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Rubber Clay Nanocomposites

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1. Introduction

RCN Nomenclature and classification of clays are first summarized, highlighting the most important clay features that affect their behaviour as fillers for rubbers. The modification of clays with organophilic compensating cations, to promote their compatibilization with the polymer matrix, is then presented. The processing methods for the preparation of RCN is then discussed and the main aspects of RCN are reviewed, namely: rheology, vulcanization, barrier and mechanical properties. Finally, commercial applications of RCN are presented.

A large scientific and patent literature is available on RCN and it was taken into consideration for the preparation of this Chapter. As the RCN applications are treated as well, press releases and news available on web sites were considered and commercial products were examined. Patents, when cited, are regarded just as publications, without considering if they were already granted or if, viceversa, they are still patent applications. Literature reporting on polymer clay nanocomposites (PCN) is available [1-13] and it has to be considered, to fully understand structure and properties of RCN. Reviews are also available, dealing specifically with rubbers [14-21].

2. Clays

2.1. Nomenclature and classification

The Joint Nomenclature Committee of the AIPEA (Association Internationale pour l'Etude des Argiles) and the CMS (Clay Minerals Society) say that a clay is a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and hardens when dried or fired. Hence, the definition of clay refers essentially to the macroscopic clay properties. Precisely determined crystallographic structures should be named as clay minerals [22].

Clays are layered: this is their most important feature. They are inorganic compounds made by stacked layers, whose atoms are joined together by ionic-covalent bonds, that are bound to each other in the perpendicular direction through weaker forces. This implies that layers can be separated from each other by applying a minor amount of energy, whereas remarkable energy is required to break the layers.

Clays are a sub-family belonging to the larger family of layered oxides (or oxyhydroxides). They are not only silicates, as some of them do not contain any silicon atom, though those applied for the preparation of polymer nanocomposites are indeed essentially silicates.

Clays can be classified according to the electrical charge of the layer, as summarized in Table 1. Clays have either (i) neutral layers or (ii) negatively charged layers or (iii) positively charged layers. In the last two cases, the layer charge is exactly compensated by an equal amount of opposite charges located in the interlayer space. Clays with negatively charged layers or positively charged layers are respectively called cationic clays and anionic clays.

Type of layers	Type of clay	Main features
neutral layers	pyrophyllite, talc, kaolinite	<i>neutral clays</i> layers joined together by van der Waals interactions and/or hydrogen bonds
negatively charged layers	phyllosilicates: e.g. bentonites (main component: montmorillonite)	<i>cationic clays</i> the negative layer charge is exactly compensated by compensating cations are located in the interlayer space.
positively charged layers	hydrotalcite (HT). layered double hydroxides (HT-like family)	<i>anionic clays</i> the positive layer charge is exactly compensated by compensating anions located in the interlayer space

Table 1. Classification of clays as a function of the electrical charge of the layer

2.2. Organization and structure of clays

Clays give rise to a multiscale organization. Examining the upper level of said organization, clays particles of micrometric size form millimetric-size agglomerates. In a polymer matrix, the dispersion of these agglomerates is one of most important feature of the polymer nanocomposite. Figure 1 reports the structure of a montmorillonite (Mt) (Figure 1a), the most applied clay for the preparation of polymer nanocomposites, thanks to its large availability, low cost and high surface area. Moreover, purified Mt, with less than 1% of crystalline silica, is considered safe and is handled as a standard powder, as its platy nanoparticles, with only one dimension at the nanoscale, appear to have little chance to cross biological barriers [23].

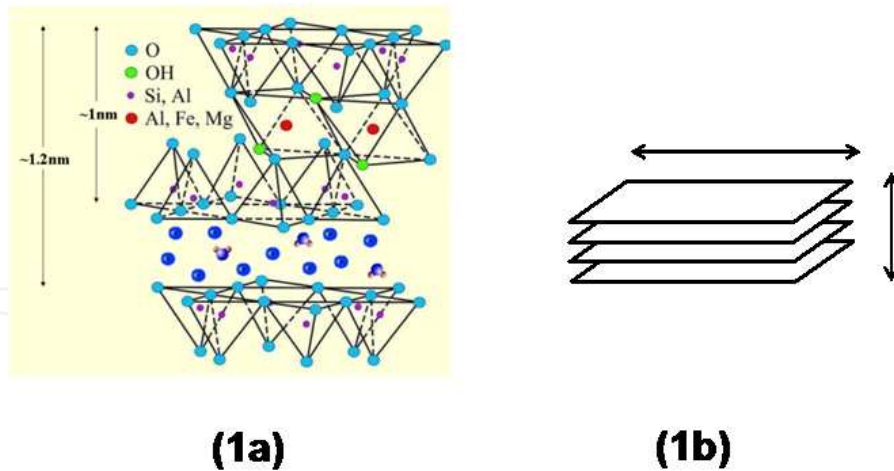


Figure 1. Structure of montmorillonite (Figure 1a) and a scheme (Figure 1b) to highlight the significant difference in length with respect to thickness of the layers

By examining a clay such as Mt at the lower level of its organization, it can be seen that a single clay layer is characterized by lateral dimensions from 100 to 1000 nm and by a thickness of about 1 nanometer. Mt is a TOT type clay mineral, with two tetrahedral (T) sheets linked to both sides to a central octahedral (O) sheet. These sandwiches are held together by weak interforces and alkaline and alkaline-earth cations are located in the interlayer space. Each silicate layer is terminated on its faces by oxygen atoms and on its periphery by oxygen atoms and hydroxide groups. The hydrophilic nature of Mt implies that a compatibilizer has to be used in order to disperse Mt in a lipophilic matrix, such as the one of most diffused rubbers. To modify a pristine Mt with a compatibilizer, the cations located in the interlayer space are exchanged with organophilic cations, preferentially with long chain quaternary alkyl ammonium cations, an organoclays (OC) are formed [24]. OC are discussed in the next paragraph. The high cationic exchange capacity (CEC) of Mt further pushes its use in polymer nanocomposites.

The term nanocomposites was many times used in previous lines. In fact, nanocomposites are defined as composite materials characterized by the presence of dispersed particles whose size is in the “nanoscale”, defined as “having one or more dimensions of the order of 100 nm or less” [25]. Mt can be considered as a nanomaterial and, as it will be discussed later on, as a nanofiller and its polymer composites are thus nanocomposites.

Figure 1 shows as well a scheme (Figure 1 b) that highlights the peculiar shape of the layers, that have a significant difference in length with respect to thickness. Considering Mt as a reinforcing filler, this means that Mt has a high aspect ratio. As it will be discussed in Paragraph 10, the mechanical reinforcement of a polymer matrix strongly depends on the aspect ratio of the filler, i.e. on the ratio between its longest and shortest dimensions. This ratio is often indicated as *shape factor f*. The higher is the shape factor *f* and the higher are the values obtained for the dynamic-mechanical moduli. It is worth commenting here that to have a high shape factor, the Mt layers have to be brought apart, that means Mt has to be exfoliated. The highest aspect ratio for a clay would be given by the ratio between the longest lateral dimension and the thickness of a single layer.

2.3. X-ray diffraction of clays

Clays are crystalline materials and X-Ray Diffraction (XRD) analysis is a technique largely used to assess clay features. In the Bragg model of X-rays diffraction, that indicates the plane spacing with d index and the plane orientation with three Miller indexes (h, k, ℓ), a constructive interference is obtained for X-rays scattered from adjacent planes when the angle θ , between the plane and both the incident and reflected beams, and the plane spacing is related with the X-ray wavelength λ . through the equation known as the Bragg law [26]:

$$2 d \sin \theta = n \lambda \quad (1)$$

From the values of θ angles detected in the XRD pattern, it is possible to determine clay features such as: d_{hkl} interlayer distance, D_{hkl} correlation length in a crystallographic direction, for example in the plane of the layers and in the direction orthogonal to the layers, and hence the number of stacked layers giving rise to a crystalline unit.

Figure 2 shows the XRD patterns of two pristine Mt available in the market: Cloisite® Na from Southern Clay and Dellite® HPS from Laviosa Chimica Mineraria.

