# Mechanical and Impact Strength of Nanoclay-Filled Composites: A Short Review

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*Authors' contributions*

*This work was carried out in collaboration among all authors. Authors GK, SP and MP designed the study and discussed the structure of the review. Authors KCK and GK performed the initial bibliographic review and extracted relevant data. Authors GK and SP wrote the initial draft. Author CS completed collection of literature and corrected the draft to submission. All authors read and approved the final manuscript.*

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## ABSTRACT

This review surveys the research work published in the field of nanoclay (montmorillonite, MMT)-filled composites with particular reference to the effect of nanoclay (NC) introduction on the tensile, flexural, impact and compressive strength of nanocomposites. The matrix most frequently used in NC-filled composites is epoxy, although other thermosetting and thermoplastic polymer materials have also been used. To make MMT more compatible with these matrices, they have been often

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subjected to organophilic modification with the use of organic cations, therefore indicated as organo-montmorillonites (OMMT). NC-filled composites are also fabricated with the most common reinforcements, such as carbon, glass, Kevlar and basalt, and more recently also biomatrices with natural fibers have also been proposed. A few studies on ceramic matrices have also been reported. The review concentrates on the maximum level of improvement obtained in the referred studies by the introduction of NC in the bare matrix or in the fiber reinforced composites, with respect to tensile, flexural, impact and compression strength, with the idea of disposing a database in comparing the best values obtained by nanoclay introduction against the benchmark composite.

## 1. INTRODUCTION

Nanocomposites are defined as materials containing nanoparticles, also referred to as to "nanofillers", which are dispersed in a polymer or ceramic matrix. Nanofillers may be of different geometry, from spherical to considerably elliptical, but at least one of their dimensions must be in the range of 1-50 nm. Nanocomposites have attracted considerable interest, also because they may exhibit remarkable variations in some material properties compared with the bare matrix or with conventional composites with the introduction of small amounts of nanofillers. For the production of polymer-matrix nanocomposites, a number of matrices have been experimented, which include mainly oil-derived ones, such as polyamides, polyolefins, polyesters and their derivatives, epoxies, acrylics and polyurethanes, and a large number of polymer blends [1].

A sub-category of nanocomposites is formed by using nanoclays i.e., nanoparticles of layered silicates, in which the stacking of layers enables the formation of complex clay crystallites [2]. The most commonly type of mineral clay used for nanoclays is montmorillonite (MMT), a 2:1 alumino-silicate, in which an alumina sheet is sandwiched between two silica sheets. MMT has smectic characteristics i.e., its liquid crystal nature allows the oriented planes of the structure to slide over one another. This property enables extensive interlayer expansion or swelling, because of the structure depicted in Fig. 1. The introduction of MMT enhances the performance of polymer composites, because the exfoliation of clay crystalline bundles (tactoids) offers an increased interfacial area between clay platelets and the polymer matrix, while resulting in more effective residual platelet structures due to their higher aspect ratio (width/thickness) [3-4].

The structure exposed above indicates the difference of nanocomposites with conventional composites. The latter usually require a reasonably high content (>10%) of the inorganic fillers to impart the desired mechanical properties: this might though create problems of interfacial compatibility between matrix and filler and affect processability. In contrast, nanocomposites show enhanced thermomechanical properties even with a small amount of layered silicate (<5%) [5-6]. This is referred to as the "nano effect": in practice, a synergic action occurs between the introduction of layered silicates on the deformation of polymer chains, due to the similar scale of the two components [7]. In sectors, such as packaging, the enhanced mechanical properties of nanocomposites can be effectively coupled with other features e.g., decreased gas permeability, and more marked hydrophobic behavior, furthermore allowing the introduction of biologically active ingredients e.g., to slow down degradation [8].

Generally clays are hydrophilic in nature. Therefore, in order to make them compatible with organic polymers, the surface of the clay minerals needs to be modified for higher organophilicity prior to their use as fillers. A number of possible modifiers have been used for this purpose e.g., organic cations from salts, such as ammonium or phosphonium ions, the latter presenting a higher thermal stability than the former [9-10]. Another possibility is the modification with sodium salts of fatty acids [11].

