

## Elastomer nanocomposites: Preparation

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### ABSTRACT

This article is a brief review of some existing studies on a new family of composites. Elastomer nanocomposites are a combination of a rubbery matrix and reinforcing fillers (silicates) that have at least one dimension in the nanometer range. The emphasis is given on the importance of modifying the silicates in organosilicates (organoclays) that are able to produce intercalated, exfoliated or intermediate nanocomposites. This transformation can be done with cationic surfactants like primary, secondary, tertiary or quaternary alkylammonium or alkylphosphonium cations. The review presents the techniques used, in general, for the preparation of polymer nanocomposites, like *in-situ* polymerization, solution, latex and melt mixing. The last two techniques are preferred in the case of elastomer nanocomposites, due to the fact that many elastomers are obtained in a latex form and the melt mixing is a common phase in the rubber technology.

**KEYWORDS:** nanocomposites, organoclays, elastomers, preparation

### INTRODUCTION

An environmentally friendly way of incorporating fillers into polymers to obtain new polymer composites is under development. A composite is a combination of two or more different materials prepared with the aim of developing a product having the best properties of both.

The introduction of inorganic nanoparticles into organic polymers has resulted in polymer nanocomposites exhibiting multi functional, high performance characteristics beyond what traditional filled polymers possess [1].

During the past 20 years, polymer-clay nanocomposites consisting of inorganic nanolayers of montmorillonite (MMT) or other clays and organic polymers have attracted a great deal of attention in material science [2, 3]. Generally layered silicate clays are particularly good candidates for the reinforcement of polymers owing to their high surface area, swelling capabilities and exceptionally stable oxide network. Because of their nanometer size features, nanocomposites possess unique properties not shared by conventional microcomposites and offer new research and industrial interest. Nanocomposites represent one area of nanoscale research that has led to marketable products.

Their advantages are:

- light weight
- low cost due to the low amount of fillers necessary
- improved properties compared with conventional composites such as mechanical, barrier, flame retardation, better thermal and dimensional stability [4].

### Nanofillers and their role in elastomers

Rubber compounding implies selecting ingredients able to lead to a processable mixture, meets the necessary requirements and can be competitive from the point of view of the price [5]. The use of fillers in rubber is almost as old as the use of

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rubber itself. The Amazon Indians and in the Spanish times were known to use black powder in the rubber latex probably to improve light ageing [6].

The reinforcement of rubber with carbon black was discovered in 1904 by More, Mathews and others. They were investigating the effects of numerous ingredients on physical properties. On average about 35-40 parts of carbon black are used for every 100 parts of rubber. The addition of this ingredient can affect virtually all phases of a rubber factory's operation as well as all the performance characteristics of the end product [7]. Rubber vulcanizates reinforced with layered silicates have emerged nowadays as a dynamic class of polymer nanocomposites.

Improvements in the physical properties are directly related to particle size, with the smaller particulate fillers imparting greater reinforcement to the rubber compound. Particle shape and particle size distribution have also significant effects in the reinforcement of rubber. A particulate with a high aspect ratio, such as kaolin clay, talc or precipitated silica provides greater reinforced composites and have great potential for new material applications because they often exhibit improved matrix properties [8].

One of the most important potential advantages of layered silicate polymer nanocomposites is strong reinforcement at low filler content. An extremely large surface contact combined with high aspect ratio is created by the exfoliation and homogeneous dispersion of individual silicate platelets in the elastomer matrix [9].

Nanocomposites are two phase materials based on a polymer matrix and dispersed mineral particulates that belong to the family of 2:1 phyllosilicates. Their crystal structure consists of an aluminum or magnesium hydroxide octahedral sheet sandwiched between two silicon oxide tetrahedral sheets. The layer thickness is around 1 nm and their lateral dimensions can vary from nanometers to a few microns and even larger depending on particular silicate [10, 11].

At present, nanocomposites based on polymer matrices and organo-layered silicates like MMT, hectorite, saponite, etc represent an interesting opportunity for the design of these new materials.

