

Natural rubber-based polymer blends and composites

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1 Introduction

1.1 What is natural rubber?

Natural rubber (NR) is rubber produced from raw materials of plant origin, and is mainly collected from the rubber tree (*Hevea brasiliensis*), native to the Amazon basin. Raw rubber is manufactured by collecting and drying an emulsion called latex, containing 30%–40% rubber powder, from a rubber tree, and exhibits various properties, depending on the rubber tree.

Research into NR began with Christopher Columbus' second voyage, in 1496, with the first NR balls that were taken from the West Indies to the Iberian Peninsula. Afterward, in 1791, Samuel Peal manufactured a waterproof cloth by coating a fabric with a solution of NR dissolved in turpentine oil, and applied for a patent on this method. This patent contributed to the gradual expansion of the application range of NR. In particular, in 1893, Charles Goodyear and Thomas Hancock devised an independent curing system for NR, by which NR was transformed to a polymer material with improved tensile strength and high resistance to organic solvents. This material modification became the cornerstone of the current global business on NR, dealing with billions of NR products. In 1908, the business of Henry Ford provided an opportunity for explosively increasing the demand for automobile tires using NR. However, Japan's occupation of Southeast Asia during World War II blocked the supply of NR, resulting in a sharp decline in industrial growth.

In the mid-1980s, as the demand for NR latex increased exponentially, and the NR latex industry moved from the West to the East, the total global consumption increased dramatically to 300,000 tons or more. In 2011, the worldwide consumption of NR and synthesized rubber (SR) comprised 42.3% and 57.7%, respectively (30% of NR was consumed by China). According to S. Evans, the former secretary-general of the International Rubber Study Group (IRSG), the expected consumption and production of NR in 2020 were 16.5 and 15.2 million tons, respectively (Chan et al., 2013; Ciesielski, 1999; Hurley, 1981; James & Guth, 1943; Mark et al., 2013; Visakh & Visakh, 2017).

NR is a representative reinforcing agent, and in particular, it has high applicability as an impact modifier in composite materials. At the early stage of research into NR, latex applications mainly utilized the intrinsic properties of NR. The actual production yield (3000 kg/ha/year) was much less than the theoretical production potential (9000 kg/ha/year), which significantly deviated from the actual industrial potential. This difference is gradually increasing due to the poor working environments in the main production areas, as well as a lack of production manpower (Chan et al., 2013).

To resolve this problem, the Bridgestone Americas Center decoded the major genome sequence of Hevea to increase NR production, and applied the outcome to the development of new production technology and growing methods for NR. However, due to fundamental issues, such as pest attack and mold discoloration of the NR wood, as well as various contaminations occurring in the handling and transportation stages, commercial applications have been restricted, and methods to resolve these problems are still under development.

The major driving force for the recent industrial revival of NR is the discovery of nanomaterials. The application of nanomaterials to conventional polymeric materials has resulted in new physical properties, expansion of the application scope, and enhanced development potential of fusion materials between various materials (Chien et al., 2010; Dong et al., 2014; Kaneto et al., 1999; Yu et al., 2006).

The combination of NR and nanomaterials facilitates the discovery of new materials, and further widens the ripple effect of materials that can meet specific customer requirements. This chapter introduces nanocomposite materials prepared from NR and various nanomaterials and describes their influences on the performance and properties of NR.

2 Natural rubber-based polymer nanocomposites

Recently reported composite materials show differentiated performances compared to conventional materials and are being developed as materials with industrial applications, focusing on high performance, resistance to extreme environment, and eco-friendliness. In the past, materials were designed and developed according to need, while the current and future industries are focused more on the convergence material industry, whose application range is not limited to any one area. Polymer nanocomposite materials are drawing increasing research attention in response to this demand.

Polymer nanocomposite materials have high performance and multifunctionality, which exceed the limitations of existing physical properties, appearance (shape), and synthesis methods of the component nanomaterial. This chapter describes the properties of NR composites added as nanofillers, such as spherical silica particles, multi-layered clay, and rod-shaped carbon nanotubes (CNTs).

2.1 *Si-based NR nanocomposites*

The mechanical/thermal properties of polymer composites are influenced by several factors, including process conditions, filler dispersion, polymer–filler interactions, and filler morphological aspects, and NR composite materials are no exception. Among them, the dispersion state of the filler is essential for determining the overall physical properties of nanocomposite materials, especially inorganic–organic nanocomposites, polymer–clay nanocomposites, metal–clay nanocomposites, etc. prepared by the sol–gel method. Studies to improve the dispersion state of fillers have been reported (Bokobza & Chauvin, 2005; Ikeda & Kameda, 2004; Poompradub et al., 2005).

The sol–gel process can be conducted before or after the cross-linking reaction. Ikeda's group performed a sol–gel reaction before hardening after immersing the unvulcanized NR sheet in tetraethyl orthosilicate (TEOS) solution at room temperature for several hours. The results show that the reference sample NR exhibits high tensile strength and elongation, while the composite material containing silica had enhanced physical properties. In particular, the reinforcing properties of the additives are remarkable at an initial elongation of 200% or more, which can be regarded as a result of the typical improvement of physical properties of composite materials due to the addition of fillers. Furthermore, there was an increase in the initial modulus of elasticity of the composite material synthesized by the simultaneous polymerization method, involving filler addition along with cross-linking of NR rubber, compared to the system fabricated by simple stirring as the filler addition method. This can be interpreted as a result of uniform distribution (variance) of fillers in the matrix (Bokobza & Chauvin, 2005; Ikeda & Kameda, 2004; Murakami et al., 2003; Poompradub et al., 2005).