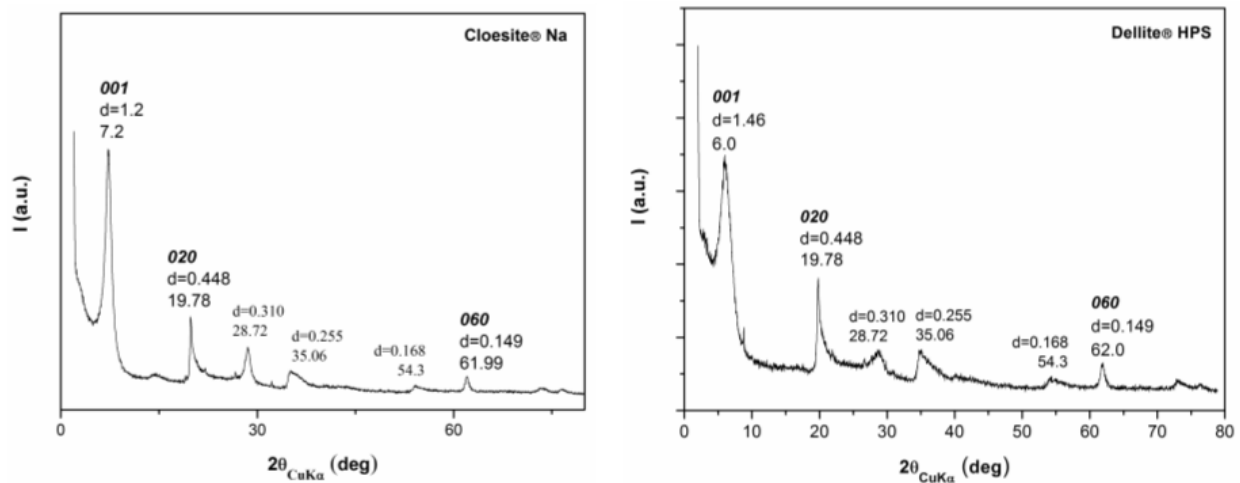


Figure 2. X-Ray diffraction patterns in the 2theta range 0-80° for pristine Mt samples: Cloisite® Na and Dellite® HPS

The d_{001} interlayer distance was determined to be about 1.20 and 1.46 nm for Cloisite® Na and Dellite® HPS, respectively. As mentioned above, from XRD data it is also possible to calculate the D_{hkl} correlation length of the crystalline domain in the direction orthogonal to the structural layer, through the Scherrer equation:

$$D_{hkl} = 0.9 \lambda / \beta_{hkl} \cos \theta_{hkl} \quad (2)$$

where: λ is the wavelength of the irradiating beam (1.5419 Å, CuKα), β_{hkl} is the width at half height, and θ_{hkl} is the diffraction angle [27]. With reference to the (001) reflection and by introducing the correction factor, to be used in case β_{hkl} is lower than 1°, a D_{001} value of about 9 nm and about 4 nm was calculated for Cloisite® Na and Dellite® HPS, respectively. Taking into account that the d_{001} interlayer distances reported above, a

number of about 8 and about 4 stacked layers was calculated for Cloisite® Na and Dellite® HPS, respectively. This elaboration demonstrates that the available pristine Mt are characterized by a pretty typical interlayer distance and by a relatively low number of stacked layers.

3. Organoclays

As mentioned in the previous paragraph, OC are prepared through the exchange reaction of a pristine clay with an organophilic ion. In the case of cationic clays, such as Mt, organophilic ammonium cations are mostly used for preparing OC for polymer nanocomposites. The intercalation of ammonium cations leads to an expansion of the interlayer distance. In the XRD spectrum, (00 l) indexes refer to a crystalline order in the direction perpendicular to the structural layers: the (001) reflection is due to regularly stacked layers and higher order reflections, e.g., (002) and (003), originate from the regular arrangement of intercalants. An expansion of d interlayer spacing corresponds to a shift of (001) reflection towards lower 2θ angle values.

Figure 3 shows two types of ammonium ions largely used as Mt compensating cations and the expansion of interlayer distance that occurs as a consequence of their intercalation. The ammonium cations are: dimethyl-talloyl-dihydroxyethyl and dimethylditalloyl and the talloyl (T) group can be optionally hydrogenated (HT).

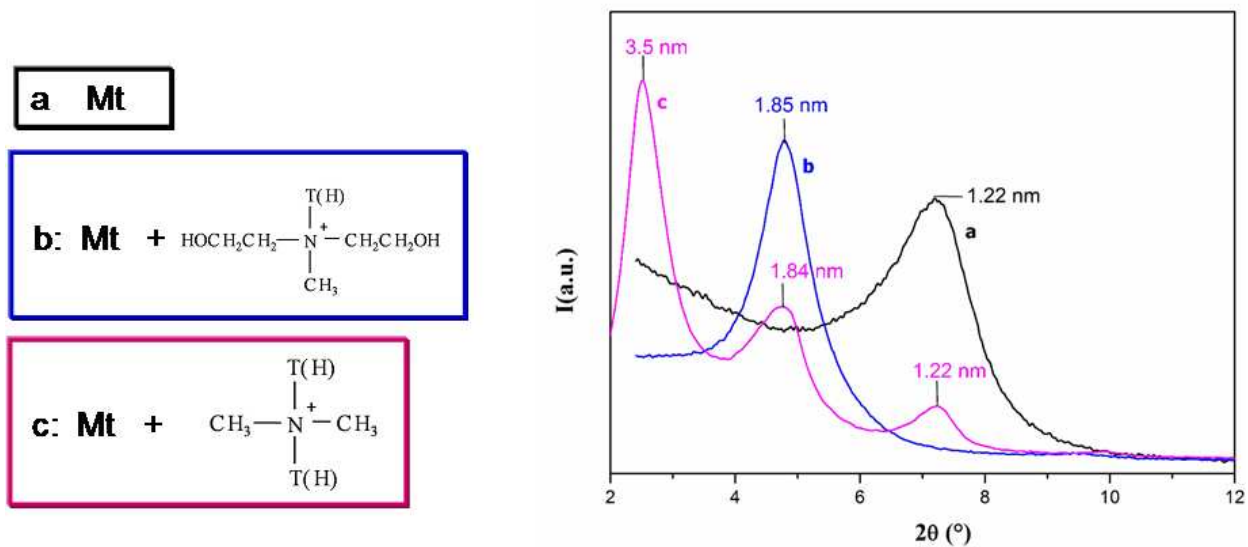


Figure 3. Expansion of Mt interlayer distance as a consequence of ammonium cations intercalation. 2(H)T and (H)T dihydroxyethyl as the ammonium cations

It is worth underlying that the same ammonium cation can give rise to different interlayer distances, as a function of its weight percent and of its bond with the inorganic layer. In fact the ammonium can be ionically bonded or can be only adsorbed on the layer surface. Table 2 reports the values of interlayer distances detected for commercially available OC with 2HT as the compensating ammonium cation.

Organoclay	% wt organic	2 θ (deg)	Hkl	d (nm)	d ₀₀₁ (nm)
Dellite® 72T	36 – 38	3.42	001	2.59	~ 2.5
		7.12	002	1.24	
Closite® 20A	38	3.57	001	2.48	~ 2.5
		7.1	002	1.25	
Closite® 15A	43	2.98	001	2.97	~ 3.0
		7.15	00?	1.24	
Dellite® 67G	45	2.50	001	3.53	~ 3.6
		4.66	002	1.89	
		7.23	003	1.22	
		9.8	004	0.90	

Table 2. Organoclays with 2HT as the compensating ammonium cation

4. Clays and organoclays used for RCN

Literature available on RCN essentially refers to cationic clays. Those used for RCN preparation were: Na-Mt, Na-bentonite, Na-fluorohectorite, rectorite, vermiculite and a fibrillar silicate such as attapulgite. Clays of the bentonite family and, among them, Mt in particular, were the most applied ones. This chapter refers thus to data based on cationic clays. As discussed in paragraphs 2 and 3, a lipophilic compensating cation promotes the compatibilization of the cationic clay with the polymer matrix. Those used for the preparation of RCN are listed as follows, indicating for the ammonium cation the substituents of the nitrogen atom: (i) cations from primary alkenylamines, (ii) ammonium cations with three methyls and one long chain alkenyl, (iii) ammonium cations with two methyls, an hydrogenated tallow and a benzyl group, (iv) ammonium cations with two methyls and two ethylhexyl or short chain alkenyl groups, (v) ammonium cations with a methyl, a tallow and polar groups such as 2-hydroxyethyl, (vi) ammonium cations with two methyls and two (hydrogenated) tallow groups.

