

Nanoclay Based Natural Fibre Reinforced Polymer Composites: Mechanical and Thermal Properties

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Abstract This chapter discussed the introduction of nanoclay into natural fibre reinforced composites (in practice, reinforced with lignocellulosic fibres from plants, therefore referred here as plant fibre composites, abbreviated as PFC) in terms of improvement of mechanical and thermal properties. A number of issues are to be accounted for, which include the specificity and hierarchical structure of the different lignocellulosic fibres, therefore their significant variability in mechanical terms, which results also in a substantial dimensional variability when introduced in the composite. More specifically, the main effects encountered by this introduction, in amounts normally variable between 1 and 5 wt %, would concern the reduction of viscoelastic behaviour of the composite and achieving improved dimensional control, provided a sufficient interaction of the nanoclay in the composite is obtained. This is particularly significant on one side aiming at an effective production of injection moulded PFCs and on the other side in connection with the use of biodegradable matrices, focusing on the production of a fully sustainable composite.

Keywords Nanoclay · Lignocellulosic fibres · Mechanical properties · Thermal properties

1 Introduction

When dealing with plastics, the addition of nanofillers can be useful to modify their properties, with notable effects on heat distortion, hardness, toughness, stiffness and mould shrinkage (Barmar et al. 2006). In the particular case of nanoclay, its use as a filler has been proposed in polymer composites, where at the expense of some increase in weight, limited by the small amount of nanoclay introduced, advantages in mechanical terms and as far as processability is concerned, were encountered.

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In principle, different ways to introduce nanoclay in composites can be proposed, in particular directly in the matrix, which is known as the melt blending process or else its addition when producing the composite: the two methods were e.g., compared in the case of high density polyethylene (HDPE) wood flour composites (Faruk and Matuana 2008). In addition, the introduction of fillers of agricultural origin, but not strictly speaking of fibrous geometry, was also proposed in combination with nanoclay: this was the case for example for almond shells, a typical waste from the confectionery industry, introduced in maleic anhydride grafted polypropylene matrix with the main limitation being a reduced impact strength (Lashgari et al. 2013). A similar introduction of empty fruit bunches (EFB) in a polyurethane foam matrix together with organic montmorillonite (o-MMT) improved by the synergy of the two fillers the stiffness of the composites, although EFB did not prove particularly effective in combination with o-MMT as far as thermal stability is concerned (Ali and Ahmad 2012).

On the other side, the introduction of nanoclay proved also beneficial also in cement-based composites, where its synergy with fibres of vegetable origin, was studied. In this case, it was observed for example that hemp fabric in the amount of 2.4 wt% had a beneficial effect on the reduction of porosity and the consequent increase of density and particularly on flexural strength and toughness, when coupled to 1 wt% of nanoclay (Cloisite 30) in a cement matrix with a cement/binder ratio equal to 0.48. A larger amount of hemp fabric (up to 6.9 wt%) was also accommodated in the composite by treating the fibres by mercerization (Hakamy et al. 2015). The addition of Cloisite was not effective though when increasing the amount of nanoclay up to 3 wt%, in which case the presence of more pores, calcium hydroxide crystals, ettringite and microcracks weaken the structure was revealed (Hakamy et al. 2014a). However, in the amount of 1 wt%, nanoclay was demonstrated to act as an activator to promote pozzolanic reaction therefore modifying cement matrix and improving the hemp fabric-matrix adhesion, promoting also thermal stability of the composite (Hakamy et al. 2013, 2014b).

In other cases, even more complex situations have been envisaged, such as the combined introduction of multiwalled carbon nanotubes (MWNT) and sepiolite nanoclay in a plant fibre composite, especially in view of obtaining a superior flame retardancy effect, a result which has been the object of specific reviews, as regards nanoclays (Kiliaris and Papaspyrides 2010). As a matter of fact, the introduction of 30 wt% hemp, using a particularly coarse fabric (areal weight 800 g/m²) in a ternary composite comprising polylactic acid (PLA), 10 wt% sepiolite + 2 wt% MWNT was measured to have a 25 % reduction in peak heat release (PHRR) under the cone calorimeter (Hapuarachchi and Peijs 2010).

Dealing with plant fibre composites (PFCs), the main synergistic effect of nanoclay with plant fibres, e.g. flax, apart the aforementioned mechanical advantages, was demonstrated in hindering the dissolution of lignin in the alkaline environment present in cement (Aly et al. 2011), an aspect that proved its usefulness also in the case of geopolymers (Assaedi et al. 2015). Also, in combination with flax fibres, different types of nanoclay indicated a significant and yet again in synergy with the natural fibres, improvement of the fire resistance in soy-based matrices (Bensadoun

