

Review On Development Of Natural Rubber/Nanoclay Nanocomposites

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Abstract— The advantages of nanocomposites containing single silicate layers uniformly dispersed in a polymer matrix were first demonstrated by researchers at Toyota in Japan, who developed nylon-6 nanocomposites and published in 1993. Polymer-nanoclay nanocomposites have attracted the attention of many researchers thereafter due to their outstanding mechanical and barrier properties. This concept is first applied to synthesis of plastics/nanoclay nanocomposites and then expanded to preparation of rubber/nanoclay nanocomposites, since few years later. The various types of synthetic rubbers, such as silicon rubber, nitrile rubber and epoxy rubber, were used to prepare nanocomposites using different techniques, namely, melt intercalation, in situ intercalative polymerization, exfoliation-adsorption and template synthesis, etc. Natural rubber (NR) was also used to prepare nanocomposites using the same techniques but with some modifications in the last decade. Now a day's nanocomposites are widely developed in NR latex industry to achieve required properties with minimum use of clay content. NR/nanoclay nanocomposites exhibit markedly improved properties when compared to pure NR or their traditional composites. Most notable properties are increased tensile properties, gas barrier properties and heat distortion temperature, resistance to small molecule permeation, increase in atomic oxygen resistance and retention of impact strength. Tensile strength and modulus were recorded in current research as enhanced by more than two times or even ten times. It was noticed that obtaining a fully exfoliated structure is not at the desired level. Nanoclay nanocomposites are considered as fully exfoliated when inter gallery distance is greater than 10 nm but it was not achieved in many research work. Establishment of exfoliated structures in nanocomposites prepared in industrial scale is the major challenge that NR industry faces at present. NR/nanoclay nanocomposites produced with existing techniques develop high property fluctuations. Therefore, it is necessary to develop a technique to minimize property fluctuations and to obtain a reliable NR based product. It is predicted by this review that co-coagulation technique is the most promising and potential technique to fulfill the requirements of developing a NR/nanoclay nanocomposite. Use of modified nanoclays like Organoclays will aid to obtain a reliable NR based product.

Keywords— natural rubber; nanoclay; nanocomposites

I. DEVELOPMENT OF RUBBER NANOCOMPOSITES

Polymer composite is made by combination of polymer/s and other different materials including synthetic or natural

fillers. In polymer/filler nanocomposites, filler has at least one dimension in the nanometer scale (<100 nm).

Commercial clays of particle sizes in macro- and micro-scales have been used as filler in rubber product manufacturing industry over many years. The first nanocomposite was invented by researchers of Toyota, published in 1993, who developed nylon-6 nanocomposite [1]. The concept was then expanded to preparation of rubber/nanoclay nanocomposites. Most of their new findings were reported since past decade. Nanoscale dispersion of filler within rubber leads to tremendous interfacial contacts between rubber and filler which causes to superior properties than those of rubbers added with conventional macro- or micro-scale fillers. Most notable properties are increased modulus, increased gas barrier properties, increased heat distortion temperature, resistance to small molecule permeation, increase in atomic oxygen resistance and retention of impact strength [2]. Rubber/nanoclay nanocomposite with a relatively low filler loading achieved required improved properties when compared to conventional fillers with higher loading [3]. Due to high demand in preparation of rubber/nanoclay nanocomposites, various techniques namely melt interaction, in situ intercalative polymerization, exfoliation adsorption and template synthesis were used in preparation of rubber/nanoclay nanocomposites [4].

II. NANOCLAY STRUCTURE AND REINFORCEMENT

Particle size, structure and surface characteristics are the main three factors that influence reinforcing ability of conventional fillers. Increase of modulus and tensile strength is dependent on particle size of the filler; smaller particle size fillers imparts greater reinforcement to rubber than coarse ones. Particle size is directly related to reciprocal of surface area per gram of filler, and therefore, an increase in surface area that is in contact with rubber matrix probably leads to increase in reinforcement.[5]. Specific area of filler particle is directly related to the shape/geometry of the filler. Spherical particles of 1 μ m have lowest surface area of 6 m²/cm³. Nanoscale platelets filler particles have the highest surface area in order of 300-400 m²/cm³ which is effective for reinforcement [6]. Rubber/nanoclay nanocomposites are made by exfoliation or intercalation of layered silicate into rubber matrix and are of main three types which are shown in Fig. 1.