5. Processing methods for the preparation of RCN

In this paragraph, distribution and dispersion of clays in a rubber matrix are discussed. They will be shown as depending on the chemical nature of the clay (pristine or organically modified) and on the selection of the appropriate processing technology.

Different methods have been developed for the preparation of RCN. A classification can be attempted, based on the type of clay used for the preparation of the nanocomposite: pristine or organically modified, as it is summarized in Table 3.

A pristine clay can be blended with rubber latexes (NR and E-SBR as the rubbers) through what is known as the emulsion blending. It can also be blended with the rubber in the melt state, performing the exchange reaction with an ammonium salt and using the rubber as the reaction medium.

For an organically modified clay, melt and solution blending can be applied. In the melt blending, the OC is mixed directly with the rubber in the melt state. In the solution blending, the rubber is first dissolved in a good solvent, adding the OC swollen in the same solvent.

Methods that use pristine clay and the melt blending of an OC are suitable for an industrial development, whereas the solution blending can be adopted in a laboratory. In this paragraph, the impact of mixing methods on clay distribution and dispersion is examined. An even clay dispersion is a crucial property for a PCN, as it allows to best exploit the properties of the layered filler.

Type of Clay	Ammonium cation	Type of blending	State of the rubber
pristine clay	=	emulsion blending	in a latex
pristine clay	added during blending	melt blending	in the melt state
organoclay	in the organoclay	melt blending	in the melt state
organoclay	in the organoclay	solution blending	in solution

Table 3. Processing methods of clays and organoclays with rubber

5.1. Emulsion blending from a pristine clay

Zhang first introduced the emulsion compounding: a mixture obtained from an aqueous clay suspension and a rubber latex was coagulated in an electrolyte solution. This approach was applied for blending Mt in rubbers such as NR [28, 29], SBR [28-32], NBR [28, 29, 33], XNBR [29]. Moreover, bentonite was blended with SBR [34-37] and SVBR (V = vinylpyridine) [34, 35] and rectorite was blended in SBR [38, 39]. Different electrolytes were used: triethylenetetrammonium chloride (2% wt solution) [29, 38, 39], diluted sulphuric acid solution [28, 30-32, 36], 1% calcium chloride aqueous solution [32], dilute hydrochloric acid solution [34, 35, 37], dilute dichloroacetic acid solution [33]. A scheme for blending a pristine clay with a rubber latex, as reported by Zhang, is shown in Figure 4.

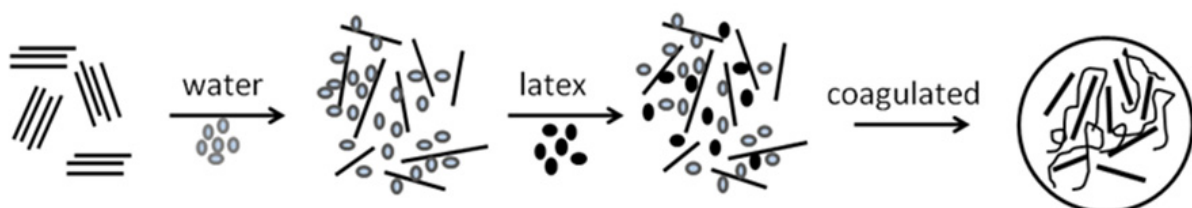


Figure 4. Emulsion blending of a pristine clay with a rubber latex

It was reported that the emulsion compounding led to nanocomposites, whereas conventional microcomposites were obtained when a pristine clay was melt blended with a rubber [28]. The Mt dispersion was commented to be excellent, up to 20 phr as concentration, and best results were obtained with diluted sulphuric acid.

Modifications of this procedure, leading to satisfactory silicate dispersion, were adopted by:

- i. adding a slurry containing further ingredients prior to coagulation, with NBR as the rubber and a sodium salt of methylene-bis-naphthalene sulphonic acid as the electrolyte.

- ii. adding further ingredients by melt mixing and avoiding the use of coagulating agents, with NR as the rubber [40]
- iii. avoiding both coagulating agents and the addition of further ingredients, with NR as the rubber [41].

Bentonite and fluorohectorite (10 phr) dispersions in NR were observed to be to some extent worse when further ingredients were added prior to coagulation and coagulating agents were not used [42, 43].

When a prevulcanized NR latex was used, a minor amount of fluorohectorite layers and stacks with an increased distance between opposite layers were observed [44]. Fluorohectorite revealed a better swelling ability than bentonite and thus gave a more exfoliated structure [45].

5.2. Melt blending from clays and organoclays

Melt blending was performed with the help of the typical processing technologies of the rubber industry, from internal mixers such as brabender® and banbury® to open mills to twin screw extruders.

The melt blending of a pristine Mt with a rubber leads to composites with undispersed agglomerates, as demonstrated for NR [46-49], IR [50], BR [51-53], E-SBR [48, 54], E-SBR/NBR blend [55], EPDM [56] as the rubbers. Analogous results were presented with fluorohectorite and attapulgite as the clays.

A satisfactory dispersion was achieved when the inorganic clays contained a lipophilic modifier [57]. With primary alkenylamines, exfoliated platelets and aggregates composed of different number of platelets were observed in the final composites, commenting that the C₁₈ alkenyl group promoted a better dispersion with respect to the shorter ones.

An even dispersion of the organoclay in the rubber matrix was achieved in any the composites, though a fully exfoliated morphology was not achieved, when an ammonium cation with either three methyls and one long chain alkenyl substituent or two methyls and two long chain substituents was used. The polar hydroxyl group as ammonium cation substituent led to some layers agglomeration. These results were independent of the type of the rubber matrix.

5.3. Solution blending from clays and organoclays

Microcomposites were prepared when a bentonite or a Mt were mixed with the help of an organic solvent with many different types of rubbers: NR [58], BR [55], SBR [55, 59-61], (H)NBR [55, 62], BIMS [63]. Big lumps of clay aggregates and agglomerates were formed. Viceversa, an even dispersion of organoclays was achieved, when a clay containing a lipophilic ammonium as compensating cation was used. As reported in paragraph 4, different types of ammonium cations were used, in many types of rubber. A rationalization is proposed in ref. [57]. To summarize, the mentioned even dispersion was achieved in NR,

BR, SBR, NBR, BIMS and EPDM with a primary alkenyl amine as the clay modifier. In NR, IR, BR, SBR, (H)NBR when ammonium cations having either two or three methyl groups and longer chain substituents were adopted as clay compensating cations. Results appeared very similar to those obtained with melt blending.

5.4. Formation of organoclays *in situ* in the rubber matrix

The preparation of the organoclay *in situ* in the rubber matrix was reported by Galimberti [57, 64-67], by adopting the melt blending approach, with all the processing technologies mentioned in paragraph 5.2. An even clay dispersion was achieved in the rubber matrix and the organoclays revealed a lower number of stacked layers. This approach was adopted for many types of rubbers: IR, NR, SBR, NBR, XIIR, EPDM.

6. Structure of RCN

In this paragraph, the overall picture of RCN structure is presented, discussing in particular the interlayer distance of clays and the type of intercalants present in the interlayer space, of low molecular mass or polymeric.

This aspect is of the utmost importance for polymer clay nanocomposites. In fact, it is largely reported [1-22] that the intercalation of polymer chains in the interlayer space is at the origin of the remarkable properties of PCN. The intercalation of polymer chains is considered not only to favour the improvement of the polymer matrix but also to promote the clay exfoliation, leading to the ultimate clay dispersion. The overall picture of RCN, that is proposed for PCN is shown in Figure 5.