The obtained materials for prospected use as the fillers of polymers are referred as to as organo-montmorillonites (OMMT). Modification causes the expansion of the interlayer space and thereby increases by a non-negligible amount (normally more than 2 nm) the distance between planes of atoms (d spacing). This enables an easier diffusion of polymer or its precursor into the interlayer space. Fig. 2 represents the schematic representation of the organic modification of clay.
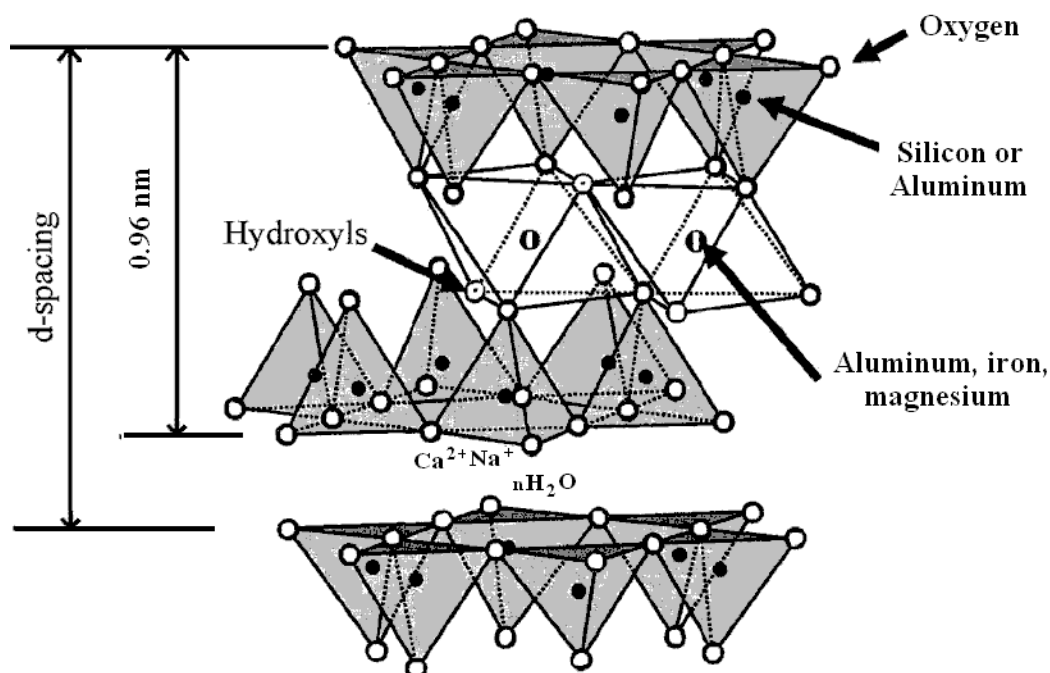
**Fig. 1. Structure of montmorillonite**

Depending on the nature of the components, processing condition and strength of the interfacial interactions between polymer and layered silicates (modified or unmodified), from the filling of polymer with clay either conventional composites or nanocomposites (intercalated or exfoliated) can be formed, as shown in Fig. 3. In intercalated nanocomposites, the clay layers retain the well ordered multi structure of alternating polymeric and clay layers with a d spacing in the region of 2–3 nm [12]. On the other hand, in exfoliated nanocomposites, the individual clay layers are well separated and randomly distributed in the continuous polymer matrix with a d spacing of more than 5 nm [13]. The intercalation and exfoliation of the clay layers in the polymer matrix can be identified through wide angle X-ray diffraction (WAXD) and Transmission Electron Microscopy (TEM).

## 2. GENERAL CONSIDERATIONS ON NANOCLAY-FILLED COMPOSITES

The initial idea of producing nanoclay-filled composites is to provide enhanced mechanical and impact properties, hardness and resistance to abrasion with respect to the bare matrix. In general terms, the effect of NC on composite strength, due to the structural rearrangement that it produces in the material, may be much more significant than the amount introduced, which normally does not exceed a few percent of the total composite weight. This occurs through the modification of the fracture modes produced by exfoliation, which results in nucleating or enhancing the localized crack tip stress fields, a procedure especially effective when nanoclay mixing is optimized [14]. Other properties that are also worth considering are the thermal ones. In particular, the coefficient of thermal expansion is markedly reduced by the introduction of OMMT [15], while the glass transition temperature of the polymer matrix is also increased [16]. Other than the amount of nanoclay introduced, also the orientation and the mutual distance of the nanoclay layers play a role in the variation of thermomechanical properties, due to the likeliness of the exfoliating effect.

