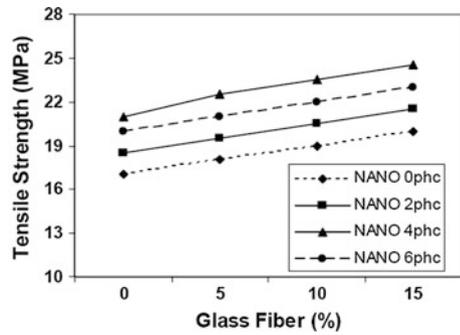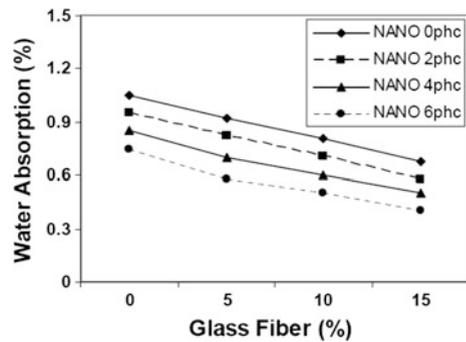function of GF and nanoclay
contents in PP-wood flour
composites

Fig. 17 Water absorption as
a function of GF and nanoclay
contents in PP-wood flour
composites

4 Foams

Foams are porous materials consisting of numerous gas bubbles which were pro-
duced in the polymer melt and then stabilized during solidification (Anadão 2013).
Foams with different morphologies are one solutions to use less amount with

satisfactory mechanical properties. Many industries, especially construction, automotive, and packaging, are interested to use foams because of their light-weight, high specific strength, as well as high thermal and sound insulation properties. Besides cell geometry, two parameters are important to characterize a foam morphology: cell size and cell density (number of cells per unit volume). According to cell size, foams can be divided into 4 categories (Anadão 2013):

1. Macrocellular have cell sizes above 100 µm. This group is attractive for sound or heat insulating properties and furniture industries. Generally and like other foams they are cost effective compared to their unfoamed counterparts.
2. Microcellular have cell sizes in the range of 1–100 µm. For over three decades now, this group has been developed due to their good mechanical properties such as impact strength and toughness compared to traditional foams. They also have better acoustic and thermal insulation properties and this is why there is still high interest to develop these foams for industrial applications like construction and automotive.
3. Ultramicrocellular have cell sizes in the range of 0.1–1 µm.
4. Nanocellular foams have cell sizes in the range of 0.1–100 nm.

Other types of foam classification are possible. Depending on their rigidity, they can be classified as rigid and flexible foams. Finally, depend on cell connections, they can be classified as open (in which cells are connected to each other and the wall between cells are broken) and closed (cells are surrounded by polymer matrix and isolated from each other) cell foams (Chen et al. 2013). Relative density (foam density divided by un-foamed density) is also an important property as it mainly controls the overall mechanical and thermal properties of the foams.

4.1 Nanocomposite Foams

The mechanical properties of polymer foams are generally lower than their unfoamed counterparts because less material is available to sustain the applied stresses. One way to overcome this limitation is to use fillers inside the foamed structure (Yousefian and Rodrigue 2015). But high filler content can bring processing issues such as dispersion and aggregation problems, as well as higher viscosity. So, nanofillers instead of larger size fillers have been used in foam structure. Besides their lower content, they can provide improved mechanical, barrier and flame retardancy properties to the foam. They also improve nucleation (crystallization and foam cell) by acting as nucleating agents leading to higher cell densities and lower cell sizes. In fact, all these improvement are directly related to the nanofiller dispersion and content, as well as interfacial bonding (Sorrentino and Iannace 2013).

4.2 Clay Based Nanocomposite Foams

Nanoclays (especially MMT) are one of the most widely used nanofillers in polymer composite foams (Ahmadzadeh et al. 2015). Indeed, they provide better conditions to control the foam morphology. Besides excellent effect on nucleation due to their flat surface and specific surface area, well-dispersed clay particles were shown to produce excellent foam structures (uniform and small cell size with higher cell density) and improved mechanical properties (Chen et al. 2013). There are several works on clay based nanocomposite foams and the most recent ones are presented next.

In a study done by Zandi et al. (2011), the effect of organophilic MMT (oMMT) on the morphological, thermal, and mechanical properties of uncrosslinked LDPE via extrusion was studied. Their results showed that the presence of nanoclay changed the foam morphology by decreasing cell size and increasing cell density (2 times increase in cell density while nanoclay increased from 0 to 0.6 % wt.). Probably due to this effect, these nanocomposite foams were shown to have lower thermal conductivity than neat LDPE (7 % reduction when clay increased from 0 to 0.6 % wt.). The mechanical results also showed that for an optimum clay content (0.3 % wt.), Young's modulus increased (31 % compared to neat LDPE) and due to presence of nanoclay, these nanocomposite foams had better fire retardancy properties (Fig. 18) related to char formation on the burning face.

