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STUDY ON THE DISPERSION OF GRAPHENE IN RUBBER MATRIX BASED ON ULTRASONIC VIBRATION

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Graphene has a wide range of potential applications in the field of rubber materials because of its special structure and characteristics. Graphene, however, can aggregate and cause uneven distribution. Graphene synthetic rubber was prepared via ultrasonic vibration, with rubber and graphene powder as raw materials in order to enhance the dispersion of graphene in the rubber matrix. Raman spectroscopy was used to characterize and analyze the dispersion of graphene in the rubber matrix following ultrasonic vibration, and scanning electron microscopy was used to determine the shape of the graphene. According to the experimental findings, the sample's Raman spectra after ultrasonic separation exhibit narrower G peak and 2D peak widths, higher G peak intensity, and lower D peak intensity compared to the original sample. The scanning electron microscope image demonstrates that the structure is complete, the flaws have decreased, and the degree of crystallization of the synthetic rubber made from graphene is essentially unchanged. It is concluded that ultrasonic vibration can successfully enhance graphene's dispersion and size consistency in rubber matrix.

Keywords: graphene; rubber/graphene nanocomposites; ultrasonic vibration; Raman spectroscopy

1. Introduction

In recent years, the emergence of various nanofillers [1-2] has propelled the rapid development of composite materials, among which graphene materials [3] have been at the forefront of material research due to their excellent physicochemical properties [4]. The interlayer adhesion of graphene is significant due to van der Waals interactions and π - π stacking effects [5]. However, graphene possesses excellent electrochemical and mechanical properties, and appropriately treated graphene materials exhibit characteristics that are more easily dispersed and less likely to aggregate [6]. When graphene is well-dispersed within a polymer

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matrix, these properties become apparent. The dispersion of graphene affects the mechanical properties of composite materials, yet characterization techniques for studying the degree of graphene dispersion in the matrix are quite limited [7].

Conventional electron microscopes can only characterize graphene that is exposed on the surface. Charge contrast electron microscopy can be used to characterize the dispersion of graphene, but this technique is only used for graphene conductive networks formed in composite materials [8]. Shojaee et al. [9] used a confocal Raman imaging system to characterize the distribution of graphene in the resin matrix using the D or 2D peaks of graphene. Zhao et al. [10] characterized the distribution of graphene in the epoxy resin matrix using the G peak of graphene. Studies have shown that confocal Raman microscopy can calibrate the dispersion of graphene in composite structures. McCrear et al. [11] linked the Raman spectroscopy characterization of graphene dispersion to fiber-reinforced composite materials, using Raman spectroscopy to characterize the dispersion of graphene in composite materials. Wang et al. [12] stacked single-layer graphene on a polycarbonate film substrate and formed a new type of graphene polycarbonate folded laminate composite material through multiple folding processes. The presence of single-layer graphene on the polycarbonate was confirmed by Raman spectroscopy. Xin Hua et al. [13] mixed graphene with natural rubber and used Raman spectroscopy to characterize the structural changes of graphene/natural rubber composite materials and investigated the mechanical properties of the composite materials. The above studies indicate that Raman spectroscopy can be well used for research in the direction of graphene composite materials.

Rubber is an elastic material primarily composed of high molecular polymers, known for its unique physical and chemical properties. It is typically made from natural rubber or synthetic rubber and possesses reversible deformation characteristics, making it widely used in various fields of daily life [14-16]. Traditional rubber materials can no longer fully meet the rapidly evolving application demands. Incorporating nanofillers into the rubber matrix to prepare synthetic materials has become an effective way to obtain high-performance rubber [17]. In summary, conventional characterization techniques can only characterize graphene that is exposed on the surface and cannot provide information on the dispersion state of graphene within composite materials. Raman spectroscopy can effectively characterize the dispersion of graphene in the rubber matrix, significantly enhancing research efficiency.

