Research progress in wood-plastic nanocomposites: A review
Irina Turku and Timo Kärki

Article

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Abstract

The interest towards wood-plastic composites (WPCs) is growing due to growing interest in materials with novel properties, which can replace more traditional materials, such as wood and plastic. The use of recycled materials in manufacture is also a bonus. However, the application of WPCs has been limited because of their often poor mechanical and barrier properties, which can be improved by incorporation of the reinforcing fillers. Nano-sized fillers, having a large surface area, can significantly increase interfacial interactions in the composite on molecular level, leading to materials with new properties. The review summarizes the development trends in the use on nanofillers for WPC design, which were reported in accessible literature during the last decade. The effect of the nanofillers on the mechanical properties, thermal stability, flammability and wettability of WPC is discussed.

Introduction

Wood-plastic composite (WPC) is common name for the polymer matrix reinforced with wood fibres. WPCs are being used in a large number of applications in different fields including building, infrastructure and transportation.[1] They combine many advantages over the row materials of wood and plastic. They possess wood fibre characteristics such as lower cost, lower density and biodegradability, while the moisture resistance and dimensional

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Lappeenranta University of Technology, Finland

Corresponding author:

Irina Turku, Department of Mechanical Engineering, Lappeenranta University of Technology, PO Box 20, Lappeenranta, 53851, Finland.
Email: irina.turku@lut.fi

stability form the polymer matrix characteristics.[2] Besides, manufacturing of WPC can be classified as 'green technology' due to possibility to use recycled plastic and waste wood. However, the major limitation in their manufacturing is associated with natural incompatibility of hydroscopic wood with hydrophobic polymer matrix. Inadequate interaction results in poor dispersion of wood particles in the matrix as well as in poor mechanical and barrier properties of the final product.

Synthetic nanocomposites are novel materials, whereas natural nanocomposites such as mollusc shells, bone, teeth and wood have been present in nature for millions of years. Nanocomposites are defined as multiphase structures, in which at least one of the components has at least one dimension in the nanometre scale range. Typically, the nanofillers used in composites have the dimension range from 1 to 500 nm, while the size of conventional fillers lies between 10 μm and 1 cm. Usually, 3–5 wt% of a nanofiller gives a better result than 30 wt% of conventional micrometre-size fillers.[3] Commonly, the ability of nano-sized fillers to reinforce a polymeric matrix is attributed to their large aspect ratio (the length of a particle divided by its diameter) and the surface area with abundant interfacial chemical and/or physical interactions. In addition, an important role in improving the properties of nanocomposites might play the *percolating interphase network* in composites that is induced by the surrounding interphase region of each nanoparticle.[4,5]

The nanofillers used nowadays are mostly natural nanoclays and synthetic carbon nanotubes (CNTs). Synthetic CNTs are known to be costly, unlike nanoclays, also known as layered silicates, which are relatively inexpensive with potential for bulk applications. Besides nanoclays and CNTs, there is a growing interest towards nanocomposites consisting of nano-sized oxides, such as titanium oxide (TiO_2) and amorphous silica (SiO_2). These chemicals are cheap, easily available, thermostable and environmentally friendly. Cellulose fibres attract an interest as reinforcing nanofillers due to their specific strength and stiffness, low density, low cost, renewability and biodegradability. Nanocellulose is known to be widely used as a reinforcing agent in polymer composites. However, to our knowledge, there are only very few works describing nanocellulose (e.g. microcrystalline cellulose (MCC)) as a reinforcing agent for the WPCs.

During the past decade, many research works were devoted to optimization of WPC properties through their hybridization with nano-sized reinforcing fillers. The objective of this article is to provide an overview of the progress in this research area. As the properties of the composites depend on the uniformity of the nanofiller dispersion, particular attention is paid to the 'structure–properties' relationship in the composite material. The processing methods of WPC nanocomposites are also observed.

Wood-plastic nanocomposite structure

Wood fibre/matrix interaction

WPCs are multiphase systems, the properties of which are dependent on the properties of the components as well as interfacial and inter-phase interactions. Common thermoplastics used in WPC design are polyethylene (PE), polypropylene (PP) and poly(vinyl chloride) (PVC). Cellulosic fibres originate from plant materials; however, wood fibres are
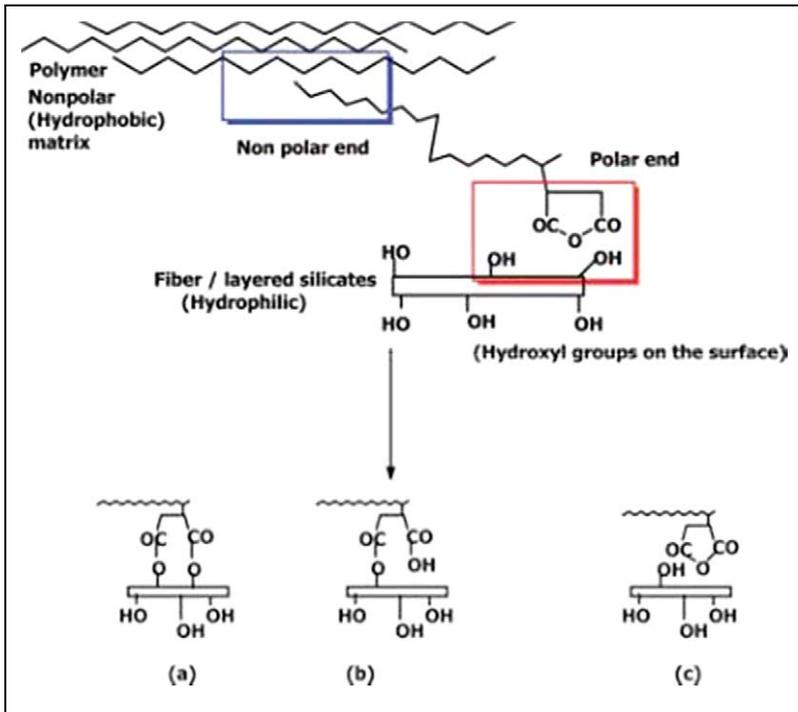
Figure 1. Possible interactions of compatibilizer with polymer matrix and fillers.[7]
Note: (a) and (b) covalent bonds, (c) hydrogen bond.

the most extensively used as fillers for WPCs. Cellulose, the main component of natural fibres, is a linear homopolymer composed of D-glucose units linked through a β-(1→4) glycosidic bond. Glucose molecules having hydroxyl groups in their structure make cellulose fibres strongly polar, and are hence not compatible with hydrophobic polymers (i.e. PE and PP). Such phase incompatibility leads to low wood/matrix work adhesion and thus poor mechanical and other characteristics of the composites. The adhesion can be improved by using compatibilizers/coupling agents. Of coupling agents, maleic anhydride (MA)-grafted polymers (maleated polyolefines (MP)) are the most commonly employed ones.[1,6] Maleated polyolefin is an amphipathic molecule whose hydrophobic tail has affinity to the matrix, and the anhydride group forms ester and hydrogen bonds with hydroxyl groups of the wood surface (Figure 1).[7] However, MP is not effective when a polar matrix, such as PVC is used.[8,9] It has been shown that the most appropriate method to improve chlorine-containing PVC/wood compatibility is by modification of wood fibres with amino-group-containing chemicals, such as aminosilane,[9] chitin and chitozan.[8,10] The mechanism of their interaction can be described according to Lewis' acid–base theory.[9] The electronegative chlorine groups (electron acceptor) of PVC react chemically and form ionic bonds with positively charged amino groups (electron donor) of modified cellulosic fibres. This interaction is shown schematically in Figure 2.
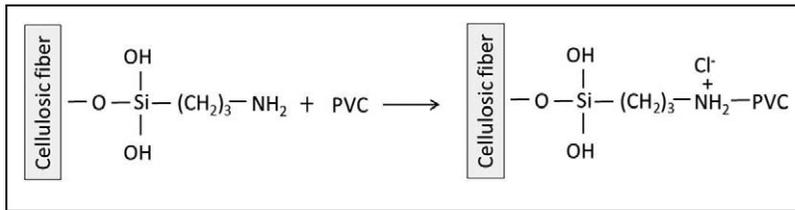
Figure 2. Possible mechanism of adhesion between PVC and aminosilane-treated cellulosic fibres (Source: adapted from Matuana[9]). PVC: poly(vinyl chloride).
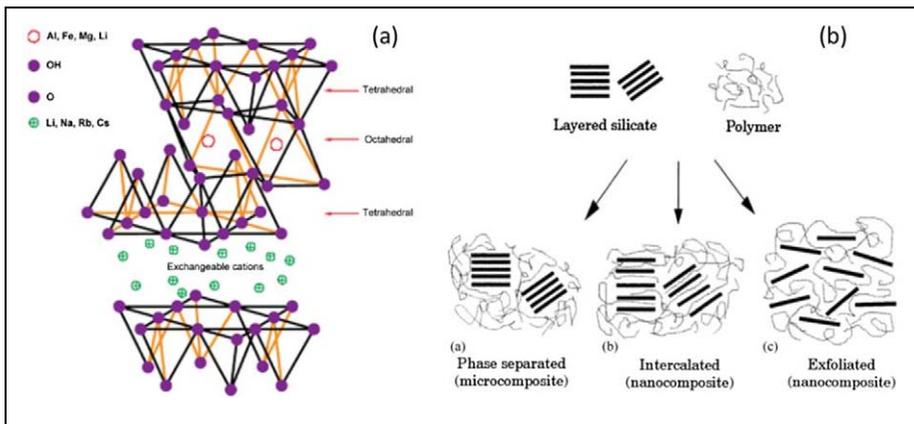
Figure 3. (a) Structure of 2:1 layered silicate; (b) different types of composites generated based on the interaction of layered silicate with polymer matrix.[11]