Increase of interlayer space in clay particles is the most important factor to disperse clay in rubber matrix. Conventional nanocomposites contain clay tactoids with the nano-layers aggregated in non-intercalated face-to-face form leads poor mechanical properties. Intercalated nanocomposite is formed by infiltration of one or more molecular layers of rubber into clay host galleries. Exfoliated nanocomposite is formed with individual clay layers that are separated in a continuous rubber matrix by an average distances that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite [2].

Clays are naturally occurring minerals with variability in their constitution depending on their groups and sources. Clays are used for preparation of nanoclays, recently; mainly belong to smectite group clays which are also known as 2:1 phyllosilicates, eg. Montmorillonite (MMT) [7]. Phyllosilicates, or layered silicates, includes natural clays and synthesized layered silicates such as magadiite, mica, laponite and fluorohectorite. Clay crystal structure consists of layers made up of two tetrahedral coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide [8, 9]. Thickness of layers would be around 1 nm and lateral dimensions of these layers may vary from 30 nm to several microns or larger. Stacking of the layers leads to a regular Van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers, for example, Al^{3+} replaced by Mg^{2+} , Fe^{2+} or Mg^{2+} replaced by Li^+ , generates negative charges that are counter balanced by alkali and alkaline earth cations (Na^+ , K^+ , Ca^{2+}) situated inside the galleries [7]. Layered silicates are characterized by a moderate surface charge known as the cation exchange capacity [10]. This charge is not locally constant, but varies from layer to layer, and must be considered as an average value over the whole crystal.

Organoclays are prepared through the exchange reaction of some pristine clay with an organophilic ion which increased the interlayer gallery space rather than normal nanoclay [11]. Clay surfaces are changed from hydrophilic to hydrophobic when inorganic cations are exchanged by organic cations. Organic cations lower surface energy and decrease cohesive energy by expanding the interlayer distance, thus facilitating wetting and interaction of rubber. The functional groups of organic cations react with rubber and improve interfacial adhesion between nanoclay and rubber. Complete dispersion or exfoliation of clay tactoids in a rubber matrix may involve three steps; wetting the surface of clay tactoids in rubber, intercalation of rubber into clay galleries, and exfoliation of the clay layers [2].

Intercalation techniques are helpful to insert organic molecule into clay gallery, effectively. Electrostatic and Van der Waals forces holding the layers together are relatively weak, and therefore inter layer space depends on charge

density on the layers, inter layer cation radius and degree of hydration [12]. Clay intercalation can be done by cation exchange reaction, anion exchange reaction, sol-gel reaction, hydrogen bonding, combine ion exchange and hydrogen bonding, carboxylic acid chelation, mechano-chemical intercalation and carbon dioxide interaction. Intercalation agents create non covalent bonding and covalent bond reactions with clay surfaces which causes improving incorporation of clay phase separation in the clay confinement. As a result, the layered structure has been considered as nanoscale galleries for encapsulating organic guest substrates such as polymers. Organic clay intercalation normally proceed in a stepwise manner that involve the first ion exchange or polar head chelation toward clay counter ions, followed by further organic incorporation by hydrophobic or hydrogen bonding forces [13]. The randomization of layered clay is the final result, which can be controllable. In the past, alkyl quaternary-ammonium salt surfactants were used as intercalating agents, but recently, hydrophobic backboned poly(oxyalkylene) amine derivatives and their corresponding amphiphilic polymers have been structurally tailored to expand the clay interlayer spacing. Various studies were done to increase the interlayer space, which are not limited to rubbers. Interlayer spaces obtained through different intercalation techniques and with intercalation agents are summarized in Table 1.

Exfoliated structure is expected when interlayer space is greater than 10 nm. It is interesting to note that the length of ammonium ions has a strong influence on the resulting structure [14]. Alkyl ammonium ions with chain length larger than eight carbon atoms favor exfoliated structures whereas ammonium ions with shorter chains lead to the formation of intercalated structures. Further, phase inversion of amphiphilic copolymer emulsifiers [15, 16] and presence of functional end-groups [17] promote exfoliated structures. However, none of the studies conducted with different intercalation techniques was successful in creating permanent fully exfoliated structures.