This study employs industrial-grade graphene semi-finished products and natural rubber extracted from pulverized waste conveyor belts [18] as raw materials. Through ultrasonic treatment technique, graphene and rubber are mixed to prepare rubber/graphene nanocomposites. Raman spectroscopy is employed to characterize and analyze the structural changes of graphene during the ultrasonic vibration process under different dilution concentrations, in order to study the dispersion of graphene in the rubber matrix and its interaction with the rubber matrix. Finally, the analysis is conducted on whether defects are produced in graphene in extracts of different concentrations after ultrasonic treatment. The analysis indicates that ultrasonic vibration effectively improves the dispersibility of graphene in the rubber matrix, enhancing its dispersion.

2. Experiment

2.1 Reagents and Equipment

Industrial-grade semi-finished graphene powder and rubber powder formed from the pulverization of waste belts were used as experimental materials, with the specific material ratios as shown in Table 1, and the experimental instruments as listed in Table 2.

Table 1

Experimental materials

Material	Typical ratio (phr)	Manufacturer
Rubber powder(sulfur content:1.5%)	100	Daqing Rubber Factory
Graphene powder	1	Xianfeng Nano
Ethanol	150	Halongxing Industrial and Trading
Molybdenum disulfide lubricating grease	1	Bihe Biochemical
Base oil	10	Daqing Refinery

Table 2

Experimental instruments

Equipment/Instrument	Model	Manufacturer
Ultrasonic Cleaner	FRQ-1008HT	Frant Ultrasonic Technology
Electronic Balance	JCS-6102A	Harbin Zhonghui Weighing Apparatus
Electric Constant Temperature Drying Oven	DHG-9075A	Shanghai Jinghong Experimental Equipment
Scanning Electron Microscope	SU3500	Shenzhen Ke Shi Da Technology
Micro-Raman Spectrometer	in Via Rflex	Renishaw, United Kingdom

2.2 Experimental Method

Graphene powder and Molybdenum disulfide lubricating grease were added to ethanol to dilute into a mixed solution; the ultrasonic frequency was set to 40kHz, and the mixture was placed into a high-pressure vessel and heated to 400°C while maintaining the temperature for 1 hour, followed by pressurization to 20MPa and then instantaneous depressurization; the product obtained after depressurization was placed into an ultrasonic cleaner and subjected to ultrasonic oscillation for 30 minutes; the ethanol mixture was distilled and dried, and the dried product was then added to the base white oil at a graphene-to-oil mass ratio of 1:5; the above material was continuously stirred for 30 minutes, followed by thorough ultrasonic oscillation dispersion; the rubber powder was devulcanized using a screw extrusion devulcanization method; the obtained graphene carrier was mixed with rubber powder to achieve uniform dispersion. The mixture was placed in a reactor for reaction and curing, resulting in rubber/graphene nanocomposites, and the synthesized rubber was filtered, washed, and dried to ultimately obtain the rubber/graphene nanocomposites. A schematic diagram of the experimental process is shown in Fig. 1.

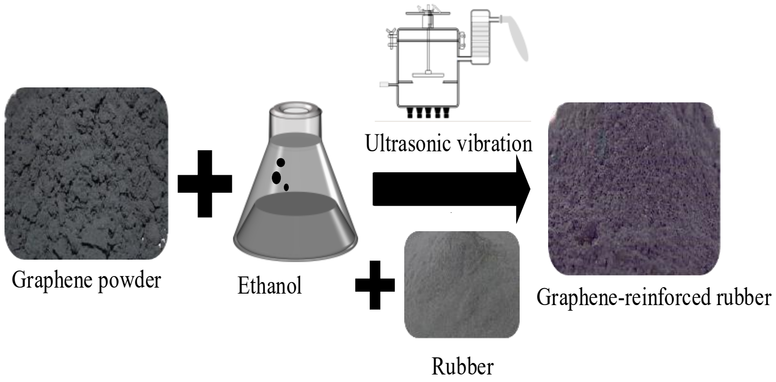


Fig. 1 Schematic diagram of preparing graphene synthetic rubber

2.3 Sample Characterization

The graphene was mixed with ethanol solution at a dispersion concentration of 0.1mg/mL and stirred for 20 minutes to form a graphene suspension. Ultrasonic vibration technique was employed to evenly disperse the mixture, resulting in a delaminated liquid that was left to stand for 48 hours. The thicker graphene flakes settled to the bottom of the beaker, and the supernatant was taken for analysis and characterization.

