

# Natural Rubber Composites – A Review

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## Abstract

*Composites play a vital role in our day today life. There are many types of composites exists among them polymeric nano composites are important in terms of their unique properties. This review paper deals with the preparation and properties of various natural rubber composites especially with carbon black, carbon nanotubes and graphene as fillers. The preparation methods of natural rubber composites are given in detail and the presence of fillers found to affect the properties of natural rubber composites drastically. The bonding of various fillers with matrix is discussed. The physical and mechanical properties were compared and found that meager quantity of filler addition in particularly the addition of carbon nano tubes and graphene, the properties of natural rubber composites were found to be enhanced.*

## INTRODUCTION

Composite material is a material consisting of two or more material. It may be comprised of a matrix (continuous phase) and a filler material (dispersed phase). Based on the matrix used composites can be classified as Polymer matrix composites, Metal matrix composites, Ceramic matrix composites. Based on the filler size present in the matrix composites can be categorized in to Nano composites. The word nano composite was appeared in the year 1994. Some of the nano fillers of interest are clay, silica, carbon nanotubes, graphene based products. The dimensional morphology of nano fillers can also vary like particles, tubes and layers. Here in this paper we are going to deal with polymeric composites.

The polymer matrix composites may be categorized in to thermosetting, thermo plastics and elastomers. Natural rubber a natural elastomeric material is made up of polyisoprene molecules. The important property of rubber including the elastic behavior i.e. tendency to regain its shape after deformation by any means, great toughness under all stresses, abrasion resistance, Impermeability to water and air and high resistance for attack to solvents and chemicals Rubber composites are becoming important strategic material can be reinforced with functional nano fillers so as to enhance the performance of the composites (1). Rubber nano composites with meager quantity of nanofillers have attracted many owing to their wide field of application. There are many number of nano particles are used as fillers to improve the properties of elastomers. Carbon black (2), Carbon Nano tubes (6-10), Graphene (1-5) are some of the fillers which attracted the researchers now a days.

## MATERIALS

## Carbon Black

Carbon black (CB) is the furnace carbon used in almost all rubber industry as a filler to enhance the property of rubber. But it requires adding a very large quantity of CB. At least a minimum of 40 or 50 phr should be added to get the desired property (2). Even though it costs less, because of higher the quantity needed, researches had been initiated long back in search for newer filler material.

## Carbon Nanotubes

Carbon nano tubes (CNT) is used as a filler element in polymeric composites for its high mechanical, electrical and thermal properties and also the processing with polymers is also easy and flexible for variety of use (8). There are two forms of CNT's available single walled CNT and multiwalled CNT. MWCNT can be Synthesized by arc discharge method, laser vaporization method (7) chemical vapour deposition (CVD) (8, 9) and catalytic chemical vapour deposition (CCVD) (10). The addition of MWCNT alone or some time with the value addition(8) found to increase the mechanical (7), electrical (8,9)and thermal properties.

## Graphene

Graphene is an isolated layer of graphite with  $sp^2$  bonding of carbon atom in a single atomic layer giving outstanding physical properties. Graphite is an allotrope of carbon with planar layered structure which is available plenty in nature. The extraction of graphene from graphite flakes is difficult and involves a big process. Some of them are chemical exfoliation, thermal exfoliation, chemical vapour deposition, solvothermal synthesis, electrochemical lithium intercalation or by methods through the oxidation of graphite as proposed by Hummer and Offerman, Bordie, Staudenmaier (6). Some researchers also used a modified Hummer's method for the production of graphene oxide. In order to improve the properties further value addition is done. In terms of electrical conductivity, graphene oxide is often described as an electrical insulator, due to the disruption of its  $sp^2$  bonding networks. In order to recover the honeycomb hexagonal lattice, and to improve the electrical conductivity, the reduction of the graphene oxide has to be achieved. It has to be taken into account that once most of the oxygen groups are removed, then it is call reduced graphene oxide. Reduced Graphene Oxide is very hard to produce, because it involves hazardous chemical reagents. L.Wu et al used a novel approach for the synthesis of reduced Graphene Oxide(rGO) (1).