In a study by Chaudhary and Jayaraman (2011), several PP-clay nanocomposites were foamed by chemical foaming agent via extrusion. The authors found that based on different melt extensional strain hardening and crystallization, different foam structures were developed. In the samples that did not stain harden, a slower crystallization rate led to the production of foams with a closed cell structure with smaller cell sizes and higher cell densities. However, in samples with noticeable strain hardening effect, the foam cells were the highest in number and smallest in size with much less cell coalescence. Overall, the best foam structure was obtained with a linear PP containing 3 % wt. clay with a compatibilizer (MAPP) to increase melt strength (see Table 3 and Fig. 19).

Another study was done by Yeh et al. (2013) on five different matrices: PET, amorphous PET (APET), thermoplastic polyurethane (TPU), thermoplastic polyether ester elastomer (TPEE), and PP which are widely used in textile applications.

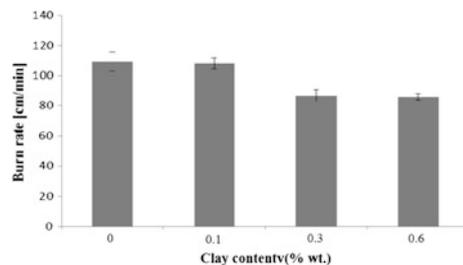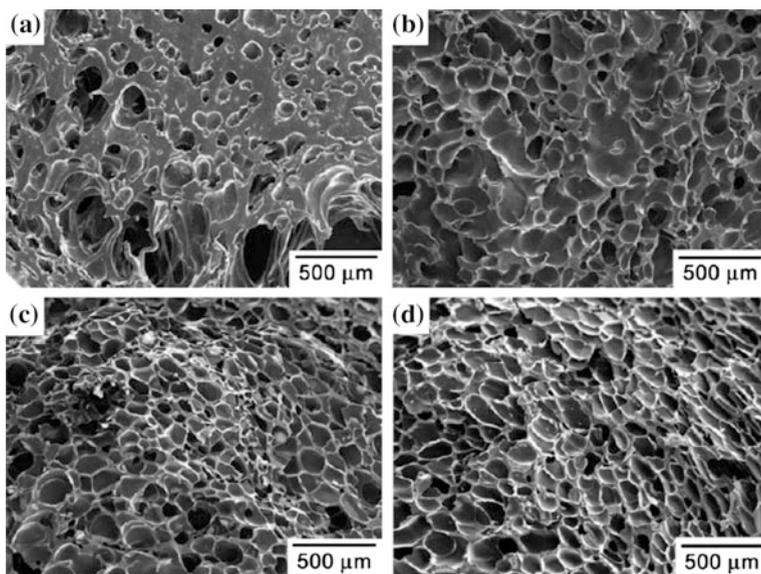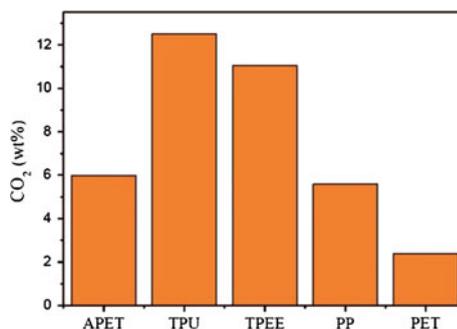**Fig. 18** Effect of clay content on the burning rate of LDPE foam

Table 3 Coding of PP-clay nanocomposites (Chaudhary and Jayaraman 2011)

Sample	PP	MAPP (% wt.)	Organoclay
PPNC-N1	68	24	8
PPNC-S1	40	52.8	7.2
PPNC-S2	76	21	3

Fig. 19 SEM images of **a** linear PP foam, **b** PPNC-N1 foam, **c** PPNC-S1 foam, and **d** PPNC-S2 foam

Fig. 20 Solubility of CO_2 in different polymers at 13.6 MPa and 40 °C for 6 h

These polymers were foamed through a batch process using CO_2 as the foaming agent. According to CO_2 solubility results in polymers (Fig. 20), PU was expected to be a good candidate for foaming and this was confirmed with experiments. This sample had the best foam structure with the highest cell density and lowest cell size.

Moreover, nanoclay was added to PU foams to improve even more on the foam structure. The authors mentioned that from their foaming results, they obtained an intercalated/exfoliated clay structure in the polymer matrix, especially at low clay content (1 % wt.). With short foaming time (5 s) at 150 °C, it was also possible to get nanocomposite foams with 1 μm in cell size and 10^{11} cells/cm^3 in cell density.