## Nanoparticles/wood fibre/matrix interactions

The properties of wood-plastic nanocomposites are greatly affected by the dispersion of the nanofiller in the composite material. Thus, the interfacial chemistry between the nano-particle and the matrix/wood is another important issue for the performance of the compo-site. The most representative nanofiller used in composites is montmorillonite (MMT; named after Montmorillon in France, where it was first identified). MMT nanoclay has a 2:1 layered structure with the composition $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$. The MMT struc-ture is schematically represented in Figure 3(a). The crystal structure of MMT consists of stacked layers of two SiO_2 tetrahedrons fused to an edge-shared octahedral sheet of alu-mina. The individual layers of silicate are attracted to each other through van der Waals forces. The space between the layers, gap or gallery spacing is occupied by hydrated N^+ or K^+ cations.[11] In this pristine state, MMT, having a hydrophilic surface, is immis-cible with a hydrophobic matrix. One possible way to improve the dispersion of nanoclay in the composite material is to apply a compatibilizer. Maleated polyolefines, which are usually used for improving the compatibility of cellulosic fibres with the matrix, are also applied for improving the silicate dispersion. The hydroxyl groups of the silicate layer

interact with the succinic anhydride groups of MP in the same way as the wood fibre hydroxyl groups (Figure 1).[7,12] Another way to facilitate the clay/matrix interaction is modification of the clay surface with polymers containing polar groups (i.e. surfactants). Due to the ion exchange reaction between the cations, which are initially present in the pristine clay interlayer and organic cationic surfactant, the hydrophilic clay surface can be transferred to a hydrophobic/organophilic one.[13,14] A negatively charged silicate layer surface is attractive to the cationic head groups of alkylammonium salt molecule, and the hydrocarbon tails radiate away from the surface due to a repulsive interaction between hydrophilic silicate layer and hydrophobic aliphatic chain (Figure 2[15]). Thus, the surfactants enlarge the *d*-spacing between the nanofiller layers and help to penetrate the polymer matrix molecules between the silicate galleries.[15–20] Also, due to the increasing silicate interlayer spacing, the interaction of the silicate layers is weakened. The strong interaction between the polymer and the MP may result in layers dispersion (Figure 5[12]). Depending on the degree of dispersion of the clay layers, the composites can be classified as *intercalated* or *exfoliated/delaminated* (Figure 3(b)). An intercalated structure can be described as an ordered layer structure, resulting from the penetration of polymer chains into the silicate gallery. Exfoliation or delamination occurs when the silicate layers are completely separated and the layers are uniformly dispersed throughout the matrix. When the polymer matrix chains are unable to penetrate between the layers, a composite with silicate microstructure is created. According to research results, exfoliated systems lead to better characteristics than intercalated nanocomposites.

To improve the interfacial interaction of WPC/CNTs nanocomposite, CNTs can be hydroxylated. It has been reported that the OH groups of CNT-OH have good compatibility with strong polar wood fibres, and on the other hand, CNT-OHs also interact readily with MP.[21] Metal oxides such as SiO_2, TiO_2 and ZnO_2 are usually modified with surfactants (e.g. cetyl trimethyl ammonium bromide (CTAB)) to increase hydrophobicity, which may result in improving the interaction with the matrix.[22–24] On the other hand, the OH groups of oxide surfaces interact with wood fibre and MP molecule functional groups, leading to strong interfacial interaction in the nanocomposites.

WPC nanocomposite manufacturing

The processing conditions of wood polymer nanocomposites do not differ from those of conventional WPCs. Wood plastic nanocomposites are usually produced by extrusion,[2,25–28] injection[9,29–32] or compression molding.[17,22–24,33–35] One of the challenges in nanocomposite manufacturing is achieving homogeneous dispersion of the nanofiller throughout the composite material. The appropriate method for the compounding, the proper choice of the extruder type and its screw design may improve the degree of nanofiller dispersion in the composite significantly, which, in turn, improves the quality of the final product.[16] Thus, along with the chemical compatibility nanofiller/matrix/wood fibres, the processing method of nanocomposites has a great effect on its performance. Typically, the direct melt compounding method, where the wood fibres, matrix, coupling agent and nanofiller are blended at the same time, is less effective at dispersing nanofillers.[20,29] One approach to facilitate the nanofiller dispersion is using the two-step 'masterbatch' process
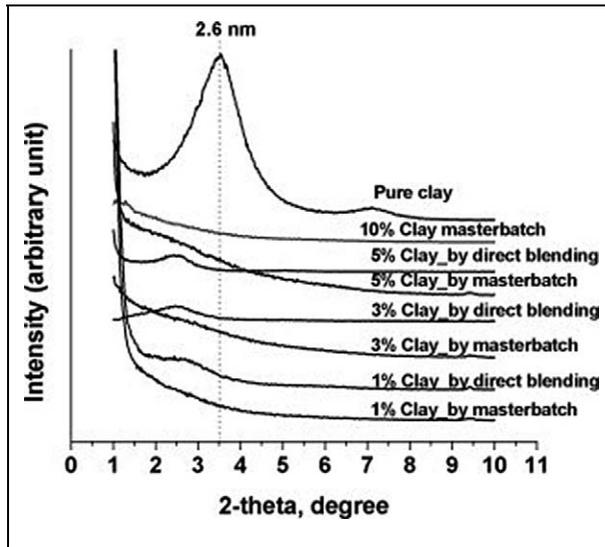
Figure 4. XRD patterns for wood fibre/HDPE/nanoclay composites with respect to preparation method of the composites and clay content.[28] HDPE: high-density polyethylene.

where the nanofiller is first premixed with the coupling agent and/or polymer matrix, followed by blending with the other composite ingredients.[2,6,10,20,25–29]

Faruk and Matuana[20] have used two methods of incorporation of nanoclay into WPC. In the 'melt blending' process, nanoclay was mixed with high-density PE (HDPE); this polymer nanocomposite was then used as a matrix for WPC processing. In the other method, 'direct dry blending', nanoclay was directly added to an HDPE/wood flour composite during conventional compounding. The authors report that the WPC manufactured by the two-step method had improved strength and modulus compared to the control WPC (no clay) and the WPC processed by direct dry blending. Direct incorporation of the clay lowered the flexural strength of the composite significantly compared to the control, due to poor dispersion of the clay in the composite material.