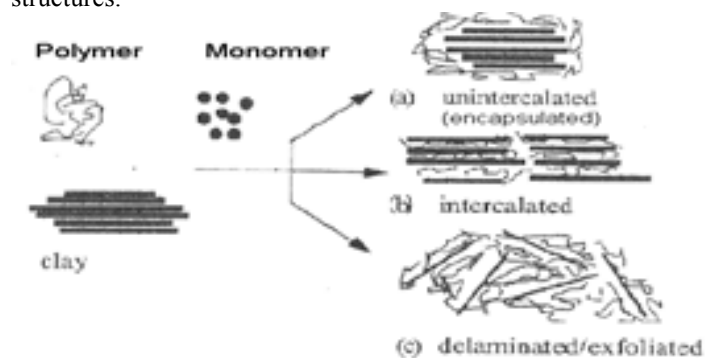


Fig. 1 Structures of nanoclay/rubber nanocomposites

TABLE I. CLAY INTERCALATIVE TECHNIQUE AND INTERLAYER SPACE

Intercalation Technique	Intercalation agent	Clay	Interlayer space (nm)	Reference
Cation exchange reaction	Low-molecular weight organics such as onium salts or liquid imidazolium salts	Na-MMT	2-5	[18, 19]
	poly(oxyalkylene)-amine	Na-MMT	1.2- 9.2	[20]
	Comb-like polymeric surfactant	Na-MMT	1.7-7.8	[21, 22]
Hydrogen bonding	Poly ethylene glycol (PEG)	Na-MMT	1.81	[23]
Combined ion exchange and hydrogen bonding	Triethylene glycol mono-n-decyl ether	Na-MMT	3.8	[20]
Carboxylic acid chelation	Sodium carboxylate, $\text{CH}_3(\text{CH}_2)_n\text{COONa}$ (n-10,16)	Mica	7.8	[24]
Carbon dioxide intercalation	Sodium carboxylate, $\text{CH}_3(\text{CH}_2)_n\text{COONa}$ (n-10,16)	M^{2+} -MMT	4.3	[25]
Amino acid chelation	Carbon dioxide	Na-fluorohectorite	1.25	[26]
Mechano-chemical intercalation	Poly(oxyalkylene)-amino acid	Na-MMT	5.1	[25, 27]
Sol gel reaction	\square -methacrylopropyl dimethyl trimethoxy silane	Na-MMT	1.26-3.04	[28, 29]
Anion exchange reaction	Poly(oxyalkylene)-amino acid	Mg-Al LDH	3.3-9.4	[27, 30]

III. NATURAL RUBBER NANOCCLAY NANOCOMPOSITES

Natural rubber (NR) is a high molecular weight polymer having chemical structure of cis 1,4 polyisoprene. Molecular weight of NR is in a range 200,000- 600,000, with a relatively broad molecular weight distribution [31]. NR vulcanizates have high tensile strength over a wide hardness range due to its strain induced crystallization [32]. It has the highest resilience which is responsible for its very low heat buildup. It shows low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear and fatigue. With these unique properties of NR, development of NR/nanoclay nanocomposites is highly important to the rubber industry, especially to produce high performance rubber products with superior properties.

NR/nanoclay nanocomposites are developed in the rubber industry starting either from dry rubber or from aqueous rubber called latex. Dry NR is a coagulated rubber from its latex form added with a coagulating agent. Properties of the resultant nanocomposites are varied with technique of incorporation of nanoclay into rubber matrix. Rubber/nanoclay nanocomposites prepared using different techniques, starting from either dry rubber or aqueous rubber, are summarized in Table 2. Property enhancements observed in nanocomposites are discussed in the following sections, separately, based on the starting material.