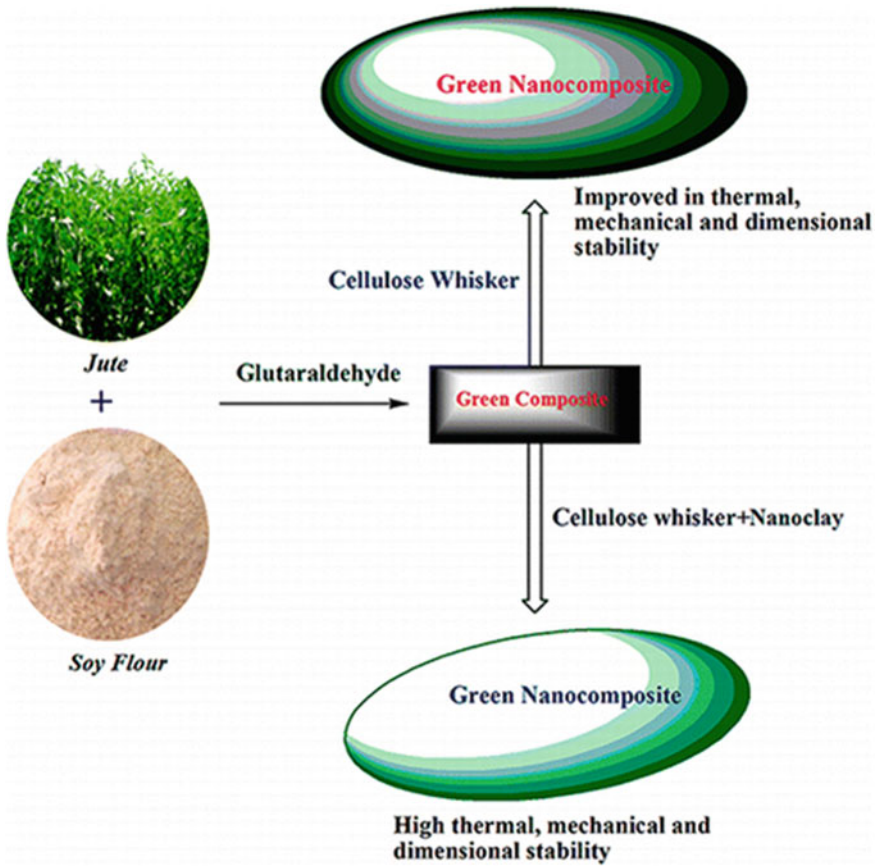


Fig. 1 System for creation of a green nanocomposite (Iman 2013)

et al. 2011). As a matter of fact, these attempts in producing nanoclay filled plant fibre composites often resort to structures of significant complexity, where a number of components need to effectively interact (the use of biomatrices in this sense can represent a further complication for the assessment of performance in the widest sense). An example suggestive of this intricate yet fascinating synergy can be offered by the diagram depicted in Fig. 1: to try and elucidate these issues, we need to refer back to the reasons for development of PFCs.

2 Plant Fibre Composites (PFCs): Perspectives and Issues

Plant fibre composites (PFCs) have been developed with the idea to replace traditional composites, in particular fibreglass, in view of their reduced carbon footprint: this is of specific interest in sectors such as automotive industry (Holbery and

Houston 2006). This drive towards improved environmental sustainability suggested that also intermediate approaches, such as the fabrication of hybrids, including both glass fibres and vegetable fibres, such as jute, flax, hemp, etc., would be of some interest for the purpose, allowing to take better control of the variables, which are essential for the success of the production and semi-structural use of PFCs, for example impact performance (Santulli 2007).

Significant problems still exist in the production and introduction into service of PFCs: on one side the importance is perceived of introducing plant fibres into bio-sourced, hence biodegradable and compostable matrices, some of which have become increasingly popular in fields such as packaging, in particular poly(lactic acid) (PLA). However, it needs to be pointed out that in other sense these materials do not always appear to be quite ready for these purposes. For example, whilst on one side PLA appears mostly suitable for packaging rigid objects, its use in soft films requires conversely the use of plasticizers, such as for example glycerol, sorbitol (Li and Huneault 2011) or limonene (Arrieta et al. 2013). This can not only ease the processing of the polymer, but also enhance some mechanical properties, particularly toughness. However, common issues encountered in biopolymers are not limited to mechanical and thermal properties. For example, also their permeability to gases and vapours and their generally scarce barrier properties are critical: amongst innovative strategies to improve these properties can be the addition of fillers such as nanoclay (Majeed et al. 2013). Of course, all fillers that are added to the polymer present a synergic effect on the properties of the composite, which is not easy to clarify. In particular, whenever nanoclay is added to PFCs, vegetable fibres are present, which present an inherent variability, due to a number of factors, which start from the ones depending on the plant species and the different agro-nomical parameters of its cropping, but are not limited to that, including the effects of extraction, treatment and fibre arrangement.

In particular, vegetable fibres are compounds combining different polysaccharides, in particular variable amounts of cellulose, hemicellulose and lignin, while pectin is normally removed during *fibre extraction* from the plant, as it is markedly non structural (Faruk et al. 2012). In particular, cellulose is a semicrystalline polysaccharide consisting of D-glucopyranose units, linked together by β -(1-4)-glycosidic bonds, therefore linearly arranged, such as those shown in Fig. 2. In contrast, hemicellulose, joined to cellulose fibrils by hydrogen bonds, has a branched structure, is fully amorphous and has lower molecular weight. Lignins are also amorphous and are mostly formed by aromatic phenylpropane polymers, whereas pectins are glue-like polysaccharide acid polymers. Passing from cellulose to

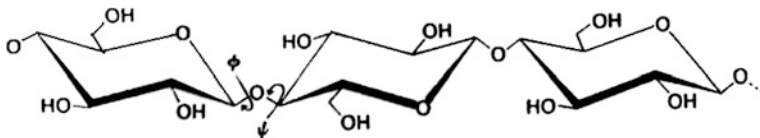


Fig. 2 Arrangement of β -1,4 glycosidic bonds

hemicellulose and lignin the hydrophilic character gradually decrease and in general terms hemicellulose, pectins and lignin are not thermally stable, tending to degrade at a temperature lower than 500 °C (Li et al. 2007).

After this, the influence of the species needs to be taken into account, often referred to as specificity (Klemm et al. 2005). Vegetable fibres can be derived from various parts of the plant, including leaf (e.g., sisal or pineapple), bast (e.g., flax, hemp and jute), seed (e.g., cotton) and fruit (e.g., coir). Once extracted the fibres, a process which mainly occurs by microbial retting, whereas only in some cases by action of enzymes, such as pectinase, these may be treated to further remove non structural parts and regularise their shape and geometry, reducing the extension of the internal voids, commonly referred to as lumens or lacunae: these are a characteristic feature of vegetable fibres and were thoroughly investigated for their effect on mechanical performance (Satyanarayana et al. 1981).

