Nanoclay and Natural Fibers Based Hybrid Composites: Mechanical, Morphological, Thermal and Rheological Properties

Hamid Essabir, Marya Raji, Rachid Bouhfid and Abou El Kacem Qaiss

Abstract The majority of the developing countries are extremely rich in natural resources such as natural fibers and clays. All these natural resources have exceptional properties and could be exploited effectively in the manufacturing of composite materials for a diversity of industrial applications. Combining two kinds of fillers is a potential way to improve the essential properties of natural filler-reinforced hybrid polymer composites. The hybridization is an efficient technique for making sustainable use of natural fillers. Natural fiber-reinforced polymers associated with particulate fillers as clay provide noteworthy advantages gains in terms of mechanical properties strength and stiffness, as well as improve the mechanical response these structural elements. Composites produced from natural resources are experiencing an increase in interest due to their high demand in the market for manufacturing, in addition to environmental and sustainability issues. This chapter focuses on the potential use of natural fibers and clay in hybrid composite materials, their availability, low cost, physical properties, structural properties and their friendless properties. The natural fiber/clay-reinforced hybrid polymer composites were prepared from Alfa fiber, Pine cone fiber, Sugarcane bagasse fiber and Coir fiber, polypropylene, and Moroccan clay named E1 using a extrusion and injection technique. Before being used, the natural fibers were alkali-treated to reduce their hydrophilicity, and the clay was purified. The chapter covers the advantages of natural fillers reinforcement in hybrid composites and future trends and applications.

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1 Introduction

In the last decade, natural fiber composites have become extremely important materials. They were used in numerous industries such as aerospace, automotive, construction, and the construction and furniture industry (Elkhaoulani et al. 2013; Boujmal et al. 2014; Malha et al. 2013). Natural fiber composites are emerging as an alternatives to synthetic fiber-reinforced composites not only in food industries, but also and especially in non-structural applications (Joshi et al. 2004; El Mechtali et al. 2015). So far, a certain number of automotive components previously made with glass fiber composites are now being manufactured using environmentally friendly composites (Pracella et al. 2006; El Mechtali et al. 2015). But, their applications are limited mostly to semi- and nonstructural components due to their inherently inferior mechanical properties such as strength and rigidity, which are typically very dominant in the conventional fiber composites. Due to their low cost and their friendless environmental character, an increasing effort has emerged on the research, development, and application of composites based polymer and natural fibers (Qaiss et al. 2014, 2015a, b; Malha et al. 2013; Nekhlaoui et al. 2014). Hybrid composites reinforced by more than one type of filler (Verma et al. 2015; Jawaid et al. 2011a, b; Kakou et al. 2015), is convenient way to achieving suitable material properties and to create a multifunctional materials. Several researchers are focusing their attention on this type of composites mainly designed and processed by the combination of natural fiber with clay fillers in the same polymer matrix, due to their easy availability (Majeed et al. 2013), low density (Pracella et al. 2006), their low cost effective (Ku et al. 2011) and also to enhance the physical and mechanical composites properties, next to that the natural fibers are recyclable and biodegradable (Taj et al. 2007). Furthermore the hybridization is a technique that can avoid the drawbacks of the composite materials reinforced either by natural fiber or clay particles, such as low durability, poor resistance of natural fibers towards water absorption which make them inequitable with non-polar polymer matrix (Saba et al. 2014) and non-degradable character of plastic materials based on clay particles (Liu et al. 2012). Many studies reported that the most famous hybrid composite applications is as food packaging materials; beer bottles, carbonated drinks, juice bottles and thermoformed containers for industrial purposes, moreover in pharmaceutical packaging applications (Majeed et al. 2013; Jawaid et al. 2011a, b; Kakou et al. 2015). The hybrid composites based on natural fillers are expected to give less health risk and environmental hazard problems for people producing the composites as compared to composite based on synthetic fibers such as glass, aramid and carbon (Ku et al. 2011), which causing an environmental damage because they are characterized by higher pollutant emissions and higher green house gas emissions and their application domain has met a real decline with the appearance of the newest wave of green materials.

Besides the advantages of natural hybrid composites, natural fibres and clay fillers as renewable natural resources poses are al challenge caused by their hydrophilic characters (Xie et al. 2010) which generate a poor interfacial adhesion with the hydrophobic matrix (Oksman et al. 2003). This poor reinforcing ability of particles create the difficulty in achieving a homogeneous dispersion into the polymer matrix. Hence, it is necessary to modify the particle surface using an organic treatment before compounding under the appropriate manufacturing process, for ensuring a good adhesion and good dispersion/distribution into polymer matrix (Fook and Yatim 2015). In general, the natural fibers surface can be modified by using a chemical modification (Cao et al. 2007), which lead to remove lignin and other non-cellulosic compounds in the fiber surface. It is also expected to disrupt hydrogen bonds in the fiber surface, thus displaying extended surface roughness, which led to the better incorporation of fiber with the matrix, that may helped to significantly enhance the fiber–matrix interfacial adhesion which then reduce the possibility of the formation of strongly bonded fillers aggregates during the composite preparation, this later can cause the lack of filler dispersion within the polymer matrix. In other hand, the most commonly used inorganic fine powder as reinforcement in several industrial products such as paper, paints, rubbers and polymers applications, is calcium carbonate, talc and clay, they are used to improve the mechanical characteristics and the dimensional stability of the end product. The clay fillers currently dominate the thermoplastic industry, as an alternative filler of $CaCO_3$ and Talc (Šupová et al. 2011).