In another study by Keshtkar et al. (2014), the effect of nanoclay on the foamability of PLA in continuous extrusion foaming with supercritical CO_2 was explored. Clay content in PLA samples varied from 0 to 5 % wt. and CO_2 from 5 to 9 % wt. A morphological analysis showed that the clays were highly exfoliated in the PLA matrix. The results on foamed samples revealed that the expansion rate and cell density were highly promoted by clay addition and dissolved carbon dioxide. The authors also showed that, by changing the temperature profile along the extruder, faster crystallization rate was responsible for higher cell density and expansion ratio. The effect of die temperature on cell size and expansion ratio can be seen in Fig. 21. This also changed the strain hardening behavior of the materials and the final foam morphology as well as reported in Fig. 22.

In another work, the effect of nanoclay surface chemistry and content on the cellular structure of poly(D,L lactic acid) (PDLLA) was studied (Tsimpliaraki et al. 2011). Three sets of composite were prepared with PDLLA and nanoclay. In the first set, extrusion was used to prepare composites with different clay contents (0, 1, 3, 5, 9, and 15 % wt.). In the second set, MMT modified with various type of alkylammonium surfactants were used. In the last set, the organic cation content (surfactants) was changed. Then, composite foam of each series were prepared through isothermal pressure quench with supercritical CO_2. Morphological analysis revealed that the foam structures were highly dependent on clay content and chemistry of the clay surface (type and content of the organic cation used for the surfactant for modification of MMT). Increasing modified MMT into the polymer matrix improved heterogeneous nucleation leader to a higher number of smaller cells, as well as increased foam density. The authors also mentioned that the foam structure can be controlled by CO_2-clay interactions and content. In each case,
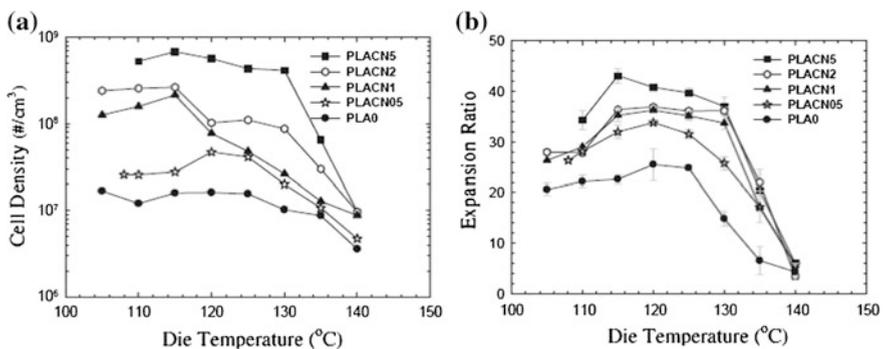

Fig. 21 Morphology of PLA and PLA-nanoclay foams obtained at various die temperatures. **a** Cell density and **b** expansion ratio
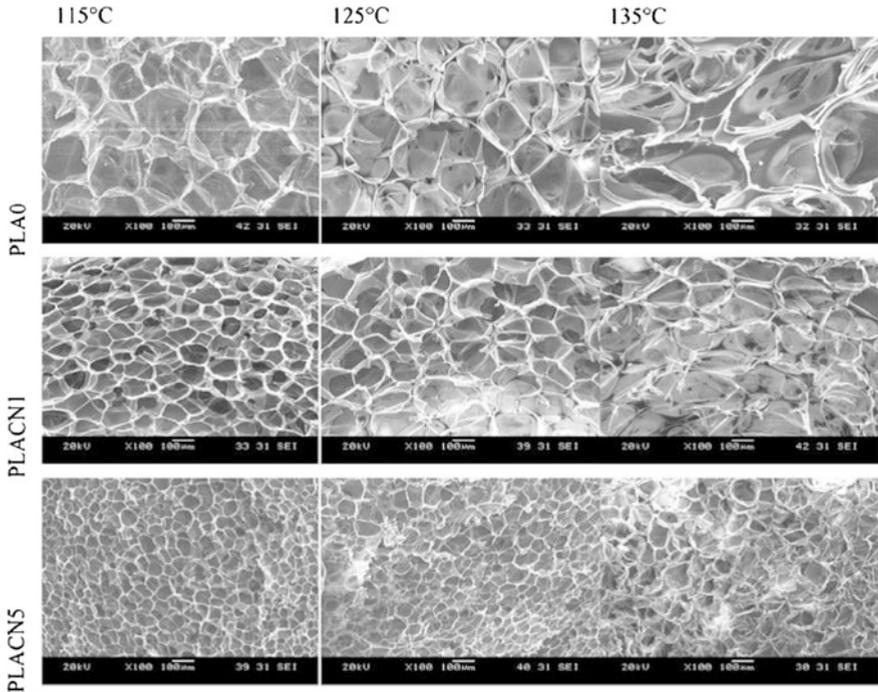
Fig. 22 Cell morphologies of neat PLA and PLA-nanoclay foams obtained at different die temperatures
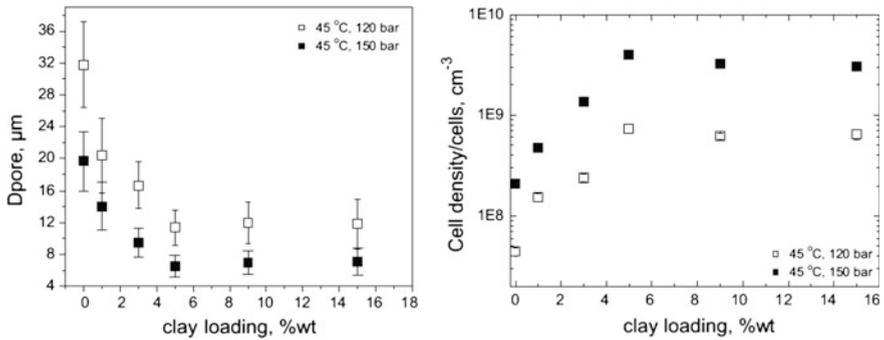