The treatment, as described above, is normally defined as primary and is essential for the manufacturing of textile products: most common primary treatments are mercerization by an alkali, such as typically sodium hydroxide (George et al. 2001), or bleaching by sodium hypochlorite (Saheb and Jog 1999), acetylation, benzylation or potassium permanganate treatment, all of which are dealt with in La Mantia and Morreale (2011). Secondary treatments may also be applied, in some cases following a primary one, which tend to be more protective for the fibres, also to reduce moisture penetration (Kalia et al. 2009). A final factor, among the principal ones contributing to the variability, is the type of fibre architecture by which the vegetable fibres are introduced in the composite: they might be in the form of short random fibres, or else to be in other randomly oriented forms, such as mats. Oriented geometries include plain weave, twill weave and satin weave, together with other forms of more complex arrangements of multiple warps and wefts, such as leno, also referred to as cross-weave.

3 General Considerations on Nanoclay

Clays are defined as phyllosilicates (from the Greek word “φύλλον” = leaf), in that they have a layered structure formed by octahedral layers formed by aluminium or magnesium hydroxide and tetrahedral silicon dioxide structure layers. They can be divided in 1:1 phyllosilicates, such as kaolinite and serpentine, in which each octahedral layer is alternate to a tetrahedral one, or 2:1 phyllosilicates, such as montmorillonite and saponite, the latter being of much more frequent use in nanocomposites, in which every octahedral layer is sandwiched and edge-fused between two layers of tetrahedrally coordinated silicon atoms. The thickness of every layered sheet is normally in the order of 1 nm with a length going from tens of nanometres to over a micron. In octahedral layers it is often possible that aluminium is replaced by iron hydroxide or magnesium by lithium hydroxide with no significant change in the geometry of the clay.

Clays are hydrophilic, because between the layers, where as an effect of stacking Van der Waals gaps are created, usually referred to as interlayer or gallery, are normally present ions of alkali metals, such as Na⁺ and K⁺, or alkaline-earth, such as Ca²⁺. These counterbalance the negatively charged platelets and therefore allow more water to be chemically linked and allocated within the structure.

Normally though, to improve the affinity between the filler and the matrix, which will have a beneficial effect on material properties, the inorganic cations located in the galleries (Na⁺, Ca²⁺, etc.) are generally exchanged by ammonium or phosphonium cations bearing at least one long alkyl chain, and possibly other substituted groups. The resulting clays are referred to as organomodified layered silicates (OMLS) and, in the case of montmorillonite (MMT), are abbreviated OMMT. As a matter of fact, most nanoclays used in composites are MMTs, with a possible competitor in synthetic fluorine mica (SFM) (patented by Tateyama et al. 1993), which is produced using 10–35 wt% of an alkali silicofluoride (possibly in addition with some alkali fluoride) and the balance of talc. Some types of nanoclay are reported in Table 1, while the characteristics that are of interest for a specific one of these are offered in Table 2.

Table 1 Main types of nanoclay

Commercial (O)MMT and their characteristics						
Commercial clays Supplier/trade name/designation		Clay type	Organomodifier type	Modifier concentration (meq/100 g)	Δw^a (%)	<i>d</i> -spacing (Å)
Southern clay products (USA)						
Cloisite [®] Na	CNa	MMT	–	–	7	11.7
Cloisite [®] 15A	C15A	MMT	N ⁺ (Me) ₂ (tallow) ₂	125	43	31.5
Cloisite [®] 20A	C20A	MMT	N ⁺ (Me) ₂ (tallow) ₂	95	38	24.2
Cloisite [®] 25A	C25A	MMT	N ⁺ (Me) ₂ (C ₈)(tallow)	95	34	18.6
Cloisite [®] 93A	C93A	MMT	NH ⁺ (Me)(tallow) ₂	90	37.5	23.6
Cloisite [®] 30B	C30B	MMT	N ⁺ (Me)(EtOH) ₂ (tallow)	90	30	18.5
Sud-Chemie (Germany)						
Nanofil [®] 804	N804	MMT	N ⁺ (Me)(EtOH) ₂ (tallow)		21	18
Laviosa Chimica Mineraria (Italy)						
Dellite [®] LVF	LVF	MMT	–	105	4–6	9.8
Dellite [®] 43B	D43B	MMT	N ⁺ (Me) ₂ (CH ₂ - ϕ) (tallow)	95	32– 35	18.6
CBC Co. (Japan)						
Somasif	MEE	SFM	N ⁺ (Me)(EtOH) ₂ (coco alkyl)	120	28	
	MAE	SFM	N ⁺ (Me) ₂ (tallow) ₂	120	41	

Tallow: ~65 % C₁₈; ~30 % C₁₆; ~5 % C₁₄

^a%Weight loss on ignition

From Bordes et al. (2009) (Table 3)

Table 2 Physical properties of nanoclay Cloisite 30B

Physical properties of the nanoclay (Cloisite 30B)	
Physical properties of Cloisite 30B	
Colour	Off white
Density (g/cm ³)	1.98
d-spacing (0 0 1) (nm)	1.85
Aspect ratio	200–1000
Surface area (m ² /g)	750
Mean particle size (μm)	6

From Alamri et al. (2012) (Table 1)

4 Objectives of the Introduction of Nanoclay in PFCs

The introduction of nanoclay in polymers does occur in two different configurations, depending on the degree of polymer polarity and Van der Waals interaction with the nanoclay, therefore the orientation of filler particles: these are respectively described as intercalated and exfoliated, as represented in Fig. 3. In any case, such an introduction produces the combination of two effects: it acts as filling the polymer with a particle-shaped reinforcement and restricts the movement of the polymer chains. While the former effect results in an increase of mechanical strength and rigidity, improving load transfer at matrix-fibres interface, reducing on the other side gas and (if relevant) moisture penetration and flammability, the latter has an outcome similar to crosslinking (Singh et al. 2009; Katschnig and Battisti 2015). To obtain these results, the uniform dispersion of nanoclay in the polymer is of crucial importance, for which mechanical stirring and sonication processes have also been experimented: of course, there is an optimal amount of nanoclay not to be exceeded to yield the best properties to the composites: this is often around 5 wt% (Chan et al. 2011).

