

# The Research Progress of Graphene-Rubber Nanocomposites

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**Abstract:** Graphene itself has a variety of high-quality properties and special characteristic structures, which provide a new direction for the research and optimization of the performance of multifunctional polymer nanomaterials. In combination with extensive research this year, graphene is one of the ideal fillers for rubber, which can help optimize the performance of high-performance rubber. Based on this, this paper summarizes the properties, characterization and preparation methods of graphene-rubber in combination with the relevant research status, and analyzes the possible development problems and trends of this kind of materials.

**Keywords:** Graphene-Rubber Nanocomposites, Research Progress.

## 1. Introduction

Graphene, as a two-dimensional carbon material, has received extensive attention since it was discovered by British scientists Geim and Novoselov [1] in 2004 and proved to exist theoretically. Graphene is a carbon material with two-dimensional sheet structure. The theoretical thickness of single-layer graphene is 0.34 nm, and the specific surface area is about  $2630 \text{ M}^2 \cdot \text{g}^{-1}$  [2], which is the thinnest of the known nano fillers. Graphene also has excellent properties due to these unique structures, with modulus up to 1 TPA [3] and thermal conductivity up to  $5.1 \times 10^3 \text{ w} \cdot (\text{m} \cdot \text{K})^{-1}$  [4], conductivity up to  $6 \times 10^5 \text{ s} \cdot \text{M}^{-1}$  [5], in addition, it has good light transmittance and gas barrier. The preparation of graphene-polymer composites from graphene and polymers is an effective way to give full play to the excellent properties of graphene [6].

Rubber is a kind of high elastic polymer material with reversible deformation. It is elastic at room temperature, can produce large deformation under a small external force, and can quickly recover after removing the external force. Compared with graphene, rubber has a very long history as a material. In recent years, rubber has been more and more widely used in all walks of life. It has become an effective way to obtain high-performance rubber by compounding nano filler and rubber to prepare nano filler / rubber composites. Relevant studies mainly improve the performance of graphene rubber composites from the following two aspects [7]: first, the improvement of the dispersion of graphene, and it is expected that graphene or its derivatives can achieve nano dispersion in the rubber matrix; The second is the enhancement of the interface interaction between graphene and rubber matrix. This paper summarizes the research progress of graphene-rubber nanocomposites, compares the advantages and disadvantages of several different composite methods, and analyzes the existing problems and future research directions.

## 2. Preparation of Graphene Oxide-carboxyl Nitrile Butadiene Rubber Nanocomposites and Their Resistance to Penetration of Organic Solvents

Graphene oxide (Go) is a two-dimensional sheet-like nano material with super large specific surface area and multiple oxygen-containing functional groups on the surface [8], which has research and application value in many fields. In the field of polymer composite materials, especially gas barrier materials doped with two-dimensional sheet graphene (GR) or go [9] and anti-corrosion coatings are more common. Z. Tang et al. [10] prepared go / styrene butadiene rubber nanocomposites by CO flocculation method. The hydrogen bond between go and the molecular chain of styrene butadiene rubber makes go disperse well in the rubber matrix, and significantly improves the gas barrier property of the composites Zheng et al. [10] compounded go and brominated butyl rubber to prepare a composite material with good protection performance against mustard gas. When the amount of go is 3 phr, the diffusion coefficient of mustard gas in the composite material can be effectively reduced. H. H.D. et al. [10] combined go modified by ferric oxide with epoxy coating, and the results showed that the anti-corrosion performance of the coating could be significantly improved due to the sheet structure and inherent plugging property of go.

In the existing cases, polyethyleneimine (PEI) is used as the "bridge molecule" between go and XNBR, so that go is uniformly and stably dispersed in XNBR matrix through the covalent bond between Pei and XNBR, to prepare go / XNBR nanocomposites, and to study the dispersion mechanism of go and the penetration resistance of organic solvents.