So far MMT is the most used silicate; it is the main component of volcanic ash [12, 13].

Two specific characteristics of layered silicates are useful for the production of nanocomposites. The first one is based on the possibility of these high aspect ratio layers to be individually dispersed, and the second one is the possibility to change their surface chemistry through ion exchange reactions with organic or mineral cations [14, 15].

It is known that a low amount of modified clay dispersed in the elastomer matrix can lead to very high surface areas of interactions. According to the strength of such interfacial interactions, following elastomer - clay composites can be obtained [16]:

- Conventional composites based on micron size fillers like carbon black,

- Intercalated nanocomposites obtained by insertion of elastomer macromolecules between unmodified clay layers. The clay particles are dispersed in an ordered lamellar structure with larger gallery height via insertion of macromolecular chains into galleries. The insertion of macromolecules into the layered silicate structure occurs in a regular fashion regardless of organically modified clay. As the forces that hold stacks together are relatively weak, the intercalation of polymer molecules between the layers is easy [17].

- Exfoliated nanocomposites. The individual layers of the nanoclay are totally delaminated and dispersed in a continuous polymer matrix. In an exfoliated nanocomposite the individual silicate layers are separated in a continuous polymer matrix by an average distance that depends on the organic modified layered silicate (OMLS) loading. Usually the OMLS content of an exfoliated nanocomposite is much lower than that of intercalated nanocomposites [18].

- Intermediate nanocomposites. These are partially intercalated and partially exfoliated.

Natural silicates have strong interaction between the layers due to negative charges and hydrogen bonding in their crystal structures. The basal space of pristine silicate is about 1 nm, which is smaller than the radius of gyration of common polymers.

This might be an obstacle for polymers to penetrate into or delaminate between the silicate layers. So, most hydrophobic polymers are limited in penetrating into layer region of hydrophilic silicates. The preparation of polymer-silicate nanocomposites is based mainly on organically modified layered silicates [19].

The strong polar nature of silicates like MMT renders it ineffective to the sorption of nonpolar polymers. To provide them an organophilic character, the hydration cations need to be exchanged. This can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary and quaternary alkylammonium (typically with chain length longer than eight carbon atoms) or alkylphosphonium cation [20]. They lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, resulting in a larger interlayer spacing [21, 22]. This is very important because minerals have neither good interaction with organic polymers to achieve dispersion nor adequate adhesion [23]. Organophilic modification improves the compatibilization between the surface of the clay and the hydrophobic polymer matrix and thus the polymers penetrate more easily into the galleries. Stacking of the layers leads to a regular Van der Waals gap between the layers called the interlayer or gallery. The clay monolayers must be uniformly dispersed (exfoliated) in the matrix as opposed to being aggregated as tactoids or simply intercalated. In the case of exfoliated monoclays the improvements of the properties are evident.

In addition to the effect of size on particle properties, the small size of the fillers leads to an exceptionally large interfacial area in the composites. The interface polymer-filler controls the degree of interaction between the polymer and filler and thus controls the nanocomposites properties. Layered silicates dispersed at a nanosized level are reported to provide effective reinforcement to both plastomers and elastomers [17].

Another approach consists in the introduction of polar functional groups such as a maleic anhydride [24] or stearic acid [25].

In the case of using organic cations, organoclays (organosilicates) are produced. Organoclays represent a group of aluminosilicate minerals that

have had their naturally occurring inorganic cations replaced by organic cations [26]. Most common minerals of the smectite group are used as the base clay for exchange; however other minerals like illite, muscovite, clinoptilolite, kaolinite and vermiculite can be used [27].

By exchanging the metal cations with long alkylammonium ions, the clay surfaces become hydrophobic and the interlayer spacing become hydrophobic and larger, a fact which facilitates the intercalation of polymer chains into the gallery between the clay layers.

The complete dispersion of clay monolayers in a polymeric matrix optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks. High aspect ratio monolayers provide properties that are not possible for microcomposites.