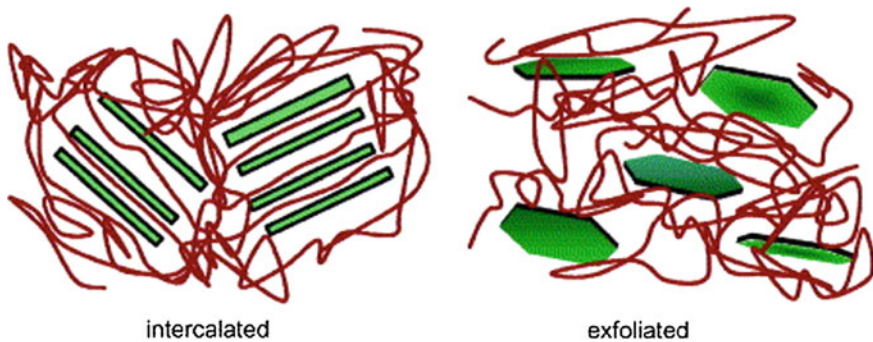


Fig. 3 Schematic illustration of two different types of thermodynamically achievable polymer/layered silicate nanocomposites (Ray and Bousmina 2005)

From what exposed above, it is clear that the introduction of nanoclay in plant fibre composites presents some additional issues, but on the other side also suggests possibilities: it has to be considered that vegetable fibres, being natural hierarchical structures, do not offer particular compactness and normally present internal gaps among the filaments, which are bound in a helical-like structure. Moreover, they have a considerable dimensional variability, which has an effect on properties. Therefore, introducing nanoclay in plant fibre composites, small quantities, such as 1 wt%, are likely to offer better stress transfer throughout the matrix, resulting typically in better impact and flexural properties: however, further increase would result in decreased properties, due to agglomeration, whose effect is worsened by the geometrical mismatches in the composites, owed to the presence of vegetable fibres (Rozman et al. 2010). In other words, optimisation of the amount and distribution of nanoclay in the composite is strongly needed. However, it is important to notice that another objective of introduction of nanoclays is the improvement of the behaviour at high temperature of plant fibre composites, which has notable effects on processing. In this sense, also studies of thermal and thermo-mechanical properties are highly required and it is important to evaluate the deviation from elastic behaviour, which tends to uncontrolled damping at high temperature. This is important, since damping behaviour is one of the great limits to the widespread application of plant fibre composites, especially as regards fatigue resistance, even for low number of cycles and low loading levels. Studies on that are limited, yet of considerable interest, in particular regarding the fact that fibre secondary treatments (Gassan and Bledzki 1997) or matrix grafting with maleic anhydride (Mohanty et al. 2006) may have a significant role in modifying this behaviour. In another sense, it is very likely that the introduction of nanoclay produces even larger effect on these properties, for this reason thermal properties of the obtained composites are of crucial importance.

5 Strategies Toward Improving the Mechanical Performance of Nanoclay-Filled PFCs

In general terms, several possibilities are open when adding nanoclay to plant fibre composites, a strategy which normally results in an increase in mechanical performance, in particular in tensile and flexural properties (Ku et al. 2011), although in some cases other characteristics might also be of crucial importance, such as for example impact performance and enhanced toughness.

A viable route is using matrices among the most diffuse for commodity uses, which are for example polyolefins, therefore practically mainly polypropylene and different grades of polyethylene, such as high density and low density. In this case, interest is concentrated on obtaining an effective moulding of these materials, despite the introduction of nanoclay essentially for mechanical purposes. This occurs particularly because thermoplastic matrices have been traditionally preferred, mainly since their processing is reasonably easy, in that manufacturing

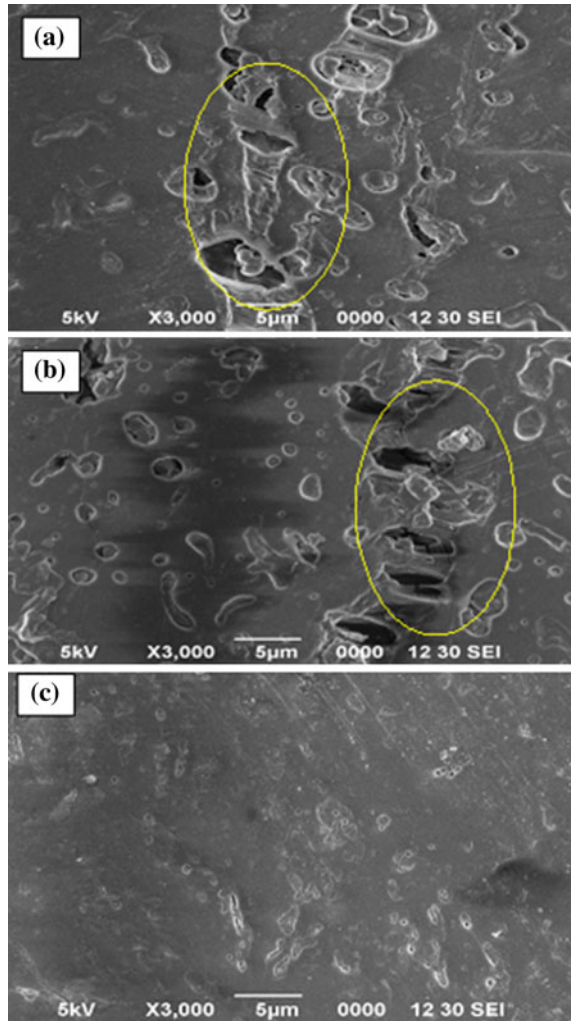
technologies such as injection moulding can be used, leading to high production rates with excellent dimensional tolerance. It is important to observe that the introduction of nanoclay has an important role in modifying the glass transition temperature of the polymer and reducing the deviation from the elastic behaviour for use at temperature higher than ambient one (Saw 2015).