As previously mentioned, the manufacturing process plays a critical role in ensuring a good dispersion–distribution and an indiscriminate arrangement of the filler into the matrix (Ben Azouz et al. 2012). The most popular manufacturing process employed in thermoplastic polymer composites is melt compounding (Ben Azouz et al. 2012). This method is capable of facilitating chemical reactions between the components during the manufacturing process, is also regarded as more economically and flexibly for the formulation and it is compatible with the frequently used industrial process, environmentally benign as well (Hietala et al. 2012). The various natural fibers types; alfa, pine cone, coir, and sugarcane bagasse are selected to prepare a hybrid composites, thus the selected fibers were ground, treated and then melt-compounded with the natural clay fillers at various concentrations using the polypropylene (PP) as matrix, in each case the filler (fibers and particles) content ranging from 0 to 30 wt%. The chose of this types of fibers is based on their availability and their performance as reinforcement agent, in previous work these types of fibers was used with the thermoplastic matrices to improve the mechanical, thermal and structural properties of the thermoplastics polymer (Arrakhiz et al. 2012a, b, c, 2013a, b, c). The extruded materials were there after ground and then injected to preparing different test samples of natural hybrid composite based on natural fibers with clay fillers. In this book chapter, we try to studying the natural fibers effects and that of clay fillers on the hybrid composite properties, which can help to develop and promote the hybrid composites. The natural fibers, and clay particles properties and also that of their composite will be characterized using the following tests; scanning electron microscopy (SEM) to obtain some information on composites morphology. Fourier transforms infrared spectroscopy (FT-IR) to evaluate their structural properties, their thermal stability using TGA test, to complete the mechanical properties taken in tensile, and torsional test.

2 Disadvantages of Natural Fillers as Reinforcement for Polymer Matrix

The hydrophilic nature of the clay particles and of the natural fibers is a responsible of the major's problem in polymer matrix composites, which was blamed on poor adhesion between components and also the surface incompatibility between them. Which may, however negatively affect the physical and mechanical properties of the resulting composite. As results, the particles content tend to agglomerate and stick to each other. Consequently, bad dispersion-distribution of the charge in the matrix. Therefore, the composites exhibited worst properties, which often reduce the potential of natural fibers and the clay particle to act as fillers and thus limits their effective application.

As previously mentioned, the hydrophilic nature of the natural fillers influences the overall composites properties, for this reason, it is necessary to perform a chemical modification of the natural fibers in order to enhance the interfacial adhesion between them and the polymer matrix. There is much type of chemical treatments, but the Alkali treatment or delignification include NaOH is one of the simplest and the effective surface modification techniques. This treatment can firstly increase the surface roughness which leads to form new hydrogen bonds between the cellulose molecular chains and secondly this treatment may increase the amount of cellulose exposed on the fiber surface. The treatment process rests on the elimination of the amphioxus substances on the fiber surface. This can help for better interlocking between matrix and fiber. Alkali treatment is a common fiber chemical method that is extensively used by researchers to enhance the fiber–matrix interfacial adhesion and to improved fiber dispersion within the polymer matrix.

$$\text{Fiber—OH} + \text{NaOH} \rightarrow \text{Fiber —O}^-, \text{Na}^+ + \text{H}_2\text{O} + \text{impurities} \quad (1)$$

Various natural fillers from mineral resources such as calcium carbonate, clay, talc, graphite were tested as reinforcement in polymer composites. Moreover the inorganic fillers such as natural talc, calcium carbonate, clay, and graphite are now a day's present trend of research to enhance the mechanical, thermal, rheological and electrical properties of the polymer composite. Clay is considered a suitable alternative to $CaCO_3$ and talc fillers as reinforcement in the plastic industries. Before using, the raw clay has been purified and chemically modified. In this work, the clay used is from Morocco and it was made by mixing 10 g of clay E1 sample with 500 ml of deionized water in a 1 L beaker for 24 h. The supernatant was scrapped and the solids were combined and then suspended twice in 500 ml of demineralized water. To get an particle size of less than 15 µm; the suspension was centrifuged with optimized requirement in terms of speed (6000 rpm) and time (10 min).

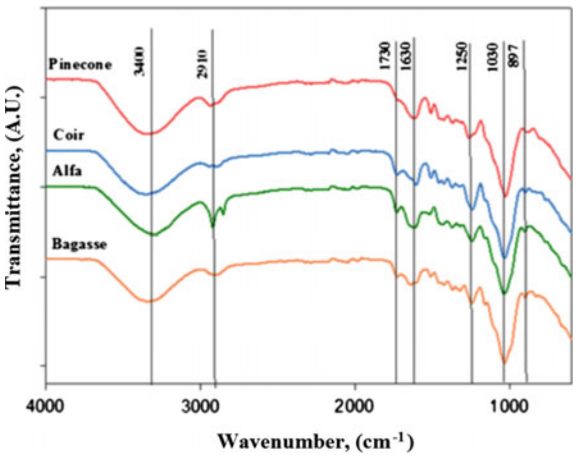
3 Physicochemical Characteristics of the Used Filler

In recent years, more attention has gone to green materials that are compatible with the environment, as well as the increment of depletion of petroleum resources, the focus of the researcher is shifted to reinforcing the polymer matrix using the natural fiber with the application areas remaining the same. Many attempts has tried to replace the conventional fiber such as glass, aramid and carbon in some application domain, even they have high strength and modulus, by the natural fiber, Due to their many advantages. To give an example, low cost, renewable, does not cause irritation when handled or they are non-abrasive and are biodegradable under certain conditions. In addition, the natural fibers have a low density compared to glass fibers which may serve to reduce significantly the density of their composites. To compare the natural fibers properties and their composites, it is necessary to understand their physicochemical characteristics.

