

# The role of organoclay and natural fibers in the performance of polysulfone nanocomposite materials

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## Abbreviations

NMP N-methyl pyrrolidone

DMSO, sulfolane dimethyl sulfoxide

TMP trimethylolpropane

PSFs polysulfones

EtO ethylene oxide

ESC environmental stress cracking

WAXD wide angle x-ray diffraction

TEM transmission electron microscopy

CN clay nanoparticles

OMMT organically modified montmorillonite

DMAC dimethylacetamide

PVP polyvinyl pyrrolidone

PSFP polysulfone

CN clay nanoparticles

PEO polyethylene oxide

MAPP maleated polypropylene

## Abstract

Advances made in the field of materials science leads to technological development. Nowadays, composite materials, used in various fields such as engineering, industry, medicine are corrosion resistance and have lightweight and high fatigue strength, and promise faster assembly –they can withstand loads, insulate or conduct heat and electricity, accept or reject magnetic flux, transmit or reflect light, be stable in hostile environments, and possesses all these characteristics cost-effectively and with minimal impact to the environment. The chosen material needs to be compatible with the manufacturing process; because even with the right materials, an incorrect manufacturing process can be disastrous. This study displays the impact of organoclay and/or natural fibers on the performance of polysulfone (PSF) nanocomposite materials for variable applications. First, PSF production and properties are outlined, and then a detailed study of organoclay and its importance as nanofiller in polymer matrices has been investigated, with a special attention to PSF. Properties of natural fibers reinforced variable nanocomposites for wide range of application together with PSF in the form of nanocomposites have also been researched and analyzed. Moreover, the recent research on the hybrid nanocomposite-based clay/natural fiber in the presence of different polymers has been also displayed in details.

**Keywords:** organoclay, natural fiber, polysulfone, nanocomposites, hybrid materials, electrical properties, neat polymer, neat polymer, clay platelets, PU chains, polysulfides, polyketones, nonsolvent, hydrophilic materials, fouling, polysulfones, plastics, cosmetics, phosphoniumcations, clay layers, polymer, biomedical applications, biomedical applications, microchemical, membrane's permeability



## Background

Polymer–silicate nanocomposites are layered silicates dispersed in a polymer matrix, which enhances the thermal, rheological, optical, mechanical, and electrical properties of the neat polymer. Many studies have explored other polymers following the research conducted by Toyota which demonstrated exceptional advancement in improving the properties of nylon-6 nanocomposites from clay, for example, polyethylene, polypropylene, polycaprolactone, polyimides, poly(ethylene oxide), poly(ethylene terephthalate), polycarbonate, polyurethane, polystyrene, polyamides, and epoxy resins, among others.<sup>1,2</sup> Yano developed polyimide/clay nano-composites from poly(amic acid) and montmorillonite and found that mixing low concentrations of montmorillonite silicate sheets decreases thermal expansion, gas permeation properties and dielectric constants of polyimide films.<sup>3–5</sup> The bio–nano interaction between clay platelets and polyurethane chains in the sample, which was spray-coated, was also investigated in some studies. Clays were intercalated with and exfoliated by polyurethane chains, which compatibly interacted with the hard segments in polyurethanes. These structural arrangements of clay define and control the reactive sites that prove effective in interacting with PU chains. This improved both physical and chemical interactions between the scattered nanoclay and the polymer matrix in the continuous phase (a layer of polyurethane).<sup>6–8</sup>

A number of studies demonstrated that the physico-mechanical properties of new, HB3-cured PU nanocomposites are extracted from toluene diisocyanate and poly(propylene glycol) and toughened and hardened either by third-generation hyper branched (HB3) polyester polyol (HBP), trimethylolpropane (TMP), or glycerol (Gy). Compared to the controlled hyper branched PU, conventionally hardened by HBP and TMP, and their nanocomposites, PU nanocomposites exhibited higher exfoliated morphology – a 23% improvement in storage modulus at 25°C along with an onset degradation temperature (5°C) improvement, which is the temperature at which maximum degradation occurred (9°C), and ~140% increase in tensile strength – when cured by HB<sub>3</sub>, which contained 8-wt% Cloisite30B.<sup>9</sup> A one-pot synthesis of the customized poly(ethyl acrylate)/organo MMT-exfoliated nanocomposites was established by Datta et al.<sup>10</sup> according to their findings, in the presence of organo MMT (Cloisite30B and Cloisite20A), the polymerization rate increased owing to the interface of the nanoclay and the carbonyl group of the monomer, which reduced the electron density of the C=C bond, thereby leading to an increase in the monomer reactivity. Compared to a neat polymer, this polymerized nanocomposite demonstrated a 17°C shift in the glass transition temperature, which was a significant finding.<sup>10</sup>

## Polysulfone

In the last two decades, thermoplastic polymers with high temperatures have been used in various applications; they have high heat resistance (200°C), strength, biocompatibility,

extremely tight tolerances, and durability and are unaffected by several cycles and doses of any kind of radiation. The need for materials with higher temperatures and higher performances has resulted in the application of aromatic polysulfones (PSFs), aromatic polyimides, aromatic polyketones, and aromatic polysulfides in medical trays and electronic components, surgical and dental instruments, drug delivery components, medical, and machined parts. Polysulfone (PSF) is a very significant membrane material because it has competent mechanical, thermal and chemical stabilities and is transparent and hydrolytically stable and is included in amorphous thermoplastics. Its hydrolytic stability is useful in applications that mandate repeated cycles of steam sterilization. Moreover, it is stiff, rigid, and tough and have high chemical and heat resistance, which enable the production of parts and products that demand high performance.<sup>11</sup>

## Polysulfone production

Bisphenol salts that react with 4,4-dichlorodiphenyl sulfone (4,4-DCDPS) can produce aromatic polysulfone, as shown in Figure 1. These types of reactions are usually conducted at temperatures ranging from 100 to 250°C in polar solvents that have a high boiling point, such as sulfolane, dimethyl sulfoxide (DMSO), and N-methyl pyrrolidone (NMP), with chlorobenzene as a co-solvent, which removes the water that is formed as an azeotropic mixture. The alkali salt is then filtered, and after the solution becomes cool, the previous mixture is poured into methanol, which is a nonsolvent. The polymer is precipitated, dried, and purified.<sup>11</sup>

