A Review on Graphene as Fillers in Rubber Nano-Composites

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Abstract—**Rubber Nano-composites is under research due to their unique properties. In rubbers/elastomers, fillers are used to gain specific improved properties for their final applications. For most of the operations, rubber has to be reinforced with certain kind of fillers such as carbon blacks, silica, and clay etc. Nanofiller-reinforced rubber exhibits high hardness, modulus, and anti-aging and gas barrier properties when compared with microfiller-reinforced rubber. Also rubber nanocomposites filled with graphene are in demand in the industrial application because of its distinctive electrical, thermal and mechanical properties. This article reviews about rubber nanocomposites, various nanofillers, advantages and challenges of rubber nanocomposites. Moreover, it summarizes the preparation techniques, innovative properties and potential applications of rubber/graphene nanocomposites.**

Keywords—Rubber/Elastomers, Micro-Fillers, Nano-Composites, Graphene Filler, Rubber Graphite Nanocomposites

I. INTRODUCTION

Nanoscience and nanotechnology can be considered as a revolutionary science in the multidisciplinary area combining chemistry, physics, material science, electronics and biosciences [1]. Generally, the term 'nano' is enclosed between the range 1-100nm sizes. With respect to diversity in technological applications, nanotechnology offers innovation and flexibility not observed in any other field.

Elastomer is a crucial commercial polymer due to its unique physical and chemical properties. In rubber, long chained polymers are arranged in random motion having amorphous solid rubbery nature. In molecular state, the atoms are cross-linked at certain points in rubber. Thus between pairs of linking, each bond can rotate freely irrespective of neighbor. As a result, rubbers possess unique physical and chemical properties. As an engineered product, rubber at some point will be subjected to external load. Due to application of external loading on rubber, molecular chain breaks down and is aligned into direction of loading. Upon unloading, the molecular chain of rubber gets cross-linked in random manner again. Due to this phenomenon, rubber possesses unique properties such as low hardness, high elasticity and high elongation at yield point. Rubber is impermeable to water but swells to more than double its size in organic solvents. These useful properties of rubber cannot be obtained until and unless a curing agent is added to modify the chemical characteristics of rubber. This process is called Vulcanization. Therefore raw rubber is usually vulcanized for its applications in the real world.

II. RUBBER NANO-COMPOSITES

In recent years researchers have focused their interest on polymeric nanocomposites which serve as a profound substitution to traditional filled polymers. In nanocomposites the reinforcement has atleast one dimension in nanometer size range (1-100 nm) when compared with traditional filled polymer reinforcements. Generally rubber nanocomposites show advantageous mechanical properties, lower water sensitivity and lower permeability to gases [2]. Over the past few years, nanocomposites have been widely deliberated considering number of various nanoelements such as layered silicates, talc, silica, nanobiofillers and carbon nanotubes. Moreover, incorporation of these nanoelements to polymer matrix provides four different structures: (i) conventional, (ii) partially intercalated or exfoliated, (iii) fully intercalated or exfoliated and (iv) fully exfoliated and dispersed.

A. Types of Nanofillers

Various nanofillers that are widely used in rubber nanocomposites are enlisted below:

1. Layered Silicates
2. Nanotubes
3. Spherical Particles
4. Polyhedral Oligomeric Silsesquioxanes (POSS)
5. Bionanofillers

The addition of the filler usually results in the improvement of the stiffness and hardness, and also of the resistance to abrasion, tear, cutting and rupture. In addition, the physical performance of an elastomeric material strongly depends on a large number of parameters, such as volume fraction, as well as the shape, size and aspect ratio of the particles. Fillers are generally classified according to their average particle size. Particles larger than 1 micrometer do not have reinforcing capabilities (at best) or have a detrimental effect, and they generally increase viscosity by a mere hydrodynamic effect [3].

Of all the ingredients used to modify the properties of elastomers, filler occupy a main role because of their significant contribution to reinforcement and processability.

The two main factors determining the interaction of fillers with elastomers are:

• Particle Size: Particle size of filler when less than 1µm have indistinct reinforcement effect on rubber. Fillers ranging from 100nm to 1µm provide a moderate reinforcement effect. While filler ranging from 1 to 100nm called Nanofillers provides a significant improvement on mechanical performance of rubber. Further the dependence of reinforcement on particle size depends on two aspects that are surface area and particle mass.