The chemical makeup of natural fibers is highly dependent on and nature of the fibers. The major components of natural fibers are; cellulose, hemicelluloses, lignin, and other non cellulosic components. The amount of major chemical constituents of the fiber varied from plant to plant, and with in different parts of the same plant. It has been already proven by many researchers that the fibers mechanical properties and their thermal properties depend largely on the fiber chemical composition which furthermore, has a vital role on the variation of overall composites properties. In order to evaluate the Moroccan resources, the Alfa, Pine cone, Sugarcane bagasse and Coir fibers were used. Alfa fibers (*Stipatenacissima L.*) with 25 cm in average length were collected from various rural areas of Morocco, the pine cone fibers were gathered from sources situated in the north of Morocco. The last Moroccan fiber used in this work, called sugarcane bagasse, obtained as a by-product of the Moroccan Sugar industry. In the other hand the coir fibers with a length of 20 cm were brought from Ivory Coast.

As the major components of the lignocellulosic fibers are cellulose, hemicelluloses, pectin and lignin, the obtained FTIR spectral bands was attributed primarily to these components. Figure 1 shows the FTIR spectra of the raw used fibers (Alfa, Pine cone, Sugarcane bagasse and Coir). The spectra shows the representing bands of the hydrogen bond and stretching of OH groups in the region of 3400 cm^{-1}, the absorptions can be assigned principally to the carbohydrates, including CO–C and CO stretching and bonds belonging to the glucoside bond and eventually the lignin from the lignin hydroxyphenyl, guaiacyl and syringyl groups, which are aromatic OH compounds (Qaiss et al. 2014, 2015a, b). The bands in the region of 2900 cm^{-1}

Fig. 1 FT-IR spectrum of the used natural fibers: Bagasse, Alfa, coir and pine cone



are due to the aliphatic saturated C–H stretching vibration in lignin/polysaccharides complex (Qaiss et al. 2014, 2015a, b). The bands in the region at 1730 cm^{-1} in all fibers are allocated to either the acetyl and uronic ester groups of the hemicelluloses or the ester linkage of carboxylic group of lignin and/or hemicelluloses (Qaiss et al. 2014, 2015a, b). The band at 1630 cm^{-1} may be due to the presence of water in the fibers. The bands in the 1250 cm^{-1} region include vibration C–O Stretching of primary and secondary aliphatic alcohols of the cellulose, hemicelluloses, lignin and extractives (Qaiss et al. 2014, 2015a, b). The peak at 897 cm^{-1} is due to β-glycosidic connections of glucose ring of cellulose (Qaiss et al. 2014, 2015a, b).

The quantitation of the main components of the understudy of fibers was carried out by conventional methods and the results have been included in Table 1. These analyses show that the Sugarcane Bagasse fibers have the superior content in cellulose (50 %). On the other hand, Alfa and Pine cone present the smaller content in lignin (23 %) and the Coir has the high content in lignin (45 %).

Cellulose the most important component of all fibers in the study may be found in the crystalline or amorphous and can be viewed by X-ray diffraction patterns. X-ray diagrams of Alfa fibers such example is shown in Fig. 2. The appearance of

Table 1 Physico-chemical properties of selected bio-filler (Paiva et al. 2007; Defoirdt et al. 2010; Geethamma et al. 1998; Bledzki and Gassan 1999; Ben and Ben 2007)

	Chemical constituents (%)			Physical properties		
	Cellulose	Lignin	Waxes	Densilty (g/cm^3)	Tensile strength (MPa)	Tensile modulus (GPa)
Alfa	45	23	5	1.2	134–220	13–17.8
Coir	43	45	–	1.15–1.25	120–304	4–6
Pine cone	42–49	23	–	–	–	–
Sugarcane bagasse	50	25	–	–	96.24	6.42

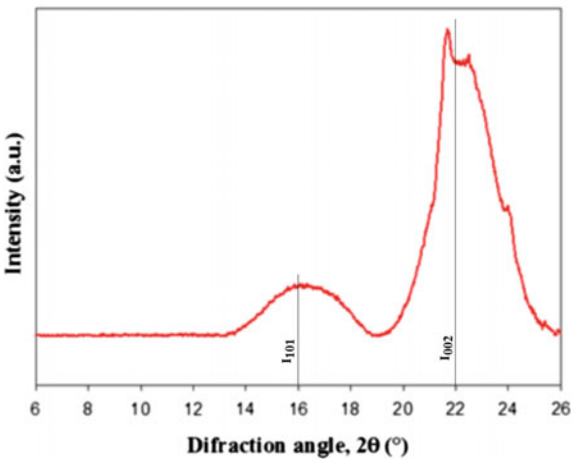


Fig. 2 X-ray diffractogram of Alfa fibers

two most intense peaks, closer to the from 2 values θ = 16° and 2 θ = 22° representing cellulose crystallographic planes I_{101} and I_{002}, respectively, can be observed. These peaks can be assigned to the crystal dissemination and diffuse background associated with disordered regions.

To improve fibers/matrix interaction, the full fibers were subjected to a chemical treatment of lignin, wax and oils that covers the external surface of fibers cell wall. Based on previous studies, the alkali treatment Removes non-cellulosic components, mining, waxes, oil, etc., from fiber surfaces. The extraction of then on cellulosic components Can be observed in FTIR spectrum, exemplified by the spectra of Coir and pine cone fibers before and alkaline after-treatment (Fig. 3).