2.2 *Clay particles*

In the case of fabricating a nanocomposite using clay, which has a typical plate-like structure, the contact area between the filler and the polymer matrix is relatively larger than that of the spherical filler, resulting in a greater filling effect than that obtained for the conventional composite material. Thus, the clay–polymer nanocomposite has the advantages of reduced dimensional stability, heat resistance, and gas permeability, and exhibits enhanced physical properties in a smaller amount compared to conventional composites. Montmorillonite (MMT) is the most actively applied filler material in the fabrication of polymer–clay nanocomposite materials. MMT is a layered mineral belonging to the smectite family, and has a hydrophilic structure in which cations, such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , are filled between the layers, and $-\text{OH}$ groups are present at the ends of the sheet; therefore, it is difficult to intercalate polymers with lipophilic properties between silicate layers. Thus, layered clay minerals are modified with organic clay, and then used in nanocomposite materials (Christidis & Scott, 1993). As a representative example, the first practical polymer–clay nanocomposite material was the nylon–clay nanocomposite reported by the Toyota Motor Company in 1987, prepared by an exfoliation phenomenon, in

which the intercalation of a nylon monomer between silicate layers increased the interlayer distance to approximately 100 Å (Wang & Pinnavaia, 1994).

Joly et al. (2002) fabricated a nanocomposite by dissolving 10 phr of an organomodified clay [dimethyl hydrogenated tallow (2-ethylhexyl) ammonium montmorillonite], an organic solvent (toluene), as a formulation component for synthesizing NR. The XRD results show a diffraction pattern typical of organoclay (OC), as well as a 001 lattice plane at $2\theta = 2.5$ degrees. However, the results suggest that the peaks of the OC lattice included in NR were shifted to a lower diffraction angle. In particular, $d_{001} = 34.0$ Å for pure OC, whereas the interlayer spacing in the composite materials increased to 40.1 Å. This phenomenon can be attributed to the increased interaction between the filler and the polymer upon intercalation of polymer chains between the silicate layers. Moreover, as shown in the TEM images, conventional clay-polymer composites exhibit low dispersion behavior due to coagulation between clays, whereas OC exhibits uniform dispersion of nanofillers in the matrix. In particular, the plate-like structure of clay can be observed partially. These results show the correlation between the dispersion of the nanofiller and the improvement in the physical properties of the polymer nanocomposite (as shown in Figs. 2.1 and 2.2).

Wu et al. (2005) further attempted uniform dispersion of the filler in rubber by cocoagulating clay and rubber in an aqueous suspension. Fig. 2.4 illustrates well this dispersion behavior. The filler and the matrix in aqueous suspension allow the rubber to penetrate into the filler by a capillary phenomenon, and subsequent coagulation enables the fabrication of a polymer nanocomposite with a uniform dispersion characteristic (as shown in Fig. 2.3).

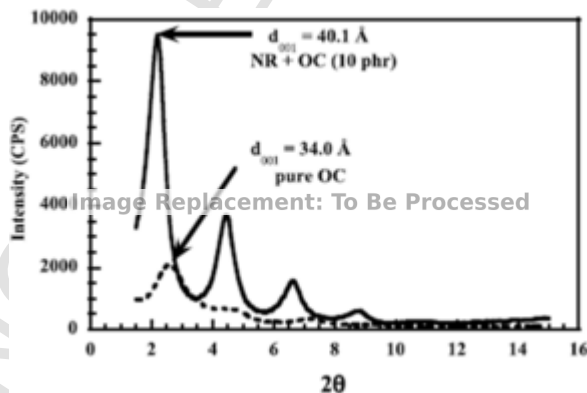


Figure 2.1 X-ray diffraction patterns for pure organoclay (OC) and for the NR composite filled with 10 phr of OC.

Reproduced with permission from Joly, S., Garnaud, G., Ollitrault, R., Bokobza, L., & Mark, J. E. (2002). Organically modified layered silicates as reinforcing fillers for natural rubber. *Chemistry of Materials*, 14(10), 4202–4208.

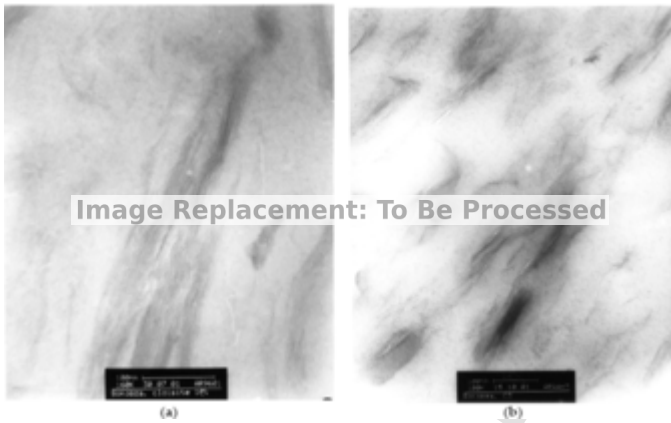


Figure 2.2 TEM micrographs of natural rubber filled with 10 wt.% of clay: (A) is for unmodified clay and (B) is for organomodified clay (Joly et al., 2002).

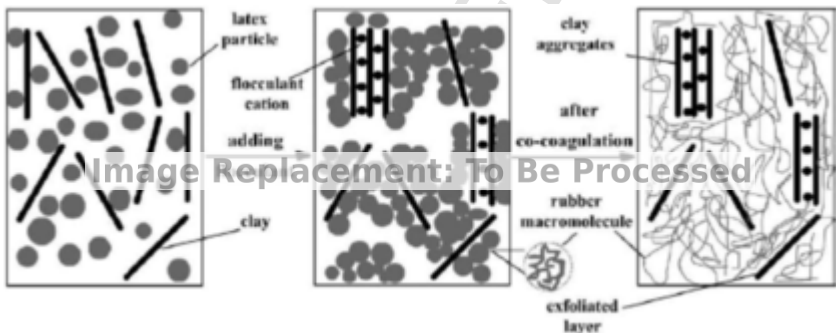


Figure 2.3 Schematic of the mixing and co-coagulating process (Wu et al., 2005).