Different types of nanoclays are available, in particular, the series of Nanomer, Cloisite, Nanofil, then bentonite, sepiolite, etc., which are in principle used for the modification of the polymer matrix. However, in a number of cases the nanoclay-filled matrix is used to include reinforcements as the most diffuse ones, namely E-glass and carbon, but also Kevlar and basalt. This offers a number of additional possibilities, for example in glass/epoxy composites, the addition of OMMT (Nanomer 1.30E) reduced

water absorption in the composite by offering a more complex tortuosity path [17]. In the case of carbon-based reinforcements, the addition of multiwalled carbon nanotubes (MWCNT) alongside MMT led to an enhanced resistance to flammability and oxidation of the epoxy resin [18]. As for basalt fibers, the insertion of MMT proved suitable to extend its field of application, since particles of different dimensions are able to more effectively coat basalt fibers [19]. More recently also natural (lignocellulosic) fibers have been proposed as the reinforcement of nanoclay-filled composites.

In most cases, traditional (oil-based) epoxy matrices are used for the production of nanoclay composites [20]: also polyamides have been experimented, especially for biomedical applications [21], or polyolefins, such as polypropylene, on which an accent on the modification of the rheological properties, hence molding characteristics, has also been placed [22]. In the cases in which lignocellulosic fibers are introduced in the composite, to provide an

improved fiber-matrix interface, polyolefins have been modified by maleic anhydride (MA) grafting (g) of the polymer [23]. Other than thermomechanical properties, also other potential properties are offered by using natural fibers: e.g., for kenaf/epoxy laminates, where MMT is a competitor against oil palm bunch short fibers [24]. Also, very recently, the need for barrier properties to be conferred upon biocomposites, also for packaging applications, suggested the use of MMT also in poly (lactic acid) (PLA)-aloe vera fiber composites [25].

## 3. STUDIES ON MECHANICAL PROPERTIES

Concentrating on mechanical properties, the introduction of nanoclay in composites in small amounts and thoroughly and uniformly mixed e.g., by sonication, offers to the composite a higher stiffness over the pure resin. This occurs especially due to the possibility to have an effective intercalation of the resin between the
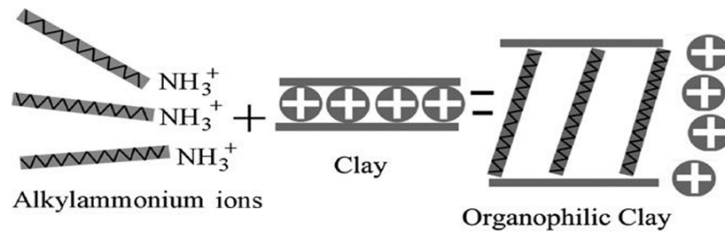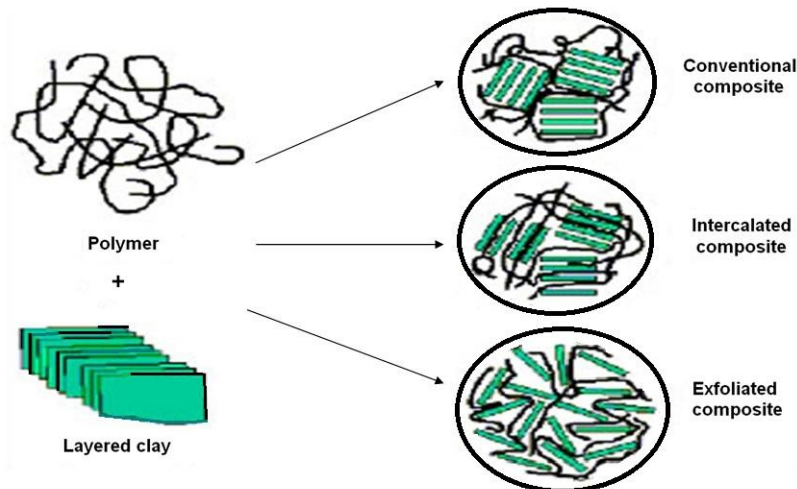