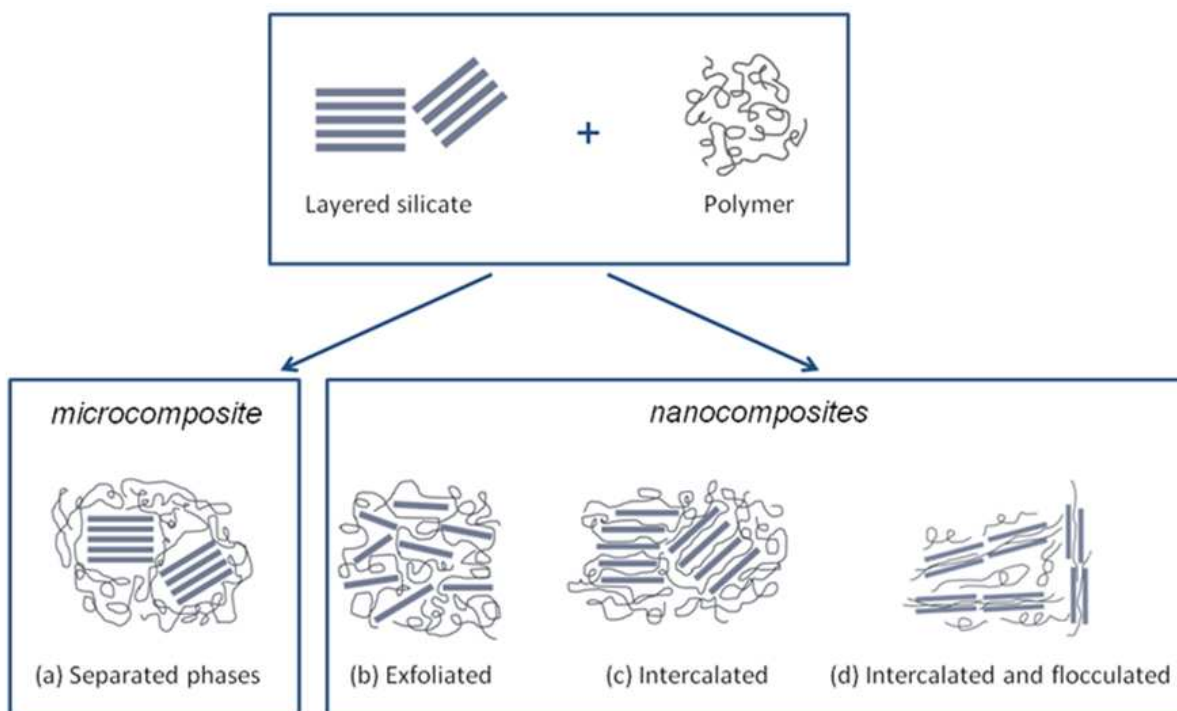


Figure 5. Overall picture of the structure of polymer (rubber) clay nanocomposites

The study of the interlayer distance is performed through XRD and TEM analysis [57]. In particular, as discussed in paragraph 3, the modification of the interlayer distance, determined from XRD patterns, is taken as the evidence of the occurring of modifications in the interlayer space. It is worth summarizing here the two mechanisms proposed in the literature to explain the occurring of clay exfoliation and the modification of the interlayer distance.

6.1. Two mechanisms for clays intercalation and exfoliation

The two mechanisms can be visualized as reported in Figure 5 and are summarized as follows.

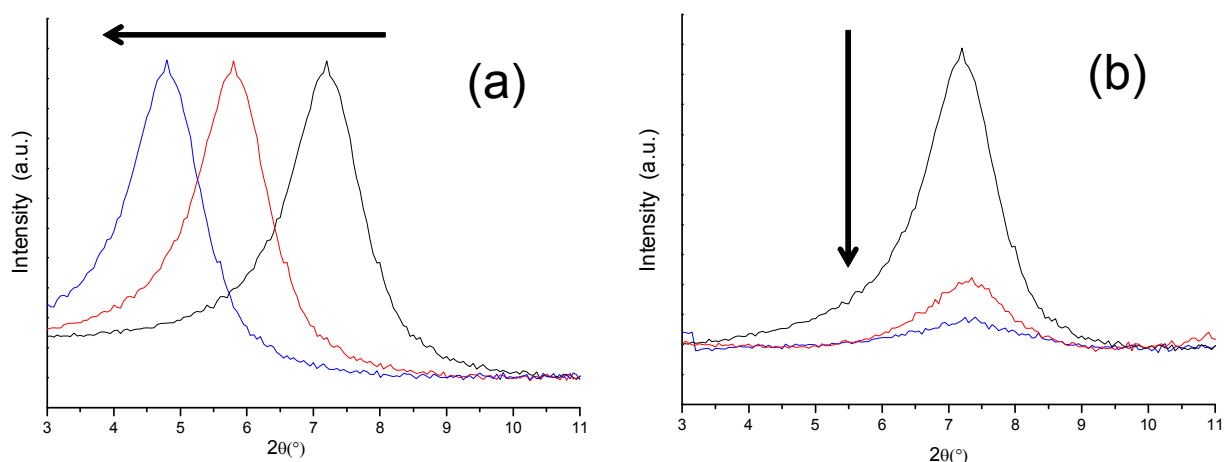


Figure 6. Schemes to visualize the two mechanisms proposed for clay intercalation and exfoliation: first mechanism (a), second mechanism (b) (see text for the explanation)

First mechanism. Polymer chains are intercalated in the interlayer space, with a consequent expansion of the interlayer distance. In Figure 6a, the position of the (00 l) reflection progressively shift towards lower values of the 2θ angle, from black to red to blue curve, as a consequence of the progressive intercalation of the polymer chains. The intercalated polymer chains are not only responsible for the expansion of the interlayer distance but also cause the separation of clay layers, promoting the ultimate exfoliation. This first mechanism, originally proposed for polystyrene as the polymer, is widely accepted in the prior art.

Second mechanism. The intercalation of polymer chains is regarded as unlikely and only low molecular mass substances are considered to be present in the interlayer space, when crystalline OC are formed. In particular, it is commented that it is hard to suppose that highly crystalline structures (as shown by the presence of several (00 l) reflections in the XRD pattern), can be generated in the presence of a polymer chain. The variation of the interlayer distance is seen as a consequence of: (i) the different arrangements of the substituents of the compensating cations, that indeed can give rise to different d_{001} values (as shown in Table 2) and/or (ii) of intercalation of guests in the interlayer space and/or (iii) of molecules absorption on clay surfaces. The clay exfoliation occurs through a progressive peeling off of the clay stacks thanks to the shear mixing. In Figure 6b, the (00 l) reflection

remains at the same 2θ value and its intensity decreases, passing from the black to the red to the black curve, as a consequence of the progressive exfoliation of the clay stacks. Authors presenting this mechanism propose the scheme reported in Figure 7, where the XRD pattern of nanocomposites in the low 2θ region (peaks are due to $(00l)$ reflections) are shown as well the mechanism hypothesized for their formation.