## PREPARATION OF COMPOSITES

There are many methods reported till now by various researchers for the preparation of natural rubber composites. The mixing plays a vital role in deciding the properties of nano composites. The interaction between filler and matrix should be ensured for better properties. A number of ingredients like curing agent, cross linking agent, processing oil, catalyst, oxidizing agent

were added in the NR/filler mixture to get the nano composite with desired properties. Each method is specific and yields a material with different characteristic.

A. Fakhrul and all (2006) discussed about solvent casting method. It involves four processes namely dispersion of filler, dissolution of rubber, mixing of rubber with filler solution, pressing and testing the sample (7).

Neena George et al (2015) briefed about Ultra sonication assisted latex mixing. In this the aqueous dispersion of filler was mixed with the compounded NR latex which needs to be sonicated to achieve proper blending. It is allowed to mature for a period then cast in trays to get the film. These were dried at room temperature and cured at 100°C for 1 hour in an air oven. They used MWCNT synthesized by CVD which was modified by H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> in a 3:1 ratio. The mixture was ultra sonicated, cooled, diluted with water, filtered, washed till neutral, dried under vacuum and named as MWCNTR. (8).

Hector Aguilar-Boladas et al (2016) used a ultrasound assisted latex mixing for the preparation of composites. Aqueous solution of filler is subjected to ultrasound for about 30 minutes at room temperature and then mixed with NR latex. This suspension is then poured in container and dried at 70 °C to form a film (6). Azmi Mohamed et al (2015) in their work used a latex based method where a surfactant solution is mixed with MWCNT dipped in different surfactant solution by sonication. Then rubber latex was added to the mixture and sonicated further. This is allowed to dry in oven (9).

Omar A. Al-Hartomy et al (2012), L. Wu et al (2015), Kenji Takeuchi and all (2015) used two roll mills for blending the filler in varying composition with rubber and other additives. It is then press formed at desired curing temperature for about 20 minutes (2, 1,10). Nang Yan et al (2014), Yanhu Zhan et al (2017) in their work used in-situ polymerization of the aqueous solution of the filler (GO) in NR latex is done by ultrasonication followed by in-situ reduction. After adding all the additives the latex was coagulated and filtered. It is then vulcanized to get the segregated network (3,5). The prevulcanised sample is blended in two roll mill to get the not-segregated network (5).

Yong Lin(2016) used a new technique known as ice-templating or freeze-drying. In this method the aqueous suspensions of filler NRL and vulcanizing agents mixed thoroughly and poured into cylindrical vial and frozen to -80°C. It is then transferred into a vacuum freezing dryer for about 3 days to remove the ice formed so as to obtain the aero gels of filler-NR. Then NRL and aqueous solution is added to fill the pores and vacuum dried and vulcanized (4).

## CHARACTERIZATION

The bonding between the elements presents in the nano composites a major role in the physical characteristics of the material, so it becomes necessary to found out the interaction between

the matrix and filler, the structure of the nano composites and the functionalization of filler. For the evaluation of the interactions between filler and matrix variety of techniques are available. Here some techniques are discussed.

Neena George et al (2015) showed in their work that the acid treatment introduced a polar carboxyl group enhanced the intensity disorder induced D band which is evident from Raman spectra. XPS provides useful information on the functional groups and presence of defects on the surface of CNT. The network of the CNT around the NR in a segregated network is evident from TEM. From the TEM of pure MWCNT and MWCNTR it can be noticed that MWCNTR is shorter than MWCNT. The fracture surface can be viewed from the SEM images. As the phr of filler increases the fracture surface is becoming rough (8).