Depending on the charge density of clay and the onium ion surfactant, different arrangements of the onium ions are possible. The longer the surfactant chain length and the higher the charge density of the clay, the further apart the clay layers will be forced. Depending on the charge density of the clay, the onium ions may lie parallel to the clay surface as a monolayer, a lateral bilayer, a pseudo-trimolecular layer or an inclined paraffin structure [28].

When the hydrated cations are ion-exchanged with organic cations it usually results in a larger interlayer spacing. The cationic head group of the alkylammonium molecule preferentially resides at the layer surface [10, 11]. Strong interactions between the polymer and the layered silicate lead to both organic and inorganic phases being dispersed at the nanometer level.

In spite of tremendous research activities in the field of polymer nanocomposites during last two decades, elastomeric nanocomposites are still in a stage of infancy as far as their application is concerned. The major challenge in this regard is the replacement of conventional fillers used in bulk amounts (sometimes above 30wt %) by small amounts (less than 10wt %) of nanofillers [29].

Vulcanized NR/layered silicate (MMT) nanocomposites prepared by melt blending with different contents of organoclay up to 20% were investigated [30].

Improvements in the physical properties are directly related to particulate size, with the smaller particulate fillers imparting greater reinforcement to the rubber compound. Like in the case of plastomers, particle shape and particle size distribution have also significant effects in the reinforcement of rubber. A particulate with a high aspect ratio, such as kaolin clay, talk or precipitated silica provides greater reinforcement than a more spherical product [31]. Due to their mineral nature the nanoparticles exhibit physical absorption with the elastomer matrix. So, in a particular interphase, the interaction clay-elastomer is weaker than in the compound with carbon black, and then the mobility of the macromolecules is higher [32]. The incorporation of organoclay reduces the vulcanization time of some rubbers like the NR due to the amine groups present in the modified clay [17].

### Preparation of elastomer nanocomposites

Three different types of polymer layered silicates nanocomposites are thermodynamically achievable: intercalated, flocculated and exfoliated nanocomposites. Flocculated ones are conceptually close to the intercalated; however stacked and intercalated silicate layers some time are flocculated due to the hydroxilated edge-edge intercalation of the silicate layers.

To produce intercalated and exfoliated nanocomposites many techniques have been tried such as:

- intercalation in a suitable monomer and subsequent *in situ* polymerization that leads to exfoliation,
- intercalation of polymer from solution and exfoliation; latex compounding in the case of elastomers [33].
- melt blending intercalation and exfoliation [4, 15, 23].

As most of the rubbers are available in solid (dry) and latex forms, melt and latex intercalations are considered to be industrially feasible techniques for preparing rubber nanocomposites. Melt blending is more preferred because it doesn't imply the use of a solvent [4, 34].

Using transmission electron microscopy (TEM) for studying some systems like EPDM/clay

composites was established the coexistence of intercalated and exfoliated clay layers with an average layer thickness in the nanometer range within EPDM matrix [35].

### *In situ*-polymerization technique

Although interlamellar polymerization techniques using modified layered silicates have long been known, the field of PLS (polymer/layered silicate) nanocomposites gained momentum due to the report of Nylon 6/MMT nanocomposites from the Toyota research group, where very small amounts of layered silicate loadings resulted in important improvements in thermal and mechanical properties [21].

In the *in situ*-polymerization technique the monomer is used directly as a solubilising agent for the swelling of the layered silicate. Subsequent polymerization takes place after combining the silicate layers and monomer thus allowing formation of macromolecules between the intercalated sheets.

The polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or catalyst fixed through action exchange inside the interlayer before the monomer swelling step. The chain growth in clay galleries triggers the clay exfoliation and the nanocomposites formation. Polymerization can take place by ring opening, controlled radical, cationic or living anionic. The nanocomposites made by this technique can have defects due to the fact that during polymerization steric hindrances made by the filler may occur [34].

