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Structures and properties of alkanethiol-modified graphene oxide/solution-polymerized styrene butadiene rubber composites: Click chemistry and molecular dynamics simulation

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ABSTRACT

Alkanethiol-modified graphene oxides (GOs) containing alkanethiol (C_xGO) molecules with varying chain lengths were synthesized through click chemistry. Then, C_xGO/solution-polymerized styrene butadiene rubber (C_xGO/SSBR) composites with different C_xGO loadings were prepared by a solution-mixing method. By combining experiment and molecular dynamics (MD) simulation, we investigated the relationship between the microstructures and properties of the C_xGO/SSBR composites. Results showed that the 1-heptanethiol-modified GO (C_7GO)/SSBR composite had the smallest fractional free volume and the least mobility of the polymer chains. Moreover, the 1-octadecanethiol-modified GO (C_{18}GO)/SSBR composite displayed the largest binding energy ($E_{binding}$). Thermal stability, gas barrier, dynamic, and static mechanical properties were improved by introducing C_xGO. The long chain length of C_xGO indicated that the composites had good performance. We believe that these results provide a basis for the design and fabrication of high-performance GO/SSBR composites.

1. Introduction

Solution-polymerized styrene butadiene rubber (SSBR) is widely used in the tire industry especially those involved in green tire production because of its low energy dissipation [1,2]. Pouring the filler into rubber is indispensable because this procedure enhances the overall performance of rubber materials. Graphene, which consists of a single layer of carbon atoms arranged into a two-dimensional honeycomb lattice, has been considered the first fabrication because of its intriguing and extraordinary physical properties [3]. Thus, graphene is an emerging filler candidate for the improvement of the mechanical, thermal, electrical, and gas barrier properties of rubber materials at low loading conditions [4]. Furthermore, graphene dispersion and graphene–rubber interactions are the two major factors influencing the properties of graphene-reinforced rubber composites [2,5]. However, experimental results and computer simulations both revealed that pristine graphene has poor compatibility with most rubber matrices [6,7]. Therefore, several attempts to functionalize graphene and subsequently enhance the compatibility between graphene and rubber have been conducted [8–10]. Alternatively, graphene oxide (GO), a precursor for the preparation of graphene by oxidation–reduction method, is also an ideal filler candidate as reinforcement of rubber [11]. The typical oxygen-containing groups (carboxylic acid, hydroxyl groups, epoxides, and ketone groups) on GO surfaces offer the possibility of further functionalization to obtain better compatibility with rubber matrices.

The oxygen-containing groups endow the GO with some polarity and dispersion stability in polar solvents, such as water, N,N-dimethylformamide, and N-methyl-2-pyrrolidone [12]. Many rubber particles can be dispersed in water in the form of the emulsion colloid, which is possibly suitable for the preparation of GO/rubber composites in water by emulsion mixing [5,8]. Extensive research suggested that emulsion mixing can significantly improve GO dispersion and the resulting properties of the composites to a greater extent than two-roll mixing [13,14]. The compatibility of GO with rubber matrices can be enhanced by decreasing the polarity of GO by surface modification, and this approach is essential in improving the interactions between GO and rubber, especially nonpolar rubber [15,16]. Some nonpolar rubbers, such as SSBR, can only be dispersed in nonpolar or low polar organic solvents in the form of rubber latex. Therefore, stabilizing dispersion in organic solvents and preparing GO/rubber composites by solution mixing are suitable approaches for nonpolar rubbers.

GO is typically chemically modified mainly by the reaction between the functional groups of GO and modifiers [11]. The carboxyl groups on

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the GO surface reacts with hydroxyl or amino groups to produce covalently bonding functional groups through the formation of esters or amides. For instance, Zhong et al. [17] developed a one-step approach to simultaneously reduce and functionalize GO via *N*-1,3-dimethylbutyl-*N′*-phenyl-*p*-phenylenediamine. The introduction of functionalized GO into SBR by emulsion mixing method endow the coomposites with high long-term thermo-oxidative aging resistance and thermal conductivity. Modifiers can also be introduced into GO by facilitating the ring opening of epoxy groups on GO surfaces. For instance, long aliphatic amine groups improve GO dispersion in organic solvents [18]. Besides, GO is capable of generating free radicals upon heating so that GO can in situ induced crosslinking and reinforcement of SBR by the fotmation of chemical bonds between GO and SBR [19]. This method can obtain better mechanical properties of SBR than SBR crosslinked with conventional sulfur. In recent years, click chemistry methods, including alkyne-azide, thiol-ene, and thiol-yne click reactions, have been used for graphene and GO modification [20,21]. In thiol-ene reactions, the thiol groups of modifiers, rather than oxygen-containing groups, react with C=C bonds on the graphite lattice. For example, Luong et al. [20] used cysteamine hydrochloride ($HS–(CH_2)_2–NH_2HCl$) as a thiol-containing compound and incorporated it to GO surface by thiol-ene reaction between the thiol groups and C=C bonds. Castelaín et al. [21] combined short-chain polyethylene brushes to graphene surfaces by thiol-ene reactions between thiol-terminated polyethylene and graphene. The click chemistry showed higher selectivity, more efficiency, and milder reaction conditions than conventional modification methods. To the best of our knowledge, click chemistry methods are rarely applied for the preparation of rubber composites filled with GO or graphene.

