Rubber Clay Nanocomposites

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List of Abbreviations

AFM	Atomic force microscopy
APTES	(3—aminopropyl) triethoxysilane
CB	Carbon black
CEC	Cation exchange capacity
CIIR	Chlorobutyl rubber
CL	Concentrated Natural Rubber Latex
Dim-Br	o-xylylenebis (triphenylphosphoniumbromide)
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric analysis
EDX	Electron dispersive X-ray spectroscopy
EG	Expanded graphite
EPDM	Ethylene propylene diene rubber
FL	Fresh Natural Rubber Latex
FTIR	Fourier transform infrared
Hal	Hallosyte
HDTMA$^+$	Hexadecyl trimethylammonium
IIR	Isobutylene isoprene rubber
M_H	Maximum torque
M_t	Montmorillonite
NBR	Acrylonitrile butadiene rubber

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NK	Nanokaolin
NR	Natural rubber
OC	Organoclay
$ODTMA^+$	Octadecyl trimethylammonium
OMt	Organomodified montmorillonite
PAS	Positron annhilation lifetime spectroscopy
PA6	Polyamide 6
phr	per hundred of rubber
PLA	Olylactide acid
SANS	Small angle neutrón scattering
SAXS	Small Angle X-Ray Scattering
SBR	Styrene Butadiene Rubber
SEM	Scanning electron microscopy
SI	Silica
$\tan\delta$	Loss tangent
t_{c90}	Cure time
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
t_{s2}	Scorch time
WAXS	Wide Angle X-Ray Scattering
W_c	Water content
XRD	X-ray diffraction

1 Introduction

The use of nanofillers allows the development of nanocomposites with improved properties and novel applications [1–7]. The technological goal is possible due to the new compounding method that allows a particle dispersion in the nanometer scale increasing the specific surface area [8].

This chapter focuses on explaining the role that nanoclays play as exceptional reinforcing particles in rubber matrices. The complexity of the analysis comes from the fact that it is a multicomponent system, which contains, for example, curing agents, co-agents, processing aids, reinforcements and fillers, affecting the final structure of a rubber/layered silicate nanocomposite. This was likely the reason for its late development compared to thermoplastic or thermoset clay nanocomposites.

The use of nanoclay in rubber allows to improve the mechanical properties (such as tensile strength and elastic modulus) [1, 8], barrier properties [9], thermal resistance [6] and, in some applications, antimicrobial properties [10]. Examples and cases of most used rubber matrices in the industrial field are presented. The methods of clays incorporation into rubber matrices as well as the final properties reached are described.

2 Reinforcement Particles

A wide variety of ingredients are used in the rubber industry for various purposes, being the most important: reinforcement, fillers and process aids. The principal reinforcement effects are increase of strength, abrasion resistance, hardness and modulus. The extents to which these changes occur strongly depend on:

(i) particle filler size
(ii) rubber-filler interaction
(iii) filler-filler interaction
(iv) filler shape and structure
(v) filler concentration
(vi) filler dispersion in the matrix.

CB and precipitate SI, with a mean diameter of 10–30 and 30–100 nm respectively, are the conventional fillers in the rubber industry, with a content that in some compounds could reach up to 40 phr of CB. Considering compounds containing carbon black (CB) as reinforcement, it is well known the so-called *bound rubber,* which refers to a microstructure seen as a gel of reinforcement particles held together in a three-dimensional lattice by polymer molecules: the amount and morphology of the bound rubber depend on the listed variables [11]. Moreover, bound rubber type also shows a dependence on the processing conditions of the compound. Bound rubber content is measured by extracting the unbound rubber with solvent, and the result is influenced by the solvent nature and the extraction temperature.

Other nanofillers have received attention for reinforcing of rubbers like organoclay (OC), nano silica, carbon nanotubes (CNT) and nano calcium carbonate due to the high aspect ratio and surface area as compared to conventional fillers. These characteristics are important to develop high-performance materials with low nanofiller content.

2.1 Carbon Black

CB is by far the most popular filler for rubber modification. CB is elemental carbon in the form of spherical particles that coalesced into aggregates and agglomerates, which is obtained by the combustion or thermal decomposition of hydrocarbons. The degree of aggregation is denoted by the term “structure”: a low-structure may have an average of 30 particles while a high structure may have around 200 particles per aggregate. The aggregates have a tendency to cluster together to form agglomerates due to van der Waals forces. During the mixing process, polymer free radicals are formed due to the shear forces generated and such free radicals react with CB to form bound rubber as CB acts as radical acceptors [12].

About 90% of the worldwide production of CB is used in the tire industry, in which acts as reinforcing fillers to improve tear strength, modulus, and wear characteristics. Commercially, CB fillers are available with different levels of structure, particle size, chemical reactivity and pH that lead to different levels of reinforcement.

2.2 Silica

SI (silicon dioxide) consists of silicon and oxygen arranged in a tetrahedral structure of a three-dimensional lattice. The use of silica as rubber reinforcement started around 1950 as an alternative to CB, shoeing sole the first applications due to the possibility of obtaining a non-black product. The incorporation of SI in heavy-service tires started in the 70's due to the improvement of cutting and chipping resistance of the compound and, also rubber adhesion to textile and metal.

The presence of hydroxyl groups in the silanol (Si-OH) on the SI results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds. Since these intermolecular bonds are very strong, the SI particles aggregate tightly, reducing the dispersion of silica in the rubber compound.

Around 1970 started the introduction of silane coupling agents such as the bis(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) and other bifunctional silanes in order to prevent adsorption of curatives on the silica surface [13]. In these cases, the silane coupling agent reacts with the silanol on the silica surface to form a siloxane bond. The silane molecule bonded to the silica surface reacts with the rubber chain to form a crosslink between the silica and the polymer.

Silica is available as fumed SI and precipitated SI, which is obtained by coagulation of SI particles from an aqueous medium under the influence of high salt concentration or other coagulants [12, 14].

In tire treads, silica yields a lower rolling resistance at equal wear resistance and wet grip than CB [15]. Rattanasom et al. [16] analyzed the reinforcement of Natural Rubber with SI/CB hybrid filler in a total amount of 50 phr. The results reveal that the compounds with 20 and 30 phr of silica in hybrid filler exhibit the better overall mechanical properties.

2.3 Clay

Clays have been known for many decades as a non-black filler type for rubber compounds [4]. These fillers are inorganic in nature and therefore incompatible with organic polymer matrices. Thus, the reinforcing effect of these fillers was lower than that of CB.

Clays have a low price and many attractive structural features such as hydroxyl groups, Lewis acidity, exchangeable interlayer cations, differences of Si–O tetrahedral sheet and Al-OH octahedral sheets [17]. Also, layered silicate nano-fillers have already been developed: the silicate layer surfaces have been effectively modified to render them organophilic so that the organically modified nano-fillers can significantly enhance the critical performance properties of polymer–clay composites. This is possible when the silicates are dispersed in nanometer- instead of micrometre-scale.

3 Layered Silicates

Galimberti et al. [18] define layered silicates as inexpensive natural mineral fillers which promote high reinforcements on the rubber matrices thanks to their high aspect ratio. They present a very thin plate-shape with low thickness (<10 nm) and width (<2 mm) [19], which permits to incorporate a relatively low amount of the filler to obtain superior mechanical properties, thermal stability, flame retardancy and gas barrier properties.

There are many works that show significant improvements in elastic modulus, tensile strength and elongation at break [8], thermal resistance [20], reduction in water/gas permeability [21] and flammability [20] for clays in their natural an modified form. The nanocomposite structure depends on the clay mineral–polymer compatibility and on processing conditions [22].

Siririttikrai et al. [19] show that clays in their natural form are easily exfoliated in aqueous suspension, which can be convenient for certain processing conditions. Depending on the compatibility with the rubber matrix, using clays in natural or pristine form can reduce the steps and cost involved.

3.1 Structure and Physical Characteristics

Figure 1 presents a typical structure of lamellar clays. Moreover, clays can be defined depending on the organization of the silicon and oxygen atoms, as well as the arrangement of the atoms within the laminar structure. The main structure consists of building blocks of tetrahedral sheets in which silicon is surrounded by four oxygen atoms and octahedral sheets in which a metal such as aluminium is between eight oxygen atoms [23, 24].

Silicate layers present oxygen atoms and hydroxide groups, giving it a hydrophilic nature. However, most rubber compounds possess a hydrophobic structure. Galimberti et al. [25] explain that, in order to achieve a compatibilization with the rubber matrix, there must be a chemical modification in the clay surface. This

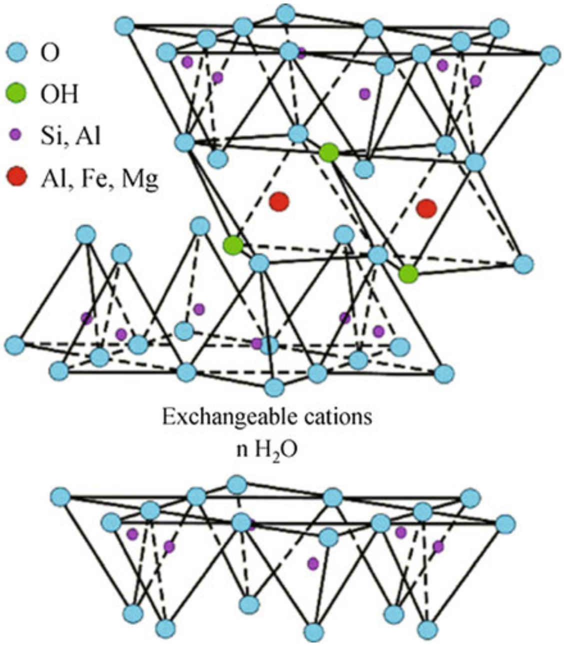

Fig. 1 General layered silicate structure [24]. Reprinted from Kievani and Edrak [24]

technique consists in an exchange reaction of alkali and alkaline earth cations, which are located inside the clay galleries with different cations, modifying the clay surface polarity and increasing the interlayer distance [25]. This process of chemical modification will be described later in the chapter. Pavlidou et al. [23] define the first structure as 1:1, in which a tetrahedral sheet is fused with an octahedral sheet, whereby the oxygen atoms are shared.