Sonochemistry was also used as a special way to initiate polymerization for producing polymer nanocomposites [35].

### Solution technique

In solution dispersion technique a preformed polymer solution (dry rubber dissolved in a suitable solvent) is mixed with the organically modified clay. This is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate is swellable. The layered silicate is first swollen in a solvent, such as water, chloroform or toluene. When the polymer and layered silicate solutions are mixed, the polymer chain intercalates and displaces the solvent within the interlayer

of the silicate. Upon removal of the solvent, an intercalated polymer/clay nanocomposite is obtained [22]. The removing of the solvent is realized by evaporation or by polymer precipitation.

Using a 1-4 polybutadiene (PB) elastomer solution an organo-MMT (in amount of 0, 3, 6, 9, 12 and 15 mass% related to the elastomer) dispersed in a solvent oil was added and the mixture was stirred at 60°C. After solvent evaporation, vulcanization additives were added in a two-roll mill [36].

In a research [37] Na<sup>+</sup>MMT was dispersed homogeneously in hot water and a solution of hexadecyl ammonium chloride salt was added to the hot dispersion of MMT under vigorous stirring to the formation of a white precipitate. This one was filtered and washed with hot water to make it chloride free. The precipitate of 16Me-MMT (hexadecylammonium-MMT) was vacuum dried, ground and sieved. EPDM clay composites having different weight percentages of 16Me-MMT were prepared by a solution blending technique. Hydrophobic organoclay dispersion was added to the solution of EPDM elastomer in toluene. The cross-linking was realized with dicumyl peroxide and the solvent was extracted under reduced pressure. Elastomer layered organophilic clay with polyepichlorohydrine was also prepared by solution-cast technique [38].

The drawbacks of *in-situ* polymerization and solution technique are the requirement of suitable monomer/solvent or polymer/solvent pairs, the high cost associated with the solvents, their disposal, their environment impact, and the co-intercalation of solvent.

### Latex technique

Most of the rubbers including natural rubber (NR) and SBR are available in a latex form. Elastomer nanocomposites were obtained by coagulating the SBR latex with an aqueous suspension of clay. The dispersion of 4% bentonite in water was mixed with the SBR latex. The mixture was coagulated with dilute hydrochloric acid, washed to a pH about 7 and dried [39]. A similar procedure was used with styrene-vinyl pyridine-butadiene latex and a dispersion of 2% clay in water [40].

Aqueous suspension of Na<sup>+</sup>cloisite with aqueous suspension of Na<sup>+</sup>MMT clay and rubber (NR or SBR) latex were mixed. After that, aqueous

dispersion of the curing agents was added and prevulcanization of latex-clay mixture was carried out and films of nanocomposites were obtained [33]. A 2% aqueous suspension of Na<sup>+</sup>MMT and an SBR latex were mixed and coagulated in an electrolyte solution (1% calcium chloride or 2% sulphuric acid solution). The SBR-nanocomposite was obtained after washing and drying. Vulcanization was done in a two roll-mill [41].

In another SBR-clay system, nanocomposites were acquired by mixing the SBR latex with a clay/water dispersion and coagulating the mixture. The clay dispersion was studied through TEM [39].

NR-MMT and polychloropren (CR)-nanoclay composites were prepared by coagulating the rubber latex and clay aqueous suspension. TEM showed that the layers of clay were dispersed in the NR matrix at a nano level. In the case of CR similar results were obtained. Compounding with vulcanizing ingredients was realized on an open mill [42].

NR latex-clay aerogel nanocomposites were produced via freeze-drying technique. This way was used to obtain prevulcanized natural rubber [43]. It is well known that the clay minerals such as Na<sup>+</sup>MMT and Na<sup>+</sup>fluoromica exfoliate in water to form a masterbatche (clay slurry, clay dispersion). Some polymer/clay nanocomposites prepared by the clay slurry were reported [44, 45].