Lee et al.[29] improved the composite properties and clay dispersion using two-step compounding. The nanofiller was first pre-compounded with the coupling agent (masterbatch), after which the mixture was blended with the matrix and wood fibres. The influence of the way nanoclay was incorporated in the clay dispersion was studied with an X-Ray diffractometer (Figure 4). As seen in the figure, the degree of the dispersion of clay was higher for the masterbatch method than that of direct blending. In direct blending, all the components were added into a batch mixer at the same time.

Yeh and Gupta[27] compared the characteristics of WPCs manufactured by one and two steps. In the two-step process, the wood fibre, polymer and other additives were pre-compounded initially; the nanofiller was introduced into the WPC material in the second step. In the one-step compounding, the nanofiller together with the wood fibres, matrix

Figure 5. Tortuous pathway of a permeant in a clay nanocomposites.[4]

and other additives were introduced into the extruder at the same time. The nanocomposite made with the two-step method showed better strength characteristics than the WPC manufactured with the single-step method. Yeh et al. explain this by the absence of competition between the clay and wood fibres for the coupling agent. Since composite strength is mainly dependent on the wood fibre/polymer resulting from the wood fibre/coupling agent reaction (Figure 1), it is important to incorporate nanoclay after compounding the matrix, wood fibres and coupling agent. However, the modulus of the WPC decreased due to the fact that the microstructure of the WPC may have been destroyed when the composite material passed through the extruder twice. The authors also compared different screws in the WPC compounding. It was shown that the counter-rotation screw gave better nanofiller dispersion in the WPC than the co-rotation one.

Co-extrusion is a novel way of WPC composite processing. WPCs manufactured with the co-extrusion system are two-layer composites consisting of a core layer completely covered with a cap layer (Figure 1[36]). Jin and Matuana[36] incorporated CNT into the outer layer (rigid PVC), which resulted in increased flexural strength and modulus compared with the control (no cap-layer) and unfilled cup layer WPCs.

Effect of nanofillers on the mechanical and physical properties of WPCs

Mechanical properties

The mechanical characteristics, such as flexural, tensile and impact properties are the most extensively studied ones in the design of WPCs. Generally, WPCs have low strength and impact properties resulting from poor interfacial interaction between the polymer matrix and wood. Also, the flexural and tensile moduli of hybrid materials are substantially lower than those of solid wood due to low stiffness of the polymer matrix. Thus, the incorporation of nanofillers into WPC aims at improving the mechanical and

other properties of the hybrids over improving the stiffness of the polymer matrix and the interfacial bonding in the composite.

In fact, the properties of nanocomposites are related to their morphology, which in turn is highly dependent on the degree of dispersion of the nanoparticles throughout the composite. Well-dispersed nanoparticles, having a large aspect ratio, provide a large interfacial area leading to better interfacial stress transfer in the composites. Hence, the structure–properties relationship analysis of composites is very important in the examination of their properties. Nowadays, there are some techniques that are successfully applied in the monitoring of the composites structure on the nano-scale level. X-Ray diffraction (XRD) analysis shows the changes in the *d*-spacing in layered silicates, which indicates the effectiveness of the clay intercalation. Transmission electron microscope (TEM) and scanning electron micrographs (SEM) provide a direct visualization of the inner composite structure.

Nanoclays and nano-oxides instead of Nanoclays. SiO2, and titanium dioxide. MMT, a hydrated alumina-silicate layered clay, is the most studied reinforcing nanofiller for WPCs. The high aspect ratio (50–1000) and large surface area (750 m^2/g) make them very suitable for the reinforcement purpose. Also, the layered structure of MMT provides additional preferences: the layered structure increases the tortuosity pathway, which may decrease the permeability of the composite and enhance its barrier properties (Figure 5). As mentioned above, pristine inorganic clay is commonly converted to organoclay for improving the compatibility with the matrix. Nowadays, different organoclays are available commercially.[13,37] Also, modification of pristine clay with a surfactant can be easily managed in laboratory conditions.[17,38]

Zhao et al.[38] have examined the effect of MMT on the morphology and properties of wood flour/PVC composite. The MMT was modified with cetylalkyl trimethyl amine bromide, and silane was used as coupling agent. An improved tensile strength of 9.7% and impact strength of 15.4% were observed for 0.5% of organo-MMT (OMMT) loading. However, the impact strength decreased when the amount of OMMT increased above 0.5%, while the tensile strength slightly increased until at 1.5% and then dropped (Figure 6(a)). This result was consistent with the morphological structure observed by TEM: at low concentration (0.5 wt%), organoclay was well-dispersed through the composite, and at high concentration (3 wt%), it became aggregated (Figure 6(b)). Obviously, incomplete dispersion of particles weakened the interfacial forces in the composite and deteriorated the mechanical properties.

Hemmasi et al. illustrated that the flexural and tensile moduli of wood flour/PP increased at a low organoclay Cloisite® 30B loading (3 phr); increasing the clay concentration further up to 6 phr resulted in leveled-off values. They also observed that the decrease in properties was related to the decreasing of clay dispersion in the composites. The XRD analyses indicated that *d*-spacing between the silicates layers decreased from 19.70 nm at 3 phr to 19.44 nm at 6 phr clay concentration. The authors also believed that the increased coupling agent loading could improve the clay dispersion, and thereby increase the interfacial adhesion in composites.
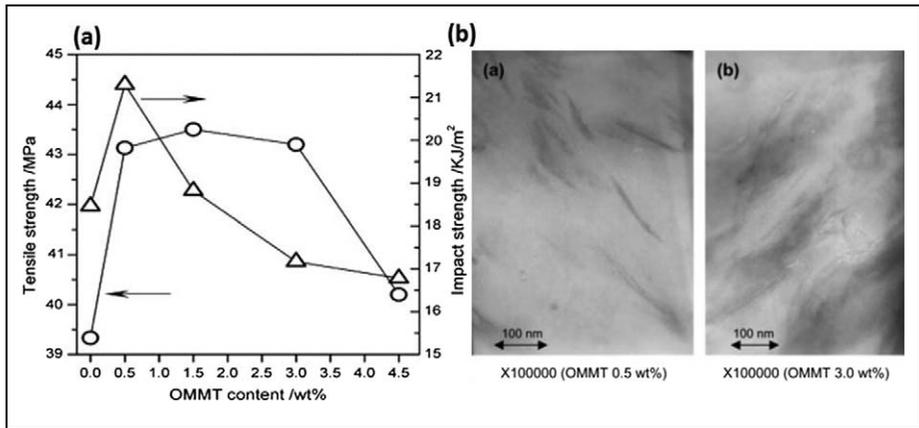
Figure 6. (a) The effect of OMMT content on the tensile and impact strengths of OMMT/STWF/ PVC, ×100,000 (OMMT 0.5 wt%); (b) TEM microphotographs of fracture surface of OMMT/ STWF/PVC composites, ×100,000 (OMMT 3.0 wt%).[38] OMMT: organo-montmorillonite; PVC: poly(vinyl chloride); STWF: silane treated wood flour.

Gu et al.[39] compared the impact of natural Cloisite Na+ and organically modified Cloisite 10A nanoclays on the mechanical characteristics of aspen fibres/PE/maleated PE (MAPE)/dicumyl peroxide (DCP). They report that a natural nanoclay-filled composite had better impact strength, tensile strength, elongation and toughness than that composited with Cloisite 10A. Researchers attribute this to the fact that natural clay exfoliates more easily in the composite material than modified clay. Inorganic natural clay and wood fibres have stronger interaction due to opposite polarities, as well as the higher density but smaller particle size of natural clay. Smaller particles disperse better in the matrix, resulting in increased interfacial interaction and improved properties. However, the moduli of the composites were similar, as the main contribution in the modulus come generally from the wood fibre.