### 2.1. Specimen preparation

#### 2.1.1. Preparation of Go

Go was prepared from GR by modified Hummers method. Put 10 g of GR and 10 g of sodium nitrate into a three necked flask, add 200 ml of concentrated sulfuric acid and stir for 30 min in an ice bath. Divide 30 g of potassium permanganate

into 5 parts, add 1 part into a three necked flask every 12 minutes, continue to stir for 40 minutes after adding 5 parts of potassium permanganate, raise the temperature to 35 °C after removing the ice bath, continue to react for 8 hours, and then slowly add 400 ml of deionized water to control the reaction temperature not to exceed 110 °C. After the deionized water is added, pour out the reactants and wash them with 2% hydrogen peroxide aqueous solution by mass. Finally, centrifuge to obtain slurry like go.

#### 2.1.2. Preparation of go / XNBR Composites

Dilute the slurry like go with deionized water to a mass concentration of 2 mg · ml<sup>-1</sup>, stir it in a large beaker for 1 h, and then sonicate for 40 min to peel off the go sheet to obtain IJGO dispersion. Weigh a certain amount of go dispersion and XNBR according to the ratio, put them in a large beaker and mix them evenly (the mass fraction of go in go / XNBR nanocomposite is 2%), and then mix them at 900 R · min. 1 for 4 h to ensure that go is evenly dispersed in XNBR. Transfer the large beaker to the ultrasonic machine. In Pei solution is added under the condition of stirring while sonicating, and the prepared calcium chloride solution is added after 1 h to flocculate the mixed latex. After the mixed latex is completely flocculated, the flocculated go / XNBR nanocomposite is precipitated and filtered with a filter screen, washed repeatedly with deionized water for 3 times, and finally dried in a blast oven at 60 °C for 24 h. After the water is completely evaporated, a massive go masterbatch is obtained for subsequent use.

### 3. Preparation of Graphene

The preparation of graphene-polymer composites requires a large amount of high-quality graphene, so how to obtain graphene using simple and efficient methods has always been a research hotspot. At present, the preparation methods of graphene are generally divided into two categories: top-down and bottom-up: the idea of the former is to directly peel or oxidize graphite to separate its sheets to obtain graphene; The latter uses various carbon sources to synthesize graphene on the substrate.

Compared with these bottom-up synthesis methods, the top-down synthesis method using graphite as raw material has a relatively high yield, so it is more suitable for the research of composite materials. The direct peeling of graphene from graphite as raw material has attracted more and more attention. With the help of peeling agents, the van der Waals force between the graphite sheets is destroyed by the action of external forces such as machinery or ultrasound, so that it is directly peeled off into graphene, avoiding the defects caused by the reduction oxidation method. In recent years, studies on the preparation of a large number of graphene by mechanical stripping have emerged in endlessly. Leon et al.[11] Introduced a method of mechanically stripping graphene by ball milling, in which graphite and melamine were ball milled together, and then the obtained product was transferred to a solvent for dispersion, that is, graphene dispersion was obtained. The multilayer graphene prepared by this method has good conductivity without oxygen-containing groups introduced by reduction oxidation method. Jeon et al. U 2J also used ball milling to prepare graphene. Dry ice and graphite were ball milled in a closed environment for 48 h, and graphite was successfully peeled off to less than five layers, and carboxylation of graphene edges was realized at the same time.

## 4. Preparation of Graphene-rubber Nanocomposites

### 4.1. Solution blending

The process of preparing graphene-rubber composites by solution blending method is to dissolve rubber in organic solvent, mix it evenly with graphene dispersion, and then dry and vulcanize it to obtain graphene uniformly dispersed composites.