Na<sup>+</sup>MMT was dispersed in water with vigorous stirring at a concentration of 5%, and the aqueous suspension of silicate was achieved. To purify it, it was kept at room temperature 24 hours and the deposit was removed. The suspension and different rubber (NR, SBR, or NBR) lattices were added into a container, stirred for 20 minutes, coagulated by adding dilute sulfuric acid (2%), washed with water until its pH was about 7, and dried at 70°C for 24 h to obtain the MMT/rubber nanocomposites [46].

Recently was studied a silicone rubber nanocomposite prepared by the masterbatche technique without any solvent in which a high MW poly (dimethylsiloxane) gum was used as a polymeric matrix [47].

### Melt mixing technique

The melt mixing does not require the use of a solvent or suitable monomer. In this case the

polymer and a layered silicate mixture are heated under either batch or continuous shear (in an extruder, roll mill, Banbury mixer, etc.) above the polymer T<sub>g</sub>. Its drawback consists in the slow macromolecules transport into the interlayer space [48].

A natural rubber-organoclay nanocomposite with a fully exfoliated structure was firstly reported in 2003. It was successfully prepared via vulcanization process [17, 49].

Using the melt technique (two roll mill) NR vulcanizates were obtained with 10 phr clay (Na<sup>+</sup>bentonite) and 2.8 phr octadecylamine. Monsanto measurements have shown that the organoclay accelerates the vulcanization process and gives rise to a market increase of the torque due to the increase of the degree of cross linking [17].

During the heating process the macromolecules diffuse from the molten mixture into the silicate galleries to form either intercalated or exfoliated systems depending on the degree of penetration. This technique has become the main stream for the fabrication of PLS nanocomposites because it is simple, economical and environmentally friendly. However melt mixing seems to be only partially successful because it is not possible to use exfoliated silicates above 4 wt% [50].

Melt mixing was recently studied for different rubbers. For instance one research concentrates on NR, 1, 4-cis-PB, 1, 4-cis synthetic PI and PBS using MMT and di (hydrogenated tallow)-dimethylammonium as the organic modifier [51]. The effect of organoclay with different modifier concentration on the vulcanization behaviour and mechanical properties of polybutadiene (PB)/organoclay hybrid was investigate [52].

Using butyl rubber (BR)-clay direct melt compounding, some researchers [53] found that the intercalation occurred in the compounding process and its degree was further enhanced during vulcanization. Hydroxyl terminated polybutadiene (HTPB)/organoclay nanocomposite was formed by melt blending in a rotary-revolutionary mixer. MMT modified with octadecyl amine, dodecyl amine or octyl amine was used [34]. To improve the interaction between poly (butylene succinate) and cloisite a new and convenient method to introduce additional functional groups to the organoclay was used [24].

SBR nanocomposites with different organoclay contents (up to 15 phr) were prepared by melt compounding followed by a compression-molding step in which the elastomer was sulphur cross linked [54].

The NBR copolymer with organic clays having different intercalates was prepared with various silicate loadings in the melt mixing process [55]. During the investigation of hydrogenated NBR/organoclay melt mixing process it was found that the recovery of agglomerates from exfoliated layers is a spontaneous process and that the condition of vulcanization is not the key factor [8]. NBR was mixed in another study with cloisite in the ratio 3:1 using an internal mixer [56].

Different combinations of the modified clay and NBR were prepared as follows: the content of NBR and admixture was fixed and the organo MMT content in the prepared nanocomposites was for different experiments 0, 1.86, 4.52, 8.70, 12.45, 15.94 wt%. The mixtures were melt-compounded at room temperature by using a Brabender Plasticoder [57]. Polychloropren was melt compounded with MMT which dispersed well in the matrix [58]. Ethylene-propylene rubber-maleic anhydride (EPR-MA) pellets and an organophilic MMT intercalated with stearyl ammonium in powder form were melt compounded at 200°C using a twin-screw extruder [59].

In order to mix ethylene-propylene-diene monomer (EPDM) rubber with MMT-ODA (MMT modified with octadecylamine) a twin-screw extruder and an internal mixer were used [60].