Gu and Kokta[40] studied the influence of Cloisite Na+ loading (5–20%) in the presence of maleated PP (MAPP) and DCP on the mechanical properties of aspen fibres/PP nanocomposites. The impact strength of the hybrid decreased monotonically with nanoclay loading. The reason for this was high nanoparticle aggregation and low surface energy, which led to increased viscosity and restricted polymer molecular chain movement. The tensile strength of the hybrid decreased slightly at lower nanoclay loading, but finally improved at high concentrations. The initial dropping was a result of stress concentration and poor nanoparticle dispersion. At high nanoclay loading, 'the penetrated nanoclay particles work as solid join-points with a strong driving force under the high viscosity which originates from the strong interfacial strength due to delamination and better dispersion. Even when an aggregation occurs, more points produced bear the stress, and lead to superior tensile strength.'[40] Also, part of the nanoparticles can deposit on the wood particles and locate lumen in the wood, which can reduce its negative effect. The tensile modulus and elongation at maximum were slightly increased

with nanoclay loading. These tendencies were attributed to the probable location of the nanoparticles on the wood fibre surface and in lumen, thereby partly eliminating the role of the particles in the movement restriction of the polymer molecular chains. The toughness of the hybrid was improved up to 17% at 20 phr nanoclay loading.

Gu and Kokta[41] studied the influence of nanoclay on birch fibres/PP nanocomposites. They report on a positive effect of clay on the modulus, but stress and strain at maximum load decreased after 10 wt% MB1001 (nanoblend concentrate, PP with 40 wt% natural MMT) was loaded. The lowered parameters were a result of the fact that the filler particles weakened the interfacial strength among the fillers, fibres and matrix (in composite material). Also, the solid particles of clay 'negatively affected the absorption of the fracture energy and made the composite more fragile due to its harder phase and its restriction for wood fibre and matrix to entangle'.[41] The impact strength did not change much after the clay loading.

Najafi et al.[42] studied the influence of Cloisite 15A and MAPP on the properties of reed flour/PP hybrid. The positive effect of the coupling agent was obvious for all studied composite parameters. The incorporation of nanoclay improved the tensile properties of the composite. This was attributed to the high dispersion of nanoclay provided by the presence of the coupling agent (Table 3[42]). The impact strength of the composite decreased at clay loading. Clay particles are potential places of stress concentration, which generally leads to crack initiation and hence dropping of the impact strength.

Kord[43] studied the influence of the Cloisite 15A (1–5%) on the properties of hemp fibres/ PP hybrid. It was shown that tensile characteristics increased with an increase in organoclay loading up to 3% and then decreased. At 3% clay loading, clay particles had the highest dispersion, which was indicated by X-Ray diffractometer measurements (Table 2[43]). The elongation at break also increased up to 3% and then decreased. Improvement at low filler content was attributed to its high dispersion in composite material. The impact strength of the hybrid decreased monotonically with the increasing clay loading amount.

Deka and co-workers[22–24,33] have published a series of works, where they examined the influence of four nano-size fillers, clay, SiO_2, and clay/TiO_2, and clay/SiO_2/ZnO_2 on the flexural, tensile and hardness properties of WPCs, where the blend of polymers, HDPE, LDPE, PP, PVC, in the ratio 1:1:1:0.5, were used as the matrix. This ratio is attributable to domestic plastic wastes. The impacts of the fillers under the scope were similar to each other: all types of nanofillers improved the flexural and tensile properties of the nanocomposites at low, 1 and 3 phr, nanofiller contents; at high content (5 phr), the flexural and tensile properties declined. The XRD analysis (Figure 7) clearly established the formation of exfoliated structures with 1 and 3 phr clay contents (no peaks), while 5 phr nanoclay pattern, having a small peak, represents an intercalated structure. Also, TEM images of WPCs loaded with different amounts of clay/TiO_2 indicated TiO_2 agglomeration at a high loading (Figure 8(c)). A comparison of WPCs reinforced with different nanofillers is shown in Table 1. One can see that the clay and SiO_2 exhibit almost equal reinforcing capacity. On the other hand, the 3 wt% of nanoclay together with same amount of TiO_2 or SiO_2 and ZnO_2 has the highest influence on the mechanical properties of WPC. This clearly shows the synergism of two and three nanofillers improving the properties of composites in a larger extent. The same authors have also
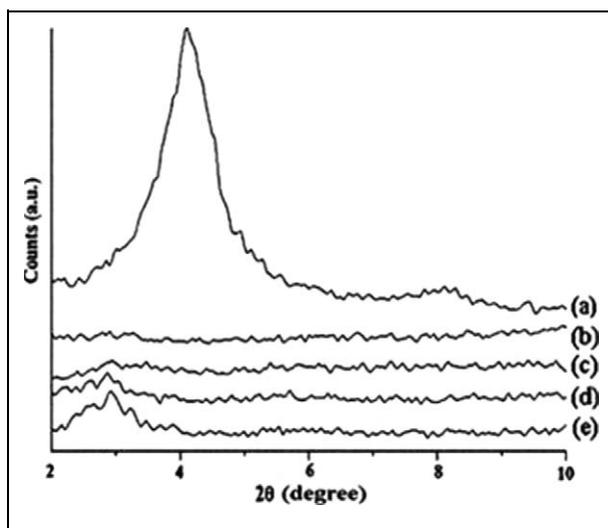
Figure 7. X-Ray diffraction of: (a) nanoclay, (b) PB/CA/W40/N1, (c) PB/CA/W40/N3,(d) PB/CA/W40/N5, (e) PB/CA/N3.[33] PB: polymer blend; CA: coupling agent.
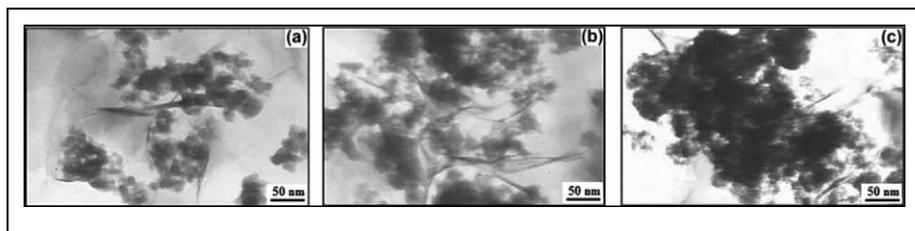
Figure 8. TEM micrographs of: (a) PB/CA/W40/N3/T1, (b) PB/CA/W40/N3/T3 and (c) PB/CA/W40/N3/T5.[22] PB: polymer blend; CA: coupling agent.

studied the changes in the mechanical properties of PB/wood/clay nanocomposites after biodegradation.[34] They found that the presence of clay promoted bacterial growth on the WPCs. Also, clay could play catalytic role in the biodegradation mechanism. The comparison of the mechanical properties of WPCs before and after a degradation period showed that the flexural and tensile properties of samples decreased. The authors note that this may be due to the loss of physical and chemical interaction in the WPC caused by the degradation effect of bacteria. Kord and Kiakojouri[44] observed the synergistic effect between nanoclay and glass fibres.

Nourbakhsh and Ashori[45] studied the influence of the coupling agent (MAPP) and Cloisite Na+ on the characteristics of a bagasse/PP composite. The tensile modulus and the yield of nanocomposites increased by 26 and 15%, respectively, with 3 wt% nanoclay loading, but then decreased at 4 wt% nanoclay content. The impact strength decreased