• Surface Activity: By compounding the nanofillers of high surface activity into elastomers, significant reinforcement can be done. Carbon black is the best example used as nanofillers in rubber industry due to high surface activity (i) Carbon black have organic functional group which promotes a high affinity of rubber to filler; (ii) due to broken carbon-carbon bonds it has chemically active site which helps in chemically reacting with the elastomer chains.
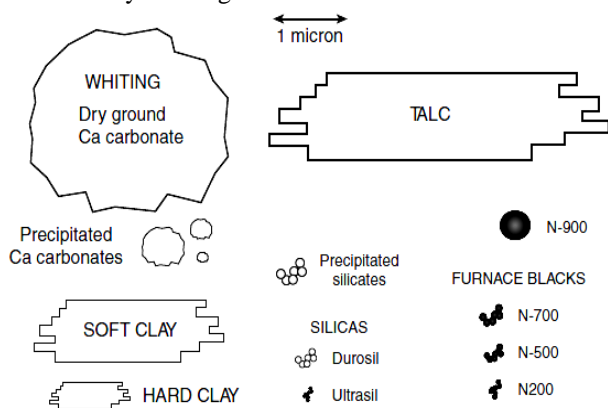

Figure I. Schematic of sizes and shapes of rubber fillers

B. *Advantages of Rubber Nano-composites*

The main advantages of nano reinforcements over traditional composites are summarized as follows:

• Smaller fraction of nanomaterial are more effective reinforcements as it causes a significant improvement of the matrix properties, leading to lightweight composites with lower cost and easy processability.

• Due to large surface area and good adhesion at interface in nanocomposites the load transfer from the matrix to the reinforcements is more efficient.

• Due to reduction in size of materials, there would be few or no internal defects in structure which provides the ability of sustaining high stress before failure.

C. *Challenges of Rubber Nano-composites*

Despite nanoreinforcements augment overall material performance, there are still challenges which are faced for nanocomposites. They are as follows:

• Nanoparticles tend to aggregate during manufacturing process. The severe particle aggregation is detrimental to the thermal and mechanical properties of the nanocomposites. The homogeneous dispersion of the nanoparticles in matrix is critical to obtain high performance nanocomposites.

• Health and environmental threats can occur from the production, use and disposal of nanoparticles. Nanoparticles can damage the body's natural defenses or

cause increased responses to common allergens. Nanoparticles used in consumer products may threaten public health. Already it is known that nanoparticles in air pollution can be up to 50 times more damaging to lung tissue than fine particles of the same chemicals.

III. RUBBER GRAPHITE NANO-COMPOSITES

Carbon is considered to be the most prominent engineering material delivering its designed application used due to its low density, thermal and chemical stability as well as exceptional high temperature mechanical properties in non-oxidizing atmosphere. Carbon can be found in a wide variety of allotropes from crystalline (diamond and graphite) to amorphous (carbon black, activated carbon, glassy carbon, etc.) and nanoscale (fullerene, nanotube, graphene, and nanoporous). Figure I display a selection of structure types of nano-carbon materials relevant for engineering applications. Diamond and graphite are the crystalline carbon materials most relevant for engineering application [5]. In past two decades, carbon found its place in nanoscale region and received great attention due to its physico-chemical properties. Nano-carbon classification refers to the structural state of the carbon allotrope (dimensionality and characteristic size). Mechanical properties of nano-carbon materials at room temperature are given in Table I.

Table I. Mechanical properties of nano-carbon materials at room temperature [5]

Carbon allotrope	Density	Young's Modulus	Strength	Heat Conductivity at room temp.
	[g/cm³]	[TPa]	[GPa]	[W/m/K]
Diamond	3.52	1.05	>1.2^t	900-2300
Graphite	2.26	0.025	0.3-0.35^c	50-500
Carbon fiber	1.7-1.8	0.2-0.7	2-6^t	20-750
Glassy carbon	1.5	0.025	0.06-0.1^b,0.1-0.3^c	<10
Fullerenes (C60)	1.7-1.9	0.017	50^c	<0.1
Nanotube (SWNT)	1.3	-1	15-60^t(95^{ZZ}/126^{AC})^t	II:3500
Nanofiber	1.8-2.1	0.5	3-30^t	1900
Graphene	2.2	(1.1)	35 (130)^t	4000(5300)
Aerogel	>0.00016	10^{-8}-10^{-5}	<0.0005^c	>0.05

Experimental (theoretical) values near rt; t=tensile; b=bending; c=compression; ZZ=zigzag; AC=armchair

Graphene is an allotrope of carbon and it is the basic structural unit of some carbon allotropes including graphite, charcoal, carbon nanotubes (CNTs), and fullerenes as shown in Figure II. Graphene is considered to be one of the prominent materials in the area of polymer nanocomposites due to its eminent material properties. Graphene is more favorable in improving the properties of matrix than CNTs for the following reasons:

• Graphene has a higher surface area and accessible to polymer molecules.

• The high surface area and rumpled nature of graphene contributes to stronger interfacial interactions with polymer matrix.