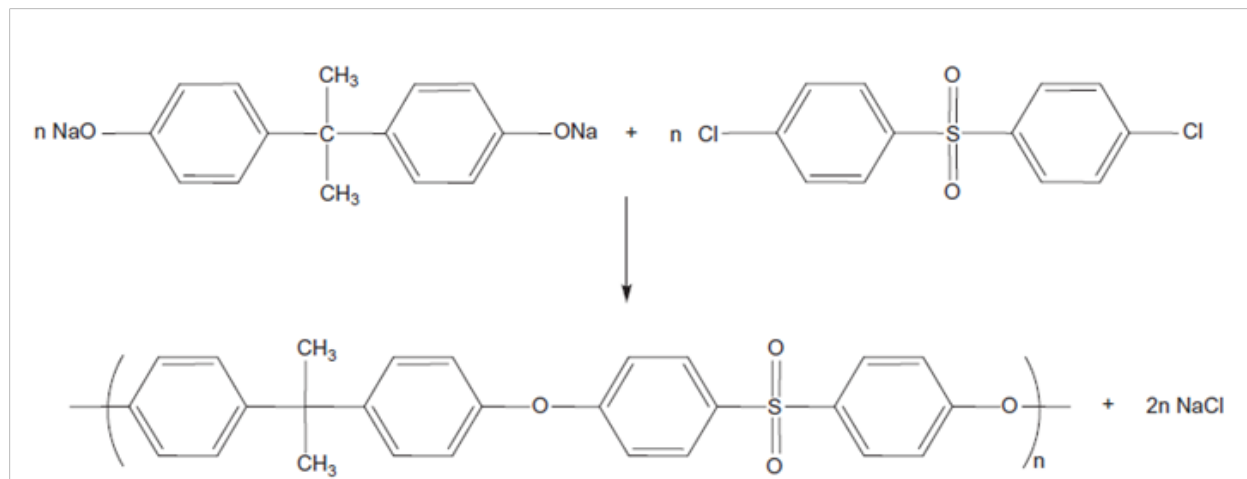
## Properties of polysulfone

Polysulfones are polymers that are transparent and amorphous. They have high heat resistance and strength and glass transition temperatures 180°C – 250°C. These properties make polysulfones receptive to repeated cycles of steam sterilization and resistant to e-beam and gamma radiations. This is mainly due to its high aromatic content. Polysulfones can be used to inject molten material into a mold or assembled in to precision parts. Table 1 describes the important properties of PSF.<sup>11</sup> This includes the physical and mechanical properties. In general, polysulfones have the following properties:

- I. They are resistant to most aqueous acids and bases but non-resistant to chlorinated organic solvents, such as dichloromethane and chlorobenzene, and ketones, such as acetone and methyl ethyl ketone.
- II. They are thermally and hydrolytically stable and suitable for both autoclave and steam sterilization; moreover, they can be sterilized with ethylene oxide (EtO) and gamma and e-beam radiation.
- III. They are used in implants, hemodialysis, and filtration membranes. Since they are hydrophobic, they are prone to membrane fouling. Hydrophilic materials such as polyvinyl pyrrolidone (PVP) can make their surfaces hydrophilic; polysulfones treated with PVP are used commercially in dialysis membranes.

Furthermore, PSFs have an important property named as welding property, through joining PSFs together. Since welding techniques with a high frequency are unsuitable to polysulfones, they can only be conjugated by vibration welding, heated tool welding, spin welding, infrared welding, and ultrasonic welding. They can also be bonded

with solvents such as NMP, dimethylacetamide (DMAC), and N.N-dimethyl formamide (DMF) as well as acrylic and epoxy adhesives. Environmental stress cracking (ESC) should be avoided at all costs with the help of precautionary measures.<sup>11</sup>



**Figure 1** Synthesis of polysulfone.

**Table 1** Typical properties of polysulfone

Fiber	Cellulose %	Lignin %	Diameter ( $\mu\text{m}$ )	Hemicellulose %	Elongation %
Coir	37	42	100-450	0.15	47
Banana	64	5	50-250	19-Jun	3.7
Sisal	70	12	50-200	14-Oct	5.1
Pineapple	85	12	20-80	16-19	2.8
Jute	71	13	15.9-20.7	13-20	3

## Clay

Clay forms a valuable composition in porcelain, bricks, tiles, sanitary ware, paper, rubber, plastics, cosmetics, paints, and medicine. They are naturally abundant and economical and are not particularly harmful to the environment. It is a finely grained natural rock or soil composed of clay minerals, such as crystalline and hydrous aluminum phyllosilicates with varying amounts of iron, magnesium, lithium, alkali metals, alkaline earths, and other cations. Clay is also made up of layered silicates and small amounts of metal oxides and organic matter.<sup>12</sup>

### Classification of clay

Clay is generally categorized into natural clay and synthetic clay. However, scholarly sources divide clay into three main types and many sub-types, as shown in Figure 2. Kaolinite clay mineral is one example of 1:1 clay; they have only one octahedral group and one tetrahedral group in each layer. Clay minerals that have one octahedral sheet between two

tetrahedral sheets are known as 2:1 clays, which include smectite (divided into montmorillonite (MMT), nontronite, saponite and hectorite species), mica, vermiculite, and chlorite.<sup>9</sup>

### Structure and properties of clay

Silicate ( $\text{SiO}_4$ ) is a basic chemical unit of clay; it has one central ion, silicon, with a charge of (+4) and each of the four oxygen ions have a charge of (-2). Each silicon-oxygen bond has one-half of the total bond energy of oxygen; hence, there is a tetrahedron-shaped anionic group with a charge of (-4). This leads the oxygen ion to bond with another silicon ion, thereby linking one  $\text{SiO}_4$  tetrahedron to another and so forth.<sup>12</sup> Mostly, phyllosilicates (2:1 layered) are used to prepare polymer nanocomposites. Since MMT is highly abundant and has a high surface area, it is typically used to fabricate polymer nanocomposites with greatly improved properties.<sup>13,14</sup> Its chemical formula, as shown in Figure 3, also makes it environment-friendly, organic, and inexpensive.<sup>12</sup> The crystalline structure of