The 2:1 layered silicates consists in two-dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedra by the tip, so the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. The layer thickness is around 1 nm and the lateral dimensions may vary from 300Å to several microns, therefore, the aspect ratio of this kind of layers (ratio length/thickness) is high, having values greater than 1000 [23]. The 2:1 structure is called pyrophyllite. Furthermore, since inside the structure, there are no substitution atoms and it has only an external surface area and no internal one, the layers do not expand in water.

When the silicon in the tetrahedral sheet is substituted with aluminium, the structure is called mica. With this type of substitution, the mineral is characterized by a negative surface charge, which is balanced by cations, such as potassium. Unlike the structure of pyrophyllite, mica does not swell in water, because due to the large size of potassium, the structure collapses and the sheets are held together only by electrostatic forces [23].

Montmorillonite (Mt) presents a structure similar to that of pyrophyllite, in which the trivalent Al-cation in the octahedral layer is partially substituted by

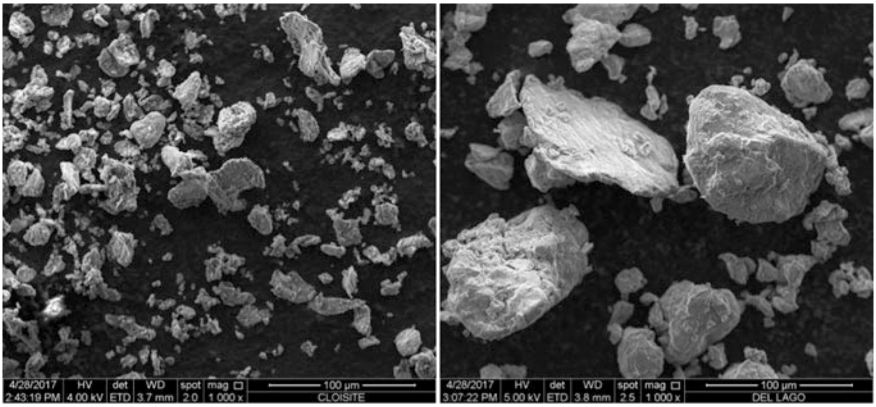

Fig. 2 SEM images of Na Mt (Left) and Raw Mt (Right)

magnesium cation. This group is called "smectites". In addition, the overall negative charge is balanced by sodium and calcium ions, which are present in a hydrated form inside the interlayer. Since the ions are not part of the tetrahedral structure, the sheets are held together by weak interacting forces, which allow the easy entry of water molecules into the clay structure [23].

As previously mentioned, depending on the type of clay different structures can be presented, which affect the size and texture of the clay. Figure 2 compares the structural differences between two types of Mts for 1000X magnification, one Na–Mt (Left) and a Raw Mt (Right). Na–Mt clay has a smaller particle size compared to the raw Mt since it undergoes a purification process to eliminate any impurities. One of the most interchangeable cations is Na^+, which is responsible for its swelling in presence of water. Moreover, the presence of Na^+ ions lets absorb a great number of water molecules resulting in the formation of a gel. If Ca^{+2} are the cations present in the interlayer, a lower amount of water molecule can be absorbed, so the clay is not able to swell. Depending on the cation presents in the interlayer, it will be determined the final application of the clay, as well as its compatibility with the rubber matrix.

3.2 Classification of Clays

The clays are classified according to the amount of silica present and the combination of tetrahedral and octahedral sites in the final structure. It can be separated into 5 main families:

(a) Kaolinite
(b) Serpentines

(c) Smectites
(d) Illites
(e) Chlorites.

Mt, hectorite and saponite belong to the smectites family and are the most commonly used clay minerals for the preparation of polymer nanocomposites [22]. Hectorite is a colloidal clay widely used in the synthetic form. Dispersed in water, Hectorite forms a colloidal suspension used in many industrial and technological applications, such as rheology modifiers in several products, like paints and cosmetics. It has a very particular anisotropy due to the nanodisc shape of the particles and to the inhomogeneity of the sheet charges [26]. The Mt presents a dioctahedral structure with predominantly octahedral substitution. On the other hand, saponite presents a trioctahedral structure with the mainly isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral sheets. This is why there are important changes in the final structure configuration; the Mt has hexagonal lamellae, while the saponite has a ribbon shape. Throughout the chapter, the discussion will focus on the use of Mt as a reinforcing, compatibilizing or property modifying agent since most of the published works use this type of clay.

- *Kaolinite*

Kaolinite is characterized by an isomorphic variation with temperature: up to 700 C, the Al^{+3} presents a tetrahedral structure (what is known as amorphous kaolin), while above this temperature has an octahedral one.

- *Montmorillonite*

It is part of the group of smectites. Their structure consists of two silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of Al or Mg hydroxide. Normally the layer thickness is around 1 nm, and the lateral dimensions may vary from 30 nm to several microns or larger. Ambre et al. [27] explain how the stacking of the clay layers leads to a van der Waals gap between the platelets called the interlayer or gallery. Also, the author described that the isomorphic substitutions within the layers generate negative charges that are counterbalanced by alkali and alkaline earth cations inside the clay galleries, and these cations are replaced by organic ones such as alkyl ammonium ions via an exchange reaction.

As it will be discussed, interlayer distance is one of the most important parameters since it defines the possibility for the polymer chains to enter inside the interlayer to effectively achieve an intercalation or exfoliation of the clay.

4 Chemical Modification of Clays

Natural clays can be well dispersed in hydrophilic polymers, such as poly (ethylene oxide) and poly(vinyl alcohol). In order to increase the compatibility with hydrophobic polymers, an ion exchange is performed with cationic-organic

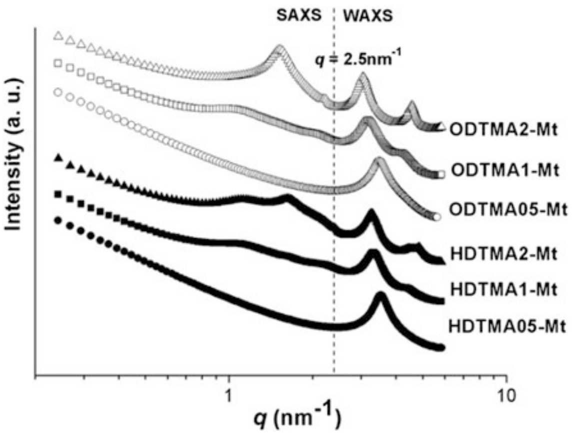

Fig. 3 Variation of the interlayer distance *q* of Mt and OMt according to the modifier concentration, determined by SAXS and WAXS. Reprinted from Bianchi et al. [28]

surfactants. Pavlidou et al. [23] referred the alkylammonium ions as the most used, but other "onium" salts can be used, such as sulfonium and phosphonium. The objective of the modification is to decrease the surface energy of the silicate and improve wetting with the polymer matrix. The long organic chains of the surfactants are tethered to the surface of the negatively charged silicate layers, promoting an increase in the interlayer gallery and therefore favouring the entrance of polymer chain between interlayer space in order to improve the mechanical properties of the nanocomposite.

During the modification process, the excess of negative charge should be considered since it is related to the ability of clay to exchange ion, this characteristic is defined as the cation-exchange capacity (CEC), expressed in meq/100 g (milliequivalents/100grams). Pavlidou et al. [23] explain how this property is highly dependent on the nature of the isomorphous substitutions in the tetrahedral and octahedral layers.

Figure 3 shows an analysis of organo modified montmorillonite (OMt) by SAXS and WAXS. In their work, Bianchi et al. characterized a Mt two with different organic modifiers: octadecyl trimethylammonium (ODTMA$^+$) and hexadecyl trimethylammonium (HDTMA$^+$) in different proportions: 0.5, 1 and 2 CEC of Mt. They obtained important changes in the final interlayer distance of the clay, which determine the final interaction with a rubber or polymeric matrix [28].

4.1 *Synthesis of Organoclays*

Due to the hydrophobic behaviour of most elastomeric polymers, raw natural clays needs to be modified in order to use them as reinforcing materials and increase the compatibility between the matrix and the nanoparticles [29]. The most common technique is by using long tallow organic ammonium cations through ion exchange of the interlayer cations. These new types of filler are commonly known as organoclays (OC).

OC preparation usually requires a two-step method, which includes a first step of purification, and a second step of the organic modification itself. Purification consists in the separation of impurities such as quartz, calcite, dolomite, talc and other clays [30]. Zhou et al. [31] described a method for purification and defibering of Chinese sepiolite. The technique consists of an acid treatment to decompose carbonated impurities and assisted by microwave-heating in order to improve the reaction kinetics with low energy consumption. Defibering aims to the de-agglomeration of sepiolite fiber bundles with the objective of obtaining nanoscale particles.