Table 1. Flexural and tensile properties of polymer blend, wood/polymer and wood/polymer/nanofiller composites.[22–24,33]
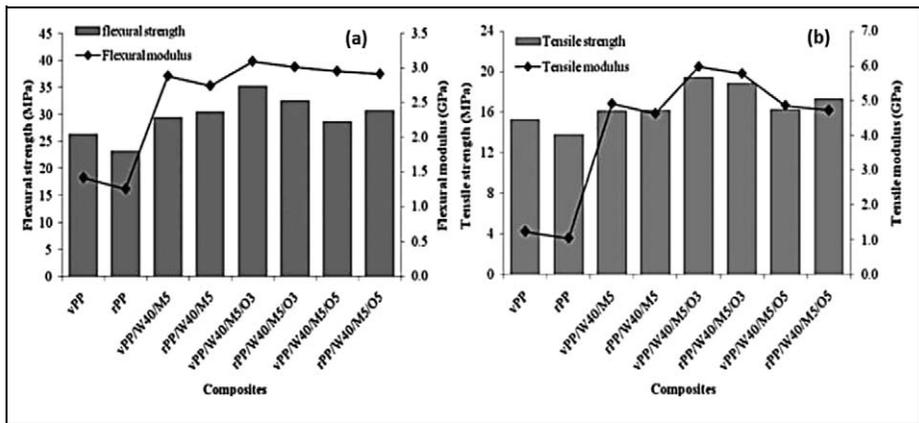
Sample	Flexural properties		Tensile properties		Hardness
	Strength (MPa)	Modulus (MPa)	Strength (MPa)	Modulus (MPa)	Shore D
PB	12.78	755.68	6.06	85.92	67.4
PB/G5/W40	16.85	3779.91	17.14	260.81	66.7
PB/G5/W40/N3	26.17	4749.53	31.57	581.40	77.0
PB/G5/W40/S3	26.46	4812.48	33.74	597.58	78.0
PB/G5/W40/N3/T3	33.85	5072.64	36.03	653.86	80.9
PB/G5/W40/N3/S3/Z3	33.99	5186.68	37.25	697.52	80.3

PB: polymer blend; G: coupling agent; W: wood flour; N: nanoclay; S: silica; T: titanium oxide; Z: zinc oxide.
[a]Number denotes amount, phr.

with the addition of clay. Noukbakhsh and Ashori also report that the presence of 4 wt% of coupling agent improved the composite properties by more than 2 wt% MAPP. Kord et al.[46] improved the flexural and tensile properties of a nanocomposite based on wood flour/PP/MAPP by the incorporation of 3 phc of Cloisite 30B. The higher amount of MMT, 6 phc, decreased the mechanical properties. X-Ray diffractograms and TEM micrographs showed that composite samples with 3 phc OMMT had higher order dispersion than those with 6 phc. However, the impact strength decreased monotonically after the clay incorporation. Kord and Tajik[47] report that the acoustic properties of WPC nanocomposites improved after clay incorporation. The time of sound propagation and sound energy absorbance of composites increased with the increase in OMMT (3-6 phc), and thereby speed of sound propagation decreased.

Recently, Khanjanzadeh et al.[48] have studied the mechanical properties of PP (recycled or virgin)/wood flour/OMMT nanocomposites. The flexural and tensile properties increased after the clay incorporation compared with the neat polymer. Better results were achieved with 3 wt% clay loading; the clay content increased further up to 5 wt%, levelling the values off (Figure 9). The XRD analysis showed that the clay was better dispersed at 3 wt% (*d*-spacing 34.49 nm) than at 5 wt% (*d*-spacing 34.1 nm). Zhong et al.[26] modified the wood flour/HDPE composite with Cloisite 20A type organoclay, improving the flexural strength from 27.3 to 44.16 MPa and the flexural modulus from 1.97 to 2.43 GPa for non-filled WPC and WPC/3 wt% clay, respectively. Lee et al.[29] have studied the influence of the dispersion degree of Cloisite 20A clay in a wood fibre/HDPE composites matrix on its properties. As shown in Figure 10(a), the presence of organocaly improved the tensile and flexural moduli of composites so that the exfoliated composites showed better improvement than the intercalated one. Also, the strengths of the composites were improved, although to a lower extent, showing an insignificant difference between exfoliated and intercalated nanocomposites (Figure 10(b)). The clay incorporation reduced the notched Izod impact strength regardless of the clay dispersion (Figure 10(c)). However, the exfoliated clay particles resulted in slightly

Figure 9. Flexural (a) and tensile properties (b) of PP (recycled-virgin)/wood flour/OMMT at different OMMT content.[48] OMMT: organo-montmorillonite; PP: polypropylene.

higher impact strength than that of the intercalated ones. Yeh and Gupta[27] have studied the properties of wood flour/PP nanocomposites reinforced with Nanomer® I.30P-type organoclay within 2–10 wt%. The nanoclay incorporation increased the tensile modulus so that the higher clay incorporation resulted in higher values. The tensile and impact strengths, however, decreased with an increased clay loading. Yeh and Gupta also observed that two-step nanocomposite compounding, allowed retaining the tensile and impact strengths at higher levels compared to single-step compounding.

The effect of different types of organically modified nanoclays on the properties of linear low-density PE (LDPE)/wood fibre nanocomposites was studied by Gu et al.[37] They observed that the characteristics of the composites were affected by the amount of clay, as well as the surfactant type used for clay modification (Figure 11). Two types of clays, pristine Cloisite Na+ and I.34 TCN, had relatively good reinforcing properties. Their strong interaction with the matrix was due to the fact that more polymer chains may fit into the empty galleries of natural clay and because of improved interaction between coupling agent MAPE and I.34 TCN, having an extra hydroxyl group (Table 1[37]). However, increasing the nanoclays loading resulted in declined properties (Figure 11(a) to (c)). Young's modulus increased monotonically with the increase in all types of clay loading (Figure 11(d)). Faruk and Matuana[20] manufactured a wood flour/HDPE composite, where the polymer matrix was reinforced with Cloisite 10A clay. The incorporation of 5 wt% of Cloisite 10A in combination with 5 wt% of MAPE coupling agent improved the flexural strength value up to 62.2 MPa, which is comparable with the flexural strength of the solid wood species (Table 1). However, the flexural modulus (3.2 GPa) was lower than that of solid wood.

Other authors have also observed improved mechanical properties of several nanocomposites with the addition of nanoclays. Tabari et al.[31] reported that the incorporation of 3 wt% pristine nanoclay to a waste poplar sawdust/PP composite improved the flexural and tensile properties of the hybrid material. The incorporation of 1 phr of
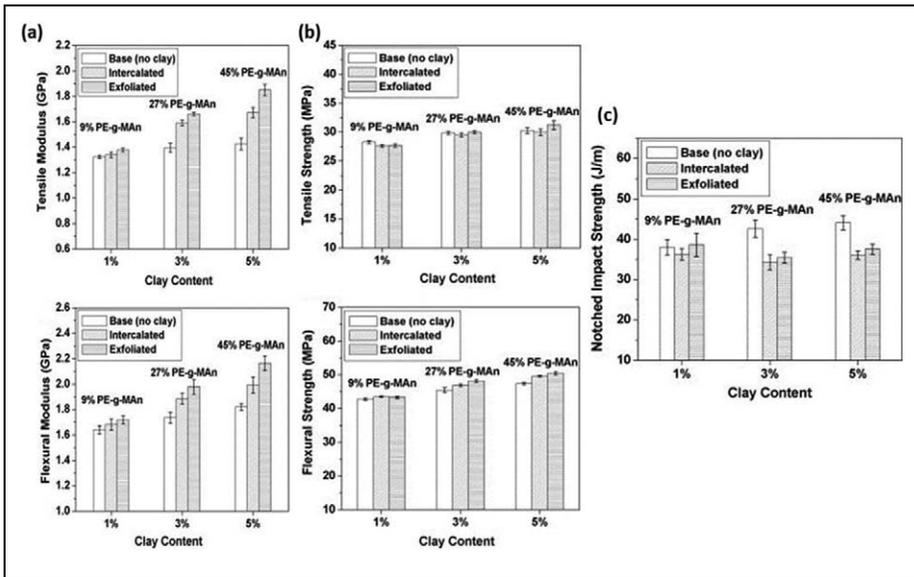
Figure 10. Effect of clay dispersion on tensile and flexural moduli (a), tensile and flexural strengths (b), and impact strength (c) of wood fibre/HDPE/clay nanocomposites versus clay percentage (weight ratio of coupling agent PE-g-MAn to clay = 9.0).[29] HDPE: high-density polyethylene; PE-g-MA: polyethylene-grafted maleic anhydride.