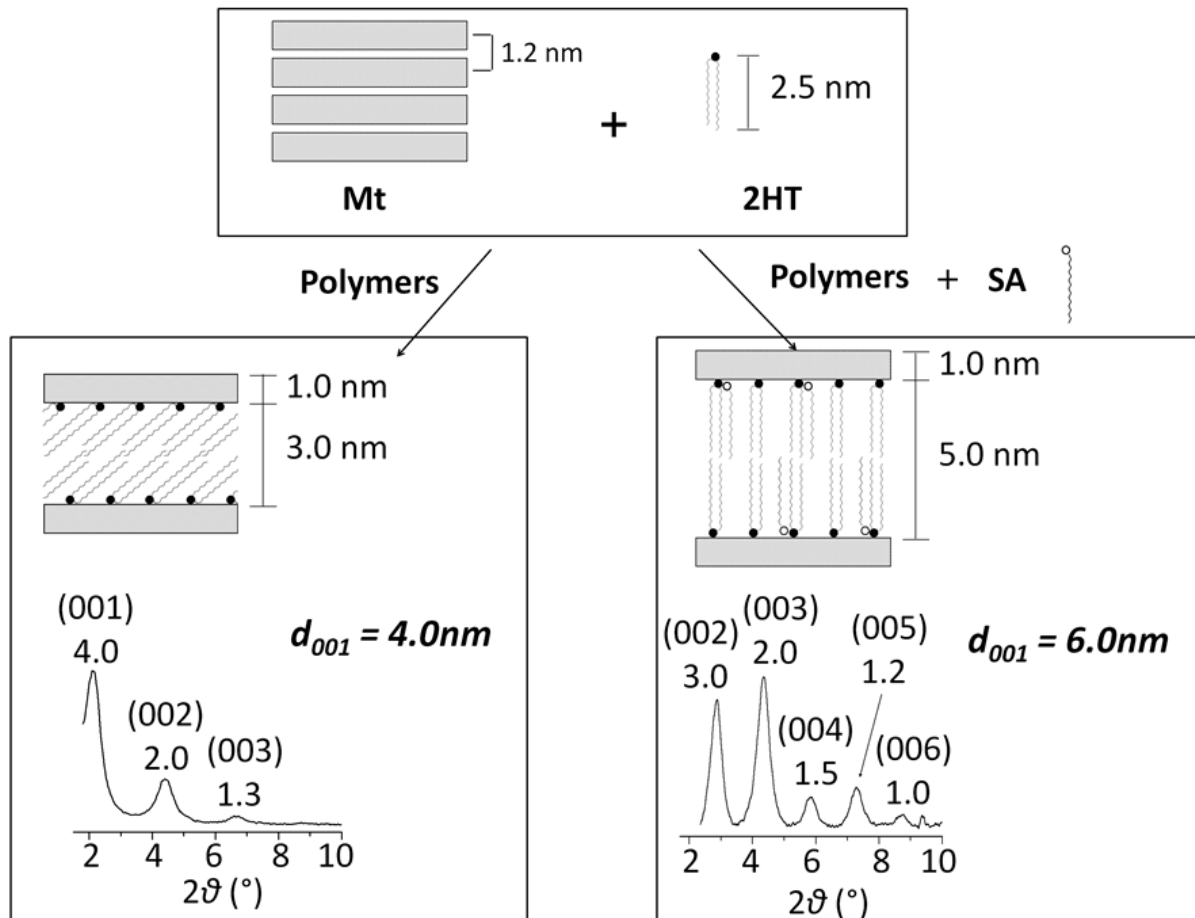


Figure 7. Schematic presentation for the formation of an organoclay by blending Na-Mt with di(hydrogenated tallow)-dimethylammonium chloride (2HT), in the absence or in the presence of stearic acid (SA) (Scheme reproduced from ref. 66)

7. Rheology of RCN

Clays compatibilized and evenly dispersed in a polymer matrix tend to build networks at low concentration. Rheological measurements, performed on RCN based on various types of rubbers, revealed the pronounced rubber-clay interaction, when measurements were taken at zero shear. The storage modulus in the low frequency region was investigated as a function of clay content and the clay percolation threshold (as wt%) was found to be about 4 (OC was Mt/methyl tallow bis-2-hydroxyethyl ammonium cation), above 5 (OC was Mt/dimethyl-dialkylammonium halide (70% C18, 26% C16 and 4% C14)) and above 7.5 (OC was Mt/ dimethyl dehydrogenated tallow quaternary ammonium chloride) for IR, EPR and EVA, respectively [68-71]. The filler networking phenomenon was observed as well in

matrices based on IR, ENR [72], SBR [73] and EPR [69]. At zero shear, the viscosity of RCN is thus higher than the one of the neat elastomer.

However, organophilic clays were shown to reduce the steady shear viscosity of RCN. Most evident results were a pronounced shear-thinning behaviour, increasing with the clay content, a higher extent of extrudate, a lower swelling and a better surface smoothness, by increasing the shear rate. These findings are of great importance, as they indicate that OC have a positive effect on the processability of rubber compounds. Data were reported for RCN based on various rubbers, such as BR [60], SBR [60], NBR [60], BIMS [74] and fluoroelastomer [75]. A compensating cation with longer alkyl chains led to a reduction of Mooney viscosity, that was not observed with a short chain substituent [76].

This behaviour of OC, that is opposite to that of traditional fillers, is attributed to the orientation, occurring at high shear rates, of clay platelets along flow direction, and to the slippage of platelets on the chains, thanks to the organophilic clay substituents. Data to demonstrate that were provided with an OC (Mt/octadecyltrimethylammonium) in BR [77] and with another OC (Mt/dimethyl hydrogenated-tallow (2-ethylhexyl) quaternary ammonium methylsulfate) in poly(epichlorohydrine) [78].

The improvement of processability brought about by OC was found to be higher when the matrix was apolar rubber such as NBR [79].

8. Vulcanization of RCN

OC promote a fast sulphur based crosslinking of unsaturated polymer chains. Moreover, they increase the delta torque value indicating a higher value of crosslinking density [80].

Many data were reported in the literature, supporting these conclusions, in rubbers such as NR (hexadecyltrimethyl ammonium, octadecyltrimethyl ammonium, tetraoctyl phosphonium, triphenyl vinylbenzyl phosphonium, octadecylamine chloridrate were used as intercalants) [81-86], SBR (Mt/octadecyltrimethylammonium) [87], (NBR (octylamine; dodecylamine and octadecylamine chloridrates were the intercalants) [76]. A reduction of the activation energy for sulphur based NR crosslinking was found by using a bentonite modified with octadecylamine chloridrate [83, 88]. OC could thus present a warning, as they could lead to premature scorching but, at the same time, they could present the chance of performing vulcanization reactions at lower temperatures.

To explain the behaviour of OC in sulphur based crosslinking, the formation of tertiary amines from the thermal degradation of ammonium cations and the enhanced mobility of sulphur accelerating anionic species were proposed [89].

9. Barrier properties of RCN

The reduction of air permeability thanks to clays dispersed in a poly(isobutene) matrix led to the first commercial application of RCN, that will be discussed in Paragraph 11.2.

9.1. The tortuous path model

Platelets with a high aspect ratio substantially reduce the diffusion of penetrating molecules in polymer matrices. The tortuous path model, represented in Figure 8, is generally accepted to explain this result.

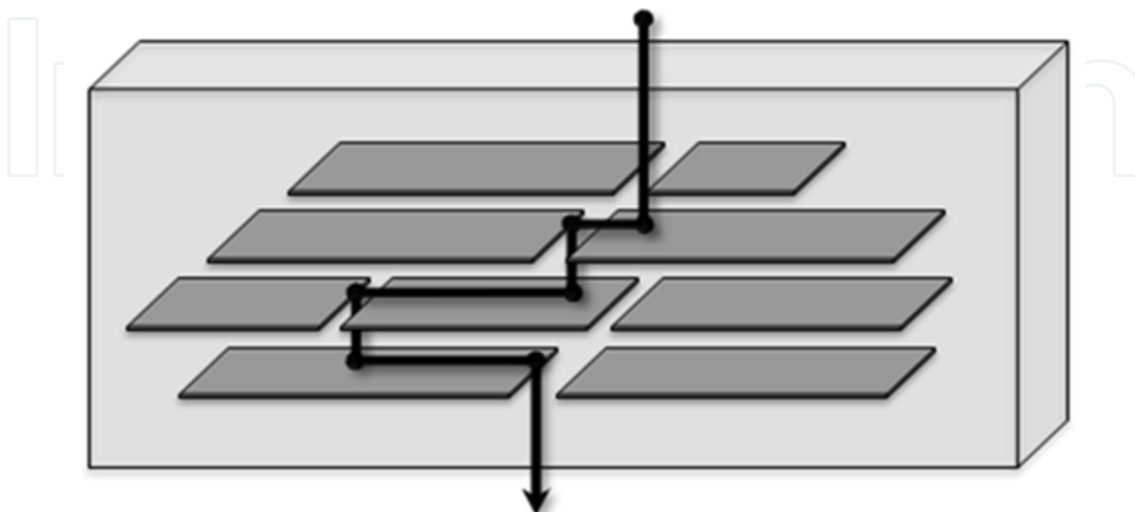


Figure 8. Tortuous path for molecules in a matrix containing platelets

Various continuum models were developed and applied to polymer clay nanocomposites, assuming in most cases a random dispersion of plates, parallel to each other and perpendicular to the direction of molecules diffusion, as summarized in refs. [90] and [91]. According to these models, reduction of permeability is enhanced by the increase of the platelet aspect ratio. These models are able to interpret the reduction of permeability in a polymer matrix, without necessarily having the presence of nano-platelets. This means that a nano-effect should not be invoked. It was commented [91] that permeating molecules have a sub-nano level and their permeation is slowed down by platelets, whatever is their size.