**Fig. 2. Organic modification of clay**



**Fig. 3 Types of polymer nanoclay composites**

nanoclay resins with occasional areas of exfoliation, a process that requires though a longer post-cure process than for the pure resins with no nanoclay [26]. In particular, the effect is very significant in the case of organophilic treatment of the resin, which results in an increase of the d spacing between the layers. This is the case for example by modifying untreated Cloisite Na$^+$ using a 1 wt.% solution of 3-aminopropyltriethoxysilane, in which d spacing was increased by 55% [27].

Dealing with fiber-matrix composites, the limitation of the maximum amount of MMT and OMMT that can be introduced not to result in a decrease of mechanical properties, especially strength, becomes more stringent. In particular, in the case of glass/epoxy composites it was demonstrated that the organophilic treatment can worsen the decrease of mechanical properties observed for amounts of nanoclay exceeding 6 wt.%, though a larger amount of OMMT, such as 10 wt.%, can assist instead in not reducing the glass transition temperature [28]. Conversely, by optimizing the fabrication method of epoxy-nanoclay composites, using hot melt processing assisted by autoclave, substantial advantage both in flexural strength and in toughness was obtained also by the introduction of very small amount of MMT like 2 wt. % in carbon/epoxy nanocomposites [29]. The application of carbon nanotubes (CNT) allowed even further reduction of MMT down to 1 wt. %, allowing substantial increase of Vickers hardness (36.4%) and impact strength (110%) over the pure matrix [30]. This was ascribed to the in-situ growth of CNT directly on clay, which was leading to a controlled exfoliation of nanoclay in the composites [31].

On the other side, an important present trend, also in nanoclay-filled composites, is trying to apply bio-based matrices to replace oil-based ones, also in the form of blends between the two types of polymer. The use of bio-matrices is convenient for the introduction of natural fibers, a possibility though explored also with conventional thermosetting matrices, such as in coir/unsaturated polyester composites with 3% MMT [32]. The application of OMMT (Cloisite 30B) to hemp fibre composites, with a matrix constituted by a blend of epoxy and epoxidized soybean oil compensated for the loss of stiffness due to the introduction of hemp: the level of toughness was maintained by an optimization of the respective contents of OMMT and bio-based resin [33]. As exposed above, other matrices than thermosetting are more adapted for the introduction of natural fibers and these proved also suitable for the successful filling with MMT. Some examples are bamboo fibers in maleated polypropylene (MAPP), using a clay masterbatch with high density polyethylene (HDPE) [34], polypropylene (PP)/pineapple leaf fiber (PALF) reinforced nanocomposites, using Cloisite 20A [35] and a typical by-product on food industry, namely bagasse from sugarcane, in PP [36]. Other attempts concerned the application of OMMT or sepiolite into extracted lignin/Arboform composites, therefore avoiding at all the use of conventional polymers [37]. Also polylactic acid (PLA)/flax fiber added with mandelic acid, benzylic acid, dicumyl peroxide (DCP) or zein and filled with an amount of 2.5 wt. % of OMMT (Nanomer) offered a substantial benefit, increasing up to several times the storage modulus [38]. In other studies, also the influence of different treatments over the properties of natural fiber/clay nanocomposites was investigated. In particular, jute/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) composites were added with up to 4% wt. of K10 MMT, showing a beneficial effect on moisture absorption, dynamic mechanical and flexural properties, though depending on the type of surface treatment of jute fibers [39].

In the following subsections, Tables 1-4 offer data about tensile, flexural, impact and compression strength, respectively, emphasizing in particular the maximum improvement in strength obtained in each study by the addition of nanoclay with respect to the benchmark offered by the composite without nanoclay. The studies are reported in the Tables being ordered according to their matrix, starting from epoxy, as the most typically used, then reporting the studies with other oil-based non renewable matrices, such as polypropylene (PP) and polyethylene and finally including the studies involving the use of natural fibers and/or bio-based matrices.