Fig. 23 Effect of clay content on cell size (*left*) and cell density (*right*) of PDLLA foams

the factors studied had a strong effect on the cell structure: higher clay content, longer organic tail of the surfactant, and higher modification level led to higher cell density and smaller cell sizes (Figs. 23 and 24). Moreover, CO_2 was believed to have a significant effect on dispersion besides its inherent role of a foaming agent.
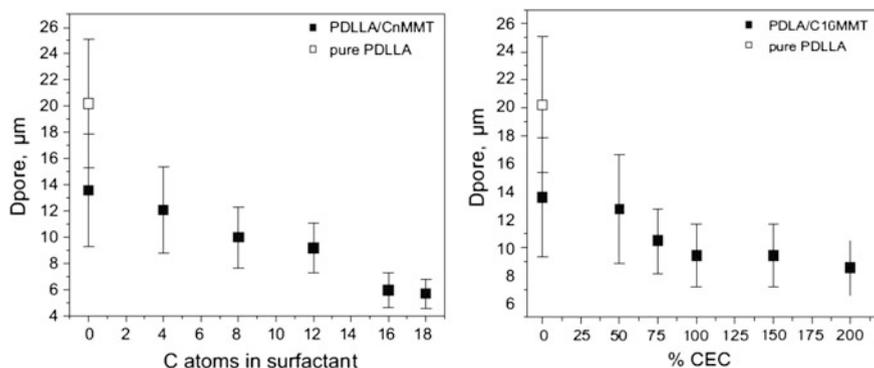
Fig. 24 Effect of surfactant type (*left*) and clay cation exchange capacity, CEC, (*right*) on the average cell diameter of PDLLA foams

Nanoclay effect was also investigated on biopolymers such as poly (3-hydroxybutyrate-co-3-hydroxyvalerate: PHBV) foaming through extrusion with supercritical CO_2 (Le Moigne et al. 2014). Two methods were used to produce foam samples. The first one was a one-step extrusion process of PHBV and nanoclay with CO_2, while the second one was a two-step extrusion method: compounding a PHBV-nanoclay composites which was foamed in a second extrusion run. The samples were analyzed in terms of physical and morphological properties. In the two-step method, compounding (masterbatch) was shown to have a positive effect on clay dispersion and limited PHBV degradation. From Fig. 25, it can be observed that mostly aggregates in the 20 % wt. clay masterbatch were obtained (Fig. 25c), while mostly intercalated and probably exfoliated structures were obtained in Fig. 25b, d where 2.5 % wt. clay was used in the matrix via the one step extrusion and the two-step with dilution, respectively. The authors also mentioned that by controlling CO_2 content, well dispersed clay was assumed to play the role of nucleating agent reducing cell coalescence and resulting in a good and homogeneous foam morphology: low cell size and high cell density by up to 50 % as seen in Fig. 26.