Another possible strategy, which is significantly different as a concept, is using biodegradable matrices, such as starch-based ones. It is worth noting that there is a partial superposition with what described above, in the sense that the success of some biodegradable polymers, such as poly(lactic acid) (PLA) in their use as matrices, also notably in plant fibre composites, is also to be ascribed to their relatively easy moulding. However, in this case the addition of nanoclay is expected to modify their degradation profile, the preservation of which is ultimately of interest, together with the maximum possible flexibility in terms of manufacturing technologies (Lim et al. 2008). The largest majority of biodegradable matrices are thermoplastics: there is nonetheless a significant amount of studies aimed at the crosslinking of some of these matrices, in particular those based on vegetable oils, such as soy, castor, palm oil, towards the fabrication of thermosetting matrices to be processed at temperatures as close as possible to ambient temperature. In this case, an additional factor of possible modification of the properties is introduced, in the sense that moulding temperatures need to undergo only limited variations as the effect of the introduction of nanoclay. A comprehensive review of these attempts, in the view of reducing environmental impact of matrices used, while retaining the initial mechanical performance was offered by Mosiewicki and Aranguren (2013): these involved the use of fillers of different size and geometries, including also nanoclay, as received or vinyl modified.

5.1 Nanoclay-Filled PFCs with Oil-Based Matrices

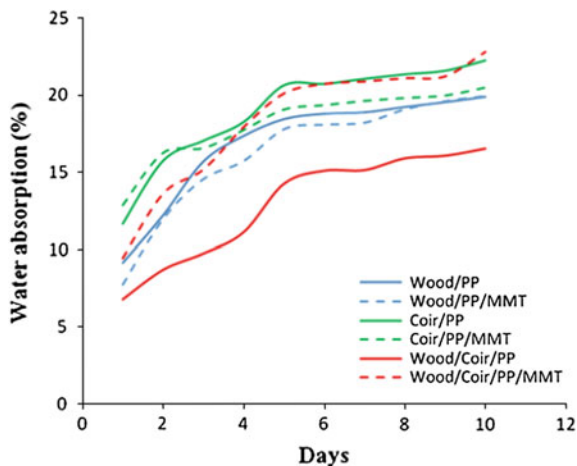
In the case of traditional thermoplastic matrices, such as polyolefines, it can be suggested that nanoclay can in a sense replace those ceramics that exert some action of making the flow of melt polymer more regular during moulding such as for example talc. This would come together with some enhancement of properties, such as rigidity, deriving from a substantial hindrance to the motion of polymer chains, provided the distribution of nanoclay platelet is uniform enough (Chen et al. 2003). It is worth noting that in most cases polyolefin-based plastics are injection moulded. In this case, to possibly create the pellet to be injected, short random vegetable fibres are used with substantial difficulties in their dispersion due to the combination between non-polar matrix and highly polar lignocellulosic reinforcement (Herrera-Franco and Valadez-González 2005). This situation can be improved in the case of introduction of nanoclay: in a composite including kenaf fibres (KF) and coir fibres (CF) in a polypropylene matrix the interfacial properties were found to be substantially improved with a number of surface micro-voids significantly reduced as the result of MMT addition and fostering the achievement of good wettability

Fig. 4 Typical SEM micrographs of tensile fracture surfaces of **a** KF/PP composite, **b** KF/CF/PP composite, and **c** KF/CF/PP/MMT hybrid nanocomposites (Islam et al. 2012a, b)



properties (Islam et al. 2012a, b), as illustrated in Fig. 4. As a matter of fact, the introduction of nanoclay has been attempted in polypropylene matrix with different amounts of kenaf fibres (20–40 wt%), with the reinforcement with the higher amount of fibres resulting in a clear decrease of tensile and Izod impact properties, despite the simultaneous introduction of nanoclay in the amount of 6 wt% (Kamardin et al. 2015). The interaction of thermoplastic polymers with two different lignocellulosic fibres (Brown Rubber bark wood and coir) in a hybrid plant fibre polypropylene composite together with montmorillonite (MMT) resulted in some kind of synergic behaviour to be better investigated. For example, interestingly enough, the addition of MMT to the bare coir fibre composite did not substantially modify water absorption profile, whereas adding MMT to the composite including both fibres

Fig. 5 Water absorption of different composites (Islam et al. 2015)



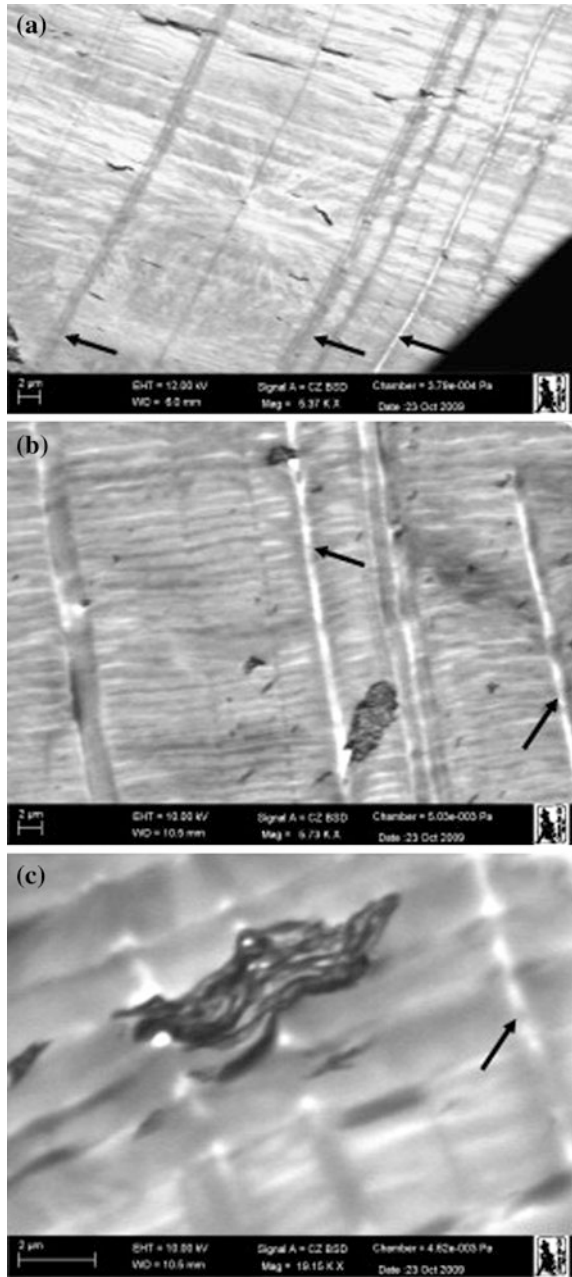
made the composite more vulnerable to water (Islam et al. 2015), as observed in Fig. 5. This observation can be a significant caveat on the modification of the effect of nanoclay depending on the very nature of the specific PFC it is introduced in.

