Polymer 55 (2014) 5389–5395

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

# Mechanical properties of polybutadiene reinforced with octadecylamine modified graphene oxide

Yan Zhang [a], James E. Mark [a, *], Yanwu Zhu [b], Rodney S. Ruoff [c], Dale W. Schaefer [d, **]

[a] Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, USA
[b] Department of Materials Science and Engineering and CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei, Anhui 230026, China
[c] Department of Mechanical Engineering and The Texas Materials Institute, University of Texas at Austin, Austin, TX 78712-0292, USA
[d] Department of Biomedical, Chemical and Environmental Engineering, College of Engineering and Applied Science, University of Cincinnati, Cincinnati, OH 45221-0012, USA

## ARTICLE INFO

*Article history:*
Received 26 June 2014
Received in revised form
18 August 2014
Accepted 24 August 2014
Available online 3 September 2014

*Keywords:*
Polybutadiene
Graphene oxide
Mechanical property

## ABSTRACT

Octadecylamine-modified graphene-oxide (OMGO) polybutadiene nanocomposites with different OMGO loadings were prepared by solution mixing. The dispersion of OMGO in chloroform is greatly improved compared to GO. Toughness and elongation of PBD–OMGO nanocomposites increase by 332% and 191% respectively compared with pure PBD. However, Young's modulus of PBD–OMGO nanocomposite decreases by 10% at 2-wt% loading. Graphene sheet crumpling accounts for the increased toughness, the absence of modulus reinforcement and the absence of a Payne effect for PBD–OMGO. The oxidation susceptibility of PBD is greatly reduced after the addition of OMGO, which is particularly desirable in the tire industry.

## 1. Introduction

Rubbers (elastomers) are an important class of commercial polymers. Classic elastomers, such as polybutadiene and polyisoprene are used as general purpose rubbers in high volume products such as tires, hoses, belting, and flexible automotive parts [1]. Rubber materials have been extensively studied because of easy processing, flexibility and excellent thermal properties [2–4]. However, rubber is commonly used in form of composites since pure rubber lacks the required mechanical properties such as wear resistance and strength.

Rubber nanocomposites are the class of filled rubbers in which at least one dimension of the fillers is on the nanometer scale. Most commonly used fillers are silica, carbon black, clay and carbon nanotubes [5–7]. Increased modulus is achieved at relative high filler loading such as 20–50 per hundred rubbers (phr), which can reduce toughness due to defects caused by the fillers [8]. However, the incorporation of small-size fillers in cross-linked elastomers results in specific nonlinear mechanical behaviors including Payne effect and Mullins effect. The Payne effect is typically observed at small strain. The dynamic storage modulus decreases strongly with increasing strain amplitude [9]. Mullins et al. first reported that the degree of softening increases with increasing stiffening ability of the fillers [10]. Some Mullins softening is observed in carbon black and silica filled rubber composites systems [11].

Polybutadiene (PBD), a synthetic rubber, has a higher resistance to wear over styrene-butadiene rubber and natural rubber, which are its main competitors in rubber-industry applications due to their lower glass transition temperatures [12]. PBD is a low cost rubber used for soles, gasket, seals and belts [13]. PBD is normally formulated with fillers, such as silica or carbon black.

Graphene is an emerging filler candidate that has been widely studied in thermoplastics, but not in elastomers. Graphene shows high thermal conductivity (5000 W $m^{-1}$ $K^{-1}$) [14–16], highest Young's modulus ever measured (1 TPa) [17] and large theoretical surface area (2675 $m^2$ $g^{-1}$) [18]. High modulus and large surface area promise dramatic improvement in mechanical properties, which as yet has not been realized. Within the few published paper on elastomers filed with graphene materials, Araby et al. [19] reported that tensile strength of styrene butadiene rubber filled with graphene increases by 230% using melt compounding. However, in order to obtain such improvement, a large amount of graphene (24%) was incorporated into rubber, which causes defects in products and increases cost.

---

* Corresponding author. Tel.: +1 513 556 9292; fax: +1 513 556 9239.
** Corresponding author. Tel.: +1 513 556 5431; fax: +1 206 600 3191.
*E-mail addresses:* markje@ucmail.uc.edu (J.E. Mark), dale.schaefer@uc.edu, schaefdw@ucmail.uc.edu (D.W. Schaefer).

http://dx.doi.org/10.1016/j.polymer.2014.08.065
0032-3861/

An effective approach to achieve graphene-based polymer composites is based on chemical transformation of graphite to graphite-oxide (GO), which readily disperses in water and exfoliates to form individual, single-layer graphene oxide sheets [20–23]. Further modification of GO is necessary to achieve fully dispersed GO in common organic solvents [24–28]. Here we demonstrate a modification scheme based on octadecylamine (ODA) modification of GO that greatly improves GO dispersion in chloroform.

We report the synthesis of ODA-modified GO (OMGO) and examine the mechanical properties of PBD–OMGO nanocomposites as a function of OMGO loading. The amino group in the ODA modifier reacts with carboxylic acid groups in GO. In contrast to the preponderance of graphene-based thermoplastic composites, we investigate the performance of thermosetting rubber materials. Toughness and elongation at break of PBD–OMGO improve by 332% and 343% respectively at 2-wt% OMGO. However, Young's modulus of PBD–OMGO decreases by 10% at OMGO loading 2 wt%.