However, this two-step method has several disadvantages such as the consumption of large quantities of water and the energy spent on repetitive techniques. In order to avoid the drawbacks mentioned, Zhuang et al. [30] proposed a one-step method combining the purification and organic modification of sepiolite into a simple and more environmentally friendly procedure. The authors stated that organic surfactants can not only be used as an organic modifier but also as flocculants, therefore organo-sepiolite was easier to be separated from the dispersion.

Daitx et al. [29] described a method for the modification of Mt and halloysite (Hal) with (3- aminopropyl) triethoxysilane (APTES). Both OC were prepared by dispersion of the clay in an ethanol solution. In the case of Mt, the pH was adjusted to 3 with acetic acid for the protonation of the amino group and to promote the cationic exchange with Na^+ located in the interlayer space. APTES was added to the clay/ethanol suspension and stirred for 2 h and later filtered and washed with 96% ethanol. Lastly, the filtered cake was dried under vacuum at 70 °C for 8 h. In this work, the modification of the nanoparticles with aminosilane increased the interaction between clays minerals and the polymer due to the amino groups that can freely interact with the matrix.

5 Characterization of Clay Nanoparticles

The characterization of the clays is quite important to determine certain properties that are fundamental to be considered before being included into a rubber matrix. For example, mineralogical and thermal properties are important to determine the composition of the clay, particularly to know the nature of the clay (hydrophilic or hydrophobic nature). Some of the most used characterization methods include X-Ray diffraction (XRD), Infrared spectroscopy (IR), Inductively coupled plasma atomic emission spectroscopy (ICP-OES), thermal analysis (DTA, TGA), Specific surface area (SSA), CEC determination, microscopic techniques (TEM and SEM), gravimetric and grain size measurements [32–34]. In this chapter, we will show some techniques that can be useful to characterize any type of clay.

5.1 X-Ray Diffraction (XRD)

XRD is a very useful technique for the study of layered type nanoparticles. Furthermore, XRD is often used for the determination of the d_{001} plane corresponding to the basal space between the layered silicates which can be calculated by the Bragg's law:

$$\lambda = 2d \sin \theta$$

were λ is the wavelength of the incident wave, θ is the scattering angle and d is the distance between the atoms of a crystalline system.

Gamoudi and Srasra [33] studied the characterization of natural clays suitable for pharmaceutical and cosmetic applications by XRD analysis. Authors determined the presence of smectite in the composition by studying the characteristic peaks of the d_{001} reflection at 12.57 Å. Moreover, they also detected the presence of kaolinite by the d_{001} = 7.12 Å and d_{002} = 3.56 Å.

Successful organic modification of clay particles produces a shift of the d_{001} plane to lower angles values. This can be explained by taking into account the increase in the basal space due to the volume of long tallow organic molecules compared to the exchangeable cations. Ezquerro et al. [35] studied the modification of Mt with organic divalent phosphonium cations. Na–Mt showed a basal reflection at 7.78° and an interlayer spacing of 1.14 nm. The organic modification with Dim-Br (o-xylylenebis (triphenylphosphoniumbromide)) shifted the basal reflection to lower angles due to the intercalation of the surface between the layers of the OC. Moreover, an increase in the concentration of Dim-Br produced a shift to lower 2θ angles.

Alves et al. [36] studied the organic modification of Mt with ionic and non-ionic surfactants. They attributed the correct intercalation to a shift of the d_{001} to lower 2θ angles. Moreover, the basal space increase when surfactant amount increases and decreased after washed.

5.2 Microscopy

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can provide information about the morphology of the clay platelets. Also, energy-dispersive X-Ray spectroscopy (EDX) can be used to study the composition after the modification with organic molecules.

Ezquerro et al. [35] studied the changes in the morphology of the Mt clay platelets. They claimed that pristine Mt shows soft surfaces and platelets tend to agglomerate. While surface modification of Na^+ for a phosphorous compound generates a rougher surface and breaks the agglomeration of the lamellas. Furthermore, EDX analysis was also conducted to study the yield of the organic modification of the interlayer cation. In their studies, the Na^+ content decreases and the phosphorous content increases with the surfactant concentration.

Figure 4 presents SEM images of Mt and OMt by Bianchi et al. [28], there can be seen the morphology modifications of the Mt surface structure induced by organic modification with alkylammonium salts ($ODTMA^+$ and $HDTMA^+$), with alters the surface structure, the curvature of the plates, and the aggregate formation.

Zhuang et al. [30] studied the purification and organic modification of sepiolite by TEM analysis, which was used to detect the presence of impurities, before and after the purification, such as calcite, quartz and talc. Also, the morphology of sepiolite fibers was studied by TEM. Sepiolite fibers form crystal bundles and rods due to hydrogen bonding and van der Waals' forces between the fibers.

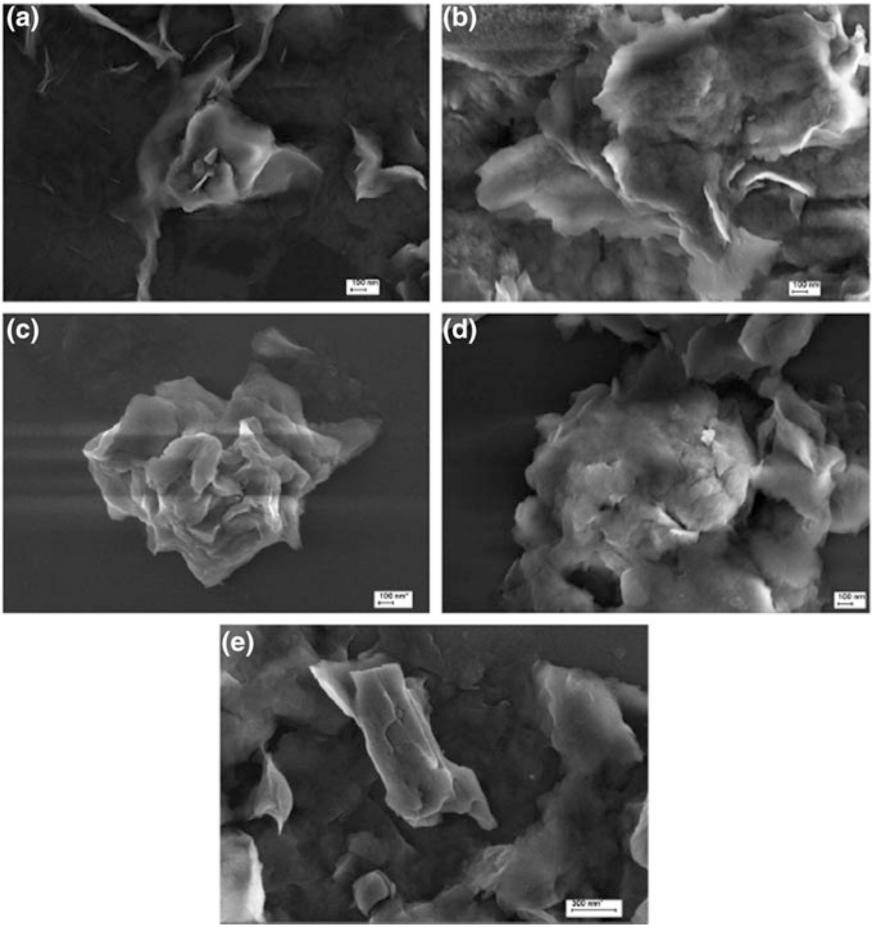

Fig. 4 SEM micrographs of Mt (A) and OMt, using as modifiers HDTMA (B and C) and ODTMA (D and F). Reprinted from Bianchi et al. [28]

5.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) can be used to characterize aluminium silicates materials. The most important bands present in clays are OH stretching (3800–3200 cm^{-1}), Si-O symmetrical and asymmetrical stretching (1200–900 cm^{-1}) and Al-O stretching (800 cm^{-1}). Moreover, FTIR could provide information about the substitution of cations from the interlayer space by organic molecules.

Hojiyev et al. [37] made an FTIR analysis of purified and cationic surfactant modified. They identified the bands corresponding to stretching vibrations of OH groups, Si-O groups, Al–Al-OH groups, and Al–Fe-OH groups. Moreover, Na–Mt spectra show the existence of free and interlayer water at $\sim$ 3400 cm^{-1} and adsorbed water at $\sim$ 1630 cm^{-1}. In addition, the spectra of cationic modified Mt show new peaks corresponding to asymmetric stretching vibration, symmetric stretching vibration and bending stretching vibration of methylene groups (2924, 2849 and 1469 cm^{-1} respectively). Also, the broad peak at 3404 cm^{-1} corresponding to free and interlayer water was removed upon modification due to the hydrophobic nature of the cationic surfactant.

5.4 Thermal Properties

Thermal analysis is also a useful tool to characterize OC due to the difference between the thermal stability of the inorganic cation and the organic surfactants. Within the thermal characterization techniques, the most commonly used ones are thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC).