A. Nanoclay Nanocomposites with Dry Rubber

Dry rubber compounds are prepared by incorporating chemical ingredients using internal mixers or mills, and are shaped later on with different techniques. Nanoclay was also incorporated in this stage, however, it was noticed that time and shear forces are not sufficient to disperse nanoclay in the rubber matrix to obtain maximum properties. Several studies were conducted with successful incorporation of nanoclay into rubber matrix with modifications of rubber and/or clay [33, 34]. Grafting of NR compatible to clay was the common modification technique. Most of such modifications were done separately before compounding stage and the modified clays were incorporated by shear blending. When clay layer surfaces are sufficiently compatible with the chosen rubber, which will

crawl into interlayer space and form either an intercalated or an exfoliated nanocomposite. In one study [35], epoxidized NR was used to incorporate organoclay. Due to high compatibility of epoxidized NR with polar clay structure, the resultant nanocomposite exhibited improved mechanical properties. Incorporation of clay with poly ethylene glycol which forms inter molecular forces with polar clay and non-polar NR was also showed improved mechanical properties [36]. The property improvements were not as high as expected. Obtaining a fully exfoliated structure is still a challenge. A new method was reported to incorporate of organoclay of particle sizes in a range 10-20 μg into dry rubber [37]. In this process, ground dried clay was sprayed on to the rolling rubber in two-roll mill by means of a pneumatic spay gun. However, this method is not practical due to release of finer particles to the factory environment. The new route of improving the interacted/exfoliate structure without using organoclay also would be important and need more attention toward it [38].

B. Nanoclay Nanocomposites with Aqueous Rubber

In aqueous rubber industry, main methods of production of nanocomposites are combining self-assembly, latex compounding or casting and shear blending followed by drying through evaporation [39, 40, 41]. The latex compounding is the widely used method, in which nanoclay and other compounding ingredients are added into aqueous rubber stage and shape of product was obtained by coagulating using particular former with aid of a coagulation agent and dried in an oven for vulcanization. The exfoliated structure found at the latex stage was destabilized while adding coagulant agent may be the significant issue in the industries and further studies require to understand this. The layers of clay structure may stack together and result inferior mechanical and barrier properties. Since no further shearing is applied after coagulation, stack layers will not be delaminated. Application of a suitable modification technique such as use of a compatibilizing agent or a surfactant or using grafting, etc. are the techniques used to minimize this shortcoming [42,43]. This would cause another problem of providing poor dispersions. Nanocomposites developed from aqueous rubber

did not exhibit expected properties and more research work is necessary to be carried, in future.

C. Co-coagulation Method

Co-coagulation method is another process practiced to develop rubber/nanocomposites. In this process, nanoclay is introduced before coagulation of aqueous rubber. Dry rubber is then produced, which can be compounded in similar to dry rubber compounding.

It was reported that agglomeration of clay layers can be prevented when incorporating rectorite clay into aqueous NR [43]. When flocculants are added, both aqueous rubber and rectorite layers were coagulated without intercalating rubber macromolecules into inter layer gallery space of clay. The competition between flocculation of rubber particles and agglomeration of silicate layers on addition of flocculants plays a vital role. Cations in flocculants probably cause re-aggregation of exfoliated rectorite layers so that the rubber particles between rectorite layers may be expelled. Re-aggregation of rectorite layers is obstructed to some extent by rubber particles around the rectorite layers when amount of rubber is more than that of rectorite layers. Dispersion level of nanocomposite depends on the ratio of rubber to rectorite, the size of rubber particles, the compatibility between rectorite layers and rubber molecules and the speed of co-coagulating. At lower rectorite loadings up to 10 phr, tensile strength of NR increased [44]. At higher loadings, tensile strength remained constant while elongation at break significantly decreased.

Main reasons for this drop can be of hindrance of stress-induced crystallization of pure NR and increase of the dispersion phase size of the nanocomposite by introduction of more rectorite layers. In a separate study [45], it was explained that a flocculent coagulated both rubber and silicate simultaneously without intercalating into galleries of clay. Further, excellent degree of exfoliation of clay was obtained through dialyzed aqueous rubber in which excess ionic species and other small non-rubber molecules were eliminated [46]. The eliminating process of ions in the aqueous rubber promotes modulus of the resultant product.