The introduction of nanoclay (in the specific case Cloisite 30B in sisal/epoxy composites) proved on the other side effective to reduce the degradation of tensile properties after water immersion, since the amount of water absorbed at equilibrium is equally diminished. This has a significant interest, although at high amounts, such as 5 wt%, of nanoclay introduced, some contrasting effect from agglomeration and not fully effective mixing is also revealed (Mohan and Kanny 2011). Agglomeration, which has the consequence to increase the viscosity of resin-clay mixture, is represented in Fig. 6, is particularly experimented in the case of addition of Cloisite Na, hence with no modifiers. As far as the study of mechanical behaviour in temperature is concerned, it can be noticed that, despite normally the introduction of nanoclay reduces the viscoelasticity of the matrix, different evidences were found with typical treatments, such as alkali and silane, on coir sheath/polyester composites. In this case, a slight increase in $\tan \delta$ values was noticed with the addition 3 wt% of clay, possibly due to non-uniform dispersion of clay and the agglomeration of residual coupling agent over the fibre surface (Rajini et al. 2013).

5.2 Nanoclay-Filled PFCs with Biomatrices

A comprehensive review on the use of nanoclay in biodegradable polymers is offered by Ray and Bousmina (2005). This review, which concentrates substantially on poly(lactic acid) (PLA) and polyhydroxybutyrate (PHB) suggests in particular

Fig. 6 TEM of sisal fibre composites with **a** 3 wt% nanoclay, **b** 5 wt% nanoclay and **c** 5 wt% Na+ microclay (Mohan and Kanny 2011)



that the incorporation of nanoclays does enhance compostability of the material, with judicious selection of the type on nanoclay. On the other side, it warns that the maximum viable amount of nanoclays for substantial increase of tensile properties

on the polymer might not exceed 5 wt%. As regards PLA, which is the most frequently used biopolymer, an important consideration needs to be done on the fact that the addition of plasticizers increases the chain motion at the same time yielding crystallization, which at the same time reduces the glass transition temperature of the polymer (Pillin et al. 2006). It is largely suggested instead that the introduction of nanoclay has an opposite effect on PLA. In the case of use of these thermoplastic biomatrices for PFCs, some importance is assigned to the fibre treatments, whose effect cannot be neglected. In the case for example of the reinforcement of chemically treated (by alkali and acetic acid) 30 wt% jute fibres into a polyhydroxybutyrate-co-valerate (PHBV) matrix with the addition of 2 %, 3 %, and 4 wt% montmorillonite K10 nanoclay: the composite with the higher nanoclay content offered lower moisture absorption, better dynamic mechanical properties, and flexural properties. It can be noticed that the rougher surface of jute fibres due to treatment resulted in a substantially improved compaction of the composites under resin infusion (Hossain et al. 2011).

On the other side, adhesion to vegetable-oil derived matrices proved effective in the case for example of partially bio-based polyurethane derived from *Mesua ferrea* L. seed, where the tensile strength was increased by about 60 % for a maximum amount of clay introduced of 5 %, obtaining notable advantages also in terms of scratch hardness, thermostability, water vapour permeability, and adhesive strength, while on the other side there a slightly positive effect on impact resistance and bending, and a limited reduction of elongation at break (Deka and Karak 2009). The addition of 21–22 wt% of industrial hemp fibres, chopped at a length of 25 mm, together with 1.5 wt% of Cloisite 30B nanoclay in a blend of traditional unsaturated polyester and epoxidized methyl soyate (EMS) was also attempted in the view to tailor the properties of the obtained composite, especially as regards stiffness, ultimate tensile stress and toughness parameters, such as impact strength and ductility (Haq et al. 2008). In this regard, coupling of jute fibres with different fillers in a soy-based matrix, which was crosslinked to confer to it quasi-thermosetting properties, was often proposed (Iman and Maji 2012). These included nanoclay in combination with cellulose whiskers (Iman et al. 2013), or else with zinc oxide, offering in the latter case a good compromise between improved dimensional stability and effective biodegradation (Iman et al. 2015). Cloisite nanoclay was also added in an amount of 5 wt% directly to a soy protein concentrate (SPC) resin, modified by 15 wt% of glycerol, in order to improve its mechanical properties and its thermal stability. To offer a general idea of the level of enhancement obtained, this allowed introducing a higher tenor of flax fibres, arranged in unidirectional yarns, up to 48 wt%, and offered tensile strength as high as 62 and 82 MPa in the warp and weft directions, respectively (Huang and Netravali 2007). In Table 3 a number of studies that are particularly significant on the role of nanoclay in modifying PFCs are reported.