Cloisite 20A slightly increased the impact and tensile strengths as well as the tensile modulus of a wood flour/PP composite.[35] Lei et al.[28] have observed that the addition of 1% of Cloisite Houston TX 15A organoclay increased the flexural and tensile strength of pine flour/HDPE composite up to 19.6 and 24.2%, respectively. Also, the tensile modulus and elongation were improved up to 11.8 and 13%, respectively. The impact strength decreased slightly after the clay incorporation. Ashori and Nourbakhsh[32] reported that the tensile and flexural strengths of a fresh poplar wood flour/PP composite increased to about 20 and 13%, respectively, when 3 wt% of Cloisite 20A were incorporated. Further increasing of the nanoclay loading up to 6 wt% resulted in decreased values. Liao and Wu[17] have studied a metallocene poly(ethylene-octene)/wood flour/ OMMT nanocomposite, prepared by the melt blending method. Incorporation of clay into the composites increased the elongation and tensile strength at break. The authors also report that the rate of biodegradability of the nanocomposite was slower than that of non-filled WPC. Kumar and Singh[7] reported that the tensile properties of an ethylene– propylene copolymer epoxy (EP)/MCC composite was significantly improved with clay loading (5 wt%). The yield stress and stress at break were decreased after adding clay to the EP/MCC composite. This was attributed to the probable agglomeration of silicate particles. Meng et al.[25] modified the poly(lactic acid) (PLA) of WPC with Cloisite 20A organoclay. The incorporation of the nanofiller from 1 to 5 wt% increased the tensile and flexural moduli and decreased the tensile, flexural and impact strengths. The
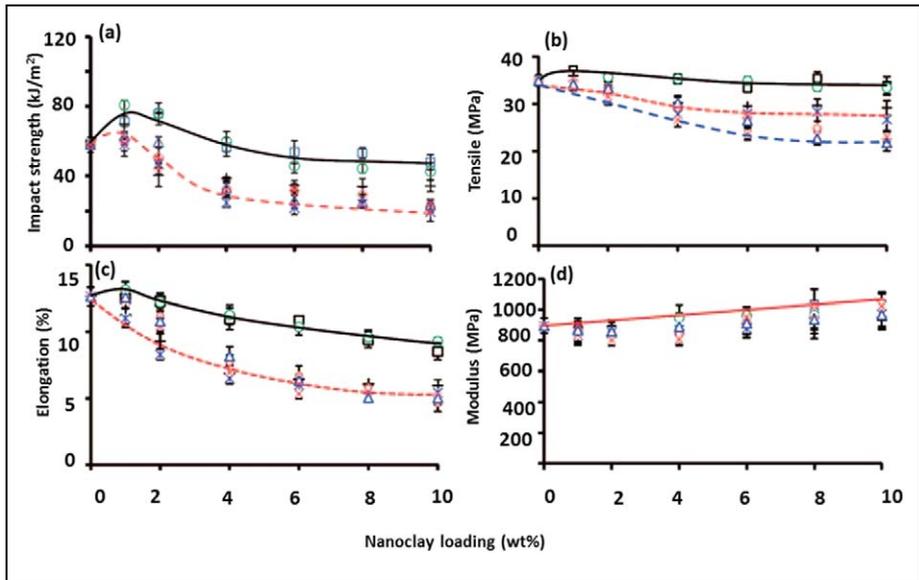
Figure 11. Effect of nanoclay on impact strength (a), tensile strength (b), elongation (c) and modulus (d) of WPC. □: Cloisite Na+; ○: 1.34 TCN; ◊: Cloisite 10A; +: 1.31 PS; ×: 1.28 E; △: 1.44 P; *: 1.30 E.[37]

XRD analysis showed that with the increased clay loading, the *d*-spacing of the clay layers decreased (Figure 2[25]). The flocculated clay introduced voids, which may have resulted in poor interfacial adhesion between the wood and the PLA matrix, and thereby reduced the tensile and flexural strengths.

CNTs/nanofibres. Faruk and Matuana[10] have used CNTs as a filler for rigid PVC for the manufacture of WPC. Chitin in the content of 6.67 wt% was used as a coupling agent to improve the adhesion between PVC and the maple wood flour phases. The flexural strength increased up to 97.8 MPa and the flexural modulus up to 7.6 GPa, when 5 wt% CNTs were loaded. These values are comparable to bending properties of solid wood (Table 2). Later, Jin and Matuana[36] have synthesized the wood flour/PVC composite with a CNT-filled rigid PVC cap layer with the co-extrusion method. On average, the presence of 5 wt% CNTs in the cap layer increased the flexural strength and modulus of the WPC up to 65 MPa and 4.9 GPa, respectively. Also, regression models evaluating the statistical effects of material compositions and processing conditions on the flexural properties of composite were developed by the authors.

Kordkheili et al.[49] improved the flexural properties of a wood flour/LDPE composite by the incorporation of single-walled CNTs (SWCNT; 1–3%). The high aspect ratio and large surface area of CNTs, as well as improved interfacial interaction between the nanotubes and the matrix were reasons for the improved mechanical characteristics of the

Table 2. Flexural properties of WPC versus solid wood species.[10,20]

	Flexural properties	
Materials	Strength (MPa)	Modulus (GPa)
Northern white cedar	45	5.5
Ponderosa pine	65	8.9
Red maple	92	11.3
Trex WPC (50% PE mix/50% wood)[a]	10.4	1.1
GeoDeck WPC (40% HDPE/60% wood)[a]	19.2	2.5
HDPE/wood-flour composite made with 5% Cloisite 10A and 5% maleated PE[b]	62.2	3.2
PVC/wood-flour composite made with 5% of nanoclay and 6.67% chitin[b]	87.4	7.2
PVC/wood-flour composite made with 5% of CNT and 6.67% chitin[b]	97.3	7.6

PVC: poly(vinyl chloride); PE: polyethylene; HDPE: high-density polyethylene; WPC: wood-plastic composite; CNT: carbon nanotube.
[a]Commercial WPC deck.
[b]Laboratory manufactured WPC.

Table 3. The thermal expansion coefficients and dimension changes of the WPCs.[35]

Sample	α_1[a] (µm/m °C)	α_2[b] (µm/m °C)	ΔL[c] (%)
W40/P60	103	194	0.69
W40/P57/C3-2	89	156	0.59
W40/P57/C3/M1	74	153	0.54

W: wood flour; P: polypropylene; C: coupling agent; M: clay.
[a]Expansion coefficient measured at 50°C.
[b]Expansion coefficient measured at 100°C.
[c]Dimension changes between 50 and 100°C.

WPC. Also the modulus of the WPC was improved due to the fact that the flexural modulus of the SWCNTs (1TPa) is much higher than those of wood and matrix. However, the impact strength increased with the increasing of CNT loading up to 2 phc, after which it decreased. This was related to the increasing probability of CNT agglomeration, which may create regions of stress concentration and crack propagation.

Zhang et al.[50] report that the incorporation of 1 wt% of CNF decreased the modulus of the wood fibres/PP/MAPP composite by 5%; the flexural strength was unchanged. SEM indicated that the dispersion of the CNFs was not completely homogeneous. Also, adhesion between the nanotubes and the matrix was poor. The poor interaction of the CNFs and the matrix was explained by the low hydrophilicity of the carbon fibre and hence their low competitivity with wood fibre in reacting with MAPP. The wood fibre had higher hydrophilicity than the CNFs, and thus the wood particles' surface

hydroxyl groups were more competitive for reacting with the MA functional groups of MAPP.

Microcrystalline cellulose. Ashori and Nourbakhsh[51] have used MCC for reinforcing of a wood fibre/PP composite. They report that the tensile strength of the composite was improved up to 39 MPa, when MCC in the amount of 8 wt% along with the coupling agent, MAPP, in the amount of 5 wt%, were loaded. Also, the flexural and impact strengths were positively affected by the MCC loading.

Considering the above examples, nanoclay is the most frequently studied reinforcing filler for WPCs. Apart from the availability of the clay, control of its surface chemistry (modification with different types of surfactants) is essential and represents interest in acquiring fundamental knowledge of the action of nanofiller.