Azmi Mohamed et al (2015) showed that increasing the number of aromatic ring per surfactant molecule from one to three leads to the effective dispersal of MWCNT in NRL by FESEM. TEM is a tool to show the bonding of nanofiller with the matrix. From TEM also it was proved the results by FESEM. The surfactant with phenyl rings have a significant role on increasing the interaction between surfactant and filler which are evident from the two bands of Raman spectroscopy bands as discussed in the previous work. The presence of phenyl group in surfactant gives a good stabilizing effect on filler in NRL (9).

Kenji Tekeuchi et al (2015) used three forms of MWCNT varying in size and heat treatment process or by crushing, the reinforcement effect was good for smaller MWCNT and the surface reactivity was improved by heat treatment. From SEM analysis of the sample it was evident that the heat treatment played a major role in the adhesion of MWCNT with rubber. The material at lower temperature shows better adhesive nature when compared with the specimen by crushing (10).

L.Wu et al (2016) in their work they studied the morphology of rGO through FITR spectra and found the presence of carboxyl, epoxide and hydroxyl group in rGO prepared by their method. A comparison XRD of three variants of GO (GO,PC-rGO,HHD-rGO) were done to identify zone in which the reduction occurs. For further study TGA, Raman spectra were also performed. FESEM was done to identify the dispersion of rGO in NR and they found that the boundary between rGO and NR is obscure since the fractured surface is rough with convex structure. HRTEM was also used to analyze the dispersion of rGO in NR. The XRD pattern of rGO-NR is similar to that of neat NR. With the increase in quantity of rGO the swelling ratio is found to decrease and cross link density is found to increase. This holds good with the results of FITR and XPS (1). Yanhu Zhan et al (2017) in their work from the results of XPS, XRD, AFM shows that GO was prepared successfully. TEM was done to confirm the segregated network of GE composites (3).

Ning Yan et al (2014) in their work they had done TEM to find out the dispersion of rGO in NR composites. From the test data it was identified that the dispersion is not uniform in one of the

sample having 4 phr of rGO. XPS was performed to found the chemical composition on the surface of composite. SAXS investigation is done to found the cross linked structure of NR. A remarkable change in scattering signal was found over the q range depending up on the filler content (5).

Hector Aguilar-Boladas et al (2016) in their work from the XRD results shows the partial elimination of oxygen group occurring in thermally reduced GO promoting exfoliation. Raman spectra show the structural defects and oxygen functionalities promote bonding between filler and NR. The important morphological changes between samples can be found by using SEM. TEM shows a considerable larger separation among the different variants of samples (6).

## MECHANICAL PROPERTIES

A. Fakhru-Razi et al (2006), Neena George et al (2015) in their work the tensile strength and Young's modulus increases by as the amount of CNT present increases but the strain of the fabricated material decreases. From this we can conclude that the ductility decreased and the material becomes stronger and tougher as the filler content increases (7, 8). Kenji Takeuchi et al (2015) also concluded with the same results as above. In addition to that they also discussed the behavior of surfactant in increasing the mechanical properties (10).

L.Wu et al (2015) also confirmed the improvement of mechanical properties by the increase in filler addition. It also dependant on the uniformity of dispersion of rGO in NR. They concluded that PC-rGO/NR is little higher than that of HHD-rGO /NR. On comparison with neat NR both rGO possess higher mechanical properties (1).

Hector Aguilar-Boladas et al (2016) showed in their work that the addition of TRGO enhances the mechanical properties of rubber .it was evident that stiffness had decreased; stress had increased in its value for the addition TRGO. Likewise Ning Yan et al (2014) also confirmed the same results with segregated and non segregated morphology (5).

## CONCLUSION

The synthesis of natural rubber composites using different filler materials like CNT and GO and their derivatives has been reviewed. The implementations of GO leads to the enhancement of physical and mechanical properties were discussed in this paper. Many techniques of preparation were considered for study and finally two roll mill process is found to be the easier method among all. There is lot of scope for researchers are there in natural rubber composites for variety of application.

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