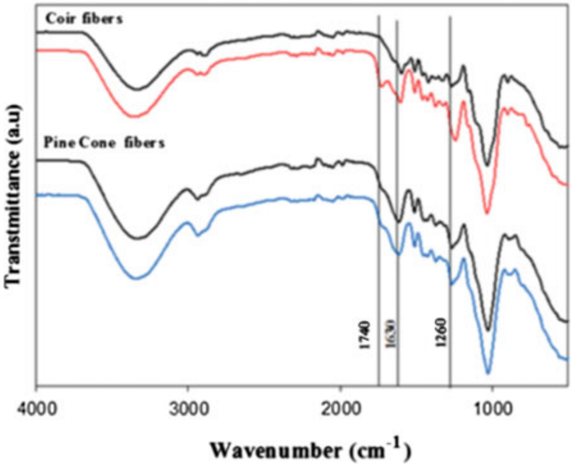


Fig. 3 FT-IR spectrum of the raw and alkali treated fibers: Pine cone and and Coir fibers

Based on previous studies, the alkali treatment eliminates noncellulosic components, mining, waxes, oil, etc., from the fiber surfaces. The extraction of the non-cellulosic ingredients can be seen in the FTIR spectrum, exemplified by the spectra of Coir and pine cone fibers before and after alkaline treatment (Fig. 3). It follows from this figure the disappearance of the band in the region at 1740 cm^{-1}, in the raw fibers assigned to the hemicelluloses and lignin, indicating a complete cleavage of these ester bonds. The intensity of the peaks is attributed to C=C of aromatic skeletal vibrations in lignin, in the region of 1500 cm^{-1}, has decreased in chemically modified fibers indicating partial removal of lignin. Also, the intensity reductions of the peak around 1260 cm^{-1} after alkalization reflects the preferential removal of hemicellulose materials instead of than lignin. Although, this chemical change in the composition of the fibers, the alkalization of lignocellulosic plant fibers changes the surface topography and their crystallographic structure.

Much research effort has explored the improvement in thermoplastic composites performance. At the Toyota research centre in Japan, the first group who worked with clay as a reinforcing phase dispersed in an engineering polymer matrix. The clay particle showed a good performance, which afford remarkable property enhancements of the polymer matrices. There are many types of clay depend on their structure. Although all clay minerals contains two types of leaves (Sheets), tetrahedron (T) and octahedron (O). In general the clay structure and the particle size of clay had an obvious effect on the composite mechanical and thermal properties. The used clay as fillers is a local variety noted E_1 (density of 1.63 g/cm^3) with diameter average of 12 μm (Fig. 4), from North of Morocco (Nador). This type of clay was more effective than talc to enhance the mechanical and thermal properties of the polymer matrix (Nekhlaoui et al. 2014). The chemical composition of the clay was determined by X-ray fluorescence (XRF) spectrometry using Axios XRF Wavelength Dispersive Spectrometer (PANalytical) (Table 2).

The recognition of the chemical components and crystallographic structure of clay noted E1 was achieved by X-ray diffraction (XRD) analysis. The diffraction patterns were analyzed using X'Pert High Score software. The X-ray diffraction pattern of the clay E_1 (Fig. 5) presents the characteristic peaks for the Quartz (SiO_2) and other associated minerals of clay such as Dolomite ($MgCa(CO_3)_2$), Illite ($(K, H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2, (H_2O)]$), and Calcite ($CaCO_3$) (Table 3).

To investigate the structural properties of the chemical nature of the clay the FTIR study was done and presented in figure. The FTIR spectra of the used clay named E_1 show intensive vibrations in the bands of 3620, 1407, 1007, 881, 874, and 778 cm^{-1} (Fig. 6). A wide absorption band at 3620 cm^{-1} matching Al-O-H stretching vibration, of attached water and Al_2OH on illite (Martinez et al. 2010). The peaks at 1407 cm^{-1} corresponds to the C–O stretching vibration in calcite (Wang et al. 2010); whilst the absorbance at 1007 cm^{-1} is typical of Si–O–Si and Si–O–Al lattice vibrations (Echeverria et al. 2005). The absorption band at 778 cm^{-1} verify the presence of a Si-translation (Martinez et al. 2010).

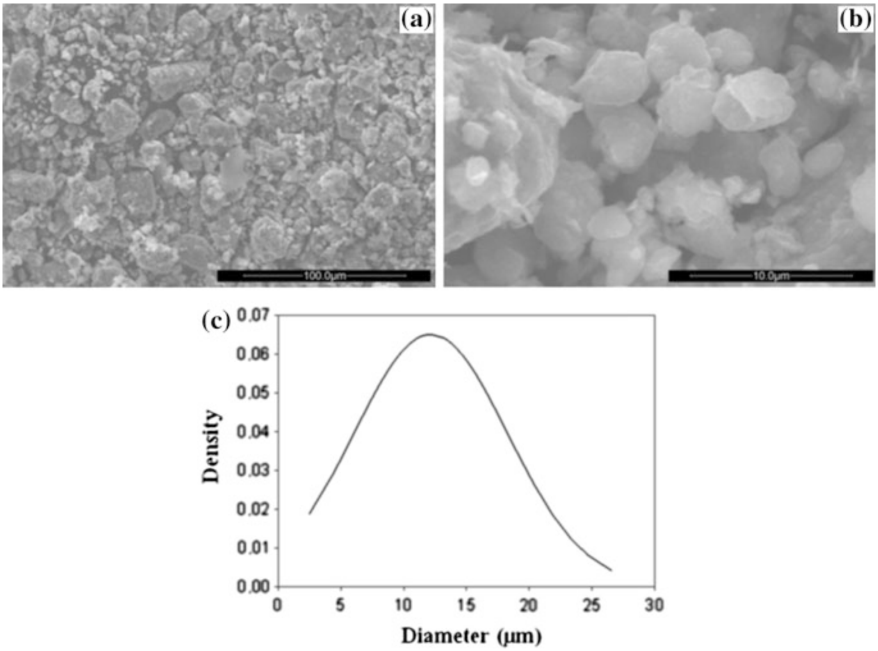


Fig. 4 **a**, **b** SEM image of the used clay (E1), **b** Diameter distribution of clay E1