Sookyung et al. [38] quantified the modification degree of Na–Mt with octadecylamine by TGA/DTG as the ratio between the mass fraction of organic weight loss owing to alkylammonium ions, and the molecular mass of the organic cation exchanged on the clay platelets surfaces. In the TGA/DTG thermograms, three different regions can be distinguished, as is shown in Fig. 5. Region I appear below 150 °C related to the loss of surface-adsorbed water and gas. Moreover, Na–Mt presents the higher weight loss in this region caused by the hydrophilic nature of sodium cation. Region II occurs in the temperature range of 150–500 °C and is attributed to the decomposition of the octadecyl amine. Therefore, region II was used to the estimation of the modifying content in the OC. Finally, region III emerge at temperatures higher than 500 °C as a result of the loss of structural water released by the dehydroxylation of the clays layers [38]. Also, the authors made DTG characterization for further study of OC in region II. They stated that samples with low contents of modifying agent present only one peak, while at higher CEC concentrations a second peak appears. This difference is caused by the location of the modifying agent in the OC.

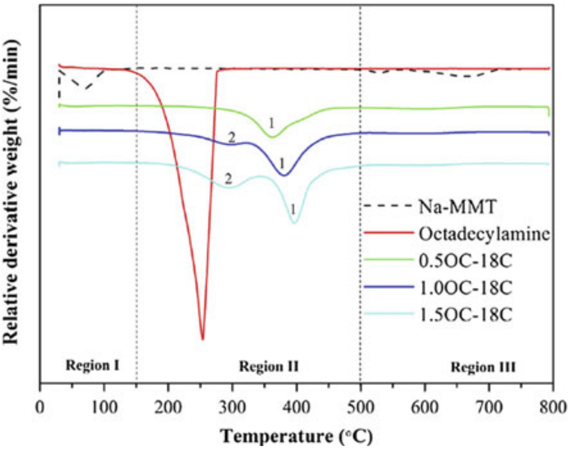

Fig. 5 DTG thermograms of Na–Mt, octadecylamine and OMt with various concentrations of modifying agent: 0.5, 1.0 and 1.5 CEC times of Na-MMT. Reprinted from Sookyung et al. [38]

Soares et al. [39] analyzed the thermal behaviour of modified anionic and cationic clays with imidazolium ionic liquid by TGA. The decomposition mass below 200 °C was attributed to the absorbed water and volatile molecules. Around 320 °C, a second weight loss region appears corresponding to the decomposition of the imidazolium ionic liquid. Also, the content of the modifying agent was calculated as the difference of loss of mass between the raw clay and the organoclay.

6 Elastomeric Clay Composites

During the last 25 years, the development of nanocomposites was intensively explored by researchers, achieving remarkable improvements in mechanical, thermal and physicochemical properties compared with those of conventional composites materials. In this section, a review of some recent works with rubber as matrix reinforced with some type of clay are presented.

6.1 Natural Rubber

Natural Rubber (NR) is obtained from the sap of different trees, almost entirely from the plant *Hevea brasiliensis*, therefore is regarded as a sustainable polymer. In the latex state, NR contains approximately 30% dry rubber content. The latex is normally concentrated, mostly by centrifugation, increasing the dry rubber content approximately up to 60% before it is distributed. NR is a hydrocarbon diene monomer whose repeating unit is cis-isoprene. The outstanding strength of natural rubber has maintained its position as the preferred material in many engineering applications. It has a long fatigue life, good creep and stress relaxation resistance and low cost [40].

Clay/NR composites have been successfully prepared by several procedures: melt mixing, latex compounding and in solution.

George et al. [6] prepared NR reinforced with different organo modified Cloisite clays (10A, 15A, 25A, 30B and 93B) in a two-roll mixing mill and studied the effect of concentration (from 1 up to 15 phr), type of clay and vulcanizing systems on the mechanical properties. They concluded that the conventionally vulcanized samples exhibited higher tensile strength and elongation at break compared to efficient and peroxide vulcanized samples. The maximum tensile strength was reached by the composite containing 5 phr of nanoclay. Among the different samples, NR containing the cloisite 25A exhibited the better properties.

Carli et al. [41] prepared composites of NR with 2, 4 and 8 phr of Cloisite 15A as a substitute for conventional silica (SiO_2). Based on mechanical properties, Authors concluded 6that 50 phr of silica can be replaced by 4 phr of organoclay without affecting the final properties even after ageing.

Siririttikrai et al. [19] prepared compounds from fresh NR latex (FL) and from concentrated NR latex (CL) with unmodified montmorillonite, due to that mixing in the latex state before being coagulated could be advantageous and this process can be carried out at the rubber plantation or at collection points nearby. Different methods yielded different results because during centrifugation process not only water is removed, also some water-soluble materials (like proteins), therefore the chemical composition of natural latex and concentrated latex are not exactly the same, an explanation of how this could affect the material properties is proposed in the scheme shown in Fig. 6. They concluded that MMT can be used to reinforce NR effectively by using fresh latex and MMT water dispersion as the starting point.

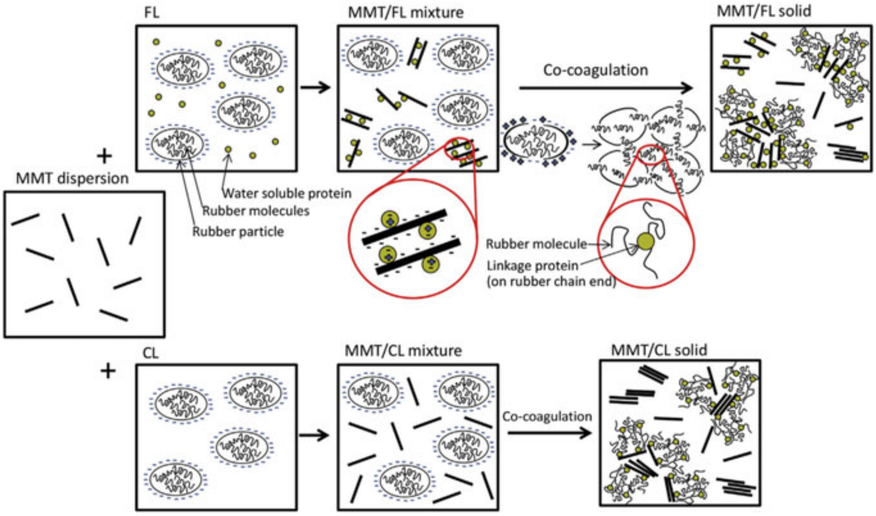

Fig. 6 Schematic illustration of Mt and rubber latex mixing and the co-coagulation processes for different types of NR latex. Reprinted from Siririttikrai et al. [19]

Sookyung et al. [38] made composites of NR with Na–Mt nanoclay modified with different concentrations of octadecylamine at 0.5, 1.0 and 1.5 times the CEC of Na–Mt, the obtained that at higher concentration value a larger *d*-spacing and a higher degree of clay dispersion in the matrix were observed. With a concentration of 1.5 times of the CEC, a faster curing reaction and a higher crosslink density were obtained and the mechanical and dynamic properties and thermal stability were enhanced.

6.2 Styrene Butadiene Rubber

Styrene-butadiene rubber (SBR) is an elastomeric copolymer consisting of styrene and 1,3-butadiene. Most SBR is produced by emulsion polymerization as well as by solution polymerization. SBR is characterized by a good abrasion resistance, ageing stability and low-temperature properties. The tire industry consumes approximately 70% of total SBR production. SBR formulations usually require a high amount of reinforcing filler, being CB the most used [40].

Praveen et al. [42] prepared SBR nanocomposites reinforced with a hybrid system of CB (N330) and OMt using octadecylamine as a modifier. The study included the variation of clay content (5, 10, 15 and 20 phr of OMt) in gum rubber and in rubber filled with 20 phr of CB, preparing in a two-roll mill. The presence of intercalated, aggregated and partially exfoliated structures were revealed through XDR and TEM. Samples containing 10 phr of OMt resulted in an increase of 153% in tensile strength, 157% in elongation at break and 144% of modulus 100%. The obtained results open up a new prospect in developing CB–OMt-hybrid nanocomposites, facilitating the possibility of partial replacement of CB with OMt in rubber products without affecting the critical performance properties.

Sadek et al. [43] studied SBR composites reinforced with sodium bentonite as well as modified with two types of surfactants: dodecyl benzene sulfonic acid (DBSA) and nonyl phenol ethoxylate (NPE), also a mixture of the surfactants was used: DBSA/NPE (50/50%). The clay content was 2, 4, 6, 8 and 10 phr, and the compounds were prepared in a two-roll mill. The presence of clays induces an increase in the minimum and maximum torque values, acceleration of the vulcanization process, and improved mechanical properties with organoclay content up to 6 phr. This effect was more noticeable in the presence of the treated clay with DBSA/NPE. Also, incorporation of 6 phr of DBSA/NPE-clay resulted in significant improvement of the degradation profile of the nanocomposites at 90 ± 1 °C for 4 days.

During the long period of service, most polymers (and composites) gradually lose their useful properties as a result of polymer chain degradation. The main harmful agents are oxygen, heat, and high energy radiation. The effects of these agents depend mainly upon the chemical structure of polymer chain. Youssef et al. [44] analyzed the effect of gamma radiation on the final properties of NR/Na–Mt and SBR/Na–Mt nanocomposites prepared by coagulating the mixture of rubber latex and clay aqueous suspension. The clay concentration was varied from 2 to 10 phr and the irradiation of the samples was carried out using a cobalt-60 gamma cell source with doses of 10, 25, 50, 75, and 100 kGy at a dose rate 5 kGy h^{-1}. XRD results indicated well dispersion of rubber latex into clay stacked layers and the platelets have a preferential orientation forming exfoliated NR/Na^+-MMT nanocomposites while SBR/Na^+-MMT form intercalated nanocomposites. Author explains that SBR have bulky benzene groups, which partially restrict the chains to intercalate into the gallery gap of the clays. Second, NR contains a higher number of unsaturated double bonds than SBR, thus the polarity of NR is higher than SBR, as a result, NR could form exfoliated whereas SBR are intercalated. Overall irradiation dose range together with clay loading, an improve of the mechanical properties of rubber/Na–Mt nanocomposites was obtained. However, SBR nanocomposite, in particular, attains its higher value at 50 kGy, then decreases; also, the thermal stability at 50 kGy is higher than 100 kGy.