Table 3 Some studies on the introduction of nanoclay in PFCs

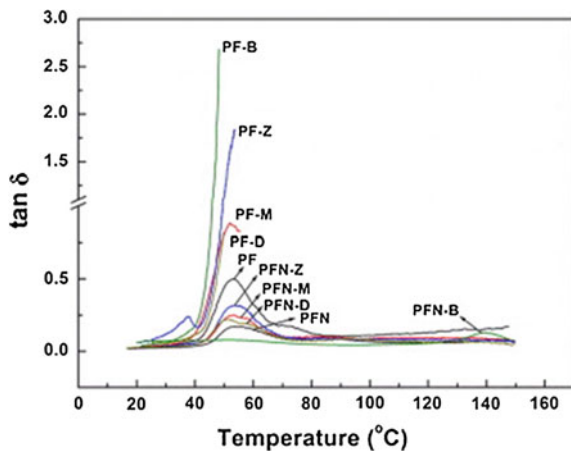
Matrix	Fibre type (and amount when available)	Nanoclay amount (%)	Improved variables by nanoclay addition	Reference
Unsaturated polyester	Coir 25 %	3	Tensile strength, Izod impact strength, compression and resin viscosity	Deepak et al. (2015a)
Unsaturated polyester	Jute 25 %	3	Tensile strength, Izod impact strength, compression and resin viscosity	Deepak et al. (2015b)
Unsaturated polyester	Jute 40 vol%	1–2	Flexural, compression, and interlaminar shear strength (ILSS) (maximum with 1 wt%)	Dewan et al. (2013)
Unsaturated polyester	Kenaf	1	Flexural and impact properties	Rozman et al. (2010)
Unsaturated polyester	Coir sheath	1	Specific wear rate (particularly with silane treatment)	Divya et al. (2014)
Unsaturated polyester	Coir sheath	1–2–3–5	Alkali and silane treated	Rajini et al. (2013)
Epoxy	Sisal	1–3–5	Water barrier effect	Mohan and Kanny (2011)
Polypropylene	Hemp	1–3–5	Tensile properties up to 3 % nanoclay	Kord (2012)
Polypropylene	Bleached red algae fiber (BRAf), kenaf fiber (KF), and cotton pulp fiber (CPF) all 40 %	5–10	Dimensional stability and dynamical mechanical properties (highest with BRAf)	Sim and Han (2013)
Polypropylene (with 5 % maleic anhydride)	Pineapple leaf 30 %	1–3	Tensile and flexural strength	Biswal et al. (2009)
HDPE (with 2, 4, 6 or 12 % maleic anhydride) (MAPE)	Bamboo up to ca. 30 %	1–3–5	Dynamical and static flexural modulus. Exfoliation with MAPE	Han et al. (2008)
Poly(lactic acid)	Short kenaf fibres 20 %	3	Impact and tensile properties	Kaiser et al. (2013)

6 Thermal Properties of Nanoclay-Filled PFCs

In general terms, as it is usually the case with ceramics, the addition of nanoclay to polymer matrices does improve their thermal stability, which can be generally indicated by the amount of residual char obtained at high temperature (such as

600–800 °C) (Alamri et al. 2012). With the introduction of vegetable fibres the problem of thermal degradation becomes even more crucial: the initial perspective was to investigate whether processing of the polymers at the usual temperatures for example for polyolefines would substantially damage the fibre structure, hence making them unsuitable for matrix reinforcement. In practice, for example on jute and flax fibres it was found that heating them at a temperature exceeding 170 °C for a period of time of 120 min resulted in a significant decrease of tenacity and degree of polymerization for the fibres (Gassan and Bledzki 2001). This was the case also on biomatrices, such as polylactic acid (PLA) in a hybrid composite with montmorillonite and kenaf fibres. Dynamic mechanical analysis at temperature ranging from –80 to 100 °C with loading frequency of 1 Hz demonstrated the increase of all parameters, including storage modulus, loss modulus and damping by an addition of up to 7 % MMT (Kaiser et al. 2011). Another study proposed that nanoclay could even act as a compatibiliser for improving the adhesion between poly(lactic acid) matrix and flax fibres (Kumar et al. 2010b). In this case the achievement of a higher compatibility by the addition of MMT was indicated by dynamical-mechanical analysis and in particular by the decrease of damping factor. The flax-poly lactide composites had been previously prepared with amphiphilic additives that served to accelerate their biodegradation to be used as compostable materials at end-of-life (Kumar et al. 2010a). Values of dynamic loss ($\tan \delta$) as a function of the temperature for these composites are shown in Fig. 7: $\tan \delta$ reduction demonstrated effective in revealing the quality of interface of the nanocomposites obtained, also for example in the case of interaction between different types of Malaysian wood fibres with nanoclay in a phenol-formaldehyde resin, as from Rahman et al. 2012. Coming back to Kumar et al. (2010a, b), the efficacy of the different additives, which are listed in the caption of Fig. 7, has been compared: this allowed demonstrating that apart from a general increase in stiffness, mandelic acid proved particularly effective owing to low water uptake, high mechanical properties and high storage modulus. This statement also holds true for

Fig. 7 Dynamic loss versus temperature of composites with different additives: PF means poly(lactic acid)-flax with no nanoclay, PFN poly(lactic acid)-flax with added 2.5 wt% of nanoclay, while B, M, Z and D represent benzilic acid, mandelic acid, zein and dicumyl peroxide (DCP), respectively



all the additives in presence of nanoclay. To confirm the interfacial adhesion between PLA, fibres and additives, morphology studies of the bio-composites were also conducted (Kumar et al. 2010a, b).