4 Processing Techniques

Different techniques have been employed in order to transform the materials to the final shape without causing any defect of product, as like in situ polymerization, emulsion polymerization, sol-gel templating and melt compounding (Fornes et al. 2001), the effective manufacturing process utilized, in producing reinforced thermoplastic hybrids is melt compounding processing methods. From the industrial point of view, this technique has great advantages related to the absence of organic solvents, environmentally unfriendly, is also considered more techno-economically viable, because of its compatibility with the frequently used industrial process, giving end-use producers of numerous degrees of freedom concerning the specifications end product (e.g. choice of polymer grade, fillers types, reinforcement level, etc.) (Qaiss et al. 2015a, b). In other words, melt processing of composites allowed to be prepared right at using conventional mixing devices like as extruders or mixers. Meanwhile, melt processing is environmentally friendly as no solvents are needed; and it enhances the specificity for the polymer intercalation, eliminating solvent-host and concurrent polymer-solvent interactions. Albeit, from a chemical point of view, one can distinguish between several ways to incorporate the particles loading into polymers matrix is their homogeneity of dispersion/distribution, depending on the degree of the interfacial strength between filler and polymer,

Table 2 Chemical composition of clay E_1

Chemical composition	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	Na_2O	K_2O	TiO_2	Pr_2O_3	P_2O_5	V_2O_5	SO_3	Cl	ZnO	MnO_2	SrO	ZrO_2	LOI
Weight (%)	48.2	11.4	10.9	3.48	2.01	0.866	0.729	0.269	0.218	0.157	0.154	0.127	0.126	0.0503	0.0255	0.0242	0.0124	21.2516

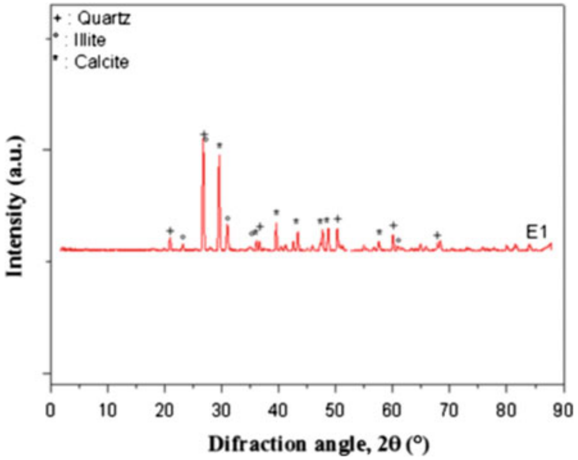


Fig. 5 X-ray Diffractogram of clay E1

Table 3 X-ray diffraction ‘d-spacing’ values of E_1

d-spacing (Å)	Mineral
4.2689, 3.3515, 2.4604, 2.2855	Quartz
3.8627, 3.0388, 2.4960, 2.2855	Calcite
4.4961, 3.5133, 3.3515, 3.1835	Illite

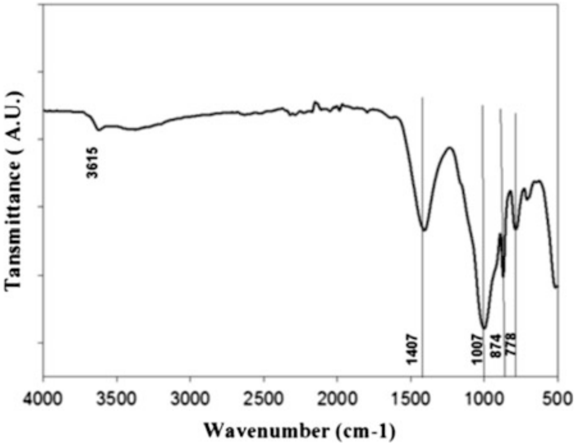


Fig. 6 FT-IR spectrum of clay E1

because they affect overall properties of the final composite (Qaiss et al. 2015b). In this direction, numerous studies have demonstrate that the melt compounding produce better composites mechanical properties, include less agglomerates, and contain fewer defects. The hybrid composites containing a natural clay fillers and the natural fibers at various concentrations using the polypropylene (PP) as polymer matrix, with the particles loading ranging from 0 to 30 wt%, were blended using a Leistritz ZSE-18 Twin Screw Extruder (Leistritz Extrusions technik GmbH, Germany) equipped with seven heating zones, the temperature profile in the various zones was set at 200, 200, 200, 200, 180, 180, 180 °C and the die temperature was 180 °C. Screw speed for melting was using a speed of 125 rpm for the main screws and a 40 rpm side-feeder screw speed for particles feeding. The melt extruded composites were cooled in a water bath and then pelletized into granules of 2–3 mm in length. Hybrid composites granules are injection molded using an Engel e-Victory injection molding machine, to produce mainly the specimens for mechanical and rheological tests. The temperature was set at 200, 200, 200 and 180 from the barrel to the nozzle while the temperature mold was set at 45 °C (Essabir et al. 2013a, b, c).

5 Properties of Hybrid Composite

5.1 Morphological Properties

The mechanical properties of material composites depends strongly on the fillers morphology, fillers content, dispersion/distribution of fillers into matrix, and fillers/matrix adhesion. A excellent fillers dispersion/distribution on the polymer matrix can be obtained by effective mixing of the various components and by a suitable mixing method (Nekhlaoui et al. 2015; Essabir et al. 2013a, b; Qaiss et al. 2015b). Regardless of fillers type (fibers or clay), the fractured surfaces of the hybrid composites (15:15) Coir fibers as exampling clearly showed a excellent fillers dispersion/distribution into polymer matrix is an indication of the relatively homogeneous nature of these hybrid composites as seen in SEM (Fig. 7). Furthermore, it is observed that the smooth surfaces of the breakage with a homogeneous matrix, as well as excellent adhesion between fillers and thermoplastic matrix, which play an important role in enhancing mechanical performance of the composite as described earlier. The fillers/matrix interface is obscure, and expenses were fully covered by the matrix. Fillers were fractured, indicating that the