4.3 Clay-Natural Fiber Hybrid Composite Foams

Nanoclays have also been used with various natural fibers in different matrices to produce hybrid foam systems. Nanoclay hybridization with empty fruit bunch (EFB) was studied in foamed PU (Ali and Ahmad 2012). Composites of PU and EFB, silane treated EFB (sEFB) and oMMT were compared with hybrid systems of EFB/oMMT and sEFB/oMMT at different ratios (1/4, 1/2, and 3/4). The authors observed that hybridization improved the barrier properties of PU. As seen in Table 4, the thermal stability was influenced by both nanoclay and EFB. Higher
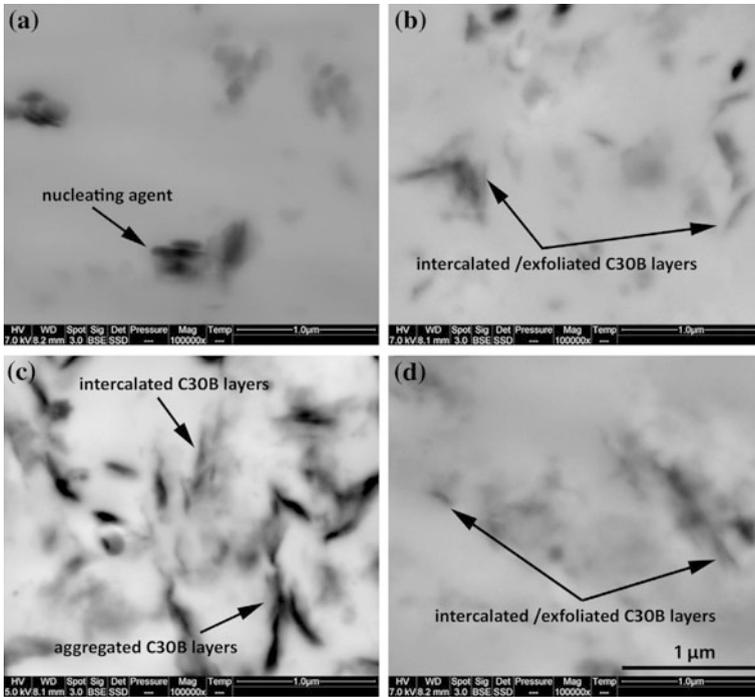
Fig. 25 SEM images of **a** extruded PHBV, **b** PHBV-clay (2.5 % wt., extruded), **c** PHBV-clay (20 % wt. extruded) masterbatch, and **d** PHBV-clay (2.5 % wt. dilution of 20 %, extruded) nanocomposite
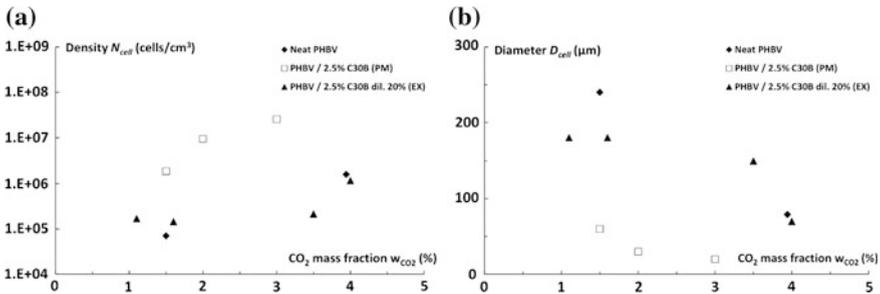

Fig. 26 Foam morphology as a function of CO_2 content for foams based on virgin PHBV, PHBV-clay (2.5 % wt., PM), and PHBV-clay (2.5 % wt., dilution of 20 %, extruded). **a** Cell density and **b** cell size

degradation temperature of the hybrid systems compared to the biocomposite shows the effect of nanoclay to improve the thermal stability of the system which is probably related to limited mobility of PU chains between the intercalated clay structures.

Table 4 Thermogravimetric analysis results of different PU composites (Ali and Ahmad 2012).

Sample	Degradation temperature (°C)	Weight loss (%)
Bio-composite	440	93.6
Hybrid bio-nano-composite	450	92.0
Nano-composite	460	93.4

Fig. 27 Effect of filler content on the compressive modulus and strength of PU
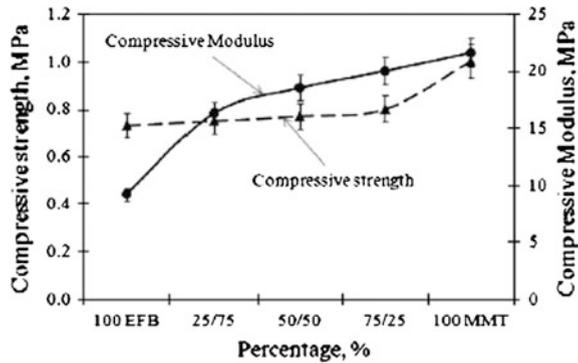
The hybridization also affected the mechanical properties by improving the compression modulus and strength (Fig. 27). Since the mechanical properties of composites mostly depend on the properties and volume fraction of each component, Fig. 27 clearly shows that with increasing nanoclay content, both modulus and strength of the hybrid systems increased (120 and 4 % respectively, at 75 % of nanoclay and 25 % of EFB). With nanoclay addition in the composite, the silicate layers can well disperse in the system and increase the available surface between the matrix and the fillers. So the mechanical properties are improved.