The relationship between the structures and properties of materials can be obtained not only by experiments but also by computer simulation. Investigation on polymer composites widely uses molecular dynamics (MD) simulation, a popular computer simulation method based on classical mechanics theory, and great progress has been achieved in the surface modification of fillers [22–24]. MD simulation is a more intuitive and flexible method for the investigation of the microstructures of materials and prediction of their macroscopic properties compared with conventional experimental methods at experimental conditions.

In this study, we synthesized alkanethiol-modified GOs containing alkanethiol (C_xGO) molecules with varying chain lengths by using click chemistry. We also prepared C_xGO/SSBR composites with different C_xGO loadings by solution mixing. C_xGO dispersion in *o*-xylene, effect of C_xGO on filler dispersion, filler–rubber interactions, and properties of synthesized composites were subsequently examined. The relationship between the microstructure and performance of the composites was explored by investigating their fractional free volumes (FFVs), fractional cavity volumes (FCVs), and mean square distance (MSDs) through MD simulation.

2. Experimental

2.1. GO synthesis and alkylation

All raw materials were present in Supporting Information (SI). We synthesized GO from natural graphite flakes by modified Hummers method [25]. We also amalgamated the alkylated GO according to a previously reported thiol-ene click chemistry procedure [21] as shown in Scheme S1. The thiol-ene click chemistry procedure was presented in SI briefly.

2.2. Preparation of C_xGO/SSBR composites

We prepared C_xGO/SSBR composites with 0.5, 1.0, 2.0, and 3.0 phr of C_xGO (phr is the abbreviation for parts per 100 parts rubber by weight) through solution mixing. The detailed preparation process was present in SI.

2.3. Characterization

All characterization methods were present in SI. In order to guide the modeling of GO and C_xGO in MD simulation, the results of XPS are firstly discussed in this section (see SI), and the other test results are given and discussed in Section 4.

3. Model and simulation details

We constructed as matrix the SSBR chain consisting of 30 repeat units with 21 wt% of styrene and 68 wt% of vinyl in accordance with the Taipol® SSBR 2466 sample. We also fabricated the single GO sheet with a width of 3.3 nm and a length of 4.2 nm and terminated the unsaturated edge configurations by adding hydrogen atoms as shown in Fig. S2a. The model construction and the simulation details were present in SI.

4. Results and discussion

4.1. Characterizations of GO, C_7GO and C_{18}GO

GO alkylation was first confirmed by FT-IR spectra as shown in

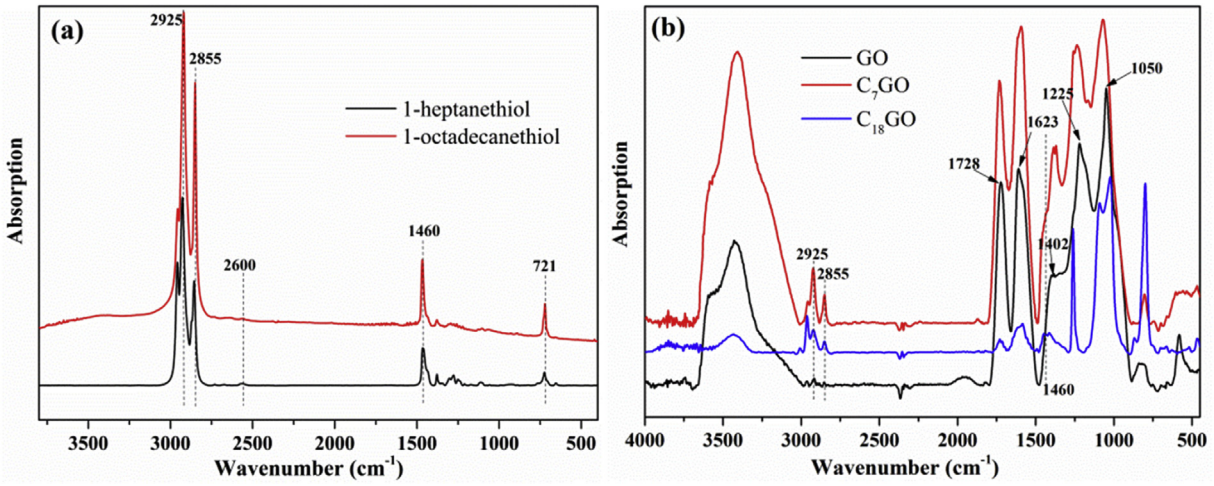

Fig. 1. FT-IR spectra of alkanethiol, GO and C_xGO.