- The flat surface of graphene diminishes the geometric contribution to thermal interface resistance.
- The cost of graphene or graphene oxide is relatively lower as they are fabricated from cheap harbinger material, graphite.
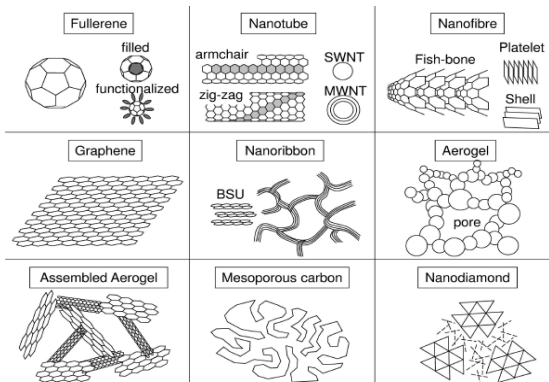

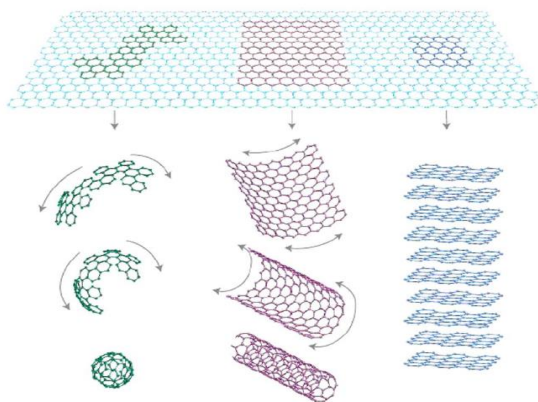*Figure II. Structures of selected nano-carbon allotropes [5]*

Figure III. Structure of fullerenes, CNTs, and graphite based on Graphene [6]

A. Preparation Techniques of Graphene Rubber Nano-composites

With the progress in study of graphene material, its preparation is more and more precise and parallel cost decreases significantly. Graphene nanocomposites are one of the fastest growing applications. Graphene and their derivatives are used as fillers in nanocomposites which are of great potential. Presently, the methods of the preparation of graphene/polymer composites are [6]:

- Solution/Suspension Mixing: It is frequently used method in preparation of polymer composites as polymers are soluble in polar and nonpolar solvent like water, acetone, hexane, and chloroform. In this method, graphene and polymer are dissolved in solvents one-by-one, and then they are mixed together with help of stirring or ultrasonic treatment. Finally, the mixture is co-precipitated by volatilizing the solvent or by adding the non-solvent. The process in this method can be easily regulated due to short work method. Also the diffusion of solvent can be controlled through ultrasonic treatment. The only defect is that solvents are not removed completely which will affect the mechanical property of the composites.

- Latex Mixing: In mechanism of Latex Mixing, graphene and their derivatives are constantly diffused in deionized water, than rubber latex is added into above solution with the help of stirring or ultrasonic treatment until graphene is exfoliated and diffused properly in the mixture. Final homogenizing-dispersing system is obtained by adding the de-emulsifier. Latex mixing as same advantages as that of Solution Mixing except it is only contented with the polymer of which latex is available.

- Direct Processing: It is also called mechanical blending which is carried out in open mixing machine or in internal mixer and widely used in industries for producing rubber composites. In this mechanism, the graphene or its derivatives and rubber ingredients are mechanically mixed with the rubber by effect of high temperature and thereafter the mixture is vulcanized to prepare the graphene/rubber composites. The process is easy to operate but the only disadvantage is graphene is not exfoliated and diffused properly in matrix.

- In-situ Polymerization: the general principle of in-situ polymerization involves mixing of inorganic fillers and monomers in a solvent, followed by in-situ polymerization. This method is less in used as rubbers are polymerized in advance and reaction of graphene with oxygen functional group could terminate the reaction.

B. Properties of Graphene Rubber Nano-compositesUnits

Graphene had considerably improved the properties of graphene-filled composites because of excellent mechanical properties and high surface area. Moreover, its properties are extremely dependent on the exfoliation and diffusion of fillers and the interfacial interaction between fillers and rubber. Researchers had determined the mechanical properties of a single layer of graphene and had concluded that it has highest modulus of elasticity and strength compared to other material as shown in Table 1. The Young's Modulus of a graphene sheet is testified on the order of 1TPa (335 N/m) and ultimate stress for single layer of graphene is 130GPa for approximate strain of 20%-25%. Also its approximate surface area is 2600 m^2/g.

