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A nitrile functionalized graphene filled ethylene propylene diene terpolymer rubber composites with improved heat resistance

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ABSTRACT

Ethylene propylene diene terpolymer rubber (EPDM) is susceptible to temperature, and heat can greatly increase the molecular mobility which degrades the mechanical properties of a rubber part. To overcome this problem, EPDM composites containing various nitrile functionalized graphene (GN-CN) were prepared and investigated for the effects of surface modification on the mechanical properties under low and high temperature. Results indicated that, the tensile strength of 3phr GN-CN filled EPDM composite reaches 11.8 and 6.0 MPa at 25 °C and 70 °C, respectively, which is 63.9% and 100% higher than that of unfilled one. Meanwhile, the strength loss of the EPDM/GN-CN composite under 70 °C is 49.1%, which is 9.2% lower than that of EPDM. It was demonstrated that, the reaction of the nitrile groups is benefit to the tensile strength and heat resistance improving of EPDM.

1. Introduction

Ethylene propylene diene monomer (EPDM), composed of ethylene, propylene and unsaturated diene, is a type of widely used synthetic rubber [1–3]. Owing to its saturated backbone, EPDM has better resistance to ozone and oxidation than other commonly used rubber such as natural rubber (NR) [4], butadiene rubber (BR) [5] and butadiene-styrene rubber (SBR) [6]. Therefore, EPDM has been widely used in high temperature-resistance conveyor belts, hoses and thermal insulators [7–9]. However, EPDM is susceptible to temperature, and heat can greatly increase the molecular mobility which degrades the physical properties of a rubber part. To overcome these problems, compounding EPDM is essential to enhance its heat resistance. Although there are no common requirements for heat resistance rubber as they are not defined by the purpose of the product in which they are used, there are some common properties that heat resistance rubber should possess, such as good mechanical properties under high temperature. Therefore, in some sense, enhance the heat resistance of rubber is equate to enhance its physical properties under high temperature.

Combining nanofillers and polymers is one of the most successful approaches at the frontiers of materials technology to achieve specific goals with the greatest efficiency in properties [10–13]. Among existing nanoscale materials, graphene (GN) is an excellent candidate for multi-functional nano-reinforcement for a variety of polymer matrices because of its remarkable electronic [14–17], thermal conductivity [18], magnetic [19,20] and mechanical [21,22] properties. To incorporate graphene into, or compatibilize with polymers, it must be appropriately modified in order to provide it with adequate functional groups able to interact with specific chemical moieties in polymeric matrices, and then subsequently mixed with the polymer. To date, the mixing of functionalized graphene with polymers covers the most of the published studies (some studies including nitrile functionalization have been summarized in Table 1). Although, among the references Wan et al. [27] reported a nitrile functionalized method to modify halloysite nanotube with phthalonitrile which used to improve the dielectric properties of polyarylene ether nitriles, nitrile functionalization of GN which used for improve the heat resistance of elastomer is somewhat less reported but quite promising.

Moreover, the dielectric properties as measured over a wide range of frequencies and temperatures can provide valuable information about the structure and dynamics of polymeric systems [28,29]. Dielectric spectroscopy, as one of the most effective methods in material characterization, is also effective in in situ and real-time investigation due to its substantial advantages including non-invasion, high sensitivity to ionic and dipolar motions, and

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Table 1
Methods for functionalize graphene and other nanomaterials.

Functional group	Form of nanomaterials	Notable findings	References
4-bromoaniline, 4-nitroaniline, 4-chloroaniline	Graphene oxide	Higher antiferromagnetic transition	[23]
Pyridine	Graphene	Improved mechanical and gas barrier properties	[24]
Carboxyl and amine	Graphene	Improved mechanical properties	[25]
Alkyl chains and benzyl moieties	Graphene oxide	Better dispersion lower electrical resistance	[26]
Phthalonitrile	Halloysite nanotube	Enhanced dielectric permittivity and relatively low dielectric loss	[27]

quick measurement [30,31]. Because dielectric spectroscopy is noninvasive and no special sample requirement, samples can be measured “as is” and dielectric spectroscopy measurement setup can be very simple. Due to its high sensitivity, subtle change of the system arising from ionic and/or dipolar motion is detectable [32,33]. A great number of successful applications have been reported in the real-time monitor of various kinetic processes, such as structure changes [34], phase separation [35], polymerization [36,37], crystallization [38–40], relaxation [41–43], cell cultivation [44,45] and even chemical reaction [46]. Although extensively studied, the application of dielectric spectroscopy in the monitor of weak crosslink of functionalized nanofillers in polymer matrix is rarely reported.