2.3 Carbon nanomaterials

NR, which does not undergo reversible deformation, is used in various industries. Because of its mechanical properties of high strength and high elasticity, NR can be utilized for different purposes (Miedzianowska et al., 2019).

Carbon materials, including carbon nanotubes, carbon black, graphene, and MoS_2 , are among the most widely explored nanomaterials (Ajayan et al., 2000; Baughman et al., 2002; Collins et al., 1997; Dresselhaus et al., 1996). Because carbon materials have high elastic modulus, excellent mechanical properties, and chemical stability, they are used in various fields such as for the development of high-strength composite materials, flame retardants, and biofields, as well as the preparation of electrochemical devices, hydrogen storage materials, field emission

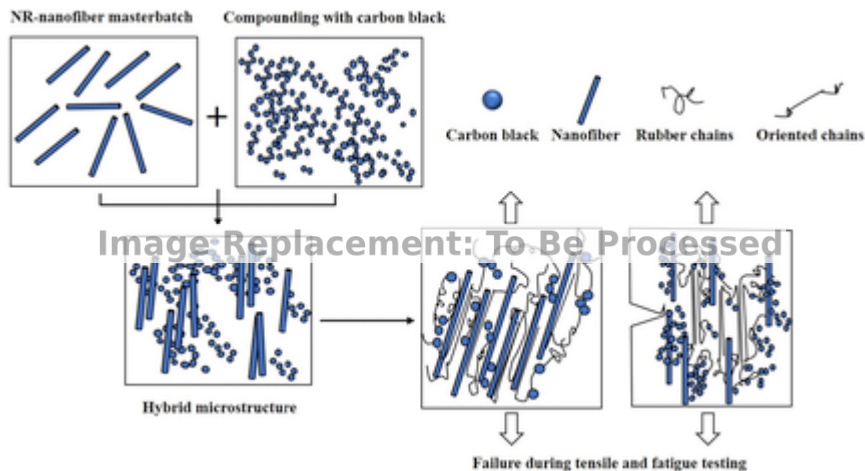


Figure 2.4 Development of hybrid microstructure and its effect on the failure resistance of composites (Parameswaran et al., 2021).

devices, gas sensors, supercapacitors, and memory devices (Baughman et al., 2002; Berber et al., 2000; Choi et al., 2003; Dzenis, 2004; Subbiah et al., 2005).

Carbon black (CB) is the most widely used reinforced filler in NR formulations, which are frequently used in static-dissipative plastics (Araby et al., 2015; Baughman et al., 2002; Bokobza, 2019; Ponnamma et al., 2014; Sadasivuni et al., 2014). In particular, the use of CB as a filler facilitates controlled conductivity, easy dispersion, improved component properties, and good surface treatment. However, a large amount of CB, that is, 10–30 times higher than that of nanomaterials, is required. Although this high amount enhances the electrical properties, it degrades the mechanical properties, thereby limiting its application. To resolve this problem, the use of nanomaterials as alternatives to CB has been widely investigated.

Zhao and colleagues (Sui et al., 2008) compared the composite formed to conventional NR by mixing CNTs and CB with NR that exhibited considerably higher mechanical strength, which was attributed to the presence of CNTs. In particular, a low tan delta value of the composite using CNTs and CB, determined through dynamic mechanical analysis (DMA), was achieved at 50–60°C, which suggests that the rolling resistance (antislip property) of the composite is high when NR is mixed with the filler (as shown in Fig. 2.4).

Furthermore, a hybrid filler system was prepared by simultaneously adding two or more different carbon-based fillers to the rubber matrix. The hybrid system exhibited higher mechanical properties than the system wherein a single filler was used, because of the physical interaction between the fillers in the rubber matrix. In particular, the composite in which CB and CNT were used showed an increase in the tensile strength value by approximately 110% compared to the one with only CB (Parameswaran et al., 2021). In addition, the tan delta value of the composite was

lower than that of the system wherein only CB was used, which could be attributed to the higher rolling resistance of the former. Thus, this NR composite can be used as a tire material. Because abrasion loss is an important property that represents high performance of tires, hybrid composites such as those including CNTs showed a significantly lower abrasion loss value than the system based on only CB.

Das and colleagues illustrated that the simultaneous addition of the two fillers (CB and CNTs) causes an increase in the mechanical properties because when the well-dispersed CNTs and CB are subjected to force, as shown in the figure 2.6, CNTs are aligned in the direction of the applied force, facilitating force transmission. In addition to mechanical property enhancement, the piezoelectric properties can be improved by fabricating rubber composites using NR, CB, and CNTs. Although the system using CB alone showed higher sensitivity than the composite with NR + CB + CNTs at the same strain value, the single system exhibited a more stable behavior during the loading–unloading cycle. This is because when CNTs and CB are mixed in an appropriate amount, the application of strain allows for the alignment of CNTs (as shown in Figs. 2.5 and 2.6) (Natarajan et al., 2017).