Nanoclay effect was also investigated for HDPE-wheat straw flour (WSF) foam system according to their mechanical, heat resistance, permeability, fire retardancy, and physical properties (Babaei et al. 2014). The samples were fixed at 40 phr WSF and the nanoclay content was selected 0, 2, and 5 phr (parts per hundred resin). An internal batch mixer was used for compounding while foaming was conducted using an injection molding machine using azodicarbonamide as a chemical foaming agent. The foams were shown to have a microcellular closed cell structure and it was observed that by using nanoclay up to 5 phr, cell density (Fig. 28) increased while cell size (Fig. 29) decreased.

It was also observed that increasing foaming agent from 0 to 4 phr increased water absorption (Fig. 30) and swelling thickness (Fig. 31) by around 19 and 26 % respectively, while for a fixed foaming agent content, due to the nucleating agent role of the nanofillers, the addition of nanoclay decreased both water absorption and thickness swelling. However, increasing foaming agent content from 2 to 4 phr decreased the overall density (Fig. 32) by around 21 %, but nanoclay addition (5 % wt.) increased foam density (around 10 %).

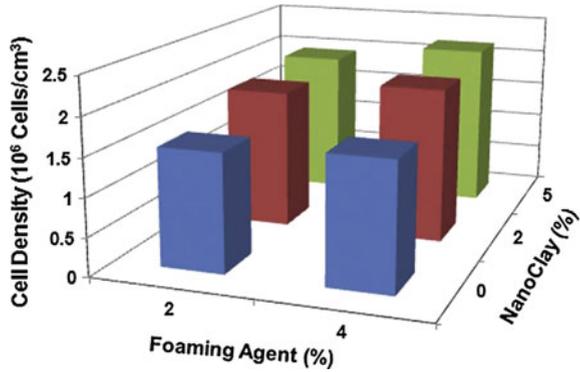**Fig. 28** Cell density of HDPE-WSF composites as a function of foaming agent and clay content

Fig. 29 Average cell size of HDPE-WSF composites as a function of foaming agent and clay content
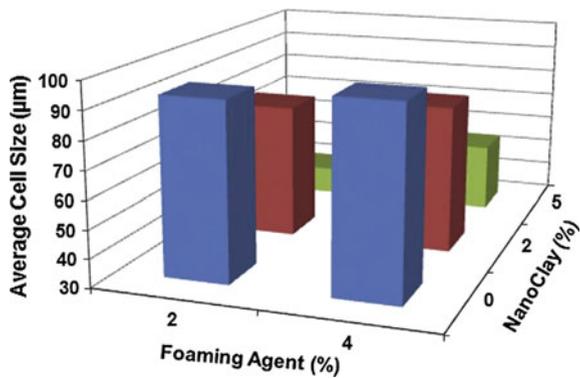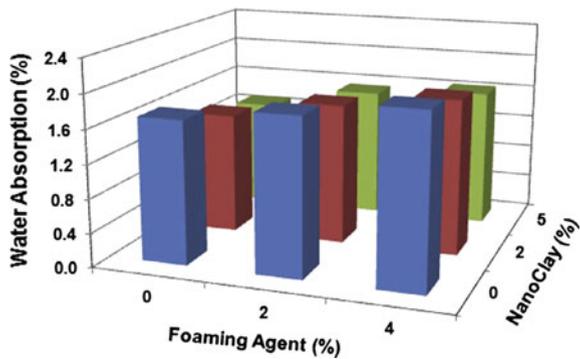

Fig. 30 Water absorption of HDPE-WSF composites as a function of foaming agent and clay content

The mechanical analysis also showed that tensile modulus (Fig. 33) and strength (Fig. 34) of the foams increased with nanoclay addition up to 2 %. However, foaming and nanoclay incorporation had negative effect on impact strength (Fig. 35) as confirmed by SEM.