## 3.1 Tensile

The studies aimed at tensile properties evaluation of nano-clay filled composites, reported in Table 1, appear to be in a larger number than those dedicated to the investigation of the effect of the other loading modes. One of the main objectives is to assess up to which amount of nanoclay the tensile properties increase over the ones of the pure matrix or of the composite. In this respect, improvement of nanoclay distribution in the composite plays an essential role, giving the difficulty of obtaining a completely exfoliated nanocomposites structure,

but rather exploiting the clustering effect of the particles in the matrix, which result in an interlocking effect, able to stop or deflect crack propagation [40]. Another significant factor to investigate on mechanical properties of nanoclay-filled composites, and specifically on tensile ones, is the effect of treatment of MMT, such as with silane, which proved effective for nanoclay particles to obtain a sounder interface with the matrix. Silane treatment can be also applied in the form of grafting with the matrix polymer, which enabled the possible exploration of other matrices for nanoclay-filled composites, such as poly[styrene–(ethylene-co-butylene)–styrene] (SEBS) [41]. Tensile properties assessment is crucial for the experimentation of other matrices not necessarily thermoplastic, as demonstrated by recent studies on the application of polyphenylene sulfide (PPS) [42]. In general terms, to provide an adaptable structure, mixed of intercalated and exfoliated sections, implies also supplying possible assets e.g., for enhanced barrier properties. For the above purpose, also hybrids with "green" matrices, such as carboxymethylcellulose (CMC) filled with oil palm empty bunch fibers have been proposed [43].

In addition, in composites tensile tests can also be considered propaedeutic to the possibility to explore fatigue studies: this has been done e.g., on basalt fiber composites, where residual tensile testing post-fatigue was also evaluated, as well as the resistance in seawater environment was elucidated [44]. A recent study investigated, after obtaining tensile data, the fatigue resistance of nanoclay-filled composites for the introduction of MMT in view of their application in other matrices, namely poly(ethylene-co-vinyl acetate) (EVA), therefore prepared by pre-swelling [45]. On more traditional matrices, such as epoxy, fatigue testing proved effective to clarify the influence of size, aspect ratio and shear stiffness in prospective service of nanocomposites [46].

Some considerations can be drawn about the data reported in Table 1, which suggest that in most cases, in the best conditions, which are those shown in the Table, an improvement of tensile strength can be obtained by the addition of nanoclay to the neat matrix, or in presence of carbon, glass or basalt fibers. In contrast, critical situations with decrease of tensile strength are indicated in some cases by the introduction of lignocellulosic materials, such as hemp [33] and Kraft lignin [58]. For comparison, data from a

study such as [56], is also reported, where clay (and not nanoclay) was introduced in a polypropylene/pine cone fibre composite, which equally brought to obtaining a lower tensile strength. A substantial improvement of tensile strength by introducing 3% nanoclay was obtained, though on a limited number of samples, in jute/polyester composites, and with not reporting any structural considerations [52]. An even larger improvement in tensile strength of up to 31%, was obtained instead by the introduction of 3% nanoclay in a composite with 30 wt. % of pineapple leaf fibers (PALF) in a maleated polypropylene matrix. This promising result was attributed to strong interaction between nanoclay, fiber, and matrix polymer, revealed by the increase of the crystallization temperature, measured by differential scanning calorimetry (DSC) [35]. As a matter of fact, the effective coupling of PALF with MMT in polypropylene matrices make these fibers becoming of interest to industries such as the automotive sector, inasmuch specific reviews for their use in that field exist already [61].

## 3.2 Flexural

In Table 2, the indications reported over flexural strength suggest, as in the case of tensile loading, an interest on a large number of fibers, including carbon, glass and some lignocellulosic fibers (among which hemp, pineapple and jute) and mainly the use of OMMT. An improvement due to the introduction of NC, in the case of flexural strength, has almost invariably been obtained, wherever the optimization of the amount of NC has been pursued. In particular, flexural strength appears to increase also in the case of natural fiber composites, for example for pineapple leaf fibers (PALF) composites with 50 wt.% fibers, tensile and flexural properties increased with an introduction of up to 2 wt.% amine-modified MMT, after which the performance declines [62].