6.3 Nitrile-Butadiene Rubber

Nitrile-butadiene rubber (NBR) is a polar elastomer, with a carboxylic group and a double bond in the rubber backbone. The polar nature of the NBR allows a higher resistance to non-polar substances such as hydrocarbons and oils. Depending on the acrylonitrile content, important improvements in abrasion resistance are obtained, therefore it has a great performance in the seal industry. Other advantages of NBR are its low cost and good processability. However, some of the negative aspects include a low ageing resistance because of the unsaturated backbone present in the chemical structure, thus is sensitive to environmental factors [45, 46].

Costa et al. [47] explain the effect of Mt in polar rubbers as NBR. The presence of the Mt offers a crosslinking effect defined as “ion cluster”. It was demonstrated that there is a chemical interaction between the NBR chains and the clay particles, especially in cases where there are metal oxides in the rubber vulcanization formula like ZnO. This reaction can be explained taking into account the acid-base reaction, where acidic ACOOH group of the NBR reacts with the ZnO producing an ionic salt and releasing water.

De Sousa et al. [48] formulated nanocomposites of XNBR with different types of clays (Na- Mt, OMt and a natural bentonite). Using XRD and mechanical properties, they concluded that the organo-modifier agent and the molar mass of rubber had a significant influence on the dispersion of the clay after the mixing process on a two-roll mill.

Finally, Yu et al. [49] presented a very interesting work combining OMt and NBR by emulsion process. TEM images of the nanocomposites exhibited uniform dispersions of the clay sheets inside the NBR matrix. Also, the XRD patterns confirmed the intercalation of the NBR polymeric chains inside the interlayer of the OMt. The final nanocomposites showed an improvement of mechanical properties and solvent resistance comparing to pure NBR. Moreover, thermogravimetry indicates an increase in the maximum decomposition rate of the nanocomposites in comparison with that of pure NBR were observed, indicating an enhancement of the thermal stability. There was also a faster curing rate and a higher glass transition temperature, storage modulus and loss modulus.

6.4 Ethylene-Propylene-Diene Rubbers

Ethylene propylene diene terpolymer (EPDM) is an unsaturated polyolefin rubber with wide applications. Due to its good mechanical properties, very low unsaturation and associated resistance to ageing and ozone deterioration, it has become extensively used in making automotive tire sidewalls, cover strips, wires, etc. In a non-polar rubber like EPDM, the presence of stearic acid in the formulation favours the dispersion of clays due to the chemical reactions leading to ester formation involving carbonyl groups of acid and hydroxyl group of clay [50]. The early works on preparation and characterization of EPDM nanocomposites included that of Usuki et al. [51] and Zheng et al. [52].

Liu et al. [17] analyzed the reinforcement of nano kaolin (NK) powder into four types of rubber: SBR, NR, BR and EPDM. The reinforcing effects were compared with those from precipitated silica (PS). The compounds were made in an open roll mill. The results showed that NK can greatly improve the vulcanizing process by shortening the time to optimum cure (t_{c90}) and prolonging the setting-up time (t_{10}), which improves production efficiency and operational security. The rubber composites filled with nano kaolin enhances the mechanical properties and thermal stability. The tensile strength of the rubber/NK composites is close to those of rubber/PS composites. The tear strength and modulus presented a lower performance compared with those containing precipitated silica.

Chang et al. [53] showed that the oxygen barrier properties of EPDM/OMt clay nanocomposites are better than that of pristine EPDM. The oxygen permeability of 10 phr layered clay filled EPDM nanocomposite was reduced to 60% as compared with the pristine EPDM compound. The gas permeability was ascribed due to the uniform dispersion of the impermeable clay layer with the planar orientation in the EPDM matrix.

Zhang et al. [54] synthesized an intercalation agent containing double bonds for modifying the interface of EPDM/clay nanocomposites, using a Na–Mt. In order to compare with the OMt containing double bonds (VMMT), the OMt modified with cetyl trimethyl ammonium bromide (CTAB) without double bonds was also prepared; in both cases, the content used were 0, 3, 5 and 10 phr. Authors analyzed the relaxation dynamics via broadband dielectric relaxation spectroscopy. In polymer/clay nanocomposites, the environment of the polymer chains inside the silicate gallery will greatly affect the molecular relaxation and mobility. According to the literature, two distinct types of dynamic behaviour may exist in such systems. One is the slower relaxation dynamics associated with glass-transition temperature (T_g) and is attributed to the large interlayer distance and the strong polymer-filler interactions. In contrast, when the polymer-filler interactions are weak, the polymer segments will exhibit the faster relaxation mode, thereby leading to the depression of T_g value. According to the XRD analysis, the VMMT containing double bonds was exfoliated, and the crosslinking reaction between VMMT and EPDM chains promotes the exfoliation of the organic layered compounds. The dielectric relaxation spectra show that the segmental relaxation of EPDM shifted to higher temperature with increasing VMMT content, and a new relaxation, which was attributed to the interfacial relaxation being confined by the MMT platelets, was detected at a much higher temperature and lower frequency, whereas that did not appear when adding OMt.

6.5 *Role of Nanofiller as Compatibilizer in Rubber Blends*

Natural and synthetic rubbers are not used very often in an isolated form. An elastomer is mixed with another one, especially in the tire industry, for three main reasons: to improve properties of the material, to improve processing or to reduce costs. Most blends of rubbers are immiscible, which leads to a non-uniform dispersion of the components in the rubber matrix. For example, in Fig. 7 can be seen images taken by TEM of unfilled NR/SBR blend with a different ratio: on the left a compound with 25 phr of NR and 75 phr of SBR (25NR/75SBR), and on the right the complementary sample (75NR/25SBR), being SBR the dark phase and NR the clear one [55].

Nanoclay also shows preferential migration to specific rubbers when used in blends, due to organoclay is more compatible with polar rubbers. By the introduction of functional groups, the polarity can be changed so as to have better filler dispersion and hence compatibilizing action.

The different solubility of two rubber is related to different polarity and level of unsaturation in the rubber components, leading to an unequal dispersion but also to

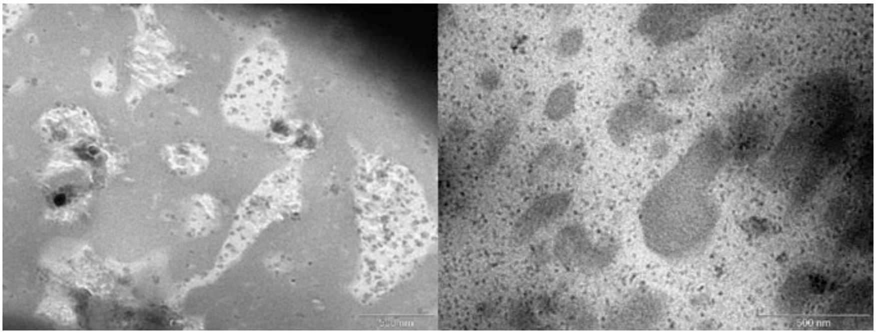

Fig. 7 TEM micrographs of vulcanized NR/SBR blends (left) 75NR/25SBR and (right) NR/SBR, being SBR the dark phase and NR the clear one

a diffusion of the components during the mixing or during the vulcanization process [56, 57], which could generate an uneven crosslinking. The presence of reinforcement particles in some cases can complicate this situation even more.

The properties of rubber blend/clay nanocomposites are strongly affected by the location and distribution of the clay in addition to the size, shape and dispersion of each rubber phase. Depending on the location of the clay in the matrix or dispersed phase, a separated or encapsulated morphology could be formed. All this can cause a narrow interphase and poor physical or chemical interactions between the two phases, influencing the mechanical properties of rubber blend.

OC particles added at a low loading level could play as interfacial compatibilizers for immiscible rubber blends reducing the domains sizes. This is due to nano level dispersion, generating a reduction of the interfacial tension between the two rubber phases [58].

Compatibilizers act through a chemical reaction (reactive compatibilization) or by its capability for interaction with blend components or by its interaction with chemicals present at the interface of blend components. Most of the interactions are intermolecular forms of attraction such as van der Waals and hydrogen bonding, based on the polarity of materials (nonreactive compatibilization). The surfactants present in organoclay also contribute to compatibilization. It is also possible that two immiscible polymer chains can intercalate the same clay platelet and play the role of a block or graft copolymer. Generally, graft or block copolymers have similar segments to blend components and hence act as compatibilizers in blends [12].

Rajasekar et al. [59] used clays as a compatibilizing agent for NR and NBR blends. They incorporated an OMt by solution mixing to promote a uniform dispersion inside the NR matrix. After that, they incorporate the first NR/OMt composite to a sulfur formulated NBR matrix, observing important changes in morphology, curing characteristics, mechanical properties, swelling and compression set. They established how the improvements in properties come from the distribution of the clay inside the rubber matrix. By their morphological studies, it was possible to determined intercalation in the whole NR/NBR composite. Also, faster scorch time and cure time, as well as an increase in maximum torque were obtained compared to the neat NBR matrix. Increases in storage modulus and lesser damping characteristics for the compounds with OMt were measured. The final reinforcing efficiency was determined comparing enhancements in mechanical properties and higher swelling resistance in oil and solvents.