It is important to note that the non-exfoliated layer aggregates without intercalation of rubber molecules in rubber/clay nanocomposites prepared by co-coagulation is different from the intercalated layer aggregates in rubber/clay nanocomposites prepared by shear blending. During shear blending, rubber molecules are first intercalated into inter gallery of Organoclay leading to decrease in interaction between layers and then the intercalated Organoclay is then exfoliated under shear forces [47]. Rubber/clay nanocomposites prepared by co-coagulation method are a kind of partly exfoliated structure, in which the rubber molecules separated clay into either individual layers or layer aggregates of nanometer thickness without the intercalation of rubber molecules into clay galleries. This separated rubber/clay nanocomposites, whose structures are different from those of intercalated and exfoliated rubber/clay nanocomposites, exhibit excellent mechanical and gas barrier properties.

TABLE II. STUDIES ON DEVELOPMENT OF RUBBER NANOCOMPOSITES

Method of preparation	Nanocomposite	Resultant properties	Ref.
Melt compounding	Ethylene propylene diene monomer (EPDM) with Octadecyl ammonium filled MMT (Organo MMT) and with Na-MMT at 20 phr loading	Tensile strength of EPDM/Na-MMT was 2 MPa and Organo MMT-EPDM was 8 MPa. 100% modulus was increased up to 2.4 MPa with Organo-MMT which is greater than that with Na-MMT. EPDM/Organo-MMT showed high toughness and stiffness.	33
Modified ball milling followed by latex shear blending	Nitrile rubber (NBR) with Na-MMT at 7.5 to 10 wt% loading	Tensile strength was 8 MPa and tear strength was 16 N/mm. Partially exfoliated and intercalated structure were obtained.	34
Co-coagulation	NBR with dimethyl ditallow ammonium filled Organo MMT at 30 wt% loading Calcium carbonate was used as the coagulating agent	Tensile strength of NBR/Organo-MMT was 10.73 MPa, which was 1.88 times higher than pure-NBR. Excellent thermal stability and swelling behavior was exhibited.	48
Latex compounding	NR and styrene butadiene rubber (SBR) with dodecylamine filled Organo-MMT at 4 wt% loading	Tensile strength for 0 phr is 15MPa and for 4phr it was 25Mpa.	39
Latex compounding	NR with sodium bentonite and sodium fluorohectorite at 10 wt% loading	High stiffness, low damping characteristics and good thermal stability was showed. The stress of 300% elongation of Bentonite, fluorohectorite and gum rubber were 4, 2 and 1 MPa respectively	40
Latex compounding	NR with Na-MMT at 5 to 30 phr loading	Tensile strengths for 10 phr 20 phr and 30 phr of Na-MMT of vulcanized NR were 6.5 MPa 9.7 MPa and 7.9 MPa, respectively. Highest young modulus of 223 MPa was at 30 phr of Na-MMT, and that of gum NR and vulcanized NR were 1.3 MPa and 3-8 MPa, respectively. Elongation at break was high at 5 phr of Na-MMT and was 599%: Gum and vulcanized NR showed 750-850% and 550-650, respectively.	41
Combining self-assembly latex compounding	NR/silica (SiO ₂) at 0 to 4 wt%	Tensile strength and modulus at 300% elongation at 4 wt% were 26.3 MPa, 5.08 MPa; those for pure NR were 15.1 MPa and 1.27 MPa. Incorporating even a small loading at 0.5 wt% showed remarkable enhancement in tensile strength and modulus.	49
Rubber compounding	NR with onium ion-modified MMT at 2 phr loading, compatibilized with epoxidized NR	Tensile strength for Organo clay alone was 18.73 MPa, for Organo clay with epoxidized NR was 28.75 MPa. Elongation at break, modulus at 300% elongation and tear strength increased with addition of epoxidized NR from 880% to 1220%, from 1.93 MPa to 2.03 MPa and from 42 to 59, respectively.	50
Rubber compounding	NR with Na-MMT by new route of	Intercalated/exfoliated structures were reported. Tensile strength for NR,	38