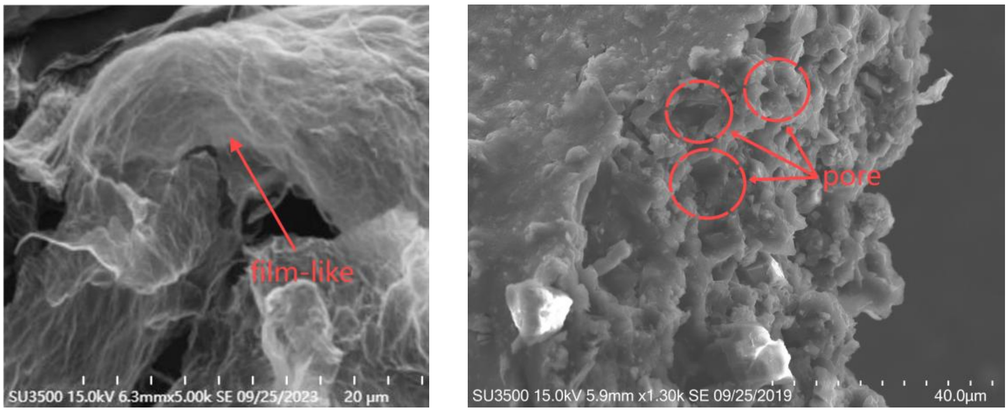
In this study, the microstructure of graphene was observed using scanning electron microscopy (SEM). Following the ultrasonic dispersion process, the graphene suspension was transferred onto conductive adhesive. After complete evaporation and drying of the ethanol, the microstructure of graphene was examined based on morphological analysis images. The molecular structure of the materials was characterized using a Raman spectrometer. The sample powder was placed on the microscope stage and scanned under stable conditions with a wavelength of 532nm. Micro-Raman spectroscopy was utilized to analyze the dispersion effect of graphene in the rubber matrix at different ultrasonic dilution concentrations and to perform Raman spectroscopic characterization.

3 Results and Discussion

3.1 Characterization of Raw Materials

SEM characterization and analysis were performed on the graphene powder and rubber raw materials used in the experiment, with the results shown in Fig. 2.

Fig. 2(a) reveals the morphological characteristics of graphene. The graphene exhibits flake-like or thin-film morphology with few layers and ultrathin thickness, demonstrating smooth, flat surfaces and semi-transparent silk-like appearance. Fig. 2(b) displays the surface morphology of rubber. The rubber surface shows pores of varying diameters, which collectively form irregular surface roughness. Rubber particles tend to aggregate into blocks or clusters, and their aggregation degree significantly influences both the dispersibility and performance characteristics of the rubber.



(a) Graphene powder (b)Rubber

Fig. 2 Morphology analysis of graphene powder and rubber

3.2 Characterization of Graphene Oxide

Graphene oxide was synthesized via the improved Hummers method. Although graphene oxide loses the electrical conductivity of pristine graphene, the abundance of oxygen-containing functional groups on its layers facilitates the preparation of graphene-polymer composite materials [19]. Incorporating graphene into the rubber matrix requires achieving uniform dispersion of graphene within the rubber matrix as a primary step.

The difference in the dispersion of graphene and graphene oxide in the rubber matrix is mainly attributed to their compatibility and interfacial interaction forces. The hydrophilicity and lower surface activity of graphene result in poor dispersion in the rubber matrix, as it cannot effectively interact with rubber and lacks compatibility. In contrast, the hydrophobicity and higher surface activity of graphene oxide contribute to its relatively better dispersion. Rubber, being inherently hydrophobic, readily interacts with hydrophobic graphene oxide, leading to improved dispersion.

Graphene, with its nearly perfectly flat and smooth two-dimensional structure lacking active functional groups, exhibits weaker interaction forces with the rubber matrix. This weakened interaction enhances the tendency of graphene to aggregate within the rubber matrix, resulting in poor dispersion. On the other hand, graphene oxide typically possesses oxygen-containing functional groups such as hydroxyl and carboxyl groups on its surface. These functional groups enhance the interaction with the rubber matrix, making graphene oxide more compatible and better dispersed within the rubber matrix.