CNTs are considered as a one-dimensional cylindrical form of graphene, in which three surrounding carbon atoms form a honeycomb-shaped lattice through sp^2 bonding of carbon atoms (Ajayan, 1999; Seidel et al., 2004). The band gap of CNTs is inversely proportional to their diameter. Single-walled CNTs with diameters of 1–2 nm exhibit conducting and semiconducting properties depending on the winding direction (Odom et al., 1998; Wilder et al., 1998). As the number of walls of the CNTs increases, the diameter of the outer wall increases to several tens of nanometers and the band gap decreases; thus, multiwalled carbon nanotubes (MWCNTs) exhibit the properties of a conductor (Ouyang et al., 2002; Van Hove, 1953). CNTs are lightweight because of their hollow cylindrical structure and are highly anisotropic owing to their nano-sized diameter and micro-sized length, which impart high electrical and thermal conductivity as well as a higher tensile force than that of iron (Baughman et al., 2002; Endo et al., 2005; Van Hove, 1953).

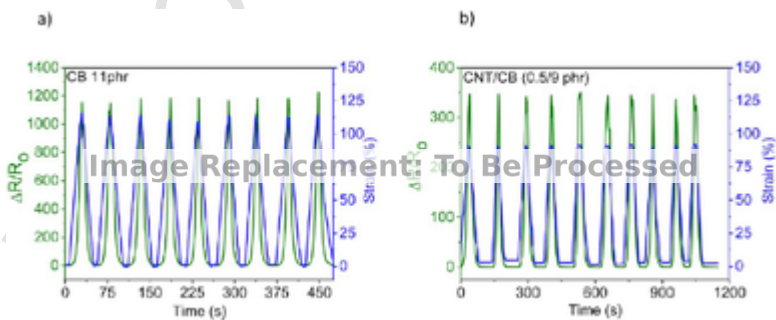


Figure 2.5 Cyclic strain experiment and plots of relative resistance and strain vs. time for (A) CB 11 phr composite and (B) for CNT/CB 0.5/9 phr hybrid composite (Natarajan et al., 2017).

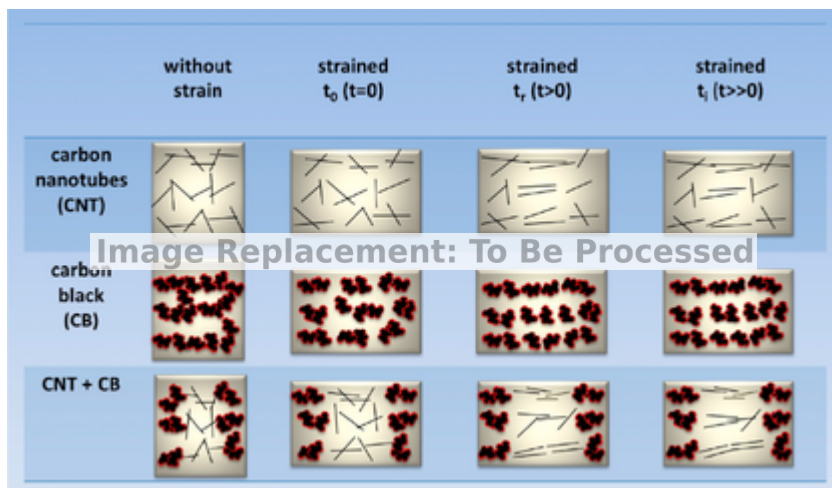


Figure 2.6 Mechanism of time dependence of NR containing CNT, CB, hybrid (CNT/CB) nanocomposites. t_0 : Breakdown of conductive network immediately upon straining ($t = 0$). t_r : Alignment of conductive particles along the tensile direction, as well as reformation of destroyed conductive network ($t > 0$). t_i : Slow and gradual reduction in interparticle distances over longer time, leading to slow decay in resistance ($t \gg 0$) (Natarajan et al., 2017).

Significant improvement in mechanical stiffness has been reported with the addition of MWCNTs in NR (Fakhru'l-Razi et al., 2006; Ruoff & Lorents, 1995).

Jean-Paul Salvetata and colleagues (Bhattacharyya et al., 2008) modified the surface of MWCNTs by strong acid treatment to introduce carboxyl functional groups, and added sodium dodecyl sulfate (SDS) into water to make a solution wherein the CNTs were uniformly dispersed. SDS used in this study is an ionic detergent with a strong negative charge, which is widely used for denaturing proteins or as a propellant for CNTs. The overall mechanical properties increased because of the uniform dispersion of the CNTs in the rubber, and the dielectric measurement result at room temperature showed a low transmission threshold (<1 wt.%), which could be attributed to the well-developed network structure between the CNTs uniformly dispersed in the matrix (as shown in Figs. 2.7–2.9).

Typically, the improvement of elongation due to the addition of the nanofiller into the polymer also causes an increase in strain energy, contributing to the improvement of the overall mechanical properties (including tensile strength, elongation, and impact resistance) of nanocomposites. Fig. 2.10 shows that the properties increase to a certain level, temporarily decrease, and then increase again. This phenomenon can be explained by the pull-out phenomenon: when the CNTs are subjected to load application in the tensile direction, the CNTs in the outermost layer are destroyed and the inner wall layer follows, resulting in the extension of the CNTs. As a result, stretching of the fibers surrounding the CNTs also occurs, which results in an increase in the

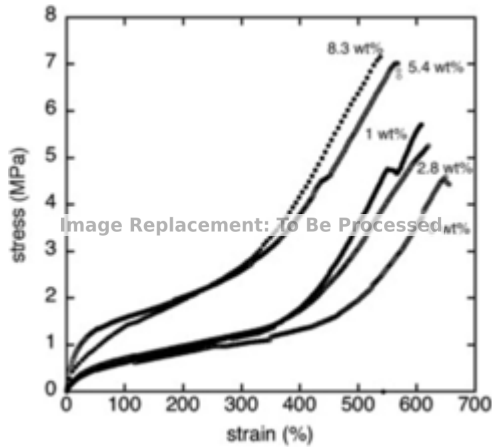


Figure 2.7 Stress–strain curves for pure latex films and composites (Bhattacharyya et al., 2008).