MMT is composed of a layer of octahedral aluminum hydroxide sheet between two layers of tetrahedral silicon oxide sheets. Each platelet has a thickness of 1 nm and a lateral dimension of approximately 200 nm. These clay platelets are heaped up on each other and bonded by Van der Waal forces, with 1 nm gaps (galleries). These galleries are usually occupied by cations, such as Na<sup>+</sup>, Li<sup>+</sup> and K<sup>+</sup>. These cations balance the negative charges generated from

isomorphic substitution within the layers (for montmorillonite, Al<sup>3+</sup> replaced by Mg<sup>2+</sup>).<sup>15</sup> Layered silicates can disperse within individual polymer layers, depending on interlayer cations, and possess surface ability toward ion exchange reactions with organic and inorganic cations; these two characteristics are necessary for the production of polymer clay nanocomposites.<sup>16</sup>

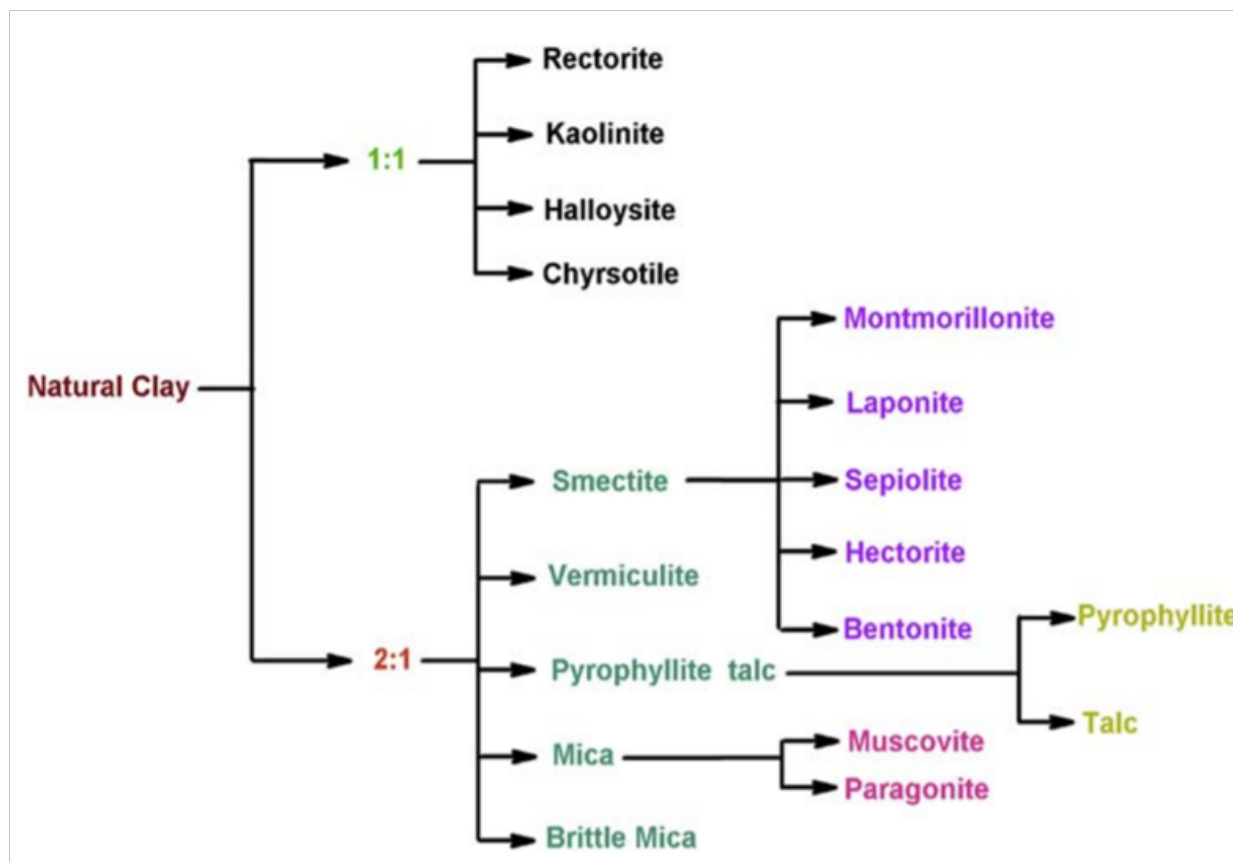


Figure 2 Classification of clay materials.

### Structure and properties of organoclay

Unlike most polymers, which are hydrophobic, clays are naturally hydrophilic. Hence, it is difficult to disperse silicates in the polymer matrix, because hydrophilic-layered silicates and hydrophobic polymers are incompatible.<sup>9</sup> Inorganic ions in the clay interlayer can be successfully replaced by organic cationic surfactant molecules through ion-exchange reactions.<sup>12</sup> This leads the interlayer spacing getting expanded, which results in the basal spacing increasing. Wettability and thermodynamic interactions, which are more improved, significant properties, can, therefore, be achieved for industrial and medical applications by chemically modifying clay.<sup>17</sup> This can be attained through ion-exchange reactions with cationic surfactants, including primary, secondary, tertiary, and quaternary alkyl ammonium or alkyl phosphonium cations. This ion-exchange reaction

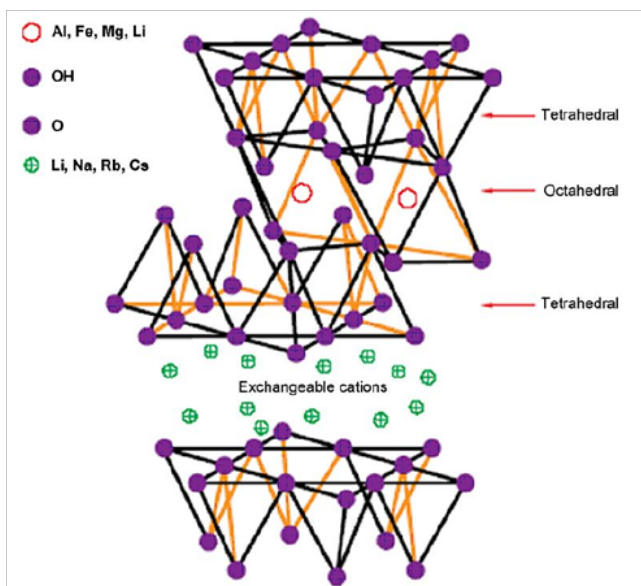
results in the formation of an organophilic clay. Added to this aqueous dispersion is an alkyl-ammonium or phosphonium salt, following they are replaced by surfactant ions; these intergallery cations are then intercalated between the layers, resulting in an increase in the intergallery height.<sup>17,18</sup> Thus, the clay surface can be modified and properties such as hydrophilicity, hydrophobicity, and others can be altered accordingly by modifying the type or length of alkyl chains or adding some polar groups in the surfactant salt.<sup>19,20</sup>