In this process, graphene oxide serves as a lubricant, effectively enhancing the compatibility and dispersion of graphene in rubber. Through the action of ultrasonic vibration, graphene oxide can better interact with rubber molecules, facilitating its uniform dispersion within the rubber matrix and preventing graphene aggregation.

SEM image of graphene oxide is presented in Fig. 3, allowing for the observation of its surface morphology and structure. The surface of graphene oxide exhibits a smooth and flat morphology, devoid of obvious particles or textures. Graphene oxide consists of multiple layers of graphene sheets, interconnected by oxygen atoms or other functional groups. Compared to graphene, graphene oxide appears relatively rough, with distinct layer structures and wrinkles, and larger dimensions. These structural changes are attributed to the introduction of oxygen-containing functional groups, which prevent graphene aggregation and enhance the dispersion of graphene in rubber.

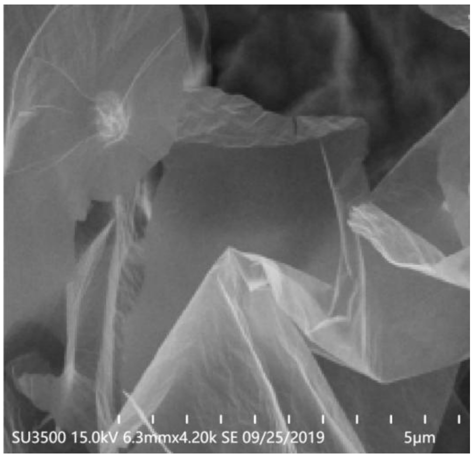


Fig. 3 Morphology analysis of graphene oxide

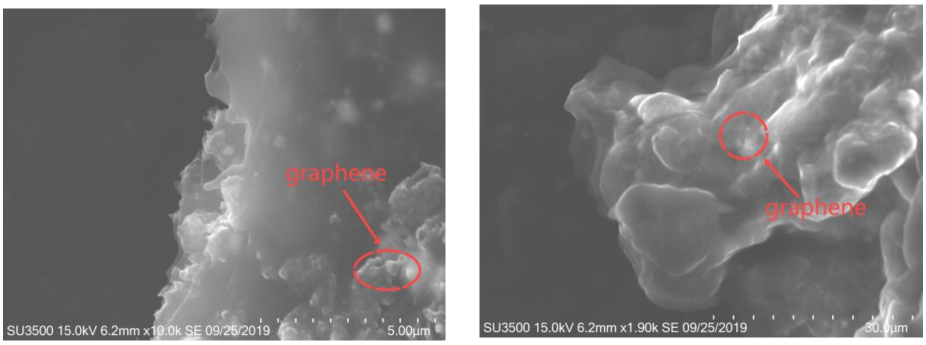
3.3 Characterization of Rubber/Graphene Nanocomposites

Using ultrasonic dispersion method, the rubber/graphene nanocomposites were separated from other substances and diluted in liquids of different concentrations. By observing the scanning electron microscope (SEM) images of the rubber/graphene nanocomposites after ultrasonic dilution at different concentrations, valuable information regarding the dispersion of graphene in the rubber matrix, morphological changes, and interface interactions can be obtained.

The morphology analysis images of the rubber/graphene nanocomposites after ultrasonic dilution at different concentrations are shown in Fig. 4.

The concentration variation of graphene in rubber can influence the surface morphology of rubber. Different concentrations lead to different morphological states.

From Fig. 4(a), it can be observed that when the ultrasonic dilution concentration is 10%, graphene particles tend to agglomerate. This is because the mutual attractive force between graphene particles is greater than the dispersing force, leading to the accumulation or agglomeration of graphene particles in the rubber matrix. As shown in Fig. 4(b), with the moderate increase in ultrasonic dilution concentration, i.e., the moderate adjustment of the proportion of graphene to the rubber matrix, graphene can be better dispersed in the rubber matrix. At this point, the mutual attractive force and dispersing force between graphene particles are relatively balanced, resulting in a relatively uniform dispersion of graphene particles in the rubber matrix.