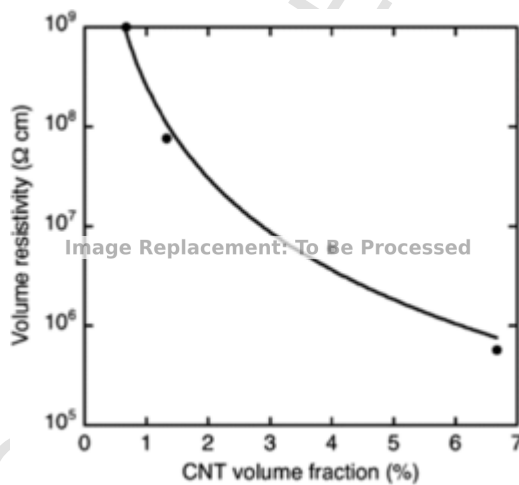


Figure 2.8 Resistivity as a function of CNT volume fraction. An electrical percolation behavior is observed because of CNT network formation (Bhattacharyya et al., 2008).

physical properties of the polyurethane–CNT composite nanowebs (Ajayan et al., 2000; Collins et al., 1997).

Moreover, the comparison between AFM images before and after the coagulation of the composite confirms the uniform dispersion of CNTs (Fig. 2.13). In the images before coagulation, many clusters of irregular size were observed on the surface of

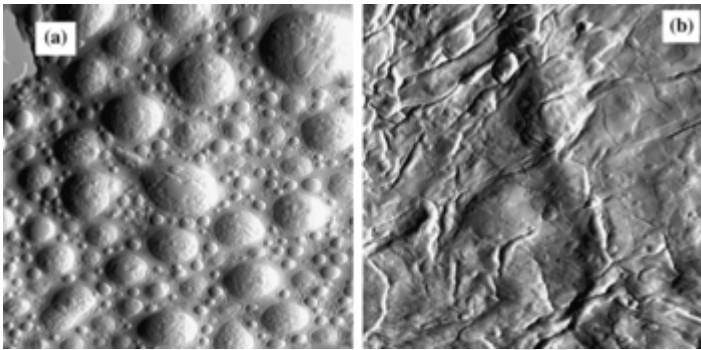


Figure 2.9 AFM image of the surface of a composite with 2.8 wt.% MWCNTs. (A) Before and (B) after coagulation of the latex beads at 60°C. The derivative of the topography signal is shown to highlight the morphology of the film after water evaporation. It was not possible to resolve individual nanotubes at the film surface. No clusters of MWCNTs were observed, showing that macroscopic dispersion was good in agreement with optical microscopy observations (Bhattacharyya et al., 2008).

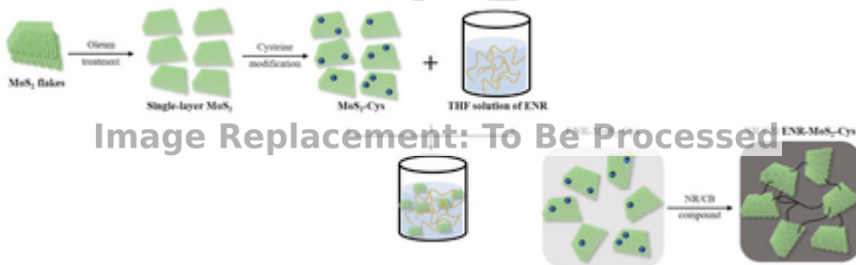


Figure 2.10 Schematic of the entire preparation process of MoS₂-Cys, ENR-MoS₂-Cys, and NR/CB/ENR-MoS₂-Cys (Jiang et al., 2020).

the composite, whereas such clusters were not observed after coagulation. In particular, after coagulation, morphological changes such as coagulation and reduced dispersion of CNTs were not identified, which is attributed to the improvement of mechanical properties and electrical properties of the composites (Grunlan et al., 2004, 2006).

2.4 MoS₂

NR is known to exhibit excellent resilience and high tensile strength, while reinforcing fillers are generally used owing to their low wear resistance (Jiang et al., 2020; Spratte et al., 2017). Molybdenum disulfide (MoS₂), a new nanofiller used to effectively respond to this demand, is composed of S–Mo–S triple layers bound by a weak

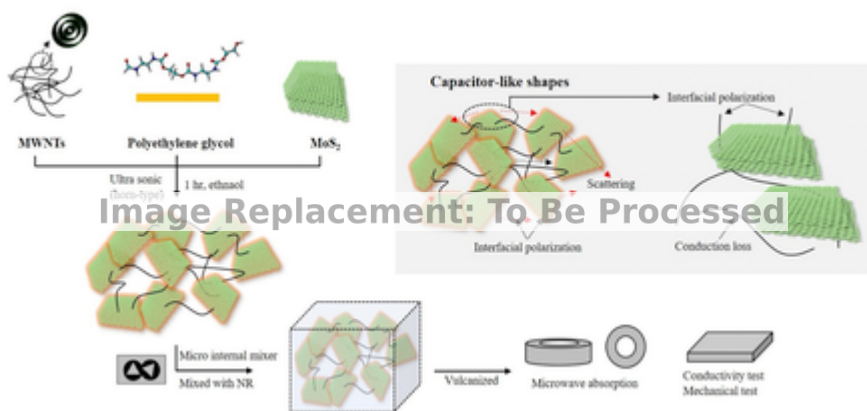


Figure 2.11 (A) Schematic illustration of the fabrication of NR composite with MW-CNTs and MoS₂ hybrids. (B) Schematic illustration of possible microwave attenuation mechanisms of the NR/MWCNTs/MoS₂ composite (Geng et al., 2020).