Arabi et al. [12]Used solution compounding to compound graphene nanosheets (GNPs) and SBR to prepare functional nano compound material. The TEM test of the material shows that the graphene in the matrix of the composite obtained by solution mixing shows a single layer or multi-layer dispersion; However, most of the graphene in the composites obtained by mechanical blending is agglomerated. Singh et al., use class II. The composites of thermally reduced graphene (RGO) and nitrile butadiene rubber (NBR) were prepared with benzene as solvent, and their microwave absorption properties were studied. It is found that when the content of RGO is 10% (mass fraction), the material shows a high dielectric loss tangent value. The results show that the composite has high reflection loss (> 10 dB) in a wide frequency range (7.5-12 GHz), and the maximum reflection loss is 57 dB at 9.6 GHz, which shows good microwave absorption performance.

### 4.2. Mechanical blending

Mechanical blending is a traditional method for rubber processing. Rubber is fully mixed with compounding agent and filler through open mill or internal mixer. The mechanical blending method is used to prepare graphene-rubber nanocomposites. At a certain temperature, graphene powder and rubber are directly mixed in an open mill or an internal mixer to obtain a mixed rubber, and then the final composite material is obtained through the vulcanization process.

Arabi et al. Focused on how to prepare graphene and rubber composites by mechanical processing. Arabi et al. Mechanically blended graphene nanosheets (GNPs) with a thickness of 3.56 nm with EPDM. The results showed that there were two states of GNPs in the rubber matrix: one was single layer or multi-layer dispersion with size less than 1 micron; The other is the agglomerated state with a size of several microns. Through the mechanical property test of the composite, it can be found that when the amount of GNPs is low, the tensile strength and elongation at break of the material are improved, but when the amount of GNPs is further increased, the strength of the material is greatly improved but the elasticity is reduced; In addition, when the volume fraction of graphene is 26.7%, the tensile strength of the composite increases by 404%, the young's modulus increases by 710%, and the tear strength increases by 270%. At the same time, the electrical and thermal properties of the material are also greatly improved, showing good comprehensive properties.

## 5. Development Trend and Existing Problems

The unique structure of graphene makes it have many special properties and broad application prospects. The graphene-rubber nanocomposite obtained by compounding graphene with rubber as a nano filler has excellent performance in mechanical and mechanical properties, electrical and thermal conductivity, gas barrier properties, etc.,

which lays a foundation for the development of high-performance rubber materials and their application in the high-tech field. Through the review of relevant studies in recent years, it is not difficult to find that the research on graphene-rubber nanocomposites mainly shows the following trends: 1) the preparation of composites pays more attention to environmental protection, latex blending and mechanical blending have. And becomes a widely used composite method. 2) There has been some progress in the industrial preparation of composite materials, but there is still a big gap from the production. 3) Through effective composite means, graphene can be kept well dispersed and show obvious nano effect. 4) More and more self-assembly concepts have been used to explain the unique properties of graphene-rubber composites and regulate their properties.

At the same time, the research on graphene-rubber nanocomposites still faces the following problems and challenges: 1) the mass production of high-quality graphene and the single-layer dispersion of graphene in the matrix are still important problems that puzzle the application of graphene composites. 2) Most of the research work has established the preliminary relationship between the properties and structures of composites, but the quantitative relationship between the number of graphene dispersed layers and properties is still lacking. 3) Although graphene-rubber nanocomposites have great advantages in performance, compared with traditional fillers such as carbon black, the research is still at the laboratory stage, and the actual application effect of graphene-rubber nanocomposites has yet to be verified.

## 6. Conclusion

To sum up, graphene has excellent properties and powerful functions, and has a very wide application prospect. Through the review of relevant research in recent years, it is not difficult to find that the research on graphene-rubber nanocomposites mainly presents the following trends: 1) The preparation of composites pays more attention to environmental protection, and latex blending and mechanical blending have become widely used composite methods. 2) There has been some progress in the industrial preparation of composite materials, but there is still a big gap between the production. 3) Through effective composite means, graphene can be kept well dispersed, showing obvious nano effect. 4) More and more self-assembly concepts are used to explain

and control the unique properties of graphene-rubber composites. It is hoped that with the unremitting persistence and efforts of relevant personnel, graphene will have a good effect on promoting China's cause.

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