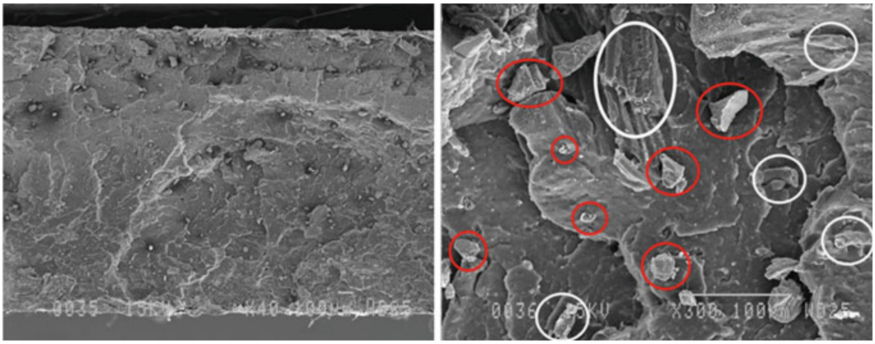


Fig. 7 SEM image of the hybrid composites 15:15 (Alfa fibers/E1)

stress was effectively transferred across the interface to the reinforcing fillers. This may be due to the interfacial interactions between the fillers and the matrix.

5.2 Thermal Properties

The thermal stability of the hybrid composites were studied using the Thermogravimetric (TGA) by determining their mass loss during heating, Thermogravimetric analysis was performed using Q500 instrument from TA Instruments. Roughly 20 mg of each sample was placed in a platinum pan and heated under air in the range of 30–600 °C at a heating rate of 10 °C/min to yield the onset temperature of decomposition (Fig. 8).

The initial weight loss in the range 100–200 °C may be due to the evaporation of water contained in the natural fiber. The thermal degradation of 30:0 composite presented in Table 4, its notice that the thermal decomposition of the polymer matrix, usually located between 320 and 370 °C (Arrakhiz et al. 2012a, b), is shifted to 386 °C with the incorporation of clay particles, more thermally stable. For the hybrid composite reinforced by the natural fibers, is located that, the thermal decomposition of the polymer composite were shifted to lower temperature raison of the reduction of the thermal stability of the melt by the incorporation of natural fibers which are lower

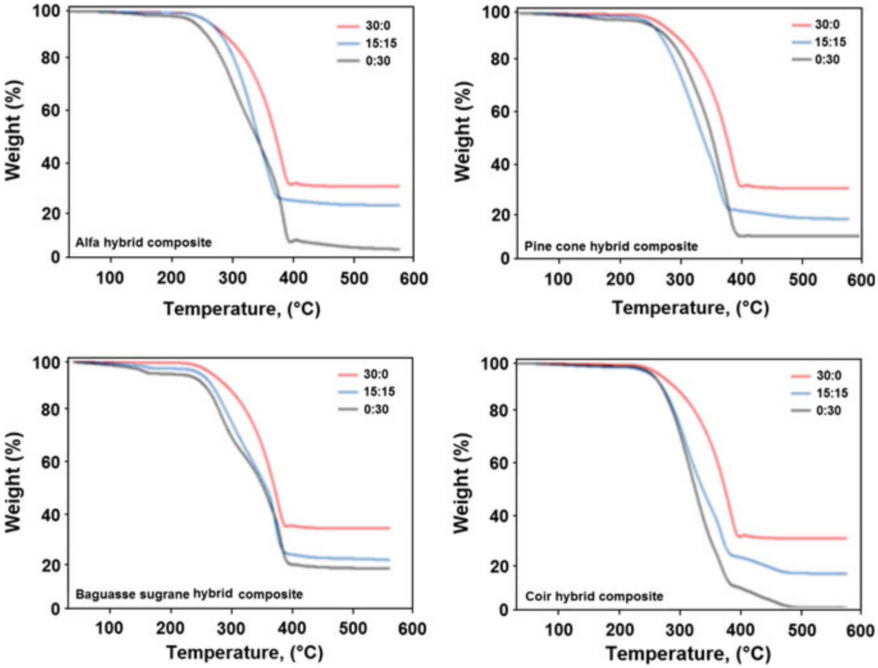


Fig. 8 TGA curves of hybrid composite: (**a**) alfa composite, (**b**) pine cone composites, (**c**) baguasse sugrane, (**d**) coir

Table 4 Thermal degradation of different hybrid composite

	T_{MAX} (°C) Alfa hybrid composite				T_{MAX} (°C) Pine cone hybrid composite				T_{MAX} (°C) baguassesugrane hybrid composite				T_{MAX} (°C) coir hybrid composite			
30:0	–	–	386	–	–	–	386	–	–	–	386		–	–	386	–
15:15	111	342	368	440	142	327	364	430	157	297	380	422	156	310	371	455
0:30	156	307	386	456	156	361	381	445	155	286	389	426	156	320	372	460

thermally stable than clay. Excluding for baguasse sugrane hybrid composite, it was found that the polymer decomposition temperature is higher, due to the high cellulose content in the baguasse sugrane fibers. The thermal decomposition of all fibers consisted of three decomposition steps; the first stage of decomposition is due to the hemicellulose degradation in the temperature range 180–310 °C. The second takes place in the range of 320–340 °C, this is due to the decomposition of cellulose, which is more thermally stable because of its crystalline nature, The third stage corresponds to the thermal degradation of lignin which occurs between 440 and 480 °C, characterized by their complex structure. The variation of the thermal degradation peak temperature is due to the variation of the natural fibers composition.

5.3 Mechanical Properties

The mechanical test is used to investigate the positive or negative hybrid effect on the composite properties. The mechanical properties of the manufactured composites were first evaluated in tension: Young's modulus, tensile strength, and strain at yield (Fig. 9). For this reason three specimens for each type of composites were tested and the average value reported. The experiment was performed under quasi-static tensile loading for all the specimens according to ISO 527-1:2012, using a universal testing machine INSTRON 8821S (Instron, USA), with a crosshead speed of 3 mm/min using a 5 KN load cell. Tensile properties such as Young's modulus, tensile strength, and strain at yield of the composites were obtained from the stress-strain curves (Fig. 9).