9.2. Improvement of barrier properties of rubber matrices thanks to the use of clays

Better barrier properties of a rubber matrix, thanks to clay addition, were demonstrated for many different rubbers. In NR as the matrix, the barrier properties were enhanced at low clay (Mt) content, preparing the nanocomposite through the emulsion blending: 1, 2 and 3 phr of clay led respectively to more than 35% and to about 45% and 50% reduction of oxygen permeability [92]. 3 phr of OC (Mt/ didodecyl methyl amine) gave a 50% reduction of the oxygen permeability and a 40% reduction of toluene absorption at 20 °C [93]. 5 and 10 phr of OC led, respectively, to about 10% and 15% reduction of the oxygen permeability, and, at 15% OC, to a 30% reduction of toluene absorption at 30°C [94]. In BR as the matrix, 5 phr OC (Mt/dimethyl ditallow-ammonium) dispersed from solution blending, led to a reduction of about 80% of water vapour permeability, whereas 10 phr OC gave about 20% reduction of toluene uptake at equilibrium [95]. In NBR as the

matrix, 1 phr of OC (Mt/dimethyl ditallow-ammonium) dispersed from solution blending brought to about 80% decrease of water vapour permeability [96]. Better barrier properties were observed by increasing the AN content of NBR: the relative nitrogen permeability was reduced by 11.5, 10.4, and 9.0% for 42NBR, 35NBR, and 26NBR (the figures indicate the wt% of AN), respectively, with 10 phr OC (Mt/dimethyl dialkyl (C14–C18) ammonium) [97].

A clay with a high aspect ratio such as rectorite was found to give better barrier than carbon black N330 [38].

10. Mechanical properties of RCN

10.1. The origin of reinforcement: nano-structured and nano-fillers

Particulate fillers are used to reinforce traditional rubber compounds: they are carbon black and silica and are made by spherical individual particles of few tenths of nanometers as the diameter, fused together to form aggregates extending up to few hundreds of nanometers. These fillers are called nano-structured as the aggregates can not be separated into individual particles by thermomechanical mixing.

Theories on the origin of reinforcement [98], developed on carbon black based compounds, led to present the modulus of a filled rubber compound as due to the sum of different contributions, as it shown in Figure 8.

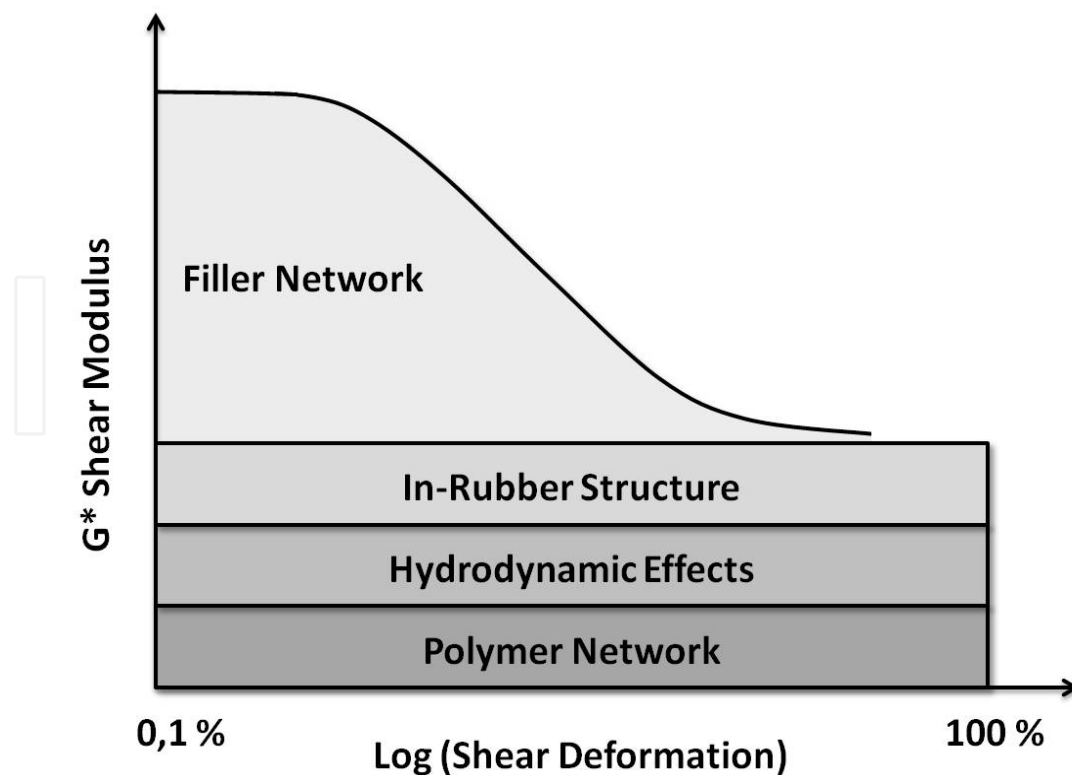


Figure 9. Contributions to the modulus of a rubber compound filled with a particulate filler

Contributions that do not depend on the strain amplitude are due to the polymer network (entanglements, physical and chemical crosslinks), hydrodynamic effects (related to the filler volume fraction and implying the strain amplification mechanism and thus the enhancement of the modulus), immobilization of rubber on filler particles (that transform a highly viscous liquid in a solid). A contribution to the modulus that strongly depends on the strain amplitude is due to the so called filler network: filler particles are joined together either directly or through polymer layers.

The Guth Equation is used to correlate the compound initial modulus with the filler volume fraction (equation 1 as follows).

$$E = E_m (1 + 0.67 f\phi + 1.62 f^2 \phi^2) \quad (3)$$

This equation holds up to a threshold of filler content, known as the percolation threshold, at which a continuous network is established in the rubber matrix and thus accounts for the sum of the three contributions commented above and shown in Figure 8 that do not depend on the strain amplitude.

In equation 1, appears the *shape factor* f , that was already commented in Paragraph 2. The *shape factor* f was introduced in the Guth model in order to account for the fact that particle aggregation (clustering) has a significant impact on stiffness at high volume fractions (higher than 0.15). These clusters are formed by the filler aggregates and the impact of the f value on the quadratic term of the Guth equation makes them much important for the total value of the modulus.

In the case of a clay, as it was shown in Figure 1b, the *shape factor* f is given by the ratio between the longest lateral side of the layer and the height of clay stacks, the highest f value being obtained in the case of a single layer. Therefore, the exfoliation of a clay not only favours a better clay dispersion but also improves the modulus of the compound. To take into account the lower contribution to the modulus of a platelet like filler, a modulus reduction factor of about 0.7 was determined [99] by fitting experimental data.

An important contribution to the reinforcement is given by the so called “in rubber structure”: fillers are able to accommodate polymer chains in the voids of their structure. This mechanism is well known in the case of nanostructured fillers such as carbon black and silica. In the case of clays, the immobilization of polymer chains would require their intercalation in the interlayer space, phenomenon that is however, as explained in paragraph 6.1, still a matter of debate.

OC give an important contribution to the polymer network. In fact, as discussed in paragraph 8, they promote a higher crosslinking density, thanks to the cation-thiolate interaction. Clay layers and aggregates could be represented as framed in a cage formed by short sulphur bonds, that prevents their slip on the polymer chains, phenomenon that occurs in uncrosslinked samples, as commented in paragraph 7.

In the same paragraph, it was commented that a low clay concentration is needed for achieving the percolation threshold in a hydrocarbon rubber matrix. This conclusion was

drawn also by determining the dependence of the Young modulus (obtained from stress-strain curves) on the OC concentration, in a SBR matrix (with Nanomer I.42E from Nanocor as OC) [100] or in an isoprene rubber matrix (OC was Mt/2HT), either synthetic [67] or naturally occurring [101]. The excess of the Young modulus was plotted versus the filler fraction [102], determining the percolation threshold, that was: 2.7 vol % in SBR [100], 2.9 vol % in IR [67] and 4 vol % in NR [101]. The excess modulus scales with a power law with an exponent between 1.8 and 2.5 above the percolation threshold, lower with respect to the one typical of carbon black (about 4). The structural difference of the filler is proposed to justify this difference. As mentioned above, the filler network is responsible for the contribution to the modulus that depends on the strain amplitude. Thanks to the easy formation of a filler network, clays promote a remarkable non linearity of the dynamic-mechanical behaviour of rubber nanocomposites, a phenomenon known as Payne effect [103]. Data that show the remarkable Payne effect of RCN, increasing with the clay content, were reported for NR [104] and IR [67] as the rubber matrices. A strong reduction of the dynamic modulus was observed also by increasing the temperature [50]. The 2-D melting of the paraffinic chains substituents of the compensating ion [105] was commented as a possible explanation [66, 101].