The adhesion at the filler/rubber interface plays crucial roles in determining the performances of the rubber compound [7]. Fillers surface area and surface properties have symbolic effects on the interface interaction. Moreover, nanoscale additives are more capable in reinforcement due to larger surface area for a given volume. Reinforcing efficiency is determined with the help of surface area-to-volume ratio factor. The ratios of surface area to volume for three kinds of common fillers with different geometries are shown in Figure III.

The reinforcement of graphene on the mechanical properties of rubber/graphene nanocomposites depends not only on the surface characteristic, lamellar thickness, and loading of graphene, but also on its dispersion in rubber matrix and the interfacial interaction between graphene layers and the matrix [6].
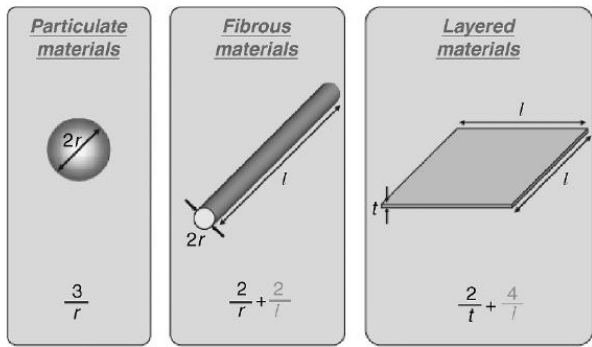
Figure IV. Surface Area :Volume relations for varying reinforcement geometries [7]

Table II. Mechanical properties for graphene-based rubber composites [6]

Matrix	Filler type	Filler loading	% increase Elongation	% increase Tensile Strength	% increase Young's Modulus
NR	GE	2.0 wt%		47	
NR	GO	0.75 wt%			250
xNBR	GO	1.2vol%		370	230
SR	FGO	0.5 wt%	175	67	
SBR	GO	7 phr			1100
EPDM	GO	0.5 wt%	30	50	130

GE=Graphene; GO=Graphene Oxide; FGO= Functionalized Graphene Oxide; NR=Natural Rubber; SR=Silicon Rubber; SBR= Styrene Butadiene Rubber, EPDM=Ethylene-Propylene-diene monomer rubber; xNBR=Carboxylated acrylonitrile butadiene rubber

C. Application of Graphene Rubber Nano-composites

Rubber Nanocomposites have achieved increased attention in both academic as well as in industrial research in recent years. Nanocomposites had shown a vast improvement in performance in comparison to conventional systems. Rubber Nanocomposites had found its application in field of Tire Engineering (tread, innerliner), Barrier Membrane Material, Sporting Goods, Airspace, Medicine and Healthcare.

Graphite holds a significant role in improving the properties of rubber materials. Also investigation has been directed with graphite and rubber intentionally for concentrating on the mechanical, tribological, thermal, electrical and other properties of their composites. Rubber materials with graphite are applicable in sealing, electro-magnetic radiation, electrostatic protection, electrodes, sensors and so on. Also the development of graphene filled rubbers provides a lightweight and high functionality composite such as conductive coating, shape memory, and light weight shielding materials.

IV. DISCUSSION

Elastomers demonstrate distinct mechanical properties such as large deformability and small viscoelasticity. The addition of nanofillers makes this nature more complex with the existence of nonlinear visco-elasticity, a strong sensitivity to strain

history, extraordinary ultimate properties such as a possible improvement of both strain and stress at break depending on the testing conditions.

A lot of research had been done on nano-carbon materials, from fullerenes to CNTs, CNFs, and graphene which have been the main focus of nano-science. There are numerous advantages of nano-carbon materials which are widely accepted in vast field areas. Also there are wide engineering application of nano-carbon materials and composites which are far away from commercial realization because of limited improvement in mechanical property and costly production technology.

V. CONCLUSION

Thus from above summary, it can be conclude that there is always two sides of coin. Nano- carbon composites had wide application and had developed widely in different fields but on other side it raises the question to environment, health and safety consideration too.

Even though much progress has been made in nanocomposite evolution, continuing growth would facilitate a wider range of applications. Further monetary of rubber nanocomposites will mostly depend on developing their structure, dispersion and interfacial properties for broader mechanical and physicochemical performance. Better economics will occur as volumes increases along with methodologies for adequate and steady manufacturing.

Also graphene has gained a lot of attention due to its unique properties. Graphene when used as nanofillers in polymers provides excellent mechanical properties with other functionality such as electrical conductivity, thermal conductivity and gas barrier properties. However diffusion and exfoliation of graphene are of considerable importance for graphene based composites.

Due to these extra-ordinary properties of graphene and wide research on graphene/rubber composites it can also be used in bearings replacing black carbon fillers or High Damping Natural Rubber. Also substitution of graphene in place of carbon black in different rubber provides more strength to composites and it reduces down the overall weight of the composite.

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