(a)10%-C13 (b) 12%-C14

Fig. 4 The morphology analysis of graphene synthetic rubber after ultrasonic dilution

3.4 Raman spectroscopy characterization

Raman spectroscopy is a commonly used, non-destructive, and high-resolution technique in the study of carbon materials, with subtle changes in the shape, intensity, and position of its spectral peaks being related to the structural information of carbon materials [20]. The quality of graphene and the presence of defects are associated with the intensity of the D peak, which primarily characterizes the double resonance Raman process of defect scattering. Therefore, the defects in graphene are reflected in its Raman D peak, and the detection of the Raman D peak of graphene can quantitatively study its defect density. Since graphene has a zero bandgap, chemical modification to introduce sp3 carbon defects on sp^2 carbon is one of the important methods to open the bandgap of graphene [21].

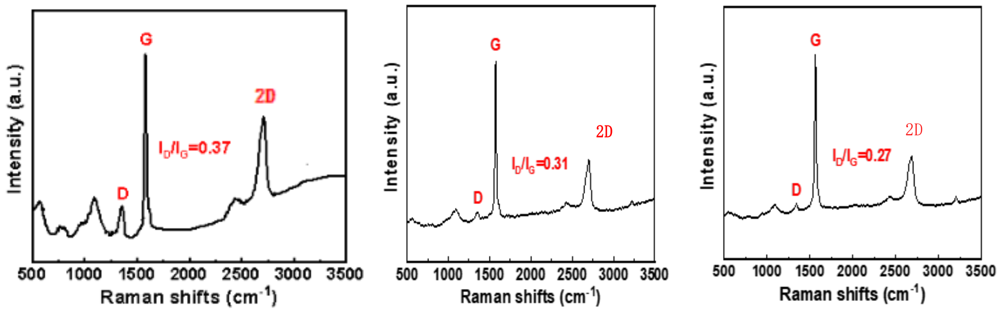
Raman spectroscopy is frequently utilized to indicate the types and densities of defects in graphene. The intensity ratio of the D peak to the G peak, known as ID/IG, is commonly used to represent the defect density in graphene. The relationship between the defect density n_D and the ID/IG value is as follows:

$$n_D = E_{L^4}(ID/IG)\left(7.3 \pm 2.2\right) \times 10^9 \tag{1}$$

The formula is related to the energy of the Raman laser and depends on the type of laser selected during testing. As indicated by Equation (1), it can be seen that the defect density n_D of graphene is directly proportional to the ID/IG value.

Raman spectroscopy was used to examine the rubber/graphene nanocomposites formed by ultrasonic vibration, with the results shown in Fig. 5. These are the Raman spectra under the same ultrasonic vibration conditions for different concentrations of the dilute solution. The D peak, 2D peak, and G peak are characteristic peaks in the Raman spectrum. The G peak reflects the in-plane vibration of sp^2 carbon atoms, the 2D peak reflects the number of layers in graphene, and the intensity of the D peak reflects the degree of disorder in the graphene structure. It is caused by the breathing mode of six-membered rings and requires a defect for its activation [22]. Therefore, the D peak can reflect the degree of defects in graphene.