7 Preparation of Nanocomposites

The incorporation process of clays into a rubber matrix influences the final properties of the nanocomposite, and the final structure depends on the nature of the rubber and the type of clay employed. Maiti et al. [4] explain the mechanism by which the nanofiller aid the rubber formulations to improve their properties [1].

The optimum improvement of the nanocomposite properties depends upon the incorporation technique, the dispersion of the clay and the concentration of the reinforcement within the rubber matrix [60].

Several techniques were used to prepare rubber/silicate nanocomposites. The most known are [1]:

- Melt mixing
- Solution blending
- Latex blending/latex compounding
- Sol-gel processing
- Emulsion polymerization.

7.1 Melt Mixing

The melt mixing technique is one of the most utilized to prepare elastomer/OC nanocomposites. The method involves internal mixers and open two-roll mills [4], which consists of blending the layered silicate with the polymer matrix in the molten state. The full exfoliated rubber/clay nanocomposites are difficult to obtain by this method because of the high viscosity of the rubber in the molten state but if the layer surfaces of the clay are sufficiently compatible with the constituent polymer of rubber, the polymer chains can crawl into the interlayer space and form an intercalated or an exfoliated nanocomposite (see Fig. 8b) [23].

The intercalation/exfoliation processes are governed by the modification of elastomers and also the chemistry involved in compounding and curing state to form elastomer-clay nanocomposites with improved properties [4]. Maiti et al. also explained how the temperature and shear rate are important variables to promote an intercalation/exfoliation phenomena. Ray et al. [61] discussed how the melt intercalation is highly specific to the polymer, leading to new rubber formulations that were previously inaccessible. Normally, polymers containing polar groups (capable of associative interactions, such as Lewis-acid/base interactions or hydrogen bonding) favour intercalation phenomena because the surfactant molecule in the OC has the same non-polar character as the polymer [62].

Several authors have utilized this technique to prepare nanocomposites. For example, George et al. [6] investigated the mechanical properties of natural rubber/OC systems by melt mixing using a two-roll mill. Authors have studied the effect of clay concentration, type of clay and vulcanizing systems on the mechanical properties. Their results show how the clay interlayer distance is increased in all samples after incorporation into the rubber matrix, as great improvements in tensile strength, elongation at break and modulus.

Most of the published works present the reinforcement of clay nanocomposites based on acrylonitrile butadiene rubber (NBR), ethylene propylene diene (EPDM) and NR [4]. Wang et al. [63] studied NBR/expanded graphite (EG)/CB micro and nanocomposites systems to compare with NBR/CB systems. Their results show an

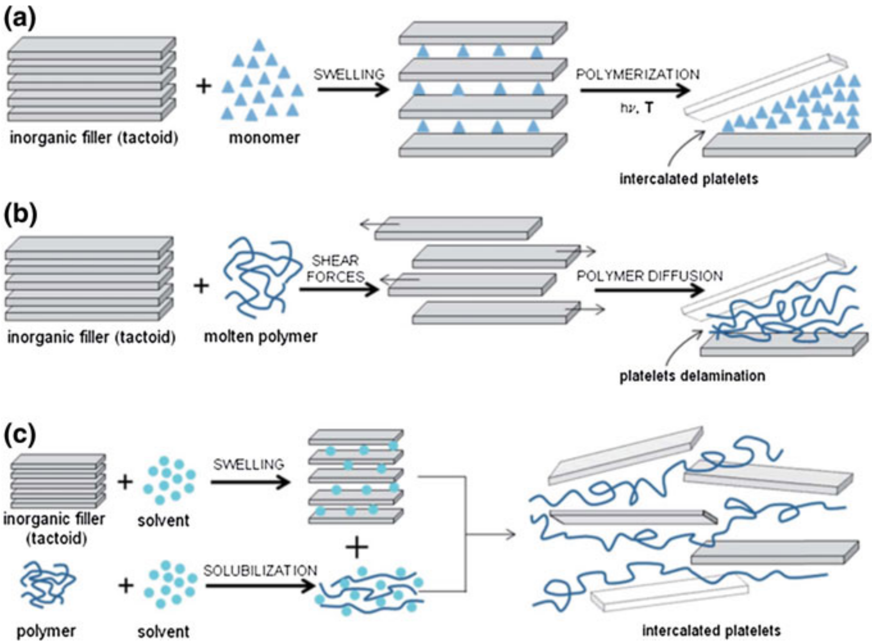

Fig. 8 Schematic representation of **a** in situ polymerization, **b** melt processing, and **c** solution casting [89]. Reprinted from Unalan et al. [90]

effect on the properties depending on the EG and CB loading content. By melt mixing, there is a better dispersion of EG, showing remarkable enhancement on tensile and dynamic mechanical properties. Przybyek et al. [63] prepared NBR reinforced with an antibacterial Mt, presenting important improvements in mechanical and thermal properties.

Melt mixing is also the preferred mode of incorporation of oxides like nano titanium dioxide, nano zinc oxide and others [4].

7.2 *Solution Blending*

Solution blending includes the solubilization of rubber in a proper solvent and then, the dispersion of the filler into the solution [4]. Later the solvent is evaporated after reaching a good dispersion of the nanofiller, usually, under vacuum or precipitation [4], the process is shown in Fig. 8c) and also in Fig. 9. The principal feature of this technique is that the layered silicates can be exfoliated into single layers using a solvent in which the polymer is soluble, overcoming the weak forces that stack the layers together [23]. The solvent allows the elastomer chains to be uncoiled and disentangled and easily enter between the layers of the clay or interact with the

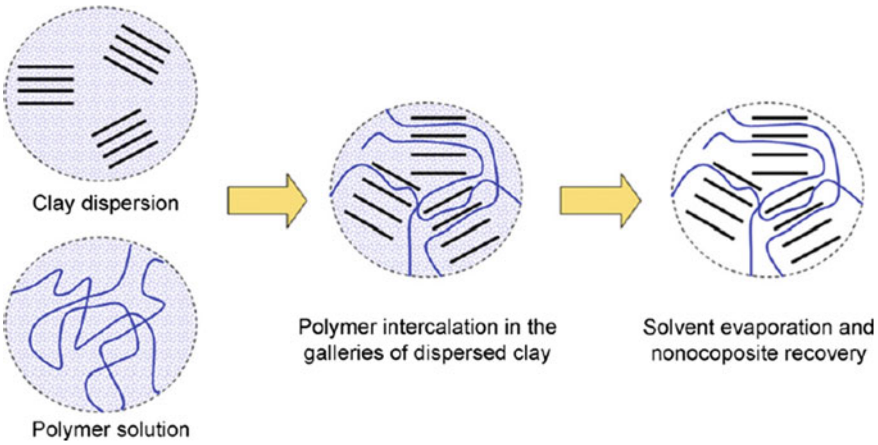

Fig. 9 Schematic representation of solution blending process. Reprinted from Pavlidou et al. [23]

particulate nanofillers [4]. In this method, the ultrasonic dispersion of clay is indispensable to increase the interfacial adhesion between clay and elastomer matrix in order to reach a high-performance rubber–clay nanocomposite. The main drawback of this method is the disposal of large quantities of solvent [23].

Usha Devi et al. [20] swelled an OMt in toluene to promote an effective method to fabricate an SBR nanocomposite, observing a complete rate of dispersion in the elastomer.

7.3 *Latex Blending/Latex Compounding*

The latex compounding method was developed to solve the problem of incompatibility between the rubber and fillers, improving the dispersion of fillers in the rubber matrix [3]. Latex is defined as a stable aqueous dispersion of fine rubber particles, with a particle size around 300–500 nm [1]. Most of the elastomers are available in latex form, so pristine clay can be added directly or in its aqueous dispersion (slurry). Moreover, an additional advantage is that the layered silicates can absorb water from the suspension, which aid to expand the interlayer space [4].

After the combination of latex and layered silicates, a co-coagulation process is carried out to produce a masterbatch product. This method allows the fabrication of latex film products, such as gloves, condoms, and coatings if the latex is mixed with the layered silicates and curatives in suspension [1].

If there is a good compatibility between rubber and clay, the formation of structures known as “house of cards” or “skeleton” can occur because of the presence of rubber particles that penetrate the clay interlayer gallery due to a polarity mismatch [64]. Rezende et al. [8] used the latex compounding method to obtain an NR/clay composite obtaining improvements in mechanical properties and characterizing the nanocomposite structure by TEM and small angle neutron scattering (SANS).

7.4 Sol-Gel Processing

In this technique, rubber/clay nanocomposite is synthesized using an aqueous solution (or gel) containing the polymer and the silicate building blocks. The precursors for the reaction are clay silica sol, magnesium hydroxide sol and lithium fluoride. The polymer aids the nucleation and growth of the inorganic host crystals and gets inside the clay layers [23].

Some authors have developed sol-gel systems. Brantseva et al. [65] used clays to improve the adhesive capacity of rubber compounds showing how both structural and pressure-sensitive adhesives (PSAs) were improved. With the sol-gel method, they ensured exfoliated or at least intercalated conditions. George et al. [6] prepared SBR/NBR/OMMT composites and notice great improvements in thermal stability and swelling properties, attributed to the barrier characteristic the clays impart to the rubber matrix.