Figure 9a shows the variation of Young's modulus values as function of particles loading for different natural fibers. It's clear that the Young's modulus of all hybrid composite increase with the clay loading up to maximum for 30:0 at 3167 MPa compared to the neat PP (1034 MPa), due to the rigid inorganic clay particles (Essabir et al. 2015a, b; Arrakhiz et al. 2013b). This is a common behavior when rigid fillers are incorporated into softer polymer matrix. These results strongly align with the results of Jawaid et al. (2011a, b), Kakou et al. (2015) and Essabir et al. (2014) which investigates that the natural lignocellulosic fillers have been reported to have a higher elastic modulus than neat polymer. Therefore, the incorporation of rigid fillers such as clay particles to a polymer matrix can improve composite stiffness because the stiffness of the inorganic particles is commonly higher than that of organic fillers such natural fibers. Some authors have also related the increase in composites rigidity with the reduction of polymer chains mobility in the presence of fillers. In the other hand, Fig. 9b shows the evolution of the tensile strength of the hybrid composite as a function of fillers content species. The tensile strength of hybrid composite exhibit an optimum at 15:15 loading (34.52 MPa) compared to that of the neat PP (33 MPa). This improvement related to the physical anchoring between polymer chains and fibers, the tensile strength presents also a high value for alfa fibers hybrid composite due to their low percentage of lignin which means by the presence of more pendant hydroxyl on the alfa surface fibers,

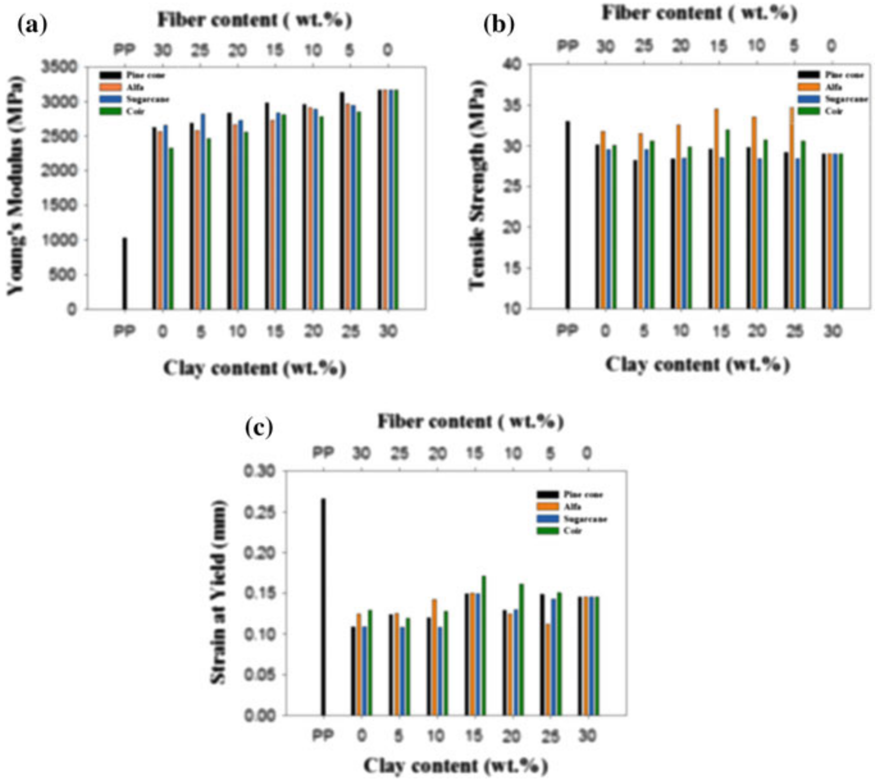


Fig. 9 **a** Young modulus of hybrid composite, **b** Tensile strength of hybrid composites, **c** strain at Yield of hybrid composite at various loading content and with different types of fibers

could lead to make the strong ester bonds between fibers and polymer matrix. This is based on the efficiency of the stress transfer between the matrix and fillers. Figure 9c present the strain at yield of the hybrid composite at various loading content and with different types of fibers. From the Fig. 9, it is clear that neat PP characterized by high strain at yield value compared to the hybrid composite made with either by alfa, coir, pine cone and sugarcane bagasse due to the rigid character of fillers content, which create a bad adhesion between fibers and PP. This debonding generates a stress concentration which accelerates the break of the sample. It's also observed that the elongation at yield values of the hybrid composites have improved until an optimum at 15:15 and then decreases with increasing amount of clay fillers result of the loss of ductility of the material with the addition of rigid particles in a ductile matrix. The increased strain at yield performance can be attributed to the good adhesion between the fibers and the matrix (Essabir et al. 2013b; 2014). The strain at yield maximum value presented for the coir hybrid composite due to their high elongation (Table 1) values which make it more flexible and easily deform.