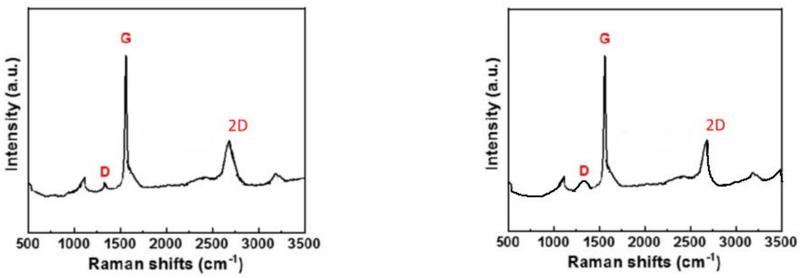
The intensity of the D peak decreases from the state of graphene powder to that of rubber/graphene nanocomposites, and the structure is relatively intact. The low intensity of the D peak indicates that the prepared graphene has no significant defects and that there is good dispersion in the rubber/graphene nanocomposite samples; the G peak shows no significant shift and remains essentially the same, suggesting that the degree of crystallinity of the graphene is consistent, and the sp^2 carbon atoms have not undergone in-plane vibrations, with the physical properties remaining essentially unchanged; the G peak exhibits a clear peak shape and relatively high intensity, indicating good dispersion; the decrease in the ID/IG value suggests that the reduction degree of graphene is higher, and the defects are smaller. The ID/IG value at a material design concentration of 12% is larger than that at 10%, indicating that the lower the design concentration of the material, the smaller the degree of defects, which further suggests that the prepared rubber/graphene nanocomposites are thinner, have very few defects, and are structurally more intact. Samples after ultrasonic separation show lower D peak intensity, relatively higher G peak intensity, and narrower widths of the G and 2D peaks, indicating that graphene has achieved good dispersion and high-quality diffusion within the rubber matrix.



(a) Graphene Powder (b) Rubber/graphene 12% (c)Rubber/graphene 10%

Fig. 5 Raman spectra of diluents with different concentrations after ultrasonic separation

The Raman spectra of graphene solutions treated with ultrasonication at different concentrations of extracts are shown in Fig. 6 for analysis.



(a)2% extract after ultrasonic treatment (b)5% extract after ultrasonic treatment

Fig. 6 Raman spectra after ultrasonic treatment

From Fig. 6, it can be observed that at an ultrasonic extraction concentration of 2%, the D peak is the lowest, indicating that the material has the lowest degree of structural defects; at an extraction concentration of 5%, the D peak is the higher, indicating that the material has the higher degree of structural defects. The G peaks at different extraction concentrations are essentially the same, suggesting that the degree of crystallinity of the graphene is consistent. The 2D peak reflects the number of graphene layers, with fewer layers resulting in a sharper peak [23].

As the extraction concentration increases, the number of graphene layers also gradually decreased. The ID/IG value is an important parameter for characterizing defects in graphene. Throughout the delamination process, it increases with the increase in extraction concentration, indicating that graphene flakes are continuously breaking down into smaller sizes and the defects are also increasing with the increase in extraction concentration. That is, the concentration of the extract will affect the degree of defects and the number of layers in graphene; the higher the concentration of the extract, the greater the ID/IG value, and the larger the defects in the graphene; the higher the 2D peak, the fewer the layers of graphene. This indicates that the concentration of the extract will have a certain impact on the quality of graphene, therefore, the concentration of the extract should be appropriately selected, and should not be too high.

4. Summary

Graphene powder semi-finished products and waste rubber belt powder are mixed with ethanol to form a diluted mixture. After heating and pressurizing with ultrasonic oscillation, the ethanol mixture is distilled and dried. The dried material is then mixed with base white oil in a certain ratio, stirred, and dispersed again using ultrasonic oscillation to form a mixture. This mixture is placed in a reactor for reaction and curing, resulting in rubber/graphene nanocomposites. The synthesized rubber is filtered, washed, and dried to ultimately obtain rubber/graphene nanocomposites.

(1) The results of SEM characterization and Raman spectroscopy both indicate that, Under the treatment of ultrasonic vibration technique, the dispersion of graphene in the rubber matrix of the rubber/graphene nanocomposites is improved.Although the SEM images did not directly reveal the micro-interface bonding situation, the morphological information obtained, combined with the spectral characteristics, comprehensively suggests that this method has practical application potential in improving the uniformity of graphene dispersion.

(2) The research results show that, under the appropriate ultrasonic dilution concentration, the number of graphene layers and their dimensions tends to be uniform, with a low level of defects. This provides a theoretical basis and experimental support for the industrial production of high-performance composites.

(3) Although this study has achieved preliminary results, advanced characterization techniques (e.g., TEM, AFM) will help to comprehensively reveal the interfacial interaction mechanisms of the composites and provide more detailed data support for the optimization of process parameters.

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