Fig. 31 Thickness swelling of HDPE-WSF composites as a function of foaming agent and clay content
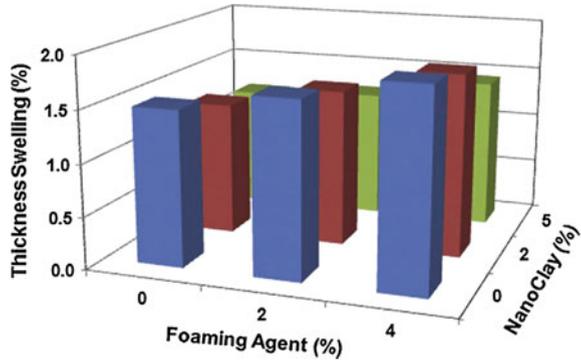
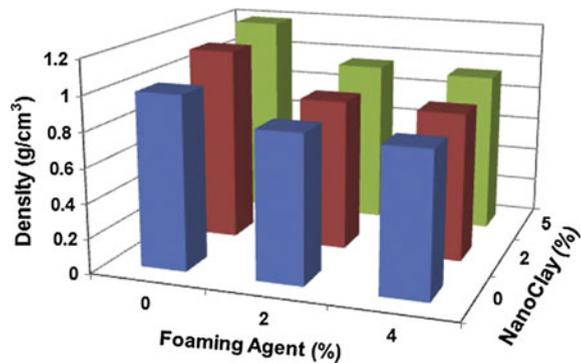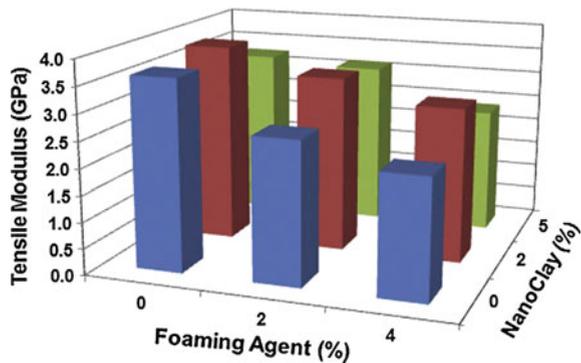**Fig. 32** Density of HDPE-WSF composites as a function of foaming agent and clay content

Fig. 33 Tensile modulus of HDPE-WSF composites as a function of foaming agent and clay content

In another study on hybrid foam systems based on clay and natural fibers, cellulose was used to produce foam trays for applications in food packaging (Ahmadzadeh et al. 2015). The process used was dissolution/regeneration, then drying by lyophilization. Different analyses on the composite foams showed that nanoclay presence brought more homogeneity to the structure of cellulose foams.

Fig. 34 Tensile strength of HDPE-WSF composites as a function of foaming agent and clay content
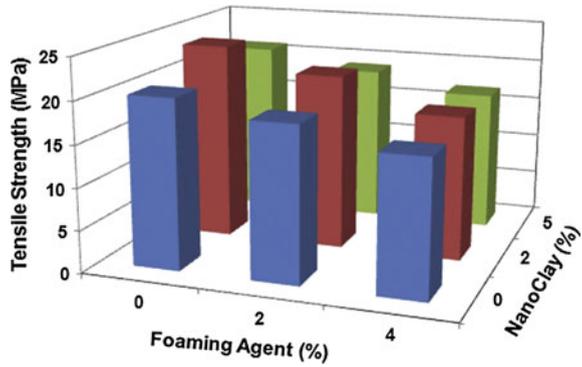
Fig. 35 Impact strength of HDPE-WSF composites as a function of foaming agent and clay content
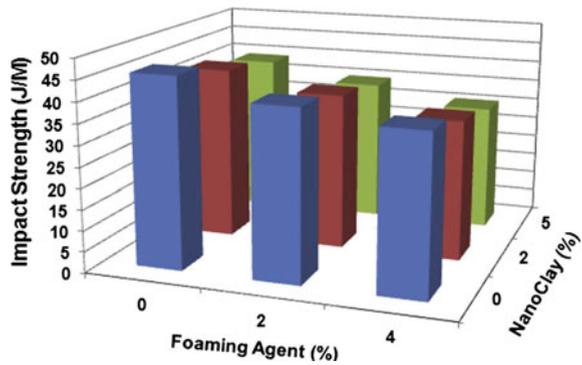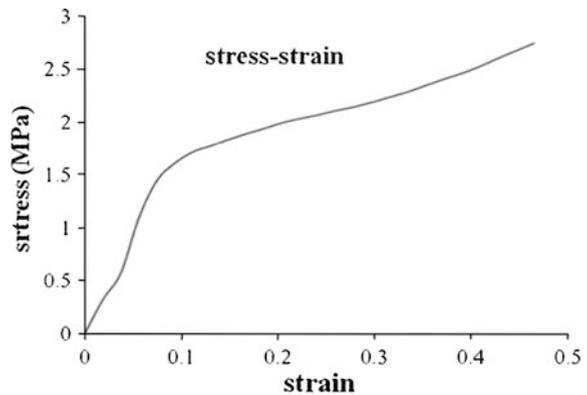
Fig. 36 Typical stress-strain curve for a cellulose foam