For the preparation of EPDM- organoclay hybrid nanocomposites different types of MMT were used; the blending was done in a Banbury type internal mixer [61].

The vulcanization kinetics of fluoroelastomer/Na<sup>+</sup>MMT nanocomposites was studied using both oscillating disc rheometer and DSC under isothermal and dynamic conditions [62].

The acceleration of vulcanization process was obtained by the melting technique by using Na<sup>+</sup>MMT and two quaternary phosphonium salts (aromatic and aliphatic) [14, 49]. Other researchers [63] applying the same technique and using MMT found that there were significant differences

between natural rubber containing modified MMT or neat MMT.

The preparation with interesting results of NR/Na<sup>+</sup>MMT nanocomposites was realized in only one step by using poly (ethylene glycol) as a dispersing agent favoring the intercalation of rubber chains into the silicate galleries [64]. The rubber mixing technique and vulcanizing process were used by many researchers [17, 32, 65-68].

The effect of two chemically opposite type of nanofillers, namely MMT and layered double hydroxide (LDH) both in pristine and organically modified forms (OMMT) and (OLDH) on the properties of CR vulcanizate have been investigated [29]. The mixing of styrene-ethylene-butylene-styrene (SEBS) block copolymer, a thermoplastic elastomer, and organic modified clay with various amounts of maleated compatibilizers and clays (Cloisite) was carried out in a batch mixer at 180°C. The compatibilizers were SEBS-gMA and polypropylene (PP)-gMA [69-71]. Unlike *in situ*-polymerization, this technique enables the polymer not to lose its characteristics. Although the separation of clay layers through melt processing is difficult, there have been many tries to exfoliate and intercalate them [34].

Silicon rubber/MMT nanocomposites were successfully prepared by the melt intercalation process [72]. Other researchers have used a two steps technique. First, silanol terminated polydimethylsiloxane (MW = 18.000) was melt blended at room temperature with dimethyldialuminumammonium - exchanged MMT. Then, the silanol end groups were cross-linked with tetrathylorthosilicate in the presence of tin bis (2-ethylhexanoate) as a catalyst at room temperature [73].

## CONCLUSIONS

Organically modified smectite clays can be effective reinforcements in the preparation of elastomer-clay nanocomposites. By inserting long chain surfactants based on alkylammonium or alkylphosphonium cations into hydrophilic galleries of native clay, the interlayer distance increases and the surface chemistry of the silicate is modified. The new galleries allow the intercalation of elastomer macromolecules and the formation of

intercalated or exfoliated nanocomposites. This also implies a strong interaction between the filler and the elastomer macromolecules. The nanolayered silicate not only exerts a market reinforcing effect but also favors the vulcanization process.

The important increase of many physical, mechanical properties and the low amount of clay will boost the future use of different elastomers and create new applications of rubber-clay nanocomposites.

Further research will furnish valuable insight into the mechanisms of reinforcement and new technique of nanocomposites design.

## ABBREVIATIONS

BR	– butyl rubber
EPDM	– ethylene-propylene-diene rubber
EPR-MA	– ethylene-propylene rubber - maleic anhydride
HTPB	– hydroxyl terminated polybutadiene
LDH	– layered double hydroxide
MA	– maleic anhydride
MMT	– montmorillonite
MMT - ODA	– MMT modified with octadecylamine
NBR	– acrylonitrile - butadiene rubber
NR	– nitrile rubber
OLDH	– organic layered double hydroxide
OMLS	– organic modified layered silicate
PB	– polybutadiene
PI	– polyisoprene
PLS	– polymer layered silicate
PP gMA	– polypropylene grafted maleic anhydride
SBR	– styrene - butadiene rubber
SEBS	– styrene-ethylene-butylene-styrene block copolymer
TEM	– transmission electron microscopy
16Me-MMT	– hexadecylammonium-MMT
gMA	– grafted maleic anhydride

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