### Polymer/clay nanocomposite morphology

It is very important to note that the relation between the performances of nanocomposites and their morphological structure. The polymer clay composite morphologies can be intercalated, flocculated, or exfoliated depending on the strength of the interfacial interaction between the clay



and the polymer matrix, as depicted in Figure 4.<sup>21</sup> The intercalation of a polymer matrix into the layered silicate structure in the intercalated nanocomposites occurs in a regular crystallographically way, by modifying the silicate layer and polymer chains. The individual clay layers in the exfoliated nanocomposites are randomly separated in a continuous polymer matrix by an average distance, depending on the clay loading.<sup>22</sup>



**Figure 3** Unit crystal structure of montmorillonite.

### Clay and polymer modification for nanocomposite formation

Poor physical interactions between polymer and clay resulted in weak mechanical and thermal properties. This can be corrected by modifying the nanocomposite formation process and the materials. Using clay organophilization and a compatibilizer can improve the distribution of different clays within the polymer matrix. A compatibilizer can often act as a polymer that is chemically compatible with both the matrix and the clay. This kind of compatibility can be achieved through grafting reactive groups or copolymerizing it with another polymer containing reactive groups. The objective of clay organophilization is to improve the clay–polymer interface through the exchange of interlamellarcations (generally, calcium and sodium ions) with positively charged organic molecules, which neutralizes the negative charges of the silicate layers and converts the clay into organophilic clay. Generally, alkyl ammonium, amino acids, and other salts of this family are used to improve clay wettability by the polymer matrix and facilitate the penetration of organic molecules between their platelets.<sup>9,23</sup> Figure 5 illustrates the process of the ion exchange and the modification of clay layers using cations salt.<sup>24–26</sup>

### Polymer/clay nanocomposite production methods

As seen in Figure 6, the methods used in preparing nanocomposites can be divided into four techniques: the first method is in-situ polymerization; here, a monomer

solution is used as a medium for clay dispersion; moreover, it is important to ensure favorable conditions, which allows polymerization to occur between the clay mineral layers. Polymerization can be initiated by either heat or radiation after diffusing a suitable initiator or a fixed catalyst inside the clay layers before the filling step with the monomer. The clay mineral layers can attract monomer units inside the galleries (until equilibrium is formed), since clay minerals have a high surface energy. Total exfoliation occurs due to the polymerization that occurs between the layers of lower polarities.<sup>23,27</sup> The second method is solvent casting, where silicate is exfoliated in single layers within the solvent system. The pre-polymer is dissolved in a solvent, such as water, chloroform, or toluene, and silicates can be easily dispersed in a suitable solvent through the increase in the entropy owing to the disorganization of the layers.<sup>23</sup> The polymer intercalates in the silicate layers; after the solvent evaporates or the mixture gets precipitated, the polymer-filled layers are reunited. For best results, an intercalated morphology or multilayer structure is usually required.<sup>28</sup> The third method is the melt intercalation method, which is environment-friendly and does not need a solvent;<sup>23</sup> in this method, the molten polymer matrix is mixed with the silicate layers. During heating, the molten polymer chains diffuse into the silicate galleries to form either an exfoliated nanocomposite or an intercalated one. Finally, in the fourth method, the clay is suspended in water or any solvent in order to increase its base spacing. Then, it is directly mixed with the polymer, leading to the intercalation of the polymer matrix in the increased basal spacing.<sup>29,30</sup>

### Morphological surface characterization techniques for polymer/clay nanocomposites

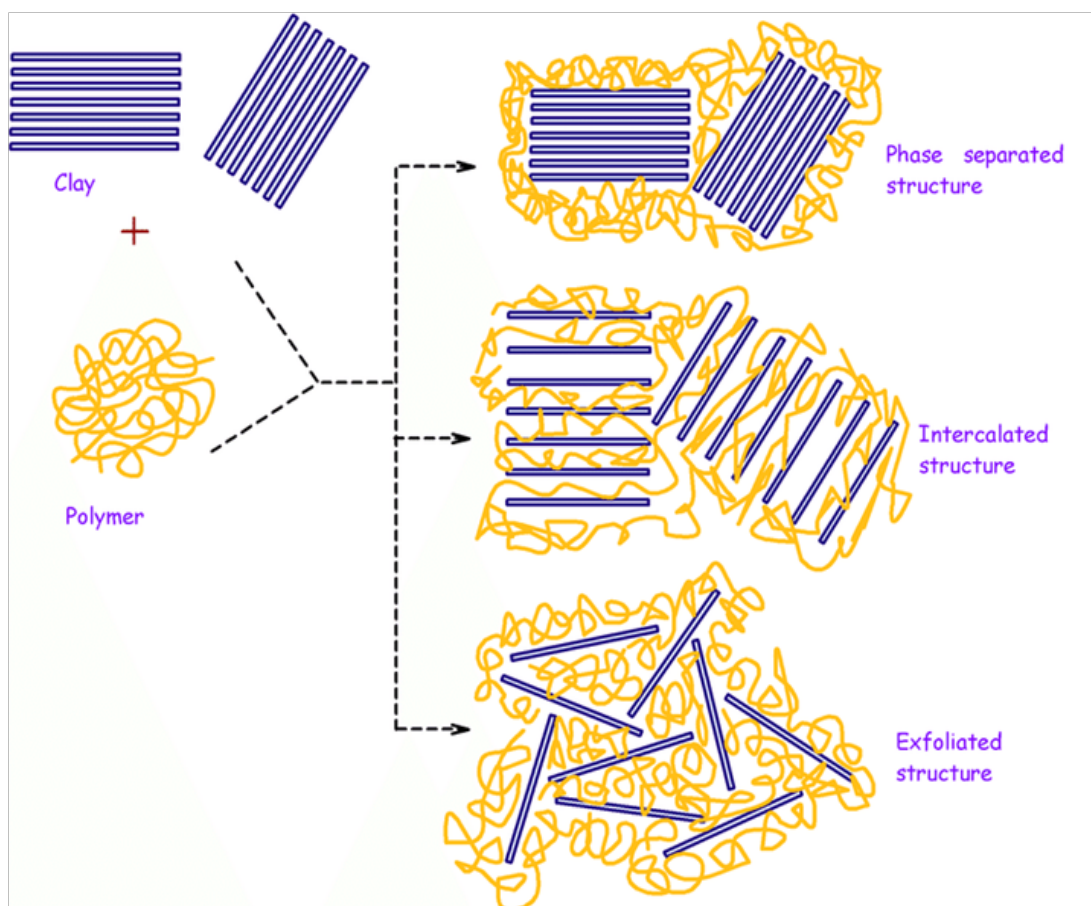
The degrees of exfoliation and interlayer spacing of polymer/clay nanocomposites can be characterized by wide angle x-ray diffraction (WAXD) analysis and transmission electron microscopy (TEM). The former identifies the structure of the exfoliated or intercalated nanocomposites by monitoring the shape, intensity, and position of the basal reflections from the distributed silicate layers. Hence, WAXD can determine the interlayer spacing of the silicate layers either in the intercalated nanocomposites or the original layered silicates. TEM, on the other hand, provides a better understanding of the internal structure and the spatial distribution of various phases and displays structural defects through direct visualization.<sup>30,31</sup>