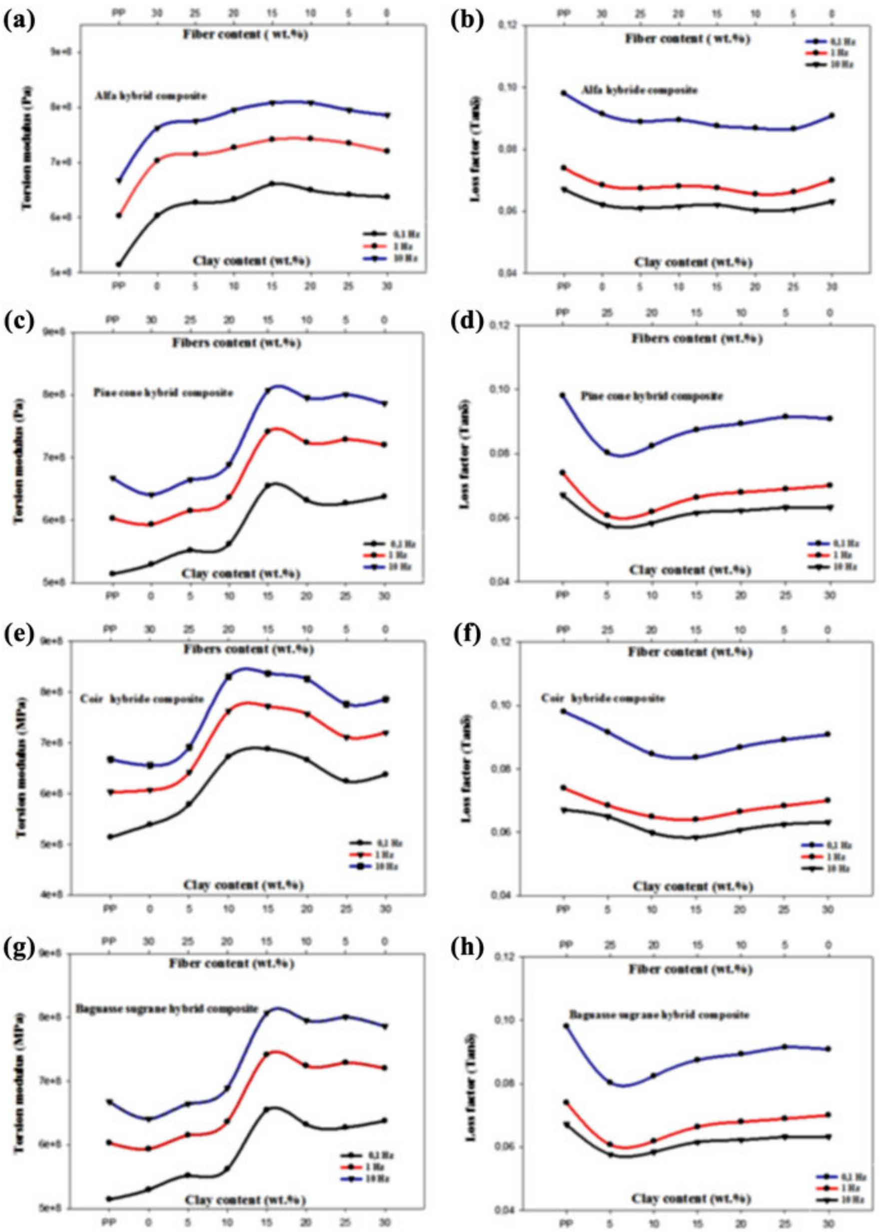


Fig. 10 Torsional properties of hybrid composite at various loading content and with different types of fibers: (**a**, **c**, **e**, **g**) torsional modulus; and (**b**, **d**, **f**, **h**) damping factor

In the other hand, torsional testing is used to describe the hybrid composites response to shear stress. Figure 10 shows the torsion modulus and the damping factor for the hybrid composite at various loading content and with different types of fibers, for all composites, the torsion modulus increase with clay particles loading (Kakou et al. 2015; Essabir et al. 2016a, b, c). On the basis of filler loading, hybrid composite with 15:15 clay/fiber content reinforced hybrid composites had the optimum set of torsional modulus among all composites manufactured. Incorporation of stiff filler as clay and oil palm fiber into the PP matrix considerably increased the torsional modulus of the manufactured composites compared to the neat PP. The variation of the torsional modulus is also marked by the variation of frequency from 0.1 to 10 Hz, leading to conclude that the hybrid composites response is like an elastic solid (Essabir et al. 2016a, b, c). This has been reported before where the elastic character of the material at higher frequency prevails over a viscous behavior. The polymer molecular time response is responsible of this enhancement in complex modulus. At higher frequency, the polymer chains do not have enough time to relax. These results agree with those observed in our previous works (Essabir et al. 2015a, b; Qaiss et al. 2015a, b) in term of the variation of rheological properties of composites as function of frequency compared to those of neat polymer matrix.

To investigate the elastic and viscous behaviours of hybrid composites, the evolution of tan δ versus frequencies and particles loading is illustrate in Fig. 10b for all composites tan δ decrease with increasing frequencies. Noteworthy is the curves in each composite have the same shape with increasing frequency from 0.1 to 10 Hz. The elastic character of the material prevails over a viscous behaviour.

Therefore, the hybrid composites have intermediate values between the composites reinforced with oil palm fibers or clay particles alone. Similar results have been reported by Jawaid et al. (2011a, b), Arrakhiz et al. (2013b), and Kakou et al. (2015). According to this result it can be concluded that hybridization has a direct effect on the mechanical properties of the composites. The hybridization of natural fibers and E_1 as clay has a positive effect on the mechanical properties of resulted hybrid composite.

6 Conclusion

The natural fibers and natural clay hybrid polymer composites have been fabricated using extrusion process followed by injection moulding technique. The prepared samples were characterized and results are reported. From this chapter, we may conclude that natural fibers (Coir, bagasse, Pine cone and Alfa) can be combinated with the natural clay as a filler in a hybrid composite material, which ultimately contributes to resolve environmental problems usually arises from natural resources. The chapter explored the potential of combination of natural fibers and clay in composites specifically hybrid polymer composites and also studied and showed the structural, morphological, mechanical and rheological properties of developed hybrid composites. This chapter also discussed the surface modification (chemical modification) of fibers which is extremely important and provides good interfacial adhesion between the fiber and matrix. Results of this study can be summarized with the following key conclusions:

Wide variety of application of natural fillers (fibers and clay) composites can also be found like packaging, doors, furniture, etc. The following application of the hybrid polymer composites can be observed, based on the achieved results, in different areas: Building component, transport sector (railway coach and Vehicle), seat and backrest and Furniture (Tables, Chairs, Kitchen, cabinet, etc.).

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