10.2. The improvement of rubber mechanical properties thanks to the use of clays

Many data are available in the literature to show that both pristine clays and OC bring about the improvement of the mechanical properties of a rubber matrix, preparing the nanocomposites from latex, melt and solution blending. Some examples are reported as follows.

Pristine Mt was dispersed in a NR latex, observing an increase of modulus for the obtained nanocomposite up to 30 phr of clay, in the presence of worse ultimate properties [41], as well as higher 300% stress, shore A hardness, tensile strength and tear strength, when Mt was at 20 phr level [29]. In a SBR matrix as well, tensile and tear strengths were improved by adding a pristine Mt via emulsion blending, up to 20 phr [29], without any improvement for a further addition [35].

OC were typically used at lower levels. In NR as the matrix, 5 phr of Mt modified by tetraoctyl phosphonium bromide led to a 3-fold increase of tensile strength [81] and best ultimate properties were obtained with 10 phr of OC (Mt/octadecyltrimethyl ammonium) [106]. In BR as the matrix, best mechanical properties were obtained with a Mt having dimethyl dihydrogenated tallow quaternary ammonium as the compensating cation [107], an ammonium cation largely diffused in RCN field. In a SBR matrix, mechanical properties improved up to 10 phr of OC (Mt/octadecyltrimethylamine, Nanomer I.28E) [87] (Mousa and Karger-Kocsis, 2001), decreasing for a further addition. In a nanocomposite based on maleic anhydride modified EPM (EPM-MA, with 0.42 wt% of maleic anhydride) about 5% of OC (Mt/octadecyl amine) gave a modulus three times higher than that of EPM-MA. Modulus increased and elongation at break decreased with clay content [108].

Reinforcement was obtained from OC also in rubber blends. 2 phr of OC (Mt/octadecyltrimethylamine) in an NR/ENR blend (10 phr ENR50) gave an increase of both strain and stress at break values [109] (Teh et al., 2004).

It was commented in Paragraph 7 the importance of sulphur based vulcanization to prevent the OC slip on the polymer chains. OC (Mt modified with hydrogenated tallow ammonium) was reported to promote a remarkable reinforcement also of a peroxide cured rubber matrix. However, in this case, the rubber was NBR, with acrylonitrile content as high as 50% [110]. It was also shown that higher values of tensile strength and better tear resistance were obtained, with a worse elongation at break, by increasing the AN content, with 10 phr of OC (Mt/dimethyl dialkyl (C14–C18) ammonium) [111].

10.3. Clays in a rubber matrix for lighter weight of the compound

The most important application of rubber compounds is in tires. Lighter rubber compounds are thus pursued, in the light of their remarkable impact on the environment. Direct comparisons were reported between OC and CB in promoting the mechanical reinforcement of rubber compounds.

In NR as the matrix, a comparable mechanical reinforcement was obtained with 10 phr OC (Mt/octadecylamine) and 40 phr CB, with almost twice elongation at break, a lower compression set and similar abrasion loss with OC [112]. With the same OC, a much lower heat build up was obtained with respect to 50 phr of CB [113].

In BR as the matrix, better mechanical performance was obtained with 3 phr OC (Mt/dimethyl dihydrogenated tallow quaternary ammonium) compared with 10 phr of CB [114]. In NBR as the matrix, a comparable tensile strength was obtained with either 10 phr OC or with 40 phr CB [115]. In EPM-MA, 5% of OC (Mt/octadecyl amine) gave the same reinforcement as 30 wt% CB [108].

10.4. Synergistics effects between clays and nanostructured fillers

An increasing number of studies is becoming available in the literature on RCN based on clays and a nanostructured filler such as silica and, in particular, CB. A large scale application of RCN could reasonably imply the use of hybrid filler systems, with a minor amount of OC added to a major part of a traditional filler. In SBR as the matrix, a hybrid sepiolite-silica filler system was adopted [116]. Hybrid OC/CB filler systems were used in the following matrices: SBR [117-119], brominated poly(isobutylene-co-paramethylstyrene) rubber [117], IR [50, 57, 120], NR [67, 121] NR/SBR blend [122], chlorobutyl rubber [123], ENR [124], EPDM [125] (Malas and Das, 2012). In some of these works [50, 57, 120-122], CB was used at a level typical of commercial applications (higher than 50 phr). A remarkable enhancement of material dynamic-mechanical properties was reported, thanks to the use of the hybrid filler system. The most important finding from these study was the synergism developed by the two fillers [118, 120, 121]. In particular, it was shown [126] that initial modulus values obtained with the hybrid CB-OMt filler system were much higher than

those calculated through the simple addition of the two initial moduli of composites with only CB or only OC. Figure 9, taken from ref. [127], demonstrates the synergistic effect between OC and CB. The dashed line indicates the initial modulus calculated by simply adding the initial moduli of composites with only CB and only OC, whereas points refer to experimental data taken from composites containing the hybrid filler system.

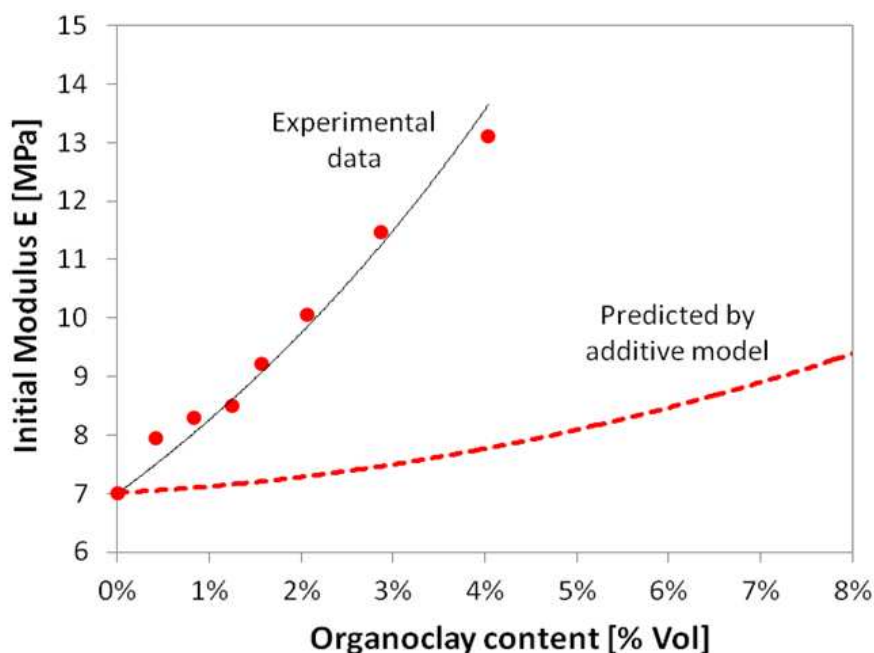


Figure 10. Initial modulus values (•) of IR based composites containing the hybrid OC/CB filler system. The dashed line refers to values predicted through the addition of initial modulus values of composites with only CB and only OC.

11. Applications of RCN

In this paragraph, applications of RCN are examined, moving from products already available on the commercial scale. The most meaningful patents were taken as the reference literature for the considered applications. RCN applications, diffused on the commercial scale, well documented and advertised, are essentially in two fields: tires and sport balls.

11.1. Applications of RCN for tyres

The most abundant application for rubbers is in tire compounds. NR is the most diffused rubber, with almost 11 million ton in 2010 [128] and SBR is the most produced synthetic rubber, with about 6 million ton. The application of both these rubbers is for about 75% in tire compounds. The world demand for tires is rising, at a pace of about 4.7 per year through 2015, achieving a number of produced tires of about 3.3 billion units. In the same period, the tire market is projected to increase, in terms of value, of about 6.5 percent annually, achieving a total value level of \$220 billion [129]. It is thus evident that the application of RCN in tire compounds can lead to a real commercial diffusion as well as to an important economic impact.