### Applications of polysulfone/clay nanocomposites

Incorporating nanoclay in the polymer matrix is applied to membrane separation and UV screens and ensures characteristics such as electrical conductivity, barrier properties, polymer blend compatibilization, impact modification, flammability resistance, and biomedical applications. Generally, materials that have always been in use are being created in the field of polymer/clay nanocomposites. However, considering the progress in chemistry and material sciences, it is not surprising to see the growth in the number and capability of new products and applications using this technology. In the literature,

some studies researching PSF/clay nanocomposites were reviewed. The first, published in 2001, showed the preparation of a polysulfone nanocomposite with montmorillonite, organically modified with dodecyl ammonium bromide, by solution dispersion in dimethyl acetamide. Exfoliated nanocomposites were produced, and these improved thermal stability and mechanical properties, though not considerably, as polysulfone is already a high-performance polymer. Moreover, the authors proposed to perform more tests in future studies so as to evaluate properties such as corrosion and diffusion properties, among others.<sup>32</sup> Therefore, another study that used solution dispersion investigated the corrosion properties of polysulfone nanocomposite membranes

prepared with Kunipia-F montmorillonite organomodified with dodecylamine. A low clay content (as 1 wt.%) produced nanocomposites with superior anticorrosion and barrier properties owing to the dispersed silicate layers, which hinder the diffusion path of oxygen and water.<sup>33</sup> Combining solution dispersion and the final step of wet-phase inversion, Anadão prepared PSF/MMT nanocomposite membranes, identifying that Na-MMT intercalated and exfoliated in the PSF matrix. Furthermore, via the mixing of MMT, the stability in thermal properties and the hydrophilicity of nanocomposite membranes were improved. Clay minerals are naturally organophobic, which makes organic modification necessary in order to provide a microchemical environment for intercalation with hydrophobic polymers.<sup>34</sup>



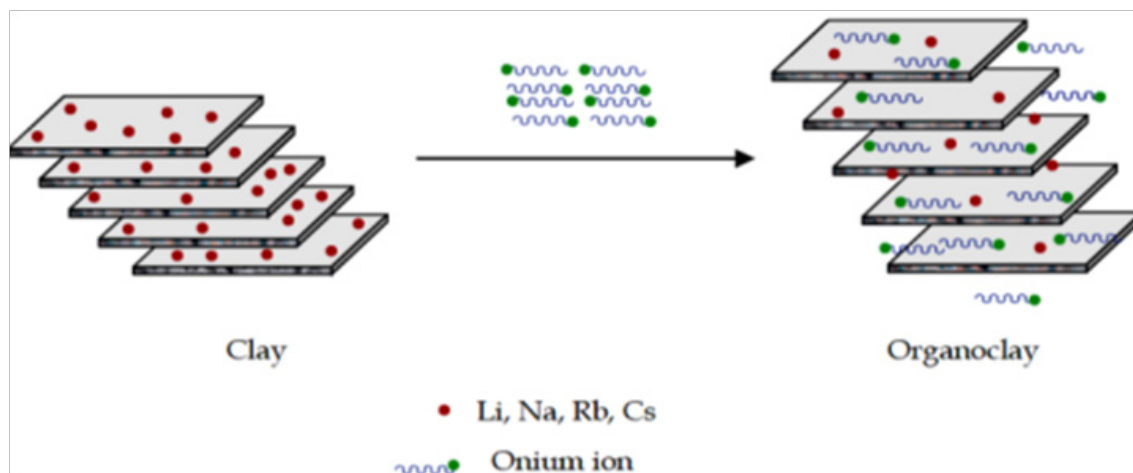
**Figure 4** Possible types of polymer-clay nanocomposite structures.

Monticelli et al.<sup>13</sup> tried to make porous membranes and films with polysulfone solutions in N-methyl-2-pyrrolidone (NMP), with different percentages and types of both unmodified and organically modified clay and without any other additives. They found that Cloisite Na and Cloisite93A formed microaggregates, and Cloisite30B led to nanostructures being composed of single sheets as well as well-ordered multilayer silicate groups. Adding Cloisite30B to the casting solution impacted the phase separation in the agglomeration bath. Furthermore, Cloisite30B improved the mechanical properties and wettability of dense films.<sup>13</sup>

Raphael researched the effect of clay nanoparticles (CN), with and without polyethylene oxide (PEO), in mixed matrix polysulfone ultrafiltration membranes in order to improve the performance of the polysulfone membrane. The results showed smoother surface, higher permeability, and less superficial charges than control. The pure water permeability of the neat PS membrane was  $15 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ . The optimal dosage of the individually doped membranes was 1.5% weight CN to PS and 5% weight PEO to PS, which resulted in permeability's of 56 and  $237 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ , respectively. Several other experiments compared the control membrane

to the membranes with 1.5% and 4.5% CN, 5% PEO, 1.5% CN + 5% PEO, and 4.5% CN + 5% PEO in order to determine the effects of dopants on pore microstructure, separation performance, superficial charge, and fouling susceptibility, as shown in Figure 7. Hence, owing to its capability to increase a membrane's permeability and rejection capacity when used alone and reduce the membrane's selectivity loss with the use of PEO as a pore former, CN is an effective additive that can be used to modify membranes.<sup>35</sup> Organoclay-embedded polysulfone (PSF) nanocomposite membranes were prepared in order to remove arsenates from contaminated surface water, as shown in Figure