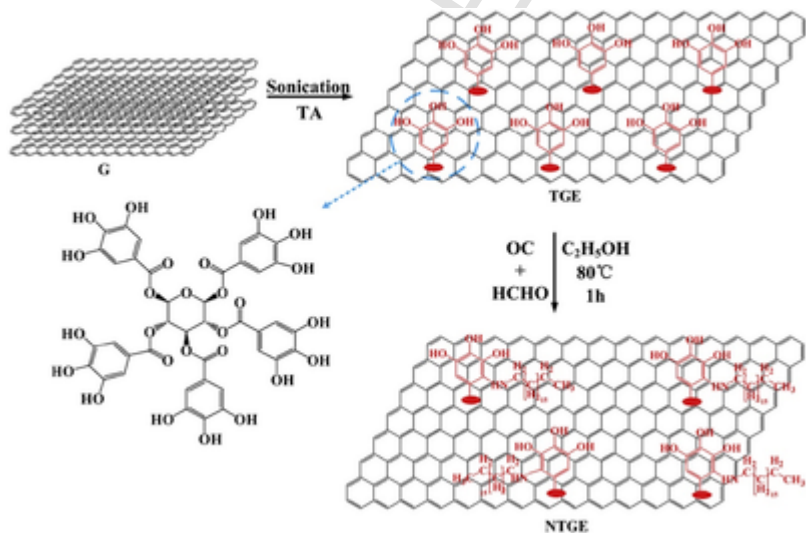


Figure 2.12 Process of liquid-phase exfoliation and mechanism of functionalization of graphene (Zhao et al., 2018).

Van der Waals force, which is widely applied in many fields, such as nanoelectronics, sensors, and catalysts.

Studies have shown that MoS₂ has excellent mechanical properties, such as a high elastic modulus, yield stress, and flexural modulus, suggesting that it is highly likely to be an effective reinforcing filler as a type of polymer composite material

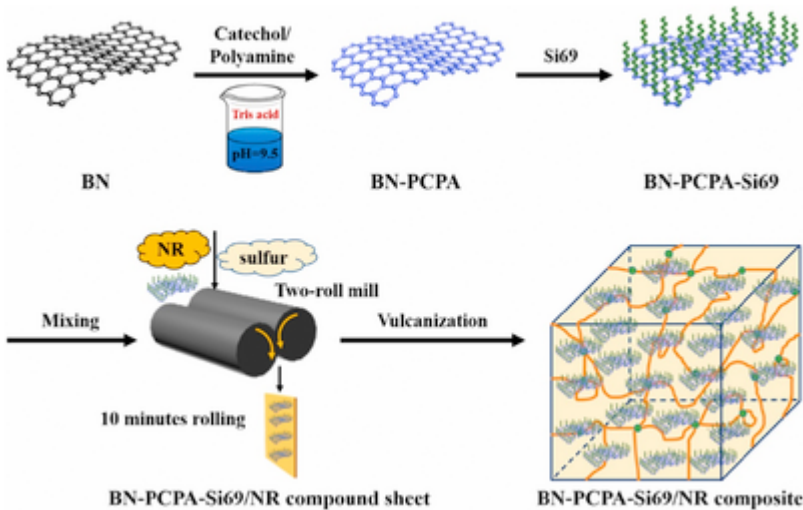


Figure 2.13 Schematic diagram of the preparation of BN-PCPA-Si69/NR composites (Yang et al., 2021).

(Cooper et al., 2013). In addition, MoS_2 has a hierarchical structure similar to graphite, with excellent electronic properties and a high probability of microwave attenuation due to dielectric and magnetic losses by polymorphism. It has been used in various polymers to improve mechanical properties and fire resistance. However, owing to poor dispersion in the matrix and weak interaction with the matrix, this application has not been sufficient for high-performance tires and requires additional application.

The study results on NR/CB/ENR- MoS_2 -Cys as an additional application were reported to resolve this problem, where a mixture of epoxide natural rubber (ENR) and cysteine (Cys) modified MoS_2 (MoS_2 -Cys) was added into the NR/CB compound (as shown in Fig. 2.10) (Jiang et al., 2020).

The ENR in the MoS_2 nanocomposite showed an excellent interaction between the modified MoS_2 -cys and NR, and the MoS_2 -cys size of NR/CB/ENR- MoS_2 -Cys was smaller than that of NR/CB/ MoS_2 -Cys. As a result, the ENR effectively increased the dispersion of MoS_2 -Cys in the NR matrix (Jiang et al., 2020). In other words, because large-sized MoS_2 -Cys may not be properly dispersed in the NR matrix, it could induce stress concentration and severe internal consumption, which can be considered as the cause of the degradation in mechanical properties. In contrast, the size of MoS_2 -Cys reduced due to ENR, and it was well dispersed in the CdsmB region, leading to uniform filler dispersion, which was advantageous in forming a hybrid network in the composite. These advantages resulted in an increase in the complexity of the tensile strength, tensile modulus (100% and 300% strain), and hardness, and further improved the wear resistance and increased cross-linking density. This allowed the control of the dynamic mechanical properties of NR. As a re-

sult, NR/CB/ENR-MoS₂-Cys improved the dispersion of the filler and the interaction between the filler and the matrix, and it simultaneously demonstrated the possibility of using MoS₂ for rubber reinforcement.