It also decreased the average cell size which mainly affected foam density, porosity, and mechanical properties. A typical stress-strain behavior of this composite foam can be seen in Fig. 36. According to the authors, the morphological results confirmed that intercalation of cellulose into clay layers improved both compressive
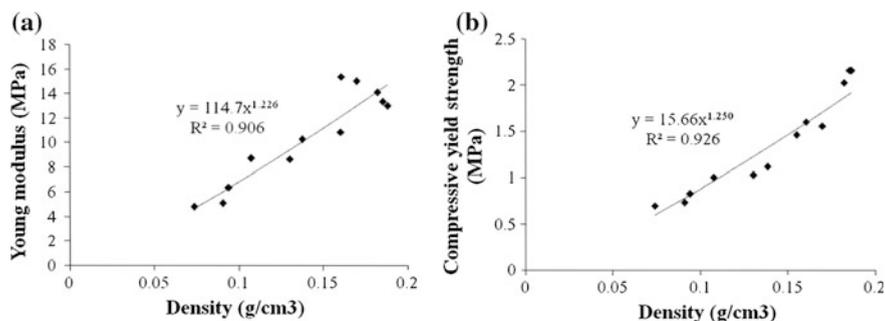
Fig. 37 a Young's modulus and **b** compressive yield strength as a function of foam density

modulus and strength (Fig. 37). Although more works are needed on this subject, it seems that nanocomposite foams based on cellulose and nanoclay could be good replacements for petroleum-based materials in food packaging industries.

Some works using only natural polymers instead of petroleum derived polymers were published, especially Vercelheze et al. (2012) using cassava starch, sugarcane bagasse fiber, and Na-MMT to produce nanocomposite trays. They were able to reach well-formed trays where the addition of natural fibers and clay resulted in lower density and rigidity. With well mixed nanoclay in the matrix, they also claimed to obtain an exfoliated structure resulting in good barrier and mechanical properties. Well dispersed clay in the starch matrix can be obtained by first making the nanocomposite in diluted aqueous solution and then plasticization (Mali et al. 2013). Vercelheze et al. (2012) and Matsuda et al. (2013) used the same method to produce starch/fiber/nanoclay nanocomposite foams and confirmed that the samples contained exfoliated MMT. The main issue while using starch base biodegradable foams is cost and performance when compared with conventional polymers. The use of natural fibers and nanoparticles such as nanoclay can help to improves on these challenges. Material performance is directly related to the type of starch, processing parameters, filler content, and foam formulations. Typical SEM images of starch foams containing different nanoclays are presented in Fig. 38.
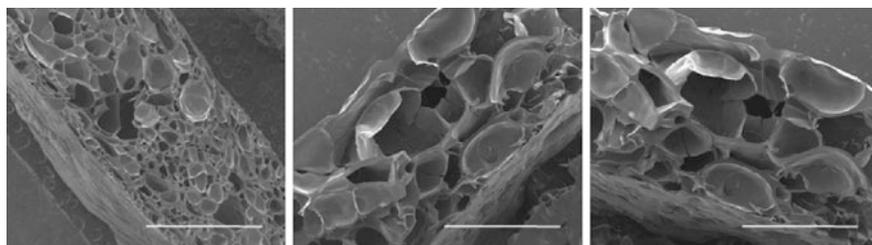

Fig. 38 SEM of foam trays cross-sections: **a** cassava starch, **b** 95 % wt. cassava starch with 5 % wt. Cloisite 10A, and **c** 95 % wt. cassava starch with 5 % wt. Cloisite 30B

Although several works have been presented here, there is still potential to develop new materials, formulations, and processes to combine clay and natural fibers in polymer matrices to produce hybrid composites foams with higher specific properties.

5   Conclusion and Prospective Works

Nanoclays, due to their specific structure (small size, high aspect ratio, and high specific area), are known to provide improved mechanical, barrier, and fire retardancy properties to polymers which is desirable for many industries, especially packaging and membrane technologies. Dispersion degree according to intercalation/exfoliation state is one of the key factors determining their reinforcing role while being used in polymer matrices.

Following numerous studies done on the incorporation of nanoclays in polymer matrices, the use of nanoclay in hybrid composite systems (with natural and synthetic fillers) was also investigated in many works as this material has the potential of being easily processed in different polymer matrices through different processing methods (extrusion, injection, compression, and solution based processes).

In the future, nanoclay combined with natural fibers (jute, hemp, flax, cellulose, etc.) to produce hybrid composites and foam systems will be further developed. The effect of different parameters such as type and amount of compatibilizer, fiber type, size, and modification as well as process conditions also need more investigation. Finally, these systems are expected to have important advantages such as: light-weight, high specific mechanical properties, high barrier properties, flexibility, well defined and controlled structure, as well as being ecofriendly, especially when using biopolymers as matrices.

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