Some of the problems this method presents are [23]:

- The synthesis of clay minerals generally requires high temperatures, which can decompose the rubber chains.
- There is an aggregation tendency of the growing silicate layers.

7.5 Emulsion Polymerization

In this method, the monomers of the polymer are dispersed in water together with an emulsifying agent and the clays, as can be seen in Fig. 8a). It is beneficial to achieve a good interaction between the rubber matrix and the reinforcement, since there is a joint polymerization between the rubber chains and the clays, leaving a nanocomposite where some of the clay sheets are embedded in the rubber particles, while some polymer chains are adsorbed on the surface of the clay particles [66], due to this, a better dispersion of the reinforcement can be obtained [67].

Polymerization is promoted with temperature, and the clay swelling process occurs directly in the polymerization medium (water) and in some cases, by the low molecular weight of liquid monomers [67]. One of the drawbacks of this method is that requires a certain time period to form the nanocomposite and depends extensively on the polarity of the monomers, the type and surface of the filler and the initiation temperature of the polymerization reaction [4].

Distler et al. [68] explained a simple procedure to perform an emulsion polymerization. The base in this type of process consists of mixing: deionized water, surfactant (for example sodium dodecyl sulfate), the reinforcement particles and the monomer. Within the process, the agitation is fundamental so that phase separation does not occur. As mentioned above, the polymerization initiator (for example sodium persulfate) is also fundamental, since the speed and the form of initiation of the process depend on it.

The polymerization system consists of a reactor with a stirrer, a reflux condenser, two lines for content the monomer emulsion and the initiator solution, and a temperature control unit which normally is rinsed with nitrogen. The reaction initiates with heat (approximately 70°C) and takes a few hours to complete. The final product is then filtered and then characterized by solid content and particle size [69].

Among the aforementioned methods, in situ polymerization and melt intercalation are considered as commercially attractive approaches for preparing polymer/clay nanocomposites [23]. In addition, the absence of a solvent makes direct melt intercalation an environmentally and an economically favourable method for industries from a waste perspective [62]. Moreover, it is compatible with the current industrial processes, such as extrusion and injection moulding. However, the dispersion of the clay in the polymer prepared by the melt mixing is not as good as that obtained by the latex compounding [69]. The main drawback is the poor dispersion within the matrix and the lack of affinity between the layered silicate and the organic polymers.

The latex compounding process is recommended when using hydrophilic clays because it occurs in an aqueous medium. While the process of melt blending is recommended when using hydrophobic clays (OMt) since with chemical modification they become more compatible with the elastomer.

8 Rubber/Clay Nanocomposites Properties

As it was mentioned above, there are numerous variables that define the final performance of a composite material, particularly when it is about a complex combination such as a vulcanized nanocomposite of rubber and clays.

The type of reinforcing the material, the shape of the particle as well as its structure, the type of rubber matrix and the preparation method play a fundamental role in the final properties of the compound. Depending on the application, it is necessary to comply with certain mechanical standards; therefore, it is necessary to consider those tests that conveniently help to determine the properties that describe how the behaviour of the material will be during its life in use.

8.1 Vulcanization Variables

The presence of nanoclay has a strong influence on the vulcanization process. The cure characterization of nanocomposites gives information about the interaction between filler and the matrix, and also the extent of filler-filler inter aggregations. George et al. [6] investigated NR reinforced with organo modified Cloisite clay and found that the t_{c90} value decreases when the concentration of clay is higher. This indicates that organophilic clays accelerate the vulcanization process in these samples due to the formation of a transition metal complex in which sulfur and amine groups of the intercalate layers may involve [65].

Siririttikrai et al. [19] studied the cure characteristics of NR containing different amounts of Mt prepared from fresh or concentrated NR latex (FL and CL respectively). Figure 10 shows the cure curves of the compounds for different Mt content and Table 1 summarizes the characteristic cure parameters. It can be seen that, for the Mt/FL series, the maximum torque (M_H) increases with increasing Mt content. No effects were observed on scorch time (t_{s2}). The Mt/CL series displays a different behaviour: the sample made from CL with 4 phr of Mt displays the maximum value for t_{s2} and also for M_H, then these values decrease when the amount of Mt is higher. When the amount of Mt is the same, the Mt/FL compound displays slightly shorter cure times (t_{c90}) than does Mt/CL compound.

Several authors proposed that high energy ionizing radiation can be considered as a cost-effective and additive–free technique [70, 71]. Moreover, it can be carried out at room temperature, so it decreases the toxic volatile releases. Shoushtari Zadeh Naseri and Jalali-Arani [72] studied SBR/EPDM blends with and without OC vulcanized with gamma radiation. The effects of the radiation dose on the interaction between phases, crosslink density, gel content, and microstructure of the prepared OC containing samples compared to those of the unfilled blends were investigated. Authors used gel content as a criterion to estimate the crosslink density and found that the OC induces an enhancement of gel content respect to the system without reinforcement (Fig. 11), which would be related with the improvement of radical-radical interaction and formation of physical crosslinks [71]. Sookyung et al. [38] analyzed compounds of NR reinforced with 5 phr of Na–Mt modified with octadecylamine in concentration values from 0.5 up to 1.5 times

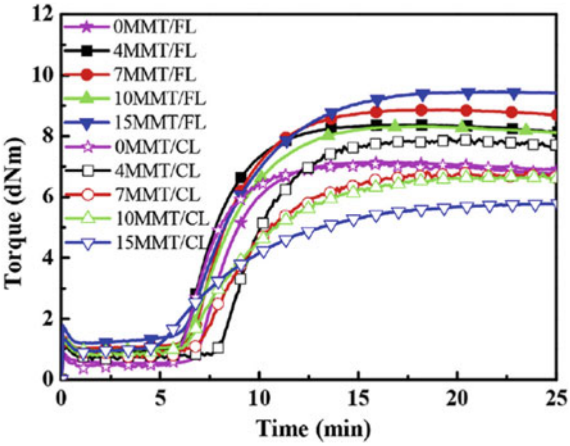

Fig. 10 Cure curves of Mt/fresh latex (FL) and Mt/concentrated latex (CL) compounds with the indicated amount of Mt. Reprinted from Siririttikrai et al. [19]

Table 1 Cure parameters of different Mt/latex compounds

Compound	M_L (dN m)	M_H (dN m)	t_{S2} (min)	t_{C90} (min)
0Mt/FL	0.54	7.15	7.60	10.88
4Mt/FL	0.91	8.37	6.83	10.65
7Mt/FL	1.04	8.86	7.33	11.67
10Mt/FL	1.00	8.32	7.32	11.93
15Mt/FL	1.20	9.42	7.15	13.21
0Mt/CL	0.44	7.08	6.65	10.15
4Mt/CL	0.71	7.94	8.79	13.10
7Mt/CL	0.78	6.72	8.18	13.86
10Mt/CL	0.83	6.76	7.75	14.82
15Mt/CL	0.94	5.79	7.43	15.09

The number in the compound indicates Mt amount in phr. Reprinted from Siririttikrai et al. [19]

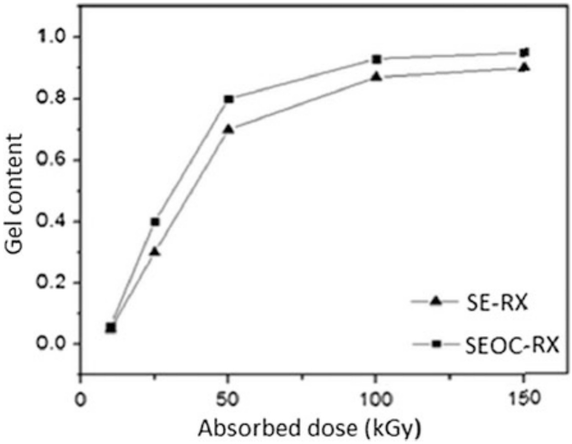

Fig. 11 Gel content of unfilled SBR/EPDM (SE) and SBR/EPDM with OC (SEOC) samples as a function of absorbed dose (RX). Reprinted from Shoushtari Zadeh Naseri and Jalali-Arani [72]

the CEC value of Na–Mt. From the rheometric curves, they obtained that t_{s2} and t_{c90} decrease when the amount of the modifying agent increases. This behaviour is attributed to the effect of the ammonium groups of the octadecylamine that causes an increase of the zinc complex content, and therefore acceleration in the vulcanization reaction. Also, a higher value of M_H was obtained with a higher content of the modifying agent, which indicates a higher interaction between the clay and the rubber chains: a higher loading of the modifying agent gives a higher interlayer spacing of OC, allowing the penetration of rubber chains or their molecular segments into the silicate. This allows to explain the improvements in mechanical and thermal properties, the tensile strength and modulus at 100 and 300%; elongation and hardness of the composites were improved with the concentration of the modifying agent.

8.2 Rheological Properties

Microstructural changes of the nanocomposites can be followed by dynamic frequency sweep tests. Maroufkhani et al. [58] performed measurements within the linear viscoelastic region ($\Upsilon = 1$) in blends of polylactide acid (PLA) and NBR reinforced with 4 phr of Cloisite 10A (OC), prepared via melt compounding. They investigated the influence of the acrylonitrile (ACN) content of NBR on the dispersion and localization of the OC; three different ACN levels content in NBR were used: low (19%), medium (33%) and high (51%). It was found that the presence of nanoclays increases the *G'* values of the samples in the low-frequency region. The plateau in this region is caused by physical interactions between the nanolayers and the rubber chains. In addition, the presence of quaternary ammonium surfactants of OC promotes a good compatibility with PLA by hydrogen bonding. Finally, this phenomenon was not altered by the ACN content in the polymer blend.