Electromagnetic pollution has recently deteriorated the performance of electronic equipment and threatened human health (Saini & Arora, 2012). A microwave absorbing material (MA) that absorbs incident electromagnetic waves and converts them into thermal energy has been presented as an effective solution (Arief et al., 2017; Cao et al., 2019; Thomassin et al., 2013). However, owing to the fundamental disadvantages of the narrow effective bandwidth, studies have recently improved the electromagnetic wave attenuation function of polymers by appropriately combining nanopillars (Cao et al., 2012; Geng et al., 2020; Kwon et al., 2014; Maiti et al., 2013).

Yanfang Zhao and Jianhe Liao developed a hybrid NR nanocomposite containing 1D- MWCNT and 2D-MoS₂ to resolve this problem (Geng et al., 2020).

The nanocomposite compounded with NR without mixing the additional filler (MWCNTs and MoS₂) could not properly address the disadvantages of the existing MA. (1) The NR nanocomposite to which MWCNTs were added exhibited a decreased interfacial adhesion between the filler and the matrix as a hole was formed in the matrix owing to the low tensile strength and decreased dispersion of the filler. (2) The MoS₂ could not achieve excellent MA capacity owing to the semiconductive properties of the filler as the matching properties became poor, showing significantly nonuniform dispersion properties. (3) The NR nanocomposite using the mixed filler showed an improved dispersion degree (as shown in Fig. 2.11).

This can be a result of reinforcing free electron transfer by inhibiting the re-coagulation of MoS₂, by infiltrating the layers of the keratinized MoS₂ sheet to form a layered structure using the long rod-shaped MWCNTs when manufacturing the nanocomposite. Simultaneously, the surface area of MoS₂ increases, resulting in a widened contact surface area between the MWCNT/MoS₂ and the NR matrix, as well as improved microwave absorption performance. Eventually, this structure had a positive effect on the mechanical, electrical, and electromagnetic properties (Fig. 2.15D) (Geng et al., 2020). In addition, the MA characteristics are superior to those obtained when using a single filler, but inferior to those obtained when using a hybrid (mixed) filler. The RL_{min} of the NR/MWCNT nanocomposite is approximately -5.34 dB at 12.08 GHz, whereas that of the NR/MoS₂ nanocomposite is only -2.24 dB, which is slightly higher than that of NR. However, the hybrid nanocomposite considerably improved the microwave absorption performance.

This characteristic induced a strong interface polarization between the two fillers, or the Maxwell–Wagner effect. In this case, the Maxwell–Wagner polarization model is the simplest for describing the polarization of particles under alternating and direct current electric fields, under the assumption of point dipole when particles and liquids have conductivity as well as a dielectric constant (von Hippel & Morgan, 1955).

This phenomenon mainly occurs in heterogeneous media because charges are accumulated on the filler's interface, and in this case, large dipoles are formed in parti-

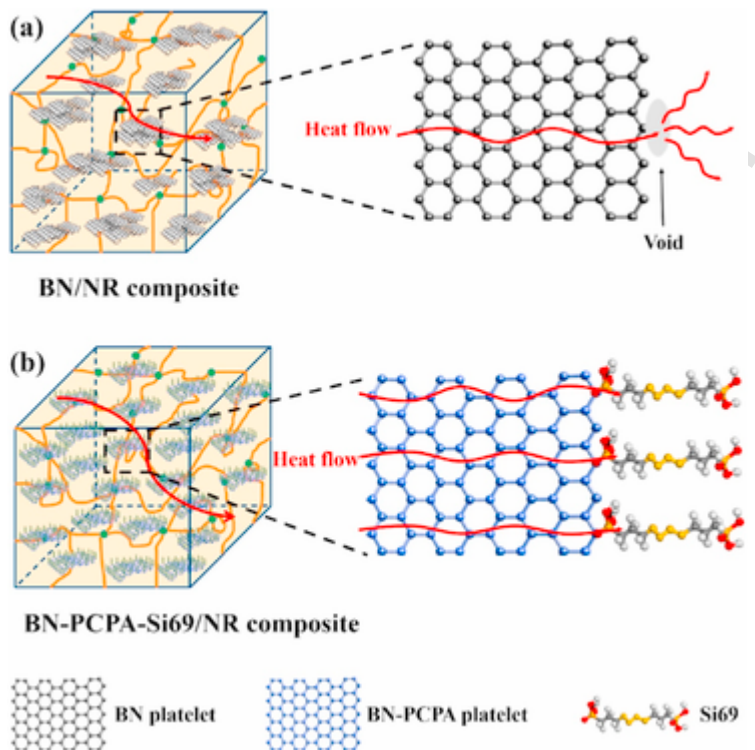


Figure 2.14 Schematic diagram of heat flow of (A) BN/NR and (B) BN-PCPA-Si69/NR composites (Yang et al., 2021).

cles or clusters. Eventually, this study could develop nanocomposite materials with a high absorption efficiency and wide effective absorption bandwidth at a small thickness by mixing fillers with different structures.

2.5 Tannic acid

Tannic acid, which is abundantly present in nature, is a type of polyphenol mainly synthesized by plants. Tannin is used as a flame retardant because it forms graphite during combustion and has the ability to deactivate radicals formed from burning materials.