In this work, in order to suppress the molecular mobility of EPDM under high temperature which improve the physical properties of a rubber part and expand various advantages and applications of GN and EPDM materials, we described a simple and efficient method to prepare nitrile functionalized graphene (GN-CN) filled EPDM composites. The EPDM/GN-CN composites exhibit much better mechanical properties than pure EPDM. Moreover, the weak crosslink between nitrile groups on GN surface in the composites were detected by dielectric spectroscopy. The results indicated that the reaction of the nitrile groups is benefit to the tensile strength and heat resistance improving of EPDM.

2. Experimental

2.1. Materials

EPDM (Trilene 77) containing 67.1 wt% ethylene and 10.5 wt% unsaturated diene was purchased from Lion Copolymer Geismar, LLC. Its molecular weight is in the range of 6500–8500. GN sheets with thickness of 10–30 nm and lateral size spanning from 5 to 10 μm were supplied by Keji Company, Deyang, China. 3-Aminophenoxyphthalonitrile (3-APN) was synthesized by our laboratory. Silicon dioxide (AEROSIL R812S) was purchased from KING CHEMICAL Company. Bis(tert-butylperoxyisopropyl)benzene (BIPB), stearic acid, zinc oxide (ZnO), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP), sulfuric acid (H_2SO_4), nitric acid (HNO_3), thionyl dichloride ($SOCl_2$) and ferrous chloride ($FeCl_2$) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. All reagents and solvents were of analytical grade and were used without further purification.

2.2. Synthesis of GN-CN

The nitrile functionalized GN was prepared through two steps (Fig. 1). Firstly, a typical reaction of chemical functionalization of GN was carried out by means of the modified Smalley method as follows [47]. 5 g GN, 300 mL H_2SO_4 and 100 mL HNO_3 were stirred together under sonication at 50 °C for 3 h. The mixture was then diluted to 1:10 by volume of acid/water, filtered through a polycarbonate membrane filter and washed with an excess of water until the pH reached 7, giving a solid paste. The paste was then dried in a vacuum oven at 80 °C for 48 h. Secondly, the paste obtained above, was refluxed in excess $SOCl_2$ at 70 °C for 20 h. The excess $SOCl_2$ was removed by distillation and remaining solid was dried in vacuum. Then, the obtained solid was reacted with 3-APN in 100 mL N,N-Dimethylformamide at room temperature for 24 h. The excess 3-APN was removed completely by washing with dichloromethane and acetone, after filtration a black solid was finally obtained.

2.3. Preparation of GN-CN filled EPDM blend

The blend formulations containing EPDM and GN-CN are presented in Table 2. The blending process was performed using a PTW252 twin-screw extruder (HAAKE, Germany) having a mixing chamber volume of 75 cm^3 with a rotor speed of 80 rpm at an operating temperature of 70 °C. The mixing sequence involved first introducing EPDM into the mixer. After 2–3 min stirring, silicon dioxide (R812S) and GN-CN as reinforcing agent was added respectively, the mixing process was continued for about 10–15 min. Then, $FeCl_2$ which used as the cure agent of the nitrile functional groups that on the GN-CN surface were add, its amount is 6 wt% of GN-CN content. For the formulation with a vulcanization agent (BIPB), stearic acid, and ZnO were added and the mixing process was continued for about 3 min. Finally, a homogeneous blend was obtained. We take some of the blends for rheological and dielectric analysis. The remaining blend was removed from the mixer and the test specimens were obtained by compression molding at 170 °C and a pressure of 20 MPa for 20 min using an electrical press. The plates were then cooled to room temperature under pressure.

2.4. Characterizations

2.4.1. FTIR analysis

Fourier transform infrared (FTIR) spectra, recorded on NICOLET 6700 FT-IR spectrometer were obtained to prove the success of nitrile functionalize treatment on GN.

2.4.2. XPS analysis

X-ray photoelectron spectroscopy (XPS) which recorded on a ESCALAB250 system with Al Kα ray, 1486.6 eV energy and 200 W power was used to measure the atomic composition of GN and GN-CN.

2.4.3. Thermal measurements

The thermal decompositions of GN and GN-CN were determined by TA Instruments TGA-Q50 thermogravimetric analyzer with a heating rate of 20 °C/min under nitrogen atmosphere.

2.4.4. Cure reaction

The cure reaction behavior of EPDM and EPDM/GN-CN blends were detected by TA Instruments Rheometer Ares-G2 and