	organophilization using PEG	NR/MMT, NR/1PEG NR/MMT/2.5PEG were 14.5, 9.05, 14.73, 18.28 MPa	
Rubber compounding	NR with modified Kaolin with sodium salt of rubber seed oil at 2 to 10 phr loading	Tensile and tear properties increased with increase in clay loading. Optimum tensile strength for 8 phr of modified Kaolin was 11.3 MPa; unmodified Kaolin was 23.9 MPa	51
Co-coagulation Rubber compounding	NR with organophillic (dodecylmethyl ammonium bromide at 20 phr loading	Tensile strength was in a range 15 to 17 MPa	52
Co-coagulation followed by rubber compounding	NR with rectorite at 5 to 20 phr, Coagulated with 2% sulfuric acid	Tensile strength increased up to 10 phr addition, elongation at break significantly decreases. The stress of 300% elongation for 0, 5, 10, 20 were about 2.5, 6.0, 8.0 and 17 MPa respectively.	53
Co-coagulation Rubber compounding	NR, SBR and NBR with RNH_3^+ -MMT and Ca^{2+} -MMT modified clay at 20 phr loading; ammonium cations from triethylenetetrammonium chloride and calcium cations from calcium chloride were used as coagulation agents	Inter layer gallery space was in a range 1.25-1.50 nm, which less than the minimum inter layer gallery space of 1.7 nm was found for Organoclay. Compared to NR, hardness, tensile strength, tear strength and elongation at break with modified clays varied from 41 to 54 Shore A, 11.6 to 26.8 MPa, 22.8 to 44.1 kN/m and 568 to 644%, respectively. Tensile strength of SBR-clay nanocomposites was 6 times higher than that with SBR.	45
Co-coagulation followed by rubber compounding	NR with Organo clay (Nanofil 8) at 4 phr loading and with precipitated silica at 0 to 40 phr loading; acetic acid was used as the coagulating agent	Optimum tensile strength, modulus at 300% elongation and elongation at break were 25 MPa, 3.0 MPa and 647%, respectively. Properties were decreased with precipitated silica.	53
Shear blending and dry process by using evaporator.	Dialyzed NR latex with Na-MMT at 10% loading	100-fold increase in elastic modulus was recorded for dialyzed NR compared to a 5-fold increase for NR	46
Co-coagulation followed by rubber compounding, Emulsion intercalation	NR/SBR with Organo (dimethyl ditallow-ammonium chloride) bentonite at 3 to 20 wt% loading; acetic acid was used as the coagulating agent	Inter layer gallery space of Organo bentonite was 3.71 nm and that for Na-MMT was 1.55 nm. Tensile strength, modulus and elongation increased with organo-bentonite up to 12 wt%. Maximum tensile strength, tear strength, 300% modulus and elongation was 4.4 MPa, 21.8 kN/m, 3.9 MPa and 388%, respectively. Mechanical and thermal properties were superior to those for pure SBR/NR.	47

IV. FUTURE TREND

Many rubber nanocomposites were synthesized in laboratory scale on interest of academics and researchers, but application of such inventions into industrial scale production is still in a challenge. None of the findings in previous studies showed optimum levels of properties in the same nanocomposite. Property fluctuation in nanocomposites was high due to non-formation of similar structures during processing and hence limits applications of nanocomposites in rubber industry. Main aim of the aqueous rubber or latex industry is to produce lightest films with remarkable mechanical properties achieved through use of small amounts of nanoclay than use of conventional clays. The demand of incorporation of nanoclay into dry rubber is increased, but is still an ideal solution due to lack of in depth analysis on current issues facing on development of nanocomposites. Reducing the gap by integration of related knowledge and technology on nanocomposites invented in various research works will be the current requirement and the objective of this review.

Co-coagulation method would be the most promising method to prepare rubber/nanoclay nanocomposites, although it was not yet extensively studied. A similar process was first developed in 1957, in order to destabilize NR latex with a clay mineral. In aqueous rubber, clay swells by hydration and makes it good dispersion at molecular level in rubber matrix. However, application of this process was limited due to lack of identified knowledge on nanoclay and clay modifications at that time. The current knowledge and technology would be helpful to develop co-coagulation concept in preparation of NR/nanoclay nanocomposites. Major advantage of this method is the ability of modification of both nanoclay and the aqueous NR during processing.

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