8. These membranes consisted of different weight ratios of organoclay to polymer, ranging from 0 to 2.0wt%. Compared to neat PSF membranes, nanocomposite membranes exhibited higher surface hydrophilicity, pure water flux, and roughness and better mechanical strength. The results showed that arsenate adsorption was most favorable in the neutral pH. The highest adsorption capacity was obtained in batch adsorption in the nanocomposite membrane containing 2.0wt% of organoclay; the applicability of the prepared membrane was also confirmed for multiple cycles.<sup>36</sup>



**Figure 5** Modification of clay layers by organic onium cations.

## Natural fiber

In many applications over the recent years, natural fibers have been utilized as reinforcers and/or fillers in the manufacture of polymer fiber composites<sup>37</sup> because they have the mechanical properties of stiffness and strength at acceptably low prices. Composites science offers significant opportunities for sourcing enhanced, sustainable materials from renewable resources. Natural fiber composites have gained considerable interest over conventional composites in this industry because of their ecological advantages, low density, and non-carcinogenic and biodegradable nature. Furthermore, they are very cost-effective, especially in building and construction, packaging, automobile and railway coach interiors, and storage devices.<sup>38</sup> However, one limitation of natural fiber composites is their relatively high-moisture absorption. In order to resolve this, the fiber surface properties are modified by various chemical treatments. Fibers mainly constitute hemicellulose, cellulose, lignin, and pectin, and the properties of each constituent contribute to the overall properties of the fiber; hemicellulose is the least resistant and is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber, whereas lignin is thermally stable but responsible for the UV degradation. The percentage composition of each of these components varies for different fibers. Generally, the fibers contain 5–20% lignin, 60–80% cellulose, and up to 20% moisture.<sup>39</sup>

## Properties of natural fibers inside variable nanocomposites

The physical and mechanical properties of composites depend on the chemical composition of a fiber (celluloses, hemicelluloses, lignin, pectin, water content, and waxes and other minors) according to the growing conditions (soil features, climate, aging conditions) and extraction/processing methods. Table 2 summarizes the chemical composition of several natural fibers. Polypropylene composites reinforced by coir fiber were also tested. The flexural properties of the coir fiber polypropylene composite were between 40 and 60wt%. Increasing the coir fiber content resulted in the flexural strength decreasing considerably. An optimal composite panel formulation for automotive interior applications was achieved through a mixture of 37wt% PP powder, 60wt% coir fiber, and 3wt% MAPP<sup>40</sup> the mechanical properties of jute fiber-reinforced polypropylene composites were also analyzed by fiber treatments such as mercerization, bleaching, and washing. By increasing % weight fraction and the NaOH percentage of fibers in the pp matrix, the tensile strength and the tensile modulus were increased. The highest tensile strength and tensile modulus were 31.48Mpa and 277.77Mpa, respectively.<sup>41</sup> Today, the production of polymer composites reinforced with wood flour is an established technology. Obtained from natural resources, wood flour is available in large quantities and in various forms. It is cheap, light,

and can be added to commodity matrices in large amounts, thereby offering economically advantageous solutions. The building and automotive industry uses wood flour-

filled composites; these composites are also applied in packaging and preparing various household articles, office appliances, furniture, and other items.<sup>42</sup>



**Figure6** Different techniques for the preparation of polymer-clay nanocomposites: (A) solution casting; (B) melt blending; (C) *in-situ* polymerization.



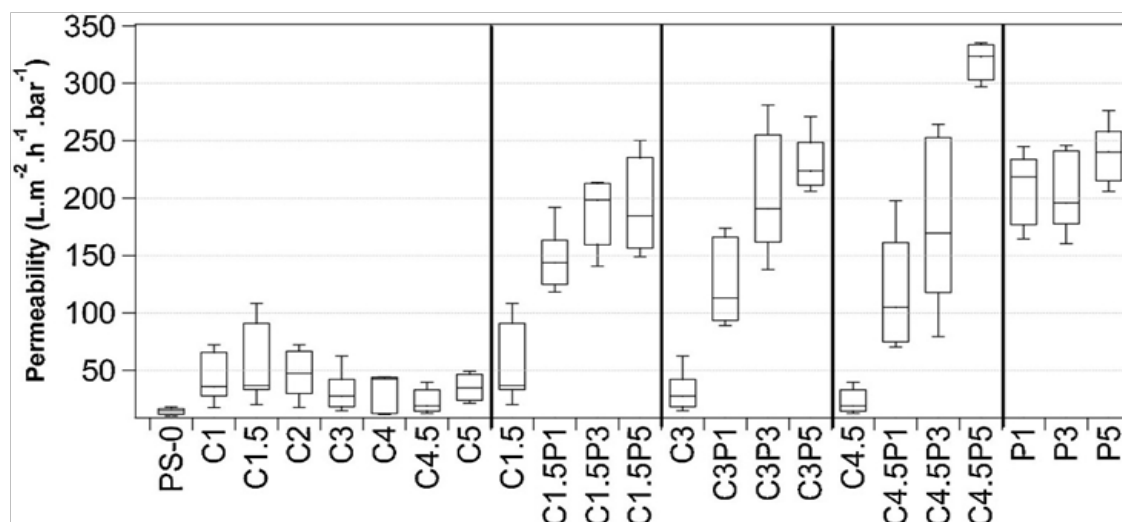


Figure 7 Cross-flow ultrapure water permeability.