Dynamic mechanical analysis (DMA) of XNBR/NR blends reinforced with nanoclays were studied by Satyanarayana et al. [73] in order to determine the T_g of the polymers. They stated that the incorporation of clays into a rubber matrix affects the rheological properties by shifting the $tan\ \delta$ peak to lower temperature values [74]. As it was explained before, this effect is influenced by the filler type and load, the type of matrix and the filler-matrix interaction. Furthermore, the authors also reported that the presence of clay lowers the height of the $tan\ \delta$ peak due to a reduction of the amount of rubber mobile during the dynamic transition process as consequence of the reinforcing effect of clay nanoparticles.

8.3 Mechanical Properties

Jahromi et al. [75] studied a ternary hybrid system consisting of polyamide 6 (PA6), NBR and OC. Compounds included an NBR and NBR activated with glycidyl methacrylate (GMA) groups. The Young modulus and tensile strength of the hybrid systems were improved by the increase of nanoclay content due to the effective reinforcing role of the inorganic filler [76]. However, the reinforcing effect was more effective for the nanocomposites including a reactive elastomer, which stems obviously from the better dispersion of nanoparticles along with nanoplatelet confinement in the thermoplastic phase domains.

A distinctive property to analyze the elastomer-filler interaction and filler-filler interaction is the non-linear viscoelastic response of filled systems, otherwise known as Payne effect [77]. Payne suggested that the formation of a three-dimensional structure was due to the filler incorporated in rubbers, which leads to higher modulus values at lower strains. Regarding the use of nanofiller, the surface area, surface modification and activity are some of the crucial factors that affect the non-linear viscoelastic response. A competition between filler-filler and polymer-filler interactions takes place in filled elastomers. If filler-filler interaction predominates, the Payne effect is more pronounced. Zachariah et al. [78] evaluated the dynamic shear storage modulus and loss modulus of NR and Chlorobutyl Rubber (CIIR) containing OC. The authors studied these systems because of their application in the manufacture of automotive inner tubes and inner liners. They found that the nanoclay loading in both matrices increases the modulus values at lower strain due to the formation of filler-filler and filler-polymer networks. These networks could break at higher strains, which results in the reduction of the modulus.

8.4 Barrier Properties

Many researchers reported on the permeability behaviour of nanoclay loaded elastomeric composites proposing that this property increases due to the creation of a tortuous path in the microstructure for the transport of gas molecules [79].

Mohan et al. [80] investigated the water uptake of NR/SBR blends reinforced with OC. The water content, W_c, in the sample was measured as % weight increase in the sample. W_c was measured until the composite specimen attained equilibrium water uptake content. The following equation was used to calculate the W_c in the specimen:

$$W_c = \frac{(W_t - W_o)}{W_o} \times 100$$

where W_t is the weight of specimen at time t and W_o is the initial weight of the sample before placing in water. Figure 12 presents the water mass uptake as a function of time (in days) of all samples, the sample that containing 3 wt% nanoclay has the lower water content value. Also, static and dynamic mechanical analysis (DMA) properties were less affected in the nanoclay filled rubber than in the base rubber. Chao et al. [1] studied gas-barrier properties of IIR/clay nanocomposites obtained via the latex method. Moreover, they compared samples prepared using latex and co-coagulating methods. It is important to remark that TEM images revealed both partially exfoliated and intercalated structures for the isobutylene-isoprene rubber (IIR)/Mt nanocomposite prepared using the latex method and, on the other hand, a purely intercalated structure in the sample prepared using the co-coagulating method. It was found that the oxygen transmission of the IIR/clay nanocomposites decreases progressively as the silicate content increase. The oxygen permeability of the compound with 10 phf of clay was reduced to 60% as compared with the neat IIR. Layered silicate is composed of many monolayers that are 1 nm thick and 200–300 nm long; this aggregated platelet structure of the layered silicates in the IIR matrix could provide an excellent barrier to the diffusion of oxygen because of the increased tortuosity of the diffusing path [1].

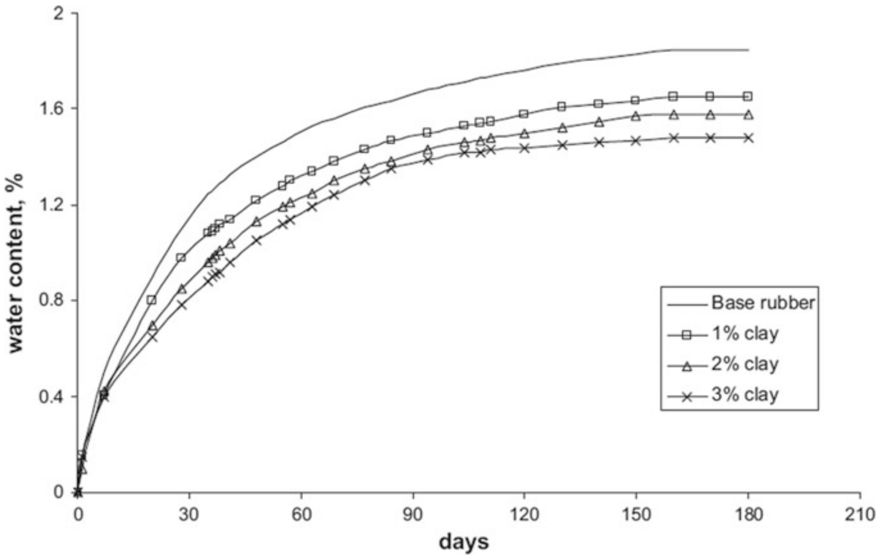

Fig. 12 Water mass uptake of rubber and rubber-nanoclay series in NR/SBR blends. Reprinted from Mohan et al. [80]

Wang et al. [81] stated through positron annihilation lifetime spectroscopy (PAS) and DSC that gas permeability in rectorite/SBR nanocomposites is mainly influenced by the free volume fraction and tortuous diffusional path effects attributed to the clay platelet-like morphology.

9 Applications

The incorporation of clays into rubber matrices comes from the need to improve the mechanical properties, such as tensile strength, elongation at break or elongation module [6, 8, 38]. There is also a need to improve vulcanization times [82, 83], as well as to extend the range of decomposition temperature [84]. There are also other properties that can be improved using rubber/clay compounds.

An important area of application of rubber/clay nanocomposites is gas and moisture barriers. The layers of clays that filled a polymer matrix serve as an impermeable medium for the gas and moisture. Although there is information about barrier properties of clay filled thermoset and thermoplastics are available in the literature, those related to barrier properties of rubber filled with clay nanoparticles are relatively few. Recently, several works were reported on the synthesis, characterization, mechanical and thermal properties.

The improvement of fatigue strength of rubber composites is also considered within automotive applications. Woo et al. [85] explain how the interest of fatigue life evaluation for rubber components such as in engine parts was increasing according to extend the warranty period of the automotive components. In their study, they developed a rubber material environmentally friendly with superior physical properties and fatigue life using a rubber-clay nanocomposite.

Other applications include structural and pressure-sensitive adhesives (PSAs). Brantseva et al. presented a paper about the uses of clays in the adhesive industry as rheological modifiers where an enhancement of barrier properties, thermal resistance and mechanical properties were found [86–89]. For example, clays have been used to increase shear strength and heat resistance of waterborne acrylic PSAs as an environmentally friendly replacement of solvent-borne acrylic PSAs [87]. Furthermore, there are reports of the use of Na–Mt and OMt to improve rheological and mechanical properties of polyisobutylene (PIB) based adhesive [87]. Results show better compatibility between PIB/OMt systems rather than PIB/Na–Mt, which was evidenced as an increase in viscosity with a 10 wt% of OMt content. On the other hand, Na–Mt did not show significant improvement of the rheological properties.

Finally, within the most innovative applications, the use of modified clays with bactericidal agents to formulate rubber mixtures with antimicrobial properties was analyzed. Przybyłek et al. developed an elastomeric nanocomposite that exhibits antibacterial and antifungal activity for the polish company Spoiwo (Spoldzielnia Pracy Chemiczno–Wytworczej ‘Spoiwo’, Radom, Poland) [20]. They used a rubber blend matrix and modified bentonite clay (Nanobent® ZR2), and noticed that by adding 1–3% of bentonite nanoparticles there was an enhancement in the elongation and tensile stress at break; they also observed improvements in thermal properties. Their work resulted significantly in the medicine, biomedical engineering and in the food industry.

10 Final Remarks

In this chapter, a review of recent works including rubber/clay nanocomposites were made. This review covers the structure and physical characteristics of layered silicates used as fillers in rubber matrices as well as the chemical and physical characteristic of the type of rubber polymers, and rubber blends, which are more likely used for nanocomposites development. Moreover, it describes several techniques for organic modification of clays nanoparticles to enhance hydrophobicity and improve the compatibility by intercalation or exfoliation of the polymer chains into the clay interlaminar space. Finally, the chapter reviews the rubber/clay nanocomposites characteristics (i.e. vulcanization and rheological, mechanical and barrier properties), and the nowadays applications, like the tire, adhesive and biomedical industries.

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