Zhao et al. (2018) developed functionalized graphene using a new eco-friendly liquid peeling method. They added tannic acid into water as a stabilizer for the dispersion, reduction, and exfoliation of graphene. Tannic acid structurally has many $-OH$ groups and can improve dispersibility in an organic solvent or matrix when combined with nanofillers. For example, when tannic acid is reacted with graphene oxide, reduced graphene is produced. This is because the catechol groups present in the end groups of tannic acid are oxidized to quinone groups, and then, they further bond

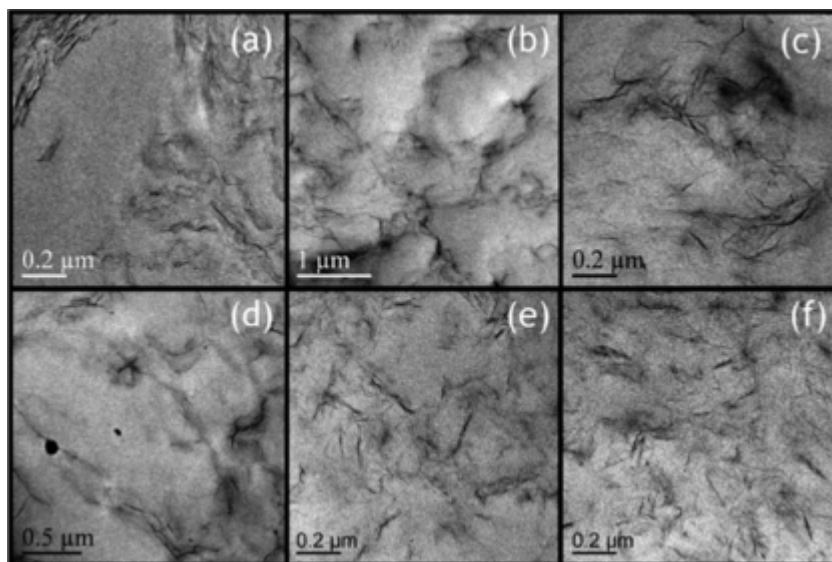


Figure 2.15 TEM micrographs of RG-O/NR nanocomposite sections. (A and B) show the “weblike” dispersion of RG-O platelets in the uncured composites, as obtained directly after latex co-coagulation. (C and D) show the dispersion in the solution-treated samples, while images (E and F) show the morphology of the milled nanocomposites (Potts et al., 2012).

to the OH groups on the graphene oxide surface or edge via self-polymerization, resulting in reduced graphene coated with TA. This reduced graphene can improve the structural defects and conductivity. In addition, because tannic acid can form graphite during combustion and can deactivate radicals formed in burning materials, it exhibits flame-retardant properties (as shown in Fig. 2.12).

3 Application of NR-based polymer nanocomposites

3.1 Thermal conductivity

Zhang and colleagues used boron nitride (BN) to increase the thermal conductivity of NR and functionalized the surface of BN to further increase the thermal conductivity (as shown in Figs. 2.13 and 2.14) (Yang et al., 2021).

According to the result, BN is functionalized with polyamine and Si69, and BN-PCPA-Si69 is formed wherein polymer chains grow on the surface of BN, and these polymer chains can be cross-linked with NR. Thus, as the heat transfer path is created and the amount of as-prepared BN-PCPA-Si69 is increased, the thermal conductivity increases. The thermal conductivity of functionalized BN-PCPA-Si69 was

higher than that of BN, showing that an increase in the filler content to 30 vol% causes an increase in the thermal conductivity from 0.15 to 0.8 W/mk. As shown in Fig. 2.14, the thermal conductivity increases as the phonon moves smoothly. As phonon scattering appears on the interface between BN and NR, the thermal conductivity may decrease. However, the functionalized BN-PCPA-Si69 inhibits phonon scattering at the interface between BN and NR, enabling an increase in the number of phonon movement paths and, thus, higher thermal conductivity.

In the following example, the thermal conductivity of NR was increased upon the addition of R-GO to NR. This study has confirmed that different properties are imparted depending on the fabrication method of rubber composites using R-GO, which includes a two-roll method using the conventional method and a “solution treatment” method using toluene (Potts et al., 2012) (as shown in Figs. 2.15 and 2.16). These two fabrication methods differed in that R-GO had different structures upon filler formation in the rubber matrix. The solution treatment method involved the use of the filler that has a “web-like” structure, whereas the two-roll fabrication method caused homogeneous dispersion after the structure was destroyed.

Because the NR composite fabricated by the solution treatment method is formed upon the addition of the filler having a “web-like” structure, the phonon movement is easier and the thermal conductivity is higher than the composite fabricated by the two-roll method (Fig. 2.16).

4 Conclusion

NR is one of the representative engineering plastics that have been continuously used throughout by numerous industries since its discovery by Christopher Columbus. In this chapter, we have described the preparation of a nanocomposite material by using

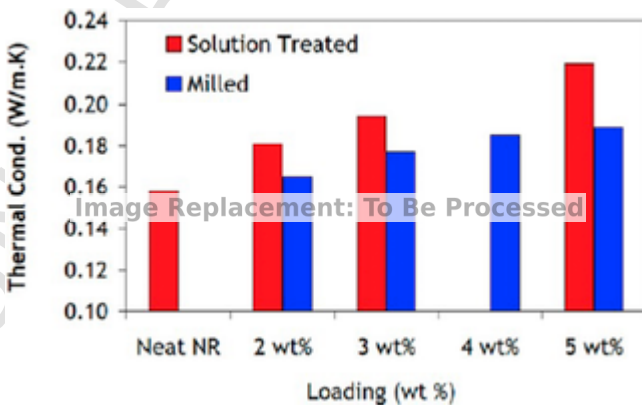


Figure 2.16 Thermal conductivities of milled and solution-treated RG-O/NR nanocomposites at various loadings (Potts et al., 2012).

various additives to overcome the shortcomings and to develop additional functionalities while maintaining the characteristics of the conventional NR. Depending on the purpose, the type of filler to be selected, as well as the application scope, may vary. This chapter will encourage the development of nanocomposite materials.

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