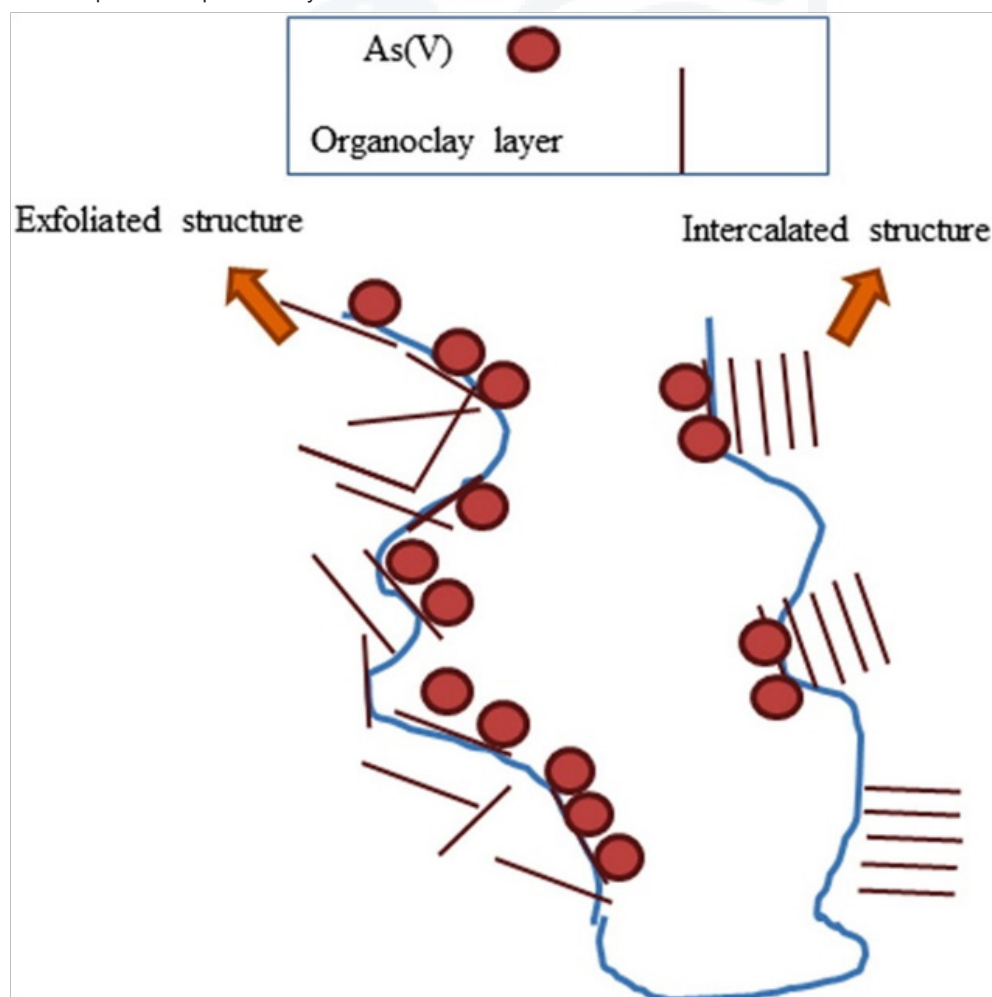


Figure 8 Schematic illustration of As(V) adsorption on the exfoliated and intercalated structures of organoclays in vicinity of membrane pore.



**Table 2** Chemical composition of natural fibers<sup>38</sup>

Properties	Unit	Polysulfone
Density	g/cc	1.24
Light transmittance	%	70
Water absorption at equilibrium	%	0.5
Glass transition temperature	°C	185
Softening point/melt temperature	°C	185
Tensile strength	Mpa	70
Elongation at break	%	50-100
Flexural modulus	GPa	2.5
Processing temperature	°C	330-385

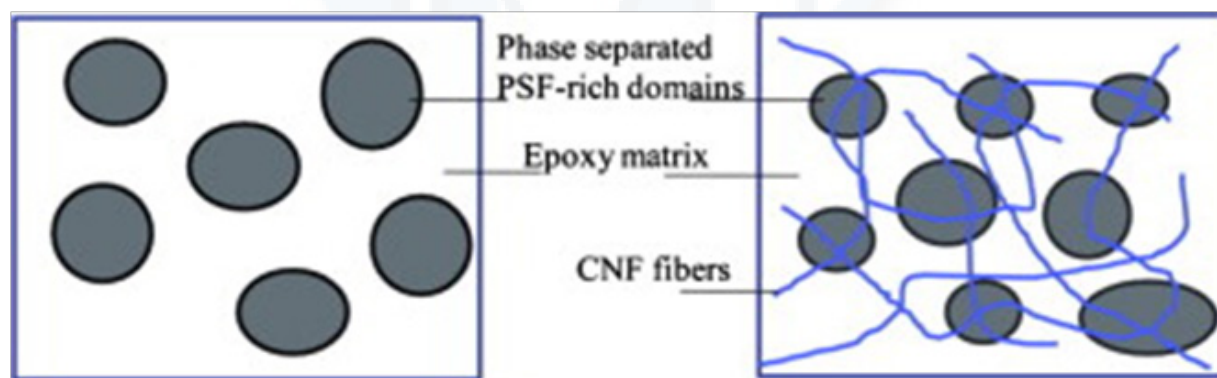
### Modification of natural fibers

Natural fibers are incompatible with the hydrophobic polymer matrix and tend to form aggregates. Because they are hydrophilic fibers, they are poorly resistant to moisture. In order to eliminate their problems related to high water absorption, they have been treated with cyclic structures and hydrophobic aliphatic. These structures contain reactive functional groups that can bond to the reactive groups in the matrix polymer, e.g., the carboxyl group of the polyester resin. Thus, natural fibers are often modified to make the fibers hydrophobic and improve interfacial adhesion between the matrix polymer and the fiber.<sup>39</sup> ZitaDominkovics and Li'viaDa'nya studied the modifiability of wood flour surface used as reinforcement in polypropylene composites by benzylolation. They determined the influence of reaction time on the degree of modification and the effect of the reaction on the structure and properties of the wood flour.