As established in the majority of the described instances, the properties of the composites are related to their morphology. In general, maximal improvements in the properties were detected in the case of homogeneous distribution of nanofiller particles throughout the composite. A large surface area to volume ratio ensures stress transfer between the phases and thereby improves the strength and stiffness of the composite material. According to the observed research examples, good dispersion of the clay generally yields enhanced moduli, flexural and tensile strengths; but the impact strength tends to decrease by the clay loading in most cases, meaning that the composite becomes more brittle.

The clear synergism of clay with TiO_2, and SiO_2 and ZnO_2 was demonstrated by Deka and Maji[22] and Deka et al.[24] The improved composite characteristics were observed when organoclay and nano-oxides were added simultaneously (Table 1). This result represents some interest, although the combination of fillers was known earlier, for example, mixtures of CNTs with clay have been used in the polymer nanocomposites.[4]

Nano-oxides and MCC have been studied to a much lesser extent, although, as shown, they have reinforcement potential for the WPCs. As can be seen in Table 1, a composite reinforced with SiO_2 has the almost identical mechanical characteristics as a composite reinforced with nanoclay.

Very promising result has been shown in an article by Faruk and Matuana.[10] They manufactured WPC reinforced by CNTs with properties close or even higher than those of solid wood (Table 2). It should be noted that they used chitin as the coupling agent. As known, chitin is an excellent coupling agent for improving the interfacial adhesion between wood and a PVC matrix.[8] Thus, so high flexural properties of WPC have been achieved due to the coupling agent effect as well.

Thermal stability and flame retarding properties

The restricted thermal stability and possible thermal dimensional changes in WPCs can limit their processing temperature range and usage. Also, a critical drawback of WPCs is their high flammability; wood fibres/flour burn easily, and the combination of wood with a matrix in WPC make them highly flammable. Many flame retardant materials have been developed for WPCs nowadays.[1] However, the use of most of them can have negative environmental effects. Their fire and smoke resistance is also limited. Besides, the

incorporation of such chemicals in a high amount (60%) may deteriorate the desirable mechanical properties of the final product significantly.[38] As reported in many research articles, nanofillers do not only reinforce the mechanical characteristics of the composites, they improve their thermal stability as well; therefore, nanofillers may become a good alternative for traditional methods.

Nanoclay and nano-oxides instead of Nanoclay and SiO_2. Guo et al.[2] found that even small amount, below 0.5 wt%, of organoclay capable of enhancing the flame retarding properties of pine wood fibre/HDPE. They also showed that exfoliated nanocomposites demonstrated better flame retarding properties than intercalated and conventional (no coupling agent) nanocomposites with the same amount of clay. The same authors found that the presence of nanoclay in wood fibre/MAPE enhanced char formation at burning, and thereby prevented the fire from spreading.[52] Lee et al.[29] reported that the presence of clay decreased the burning rate of a wood fibres/HDPE nanocomposites specimen significantly. When the clay content increased, the burning rate decreased. The authors observed the more pronounced decline in the burning rate for exfoliated clay than for intercalated one. They also noticed that the presence of the coupling agent PE-grafted MA enhanced the melt viscosity of the composites that could also decrease the burning rate. The thermal stability of the wood flour/HDPE nanocomposite was improved with organoclay (3 wt%) incorporation so that the coefficient of thermal expansion (CTE) decreased by 60% and the heat deflection temperature (HDT) increased by 10°C.[26] The further increase in clay loading up to 5 wt% did not improve the thermal properties of the composite. This was explained by the limit in the coupling agent so that the dispersion of clay at higher concentration was poor. However, Lei et al.[28] reported that the presence of nanoclay in the amount of 2% slightly lowered the temperature of the degradation of wood flour/HDPE nanocomposites, possibly due to released low-molecular-weight compounds, by which the clay was treated to become organophilic. Lee and Kim[35] reported that the presence of well-dispersed 1 phr of nanoclay shifted the initial thermal decomposition temperature of a wood flour/PP nanocomposite from 279°C to about 291°C. Homogeneously dispersed nanofiller particles could act as a barrier for oxygen permeability and heat transfer through the PP matrix, resulting in retarded thermal degradation. The storage modulus and glass transition temperature (T_g) were found to be improved by the addition of clay. It was associated with the confinement of the matrix polymer chains within the organoclay galleries that prevent the segmental motions of polymer chains. The dimensional stability parameters (Table 3) of the composite were improved with the nanoclay incorporation due to the improved interfacial adhesion and restricted molecular motion of polymer chains. Kord[43] improved fire-retardant properties of the hemp/PP hybrid by organoclay loading (1–5%). Burning rate was significantly decreased and time of ignition increased with the increase in clay loading. Also, total smoke production decreased significantly. The flammability of wood /PVC was significantly improved with the incorporation of MMT, especially at its low content, 0.5 wt%.38 The incorporation of organoclay suppressed amoke discharging as well.

Meng et al.[25] have observed that the thermal decomposition temperature (T_D) of wood flour/PLA composites with 3–5 wt% nanoclay loading increased by about 10°C

compared with that of unfilled wood/PLA composite. The thermal dimension stability was the highest at the lowest, 1 wt%, nanoclay loading for all examined temperatures (40–80°C). At a higher clay loading, 3 or 5%, the thermal expansion coefficient of the WPC was enhanced. Also, the addition of clay did not result in large variations of T_g, melting temperature (T_m) and HDT compared to those of pure PLA and a unfilled wood/PLA composite. Kumar and Singh[7] reported that the thermal stability of wood fibre/EP increased with the addition of layered silicates and cellulose fibres. The melting point T_m increased from 166 to 170°C for a neat polymer and a hybrid with the maximal amount fillers, respectively. The decomposition temperature T_D of WPC achieved maximal 283°C when 10 wt% of cellulose fibres were added to the hybrid. Deka and Maji[23] reported that SiO_2 nanoparticles improved the thermal stability of wood flour/PB composites. Thermogravimetric analysis showed that T_D achieved maximal value at 3 phr SiO_2 loading, beyond which T_D decreased. Well-dispersed nanoparticles resulted in difficulties of heat and mass transfer through the material, thereby preventing fast degradation. At high loading, SiO_2 particles became agglomerated and their effect decreased. Also, the thermal properties of the same wood flour/PB nanocomposites were improved after the incorporation of clay/TiO_2 nanopowder.[22] The authors note that the thermal barrier effect of nanoclay particles could be enhanced by TiO_2 because of the higher thermal diffusivity of TiO_2, which could provide a better dispersion of heat inside the composite. However, at high percentage, TiO_2 became agglomerated and its effect on thermal stability was reduced.

Carbon nanotubes. Fu et al.[21] reported that the addition of 1 to 2 wt% CNTs or hydroxylated OH-CNTs improved the thermal stability of wood flour/PP nanocomposites. Both CNTs and OH-CNTs were found to be enhanced the initial degradation temperature (T_{onset}) and maximum weight loss temperature (T_{max}). They also proposed a combustion model for WPC and WPC/CNT based on the morphology and chemical analysis of char residues. The incorporation of CNT and CNT-OH could enhance the char formation of composites when burned, and on the other hand, they could terminate the active radicals created in the process of the thermal degradation of the PP matrix, both of which could contribute to the flame retardancy mechanism. However, the thermal conductivity of PVC/wood flour composite was increased up to 0.206 W/(m K) after the CNTs incorporation which is not desirable for WPC, as they are mainly used as building materials.[10]

Microcrystalline cellulose. Ashori and Nourbakhsh[51] reported that partial replacing of wood flour with MCC did not improve the thermal stability of a wood flour/PP nanocomposite. They explained it by the low thermal stability of cellulose compared to lignin, which is the most stable component of wood.