Dealing with more traditional and consolidated materials such as fiberglass, the application of MMT has been also suggested to improve other properties of the composite, such as flame retardancy. In these cases, also the introduction of low amounts of MMT resulted in a lower flexural strength, such as e.g., in [63], where commercial calcium sulfate fibers were used, and in [64], where a combination with magnesium oxide was selected.

**Table 1. Highest tensile strength (TS) obtained (MPa) in the single studies with nanoclay (NC)**

| Matrix | Fibers/fillers (wt.%) | NC (wt.%) | TS with NC (MPa) | TS without NC (MPa) | Ref. |
|---|---|---|---|---|---|
| Epoxy (DGEBA) | - | 3% Cloisite30B | 41 | 63 | [15] |
| Epoxy (YD115) | - | 10% silane modified MMT | 42 | 72 | [27] |
| Epoxy | 58% glass | 1% OMMT | 390 | 373 | [28] |
| Epoxy (E51) | 5% nanosilica | 5% OMMT | 56 | 61 [47] | [47] |
| Epoxy | 1% treated zirconia | 1% Cloisite30B | 27.5 | 35 | [48] |
| Epoxy (Araldite GY250) | | 1% Cloisite93A | 62 | 51 | [49] |
| Epoxy (100)/polyester (10) | | 5% purified OMMT | 85.8 | 59.1 | [50] |
| Polyester | 22% hemp | 1.5% Cloisite30B | 24 | 29.5 | [33] |
| Polyester | 50% glass | 2% OMMT | 144 | 118 | [51] |
| Polyester | 25% jute | 3% Garamite | 40.7 | 31.3 | [52] |
| PA6 | 30% basalt | 1% Nanofil919 | 123.7 | 109.2 | [53] |
| Aramid | -. | 6% MMT K-10 | 51.85 | 35.61 | [54] |
| PP | 67% carbon | 2% Nanomer I.30E | 2720 | 2485 | [55] |
| PP | 25% pine cone fiber | 5% clay | 24 | 26.5 | [56] |
| HDPE | 40% wheat straw flour | 2% Cloisite15A | 23 | 18 | [57] |
| MA-g-HDPE | - | 7% clay masterbatch | 22.74 | 21.19 | [34] |
| MA-g-HDPE | 28.5% bamboo | 1.7% clay masterbatch | 28.62 | 24.94 | [34] |
| MA-g-PE | 15% Kraft | 11% Cloisite93A | 25 | 31 | [58] |
| MA-g-PP | 30% pineapple | 3% Cloisite20A | 45.14 | 25.97 | [35] |
| MA (4%)-g-PP | 30% bagasse | 3% CloisiteNa$^+$ | 43.95 | 38.42 | [36] |
| PA-6+PP-g-MA | - | 4% Cloisite30B | 60 | 47 | [59] |
| PPS | - | 0.5% Bz-MMT | 123.8 | 76.5 | [42] |
| PLA | 30% flax | 2.5% Nanomer | 21.2 | 18.4 | [38] |
| MFC | - | 7.5% Hydrophilic bentonite | 102 | 87 | [60] |

*MFC=Microfibrillated cellulose; MA-g=Maleic anhydride grafted; PA=Polyamide; PP=Polypropylene; PE=Polyethylene; PLA=Poly(lactic acid); PPS=Polyphenylene Sulfide; Bz= 1,3-dihexadecyl-3H-benzimidazolium bromide; DGEBA=DiGlycidyl Ether of Bisphenol A*