PP composites were prepared from the modified wood. The chemical modification of wood flour slightly improved processability and the surface appearance of the products and largely decreased their water absorption.<sup>40</sup> Ayfer DCavdar investigated the effect of chemical modification of wood flour with various anhydrides on the mechanical and thermal properties of high-density polyethylene composites filled with wood flour. Wood flour was chemically modified with varying concentrations of propionic, maleic, and succinic anhydride. The improved samples were thermally and mechanically more stable than control samples.<sup>41</sup> Hu and Lim showed that alkali treatment significantly improved the tensile properties of hemp fiber-reinforced polylactic acid (PLA) compared to those that were untreated. The composites with 40% volume fraction of alkali-treated fiber have the best tensile properties. The tensile strength and tensile modulus of the composites with 40% treated fiber are 54.6MPa and 85GPa, respectively, which are much higher than neat PLA, especially for the tensile modulus, which is more than twice of that of neat PLA (35GPa).<sup>42,43</sup>

### Application of PSF/natural fiber nanocomposites

Natural fiber-reinforced composites are an emerging area of study in polymer science. These natural fibers have low density and high specific properties. However, there is a lack of research on polysulfone/natural fiber nanocomposites. Solvent exchange and melt mixing led to CNF being introduced into epoxy/polysulfone (PSF) binary blends, as shown in Figure 9. Results show that epoxy/PSF binary blends can enhance impact toughness and tensile strength due to improved interfacial adhesion, by adding small amounts of CNF, as shown in Figure 10.<sup>44</sup>


**Figure 9** Schematic illustration for the morphologies of PSF10 blends (left) without and (right) with CNF.

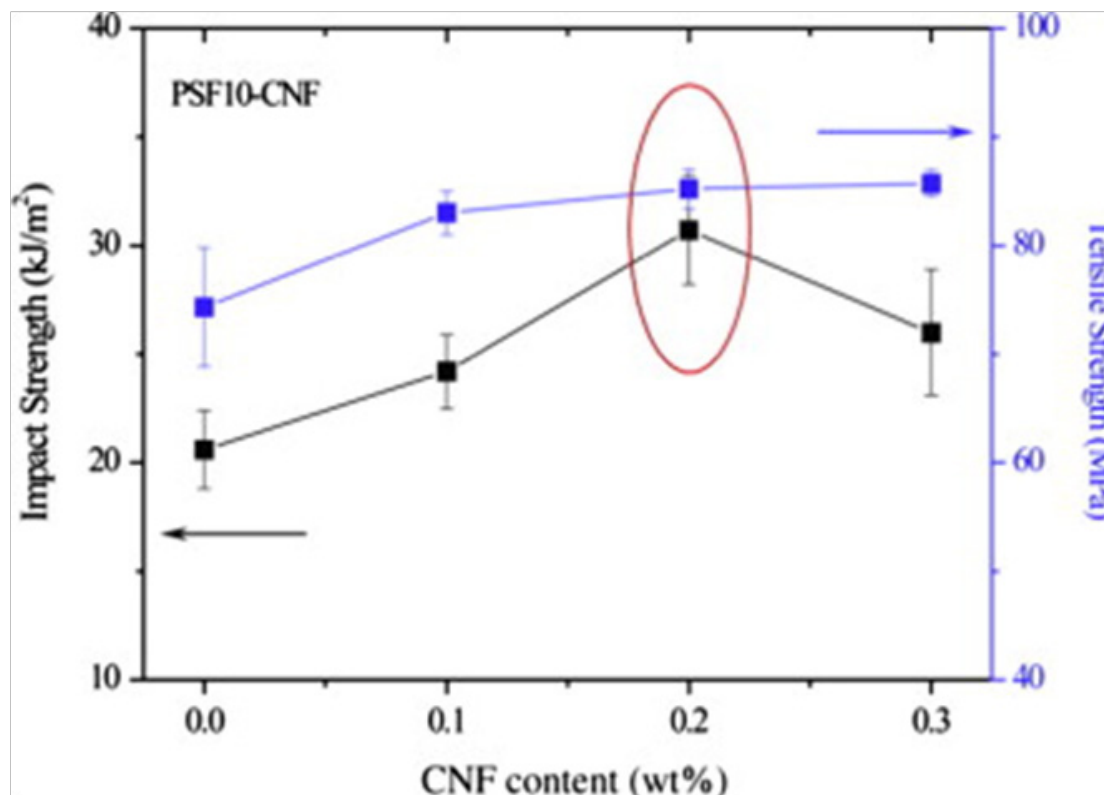
### Polymer/clay/natural fiber hybrids nanocomposites

Hybrid composites have a combination of more than one reinforcing phase and a single matrix phase or a single reinforcing phase and multiple matrix phases or multiple reinforcing and multiple matrix phases. They have more flexibility compared to composites that contain a single

fiber. Their poor resistance to water absorption can have undesirable effects on their dimensional stability and mechanical properties and, in the long-term, loss of ductility during hydrolysis, owing to the degrading macromolecular skeleton. Therefore, it is crucial to research its water absorption behavior extensively in order to determine the consequences that the water absorbed may have and understand how this water uptake can be minimized

in practice. Several experiments have been carried out in order to reduce the water absorption of wood plastic composites; to resolve this, scholars have reported the use of nanoscale fillers in wood plastic composites. Hetzerblended maleatedpolyethylenes (MAPE) with high and low molecular weight to maximize the effects of

their compatibility on WPC/clay nanocomposites. Their results showed that the addition of organically modified montmorillonite (OMMT) to a wood/polymer composite in the presence of MAPE reduces its linear coefficient of thermal expansion and increases the heat deflection temperature without affecting the processability.<sup>37</sup>



**Figure 10** Tensile strength and impact strength of PSF10 with different CNF contents.

Ismaeil Ghasemi & BehzadKord<sup>36</sup> investigated the effect of nanoscale fillers on the long-term water absorption behavior of polypropylene/wood flour composites. Hybrid composites of polypropylene/wood flour/nanoclay with varying concentrations of nanoclay and maleated polypropylene (MAPP) as the compatibilizers were fabricated in an internal mixer.<sup>36</sup> The long-term water absorption of the composites was evaluated by their immersion in water at room temperature for several weeks. Water absorption of the hybrid composites increased with immersion time, reaching a certain value at saturation point, while the water content of the composites remained unchanged. Water absorption decreased with an increase in the organoclay and MAPP content in the composites. Moreover, the intercalation morphology of hybrid nanocomposites were observed.<sup>37</sup> Recently, Alosaimi et al.<sup>44</sup> manufactured hybrid nanocomposite films based on polysulfone/wood flour/nanoclays, showing that the addition of nanoclay particles decreased water absorption; moreover, the tensile and flexural properties were improved by adding organoclay.<sup>44</sup> Moreover, the potential of PSFWBP to remove dye was

demonstrated; these sorbent removed increasing amounts of MB dye from aqueous solutions by increasing the pH, contact time, and amount of PSFWBP used.<sup>45</sup>

## Conflicts of interest

The author declares that there is no conflict of interest.

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