With progression of use and development of PFCs, other more complex requirements were suggested as far as thermal stability is concerned: in practice, it is considered important to get sounder information about the physical interaction between the matrix, the vegetable fibres present and the nanoclay introduced. Particularly important are the observations obtained on kenaf/coir hybrid polypropylene composites with the addition of organic montmorillonite, in that these really clarify the extent and importance of respective interactions within the material: compared Fourier transform infrared spectroscopy (FTIR) are reported in Fig. 8 (Saiful et al. 2015). In this case, the spectrum of pure polypropylene (Fig. 8a) displays the characteristic absorption peaks in the region of 2936 cm^{-1} for alkyl C–H. Other peaks in the further spectra (at 3400, 1700, 1150–950 and 470 are most likely to be related to the stretching vibrations for hydroxide (–OH), carbonyl (C=O), C–O in alcohol and Si–O–Si, respectively). The absorption peaks of polypropylene were slightly shifted after fibre loading as clearly observed from Fig. 8c, e, g. Spectra in Fig. 8b, d, f, h indicated that polypropylene peaks changed after blending with nanoclay, so that another peak was observed at around 470 cm^{-1} due to Si–O–Si stretching vibration for all nanocomposites. This peak is expected, due to the

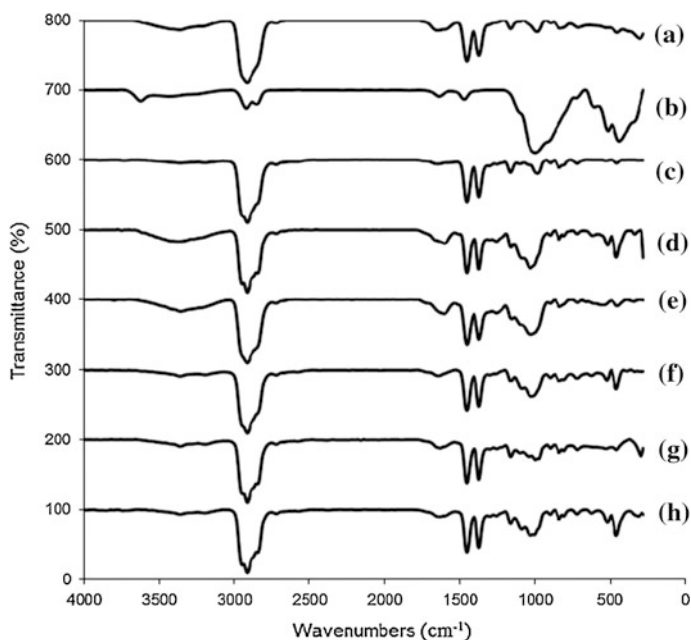


Fig. 8 FTIR spectra of **a** polypropylene, **b** nanoclay, **c** coir/PP composite, **d** coir/PP/MMT nanocomposite, **e** kenaf/PP composite and **f** kenaf/PP/MMT nanocomposite, **g** kenaf/coir/PP hybrid composite and **h** kenaf/coir/PP/MMT hybrid nanocomposites

incorporation of MMT into the composites, and was reported by Ray and Okamoto (2003) and is a sign of good incorporation. Another sign of good incorporation of MMT improving fibre–matrix interfacial adhesion in the composites was the slight shift of C=O C–O peaks and –OH peaks toward higher wave numbers after addition of MMT (Islam et al. 2012a, b). 2

7 Conclusions and Future Perspective

Plant fibre composites, though their production may be desirable for a number of reasons, including the possible obtainment of fully biodegradable composites with the use of biomatrices, present a number of issues that are not completely resolved, so that their use in semi-structural composites and possible replacement, even if partial, for glass fibres is not always practicable. In terms of mechanical properties, what is particularly required is the achievement of sufficient impact properties and effective dynamical-mechanical behaviour, so that damping is not excessive, when inserted in visco-elastic matrices, which would lead to limited dimensional stability.

Factors for concern include in particular the significant sensitivity to moisture content, which is also linked to the presence of internal voids in the fibres, known as lumens or lacunae, and the dimensional variability of the fibres. These can be arranged in different architectures, among which the incorporation of short fibres in pellets is desirable for the purpose of injection moulding, the preferred manufacturing process for commodity items. Dimensional variability, which has the effect of limiting the amount of vegetable fibres that can be introduced in the composite, can be reduced by the application of a number of different surface treatments on the fibres, among which are alkali treatment, typically with sodium hydroxide, bleaching or less aggressive ones, such as silane treatment. These are adapted for the purpose, although they introduce yet another factor of variability in the fibre properties and on the composites produced by their use. With the idea of end-of-life recycling and reprocessing, the thermal degradation of plant fibres has also been widely studied and represent another factor for concern. In practice, the most used fibres are flax, hemp, jute, kenaf, sisal and coir, for their inherent properties and the availability of different fibre arrangements: however, in principle the number of possible crops from which fibres for composites can be obtained is very large, being based on specific local productive systems.

All of the above reasons contribute to suggesting that the introduction of nanoclay in small amounts, normally not exceeding 5 wt%, but in some cases considerably less, may be beneficial for plant fibre composites. The main improvements were obtained as far as dimensional stability and ease of processing is concerned. This had also normally a non negligible effect on dynamical-mechanical properties and on tensile and flexural strength, although the balance between improved rigidity and avoiding the possible induction of a brittle behaviour was not always obvious. This difficulty was observed often in impact loading, usually performed by Izod or

Charpy tests, where the variability of the absorbed energy could even conceal the advantage obtained in terms of properties. It is noteworthy that the improvement is notable only in the case a sufficient interaction between the matrix and nanoclay exists. This is not always easy due to the fact that most frequently used matrices are not polar, such as polyolefins, whilst nanoclay is quite strongly polar. On the other side, the use of biomatrices, both based on polysaccharides and on vegetable oils, would pose other problems, such as the possible penetration of water in the material, which would have an effect also on agglomeration of nanoclay. This is a very sensitive issue at amounts of these exceeding a few percents.

Further developments of plant fibre composites including nanoclay would possibly go along the following lines:

- Combined use of different vegetable fibres possibly arranged in more complex and 3-D geometries so to have more effective interaction even in presence of a limited amount of nanoclay
- More widespread studies of loading simulating service (e.g., fatigue testing, falling weight impact) with the idea of extending their useful life even in harsh conditions (measurement of residual properties after being subjected to water absorption would e.g., be useful)
- The development of new biomatrices (particularly, real thermosetting matrices from vegetable oils) would improve the profile of use of plant fibre composites and this could include more diffuse application of nanoclay

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