**Table 2. Highest flexural strength (FS) obtained (MPa) in the single studies with nanoclay**

| Matrix | Fibers/fillers (wt.% [1]) | NC (wt.%) | FS with NC (MPa) | FS without NC (MPa) | Ref. |
|---|---|---|---|---|---|
| Epoxy | 40% vol. glass | 1% OMMT | 390 | 372 | [28] |
| Epoxy | 60% carbon | 2% Nanomer I.30E | 1220 | 890 | [29] |
| Epoxy | 70% carbon | 2% Nanomer I.28E | 498 | 380 | [65] |
| Epoxy | Ca. 75% glass | 2% NC | 1033.4 | 915 | [66] |
| Epoxy | - | 3% OMMT | 131 | 117.5 | [67] |
| Epoxy | 35% carbon | 3% Nanomer I.30P | 720 | 660 | [68] |
| Epoxy (Araldite GY 250) | | 1% Cloisite 93A | 78.5 | 64 | [49] |
| Epoxy/polyester (100/10) | | 5% OMMT | 153.8 | 102.6 | [50] |
| Epoxy/Soybean oil | 25% calcium sulfate | 10% Cloisite30B | 195 | No data | [51] |
| Polyester | 75% glass + 8% MgO | 0.2% MMT | 220 | 285 | [64] |
| Polyester | 50% glass | 2% Silane treated | 208 | 174 | [43] |
| MA-g-PP | 30% pineapple | 3% Cloisite20A | 65.01 | 38.51 | [35] |
| Lignin | Arboform | 5% Nanomer I30E | 37 | 35 | [29] |
| PHBV | 30% jute | 4% MMT-K10 | 40.87 | 33.88 | [39] |
| PA-6+PP-g-MA | - | 6% Cloisite30B | 88 | 37 | [63] |
| MFC | - | 2.5% Hydrophilic bentonite | 120 | 125 | [60] |
| Cement | 2.5% hemp | 1% Cloisite 30B | 8.84 | 6.88 | [69] |

*PHBV = poly (3-hydroxybutyrate-co-3-hydroxyvalerate)*

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[1] *Unless stated otherwise*

**Table 3. Highest impact strength (IS) obtained (kJ/m$^2$) in the single studies with nanoclay**

| Matrix | Fibers/fillers (wt.%) | NC (wt.%) | IS with NC (kJ/m$^2$) | IS without NC (kJ/m$^2$) | Ref. |
|---|---|---|---|---|---|
| Epoxy | - | 1% Polymerized MMT | 42.6 | 19.9 | [30] |
| Epoxy | 5% nanosilica | 5% OMMT | 5.1 | No data | [48] |
| Epoxy (cured at 120°C) | - | 5% OMMT | 5.77 | 4.72 | [67] |
| Epoxy/polyester (100/10) | | 5% OMMT | 10.87 | 9.28 | [50] |
| Polyester | 40% coir | 3% Garamite | 17.94 | No data | [32] |
| Polyester/soybean oil | 21% hemp | 1.5% Cloisite30B | 3 | 2.6 | [33] |
| Polyester | 33% coir- 17% glass | 2% Alkali treated NC | 13.8 | 8.4 | [51] |
| Polyester | 50% glass | 2% Alkali treated NC | 15.9 | 14.7 | [51] |
| PA6 | Basalt | 1% Nanofil919 | 352 | 303 | [53] |
| HDPE | 40% wheat straw | 2% Cloisite15A | 2.35 | 2.63 | [57] |
| MA-g-HDPE | 29% bamboo | 1.7% NC masterbatch | 3.44 | 3.90 | [34] |
| MA-g-PP | 30% pineapple | 2% Cloisite20A | 2.27 | 1.49 | [35] |
| MA (4%)-g-PP | 30% bagasse | 1% CloisiteNa$^+$ | 110 | 117 | [36] |
| PA-6+PP-g-MA | - | 2% Cloisite30B | 9.23 | 11.61 | [59] |
| Cement | 2.5% hemp | 1% Cloisite30B | 2.45 | 1.99 | [69] |
| Phenolic | Aramid/Rockwool/ Graphite | 2.25% | 5 | No data | [73] |