As can see from the examples given above, nanofillers can enhance the thermal stability and decrease the flammability of WPC significantly. Commonly, uniformly dispersed nanoparticles act as a barrier for the transport of volatile gases, which are produced as a result of WPC decomposition, and also limit the diffusion of atmospheric oxygen into the material, inhibiting decomposition. The reduced thermal dimensional changes in

composites are associated with improved interfacial adhesion that restricts thermally induced molecular motions. Also, nanoparticles facilitate char formation during burning insulating the underlying material and thus slowing down the mass loss rate of decomposition products.[53] Similarly, nanoparticles reduce the amount of smoke released during burning. On the basis of this fact, it can be suggested that flame retardancy occurs primarily by the modification of the burning process in the condensed phase and not in the gas phase.[54]

Water absorption

The water absorption behaviour of WPC has been intensively studied because of its importance for the durability of the final product. An enhanced water content can result in dimensional changes in the composites, facilitate microbial growth as well as biological decay.[55] Moisture absorption reduces the adhesion between the matrix and the wood phases, and thereby reduces the mechanical properties.[56–58] The incorporation of a coupling agent, for example, maleated polyolefin, can remarkably reduce the moisture uptake of WPC; coupling agents improve interfacial adhesion, reduce gaps and block the hydrophilic groups in the wood phase. But, as this problem still exists, new approaches to resolving it are clearly needed.

Gu et al.[37] report that water uptake was decreased at a low nanoclay loading of wood fibre/LDPE nanocomposites. This decrease was attributed to the blocking of pores affecting the moisture uptake. A further increase in the nanoclay concentration caused agglomeration of the clay particles and resulted in increased water absorption. Also, the wettability of the nanocomposites depended on the type of surfactant, with which the clay was modified. The composites reinforced with organoclay improved the interaction between the nanoclay, fibres and matrix, and relatively more hydrophobic organoclay had lower water uptake capacity. Yeh and Gupta[27] found that the rate of water absorption of a wood flour/PP composite increased with the increase in the clay loading after the initial decrease at a small (2%) clay content. They also established that the wettability of the composites was influenced by their processing method. Deka and Maji[22,23,33] have shown that small amounts of clay, SiO_2 and clay/TiO_2 reduced the water uptake capacity of a wood flour/PB nanocomposite. Uniformly dispersed nanoparticles are a barrier for water transport. On the other hand, the agglomerated particles are responsible for the decreasing protective properties against the wetting of composites.

Kumar and Singh[7] reported that the water uptake capacity of a MCC/EP composite was reduced by 3 wt% nanoclay loading (Figure 12). A positive influence of a coupling agent and clay on the wettability of wood flour/PP nanocomposites was observed by Ashori and Nourbakhsh.[32] However, the decreased wettability of the composites was associated rather with the coupling agent action, which could improve the bonding of the WPCs interfaces and thereby decrease the water penetration. Tabari et al.[31] showed that waste poplar sawdust/PP composite with 3 wt% nanoclay had a lower water uptake capacity compared to the unfilled composite. The authors suggest that well-dispersed nanoparticles act not only as water transport barrier, but also the clay hydrophilic particles tend to immobilize moisture and thus inhibiting water transfer through the
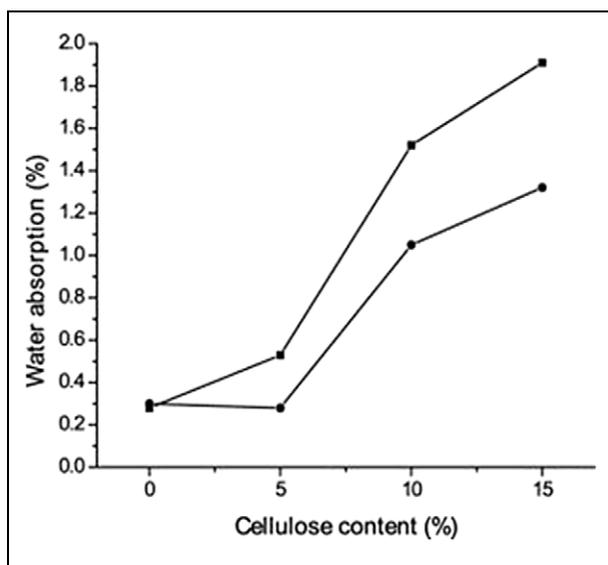
Figure 12. Water absorption behaviour of neat MCC/EP composite (●) and MCC/EP/organoclay nanocomposites (●).[7] MCC: microcrystalline cellulose; EP: epoxy.

composite. Khanjanzadeh et al.[48] found that wood flour/PP nanocomposites including a recycled PP (rPP) matrix had a lower degree of water absorption compared to a virgin PP (vPP) matrix. This was attributed to chemical impurities present in the rPP. Also, the presence of different hydrophilic groups derived from the chemical or photochemical oxidation of aged PP could improve the interaction between the hydrophilic wood and polymer matrix. Besides, increasing the nanoclay percentage (3–5 wt%) resulted in a decreased water uptake for both the vPP and rPP containing WPCs. Nourbakhsh and Ashori[45] report that the water absorption of bagasse/PP nanocomposites decreased with nanoclay and coupling agent loading.

Kord[43] reports improved hydroscopic properties of a hemp fibres/PP composite with Cloisite 15A loading (1–5%). The researcher attributes this to the increased barrier properties of the composite, the hydropholic nature of the silicate and increased crystallinity of the hybrid due to the presence of nanoparticles. Clay presence decreased water absorption and swelling of reed flour/PP/MAPP hybrid.[42]

Kord et al.[59] report that nanoclay decreased the water absorption in a vPP and rPP/newspaper composite. According to them, a WPC containing virgin polymer had lower water absorption than a WPC with a recycled matrix. Probably, the impurities present in rPP can influence the interfacial adhesion and change the polymer structure (melt flow index and crystallinity). Kord et al. also report that the water absorption kinetics in nanocomposites followed the Fickian low of diffusion.

The water absorption and thickness swelling of the composite were significantly reduced due to the SWCNT incorporation (1–3 phc).[49] The reduced hydroscopicity was

attributed to the improved barrier properties of the composite due to CNT filled voids in the composite material, and another reason was that hydrophilic CNTs tend to immobilize some of the moisture and thereby inhibit water penetration into the composite.

From the above examples, it can be concluded that nanoparticles can be successfully used for the reduction of the hydroscopicity of the composite. The layered structure of the silicates allows improving the barrier properties of the composites significantly. Well-dispersed nanoparticles induce the tortuous pathway (Figure 1) that retards the water diffusion through the composite. As it was observed in most cases, the maximal effect was achieved for the exfoliated composites when particles uniformly dispersed in the hybrid. Another important factor for the water resistance is the chemistry of the filler (hydrophilic/hydrophobic). The highly hydrophilic nanoparticles have a tendency to immobilize some of moisture, and thereby reducing the rate of water uptake. Also, particles can physically block the pores, voids and capillaries, and thus prevent water penetration into composite.

Conclusions

The combination of different types of materials in order to synthesize new materials with specific properties has attracted considerable interest among researchers. In this article are reviewed the studies where WPC were modified using nano-sized fillers. Nano-sized fillers, having a large surface area, high mechanical strength and stiffness exhibit a great opportunity for improving the quality of composites at small amounts of incorporation. As it was detected, the characteristics of the WPC were directly related to their microstructure. Maximal improvements have been observed in exfoliated hybrids, where the filler particles are uniformly dispersed throughout the composite. Good dispersion results in the reinforced matrix as well as improves the interfacial bonding, which insures interfacial stress transfer in the composites. According to the observed instances, good dispersion generally yields enhanced moduli, flexural and tensile strengths.

The nanoparticles exhibit a remarkable increase in thermal stability of the composite. Well-dispersed filler acts as a mass transport barrier to oxygen and volatile decomposition products. Also, the flammability of the composite can be significantly reduced due to fact that nanofiller can assist in the formation of char during burning, which protects the inner material from further decomposition.

The incorporation of the nano-sized filler reduces the hydroscopicity of the composite. The permeability of water is reduced mainly due to the formation of the tortuous pathway for water transport in the presence of the nanoparticles.

However, one of the major challenges in the manufacturing of nanocomposites is achieving a homogeneous dispersion of the nanofiller. Despite on many efforts in the development of production techniques and the availability of nanofillers with different surface chemistries, the predictability of the properties of the composite is very limited. Thus, for large scale manufacturing of WPCs reinforced with nanofillers, deeper knowledge in the acting mechanism of nanofillers is clearly required.

Funding

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