A tire can be defined as a toroidal high performance composite behaving as a flexible membrane, able to contain gases under pressure and with the following capabilities: load carrying, cushioning, road handling. Figure 9 reports the structure of a tire, with the name of constitutive parts.

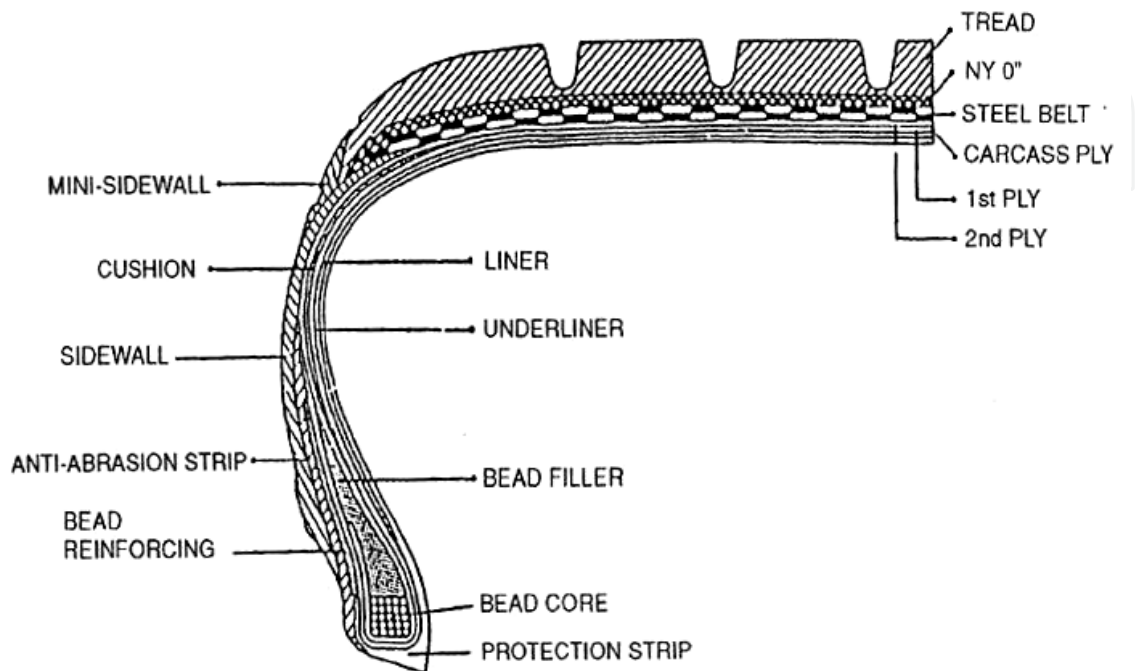


Figure 11. Structure of a tire

RCN have been so far essentially applied in three parts of a tire: tread, base (i.e. a compound immediately before the tread in contact with the road), liner. Table 4 explains the position in a tire of such compounds and clarifies their role.

RCN in tire compounds are used to achieve the following properties and performances: reduced weight, reduced energy dissipation, enhanced air retention and extension of the balance of the so called magic triangle performances for a tire tread: rolling resistance, traction, wear.

RCN in tire treads. By examining the patent literature [130-132], it appears that clays were used in tire tread compounds aiming at longer life of the compound and lower fuel consumption without negatively affecting the tread grip on the road at low temperature. Clays were used with or without an ammonium cation modifier, in the former case in the presence of a large amount of silica. Compound properties claimed in patents are: better ultimate properties, lower abrasion and an hysteresis that remains analogous at low temperature and is lower at medium – high temperature.

RCN in base compounds. OC were used in base compounds of tires commonly referred to as "HP" (High Performance) or "UHP" (Ultra high performance) tires, belonging to classes "V" or "Z", designed to experience extreme driving conditions, as they achieve maximum speeds in a range from 210 to 240 km/h and higher than 240km/h, respectively. In this type

of tires, a low thickness base compound is used to favour performances such as tread block stability, road grip, steering stability, cornering stability and ride comfort. This base compound should have high tensile and dynamic-mechanical properties. OC were reported in the patent literature to give a remarkable improvement of the compound dynamic mechanical properties [133-136] and Pirelli Tire launched in 2007 P Zero tires for the HP and UHP segments, with a base compound containing an OC. In particular, it was reported that OC was able to give a much more isotropic behavior (i.e. an equal performances in longitudinal and lateral directions), with respect to traditional reinforcing fibers, such as the aramide ones.

Tyre compound	Position in the tyre	Performances
Tread	In contact with road	Dry, wet, ice and snow traction. Stability at high speed. Abrasion resistance. Protection of compounds below.
Base (tread cushion)	Below the tread. Between tread and nylon 0°	Low hysteresis. Good adhesion. Good fatigue, tear and durability. Compatibility
Liner or innerliner Thin layer of impermeable rubber.	Under the carcass	Impermeability to air and moisture. Prevention of degradation of tire structure (due to air and moisture). Good flex fatigue, crack, long term aging resistance.

Table 4. Tyre compounds explored for RCN application

RCN in innerliner. Most research efforts were dedicated to develop OC based innerliner compounds, with the aim to exploit the barrier property provided by clay platelets, trying in particular to achieve a high clay dispersion. In order to have the best barrier, the following technical solutions were adopted: use of clays with a high aspect ratio, control of the clay organization (stacks of exfoliated layers), use of reactive rubbers to promote the clay exfoliation, use of coating layers with a high impermeability.

A kaolin [137] and a mica [138] with high aspect ratio (at least 50) were used in butyl and in butyl, butadiene and natural rubber, respectively.

Stacks of OC were used in BR [139], in BIMS [140] and in SBR [141]. With an OC content as low as 9 phr, the oxygen transmission was reduced to about one fourth [139].

The clay exfoliation was promoted either by dispersing clays in the emulsion where polymerization of monomers such as isoprene and styrene was performed [142], or by performing the exchange reaction with a cationic polymer latex [143], or by mixing the clay (in a BIMS matrix) in the presence of a tertiary amine. In this latter case, with only 3 phr of clay, a reduction of 20% permeability was detected [144].

An amine terminated oligomer (e.g. a butadiene-acrylonitrile copolymer) was used as the reactive polymer to prepare a 25/75 clay/SBR blend and the oxygen transmission was reduced to less than one half [145]. A clay was mixed with a aqueous dispersion of a diene-based elastomer, with one or more functional groups such as acid or an anhydride [146].

OC was melt blended with poly(isobutylene-co-p-alkylstyrene) and poly(isobutylene-co-isoprene) elastomers and at a concentration of 10 phr the permeability was reduced to one half [147]. OC was melt blended with an halogenated copolymer of isobutylene and p-methyl-styrene and, at an OC level of 5 phr, the air retention was improved up to 30% [148]. Poly(isobutylene-co-N,N-dimethylvinylbenzylamine) copolymer was blended with an OC and an improvement of impermeability up to 70% was reported [149].

Barrier coating mixtures were prepared by mixing an elastomer (butyl rubber) an exfoliated clay with a high aspect ratio (preferably a vermiculite) and a surfactant, adopting a polymer/clay ratio from 1:1 to 20:1 and obtaining a permeability reduction of about 25%. This technology found a large commercial success in tennis ball and it will be discussed in the following paragraph [150].

11.2. Applications of RCN for sport balls

As mentioned above, a clay based barrier coating technology was developed [151-154], and applied to sport balls, with the aim to drastically improve the pressure retention without negatively affecting properties such as the bounce, the feel and the reproducibility of performances. A relatively thin coating layer (about 10-30 micron) was deposited, made by an elastomeric nanocomposite prepared by combining aqueous dispersions of a vermiculite (having a aspect ratio up to 1000) and butyl rubber. In a laboratory study [90] (Takahashi et al., 2006) a coating layer containing vermiculite (20 - 30 wt%) in butyl rubber led to a reduction of the diffusion coefficients by two orders of magnitude and of gas permeability by 20–30 fold. This technology was developed by InMat company and Air D-Fense products were commercialized.

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