**Table 4. Highest compression strength (CS) obtained (MPa) in the single studies with nanoclay**

| Matrix | Fibers/fillers (wt.%) | NC (wt.%) | CS with NC(MPa) | CS without NC (MPa) | Ref. |
|---|---|---|---|---|---|
| Epoxy/vinylester | - | 5% Nanomer I.30E | 108 | 105 | [26] |
| Epoxy | 75% glass | 2% MMT | 493 | 414 | [49] |
| Epoxy (Epikote828) | | 5% Nanomer I.28 | 231.26 | 211.47 | [75] |
| Epoxy (ML-506) | 50% basalt | 5% silane mod. MMT | 780 | 590 | [76] |
| Epoxy | - | 1% Na-MMT | 129.22 | 89.02 | [77] |
| Polyester | 33% coir | 3% Nanoclay | 39 | No data | [32] |
| Low carbon fly ash | | 2% Cloisite 30B | 45.9 | 37.2 | [78] |

## 3.3 Impact

Charpy or Izod (ASTM D256) impact tests appear fundamental in the case of the introduction of MMT, since nanoclay particles are supposed to modify the velocity and orientation of crack growth, possibly deflecting it, hence delaying fracture. Toughness is an easy and fast measurement, yet it is also dependant on the distribution of the filler, a factor that is particularly critical when a very limited amount of it is usually inserted, such as it is the case for nanoclay. The measurement of toughness in composites is sufficiently accurate only in the case that an effective interface between the particles and the matrix is obtained. The use of other matrices and reinforcements than the usual ones for composites may complicate this issue, so that also cases of decrease of impact strength are reported e.g., with bamboo fibers [34] or with bagasse [36]. As an example, in [70], the use of nano-keratin from chicken feathers is also proposed as a matrix for MMT and/or cellulose nanocrystals (CNC): here, the increase in strength of MMT would be compensated by the higher elongation allowed by CNC. In practice, these tests for nanocomposites were revealed to be particularly of interest in situations for example of application of innovative polymer blends as the matrix, with the idea e.g., to lead to an improved control of the exfoliation/intercalation behavior of MMT, with blending of epoxy with hydroxyl-terminated polybutadiene (HTPB) [71]. As in loading cases illustrated in the above sections, the investigation of particular questions, for instance in [72] the success of injection molding of a thermoplastic blend (polypropylene/thermoplastic vulcanizate) filled with MMT, make impact tests particularly suitable for an initial investigation of the modifications into crack arrest characteristics with respect to the usual thermosetting matrices.

## 3.4 Compression

Finally, the attention over compression strength of MMT nanocomposites has been limited so far, so that a specific trend is difficult to be indicated, although here again the improvement appears substantial in the few cases presented in Table 4. An obvious indication of this relative lack of interest is that until very recently the mixed use of polymers and concrete as the matrix, in which nanoclay could play a role, has been seldom investigated [74]. It is noteworthy though that compression testing of nanoclay composites has also concerned studies where also natural fibers, in the specific case coir, have been used as matrix reinforcement, a trend that is likely to increase more recently as the consequence of the more general re-use of agro-waste in composites.

## 4. CONCLUSION

The use of nanoclay (NC), normally montmorillonite (MMT), often modified to make it more adapted to organic molecules (organophilic) (OMMT), in composites is gradually expanding. This application can take place either with only polymer (or rarely cement) matrix, or in combination with other fibers, more traditional ones, such as carbon, glass or basalt, or more innovative ones, such as hemp, coir, flax, jute. The introduction of MMT is often linked to the improvement of mechanical properties and wear resistance of the composite, together with the modification of its thermal properties (e.g., glass transition temperature of the resin). These changes in behavior depend in turn mainly on the exfoliated/intercalated balance of the nanoclay filler introduced. This review indicates that for the four properties investigated (tensile, flexural, impact and compression strength) a wide range of solutions and of resistance is possibly offered, also due to the large sensitivity of these properties to the introduction of small amounts of nanoclay. In most cases, a substantial improvement in strength was obtained, at least with the addition of an optimized amount of NC: problems have been evidenced with some natural fibers and whenever other properties are also aimed at, such as flame resistance by the introduction of other ceramic filler, which may hinder the increase of mechanical strength. The number of studies is likely to grow significantly in the near future, for the increasing availability and technological maturity of a larger number of polymers and fibers, also natural ones coming as secondary raw materials.

## COMPETING INTERESTS

Authors have declared that no competing interests exist

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