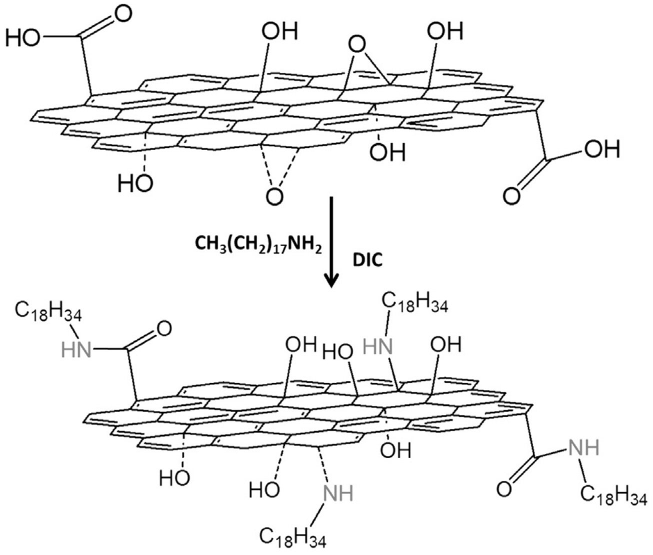
## 2. Experimental section

### 2.1. Materials

GO, prepared by a modified Hummers method [20]. ODA and N, N′-diisopropylcarbodiimide (DIC) were purchased from Sigma–Aldrich Co. Chloroform was purchased from Tedia Company Inc. Anhydrous acetonitrile was purchased from Acros Organics. High *cis*-1, 4-polybutadiene (*c*-PBD) was purchased from Sigma–Aldrich Co. Dibenzoyl peroxide (BPO) was purchased from Acros Organics. All reagents were used as received.

### 2.2. Preparation of OMGO

ODA-modified GO (OMGO) was made using the reaction between carboxylic acid groups and epoxy groups from GO and amino groups (using DIC to activate carboxylic groups), as shown in Scheme 1. The selectivity of carboxylic acid groups and epoxy groups remains an open question [29,30]. Briefly, the desired amount of GO was dispersed in 40 ml anhydrous acetonitrile followed by ultrasonication for 1 h. DIC was added into graphene oxide dispersion followed by reaction for 4 h at 70 °C to activate the carboxylic acid groups. Then ODA was added into the mixture followed by refluxing at 75 °C overnight under nitrogen atmosphere. After the reaction, the OMGO was purified by washing with dimethyl formamide and acetone successively to remove residual DIC and unreacted amines. Black, solid OMGO was obtained after vacuum drying at 50 °C overnight.



**Scheme 1.** Synthesis of OMGO with octadecylamine.

### 2.3. Preparation of the unfilled cis-PBD networks

The desired amounts of polymer were first dissolved in chloroform. After a clear solution was obtained, 2-wt% BPO was added [31]. The solution was stirred at room temperature for 2 h and then transferred into Teflon™ dishes that were covered with aluminum foil for overnight solvent evaporation. Films were pressed at approximately $1.2 \times 10^4$ psi, 130 °C for 2 h. The final samples were approximately 1.0 mm thick.

### 2.4. Preparation of PBD–OMGO nanocomposites

The PBD–OMGO nanocomposites were prepared with various loadings of OMGO. Firstly OMGO was dispersed in chloroform with the aid of ultra-sonication for 1 h to yield a well-dispersed solution. Secondly, the well-dispersed OMGO solution was mixed with *c*-PBD with 0.50, 1.00 and 2.00 weight ratio for 2 h following the same procedures as for unfilled *c*-PBD discussed above.

### 2.5. Characterization

Fourier transform infrared spectroscopy (FTIR) recorded on a Nicolet 6700 (Thermo Scientific) spectrometer was used to characterize the chemical structure of GO and OMGO. Samples were measured under a mechanical force by pressing the un-exfoliated sample's surface against a diamond window. FTIR spectra were collected in the range 4000–450 $cm^{-1}$.

Thermo-gravimetric analyses (TGA) were done on the GO and OMGO powders using a TA Q500 instrument (TA Instruments) under a nitrogen atmosphere with a heating rate of 5 °C $min^{-1}$. Degradation temperatures of PBD–OMGO nanocomposites were measured using NETZSCH STA 409 instrument under a purge flow of 20 ml/min argon at heating rate of 20 °C $min^{-1}$ from 25 to 700 °C.

Powder X-ray diffraction (XRD) measurements were carried out using a PANalytical X'Pert Pro MPD diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.541$ Å) at 45 kV and 40 mA. The diffraction angle was increased from 5° to 35° with the scanning rate of 0.05°$min^{-1}$.

Scanning electron microscopy (SEM) was conducted with an FEI Phillips Electroscan XL30 ESEM–FEG microscope using an acceleration voltage of 15 kV. OMGO suspensions (0.03 mg $ml^{-1}$) were spin-coated onto a flat aluminum plate at 2000 r.p.m. for 30 s. Then the OMGO-coated aluminum plate was mounted on a standard specimen holder using a double-sided carbon conductive tape for SEM imaging. A transmission electron microscopy (TEM) sample was prepared by placing a few drops of dispersion onto a lacey carbon film support on a Cu grid. Images were acquired in a JEOL 1230 transmission electron microscope operated at 80 kV.

Atomic force microscopy (AFM) images were obtained using a Dimension 3100 AFM made by Veeco Instruments Inc., operated in tapping mode using Veeco RTESP type silicon cantilevers with a resonance of frequency of 360 kHz. The samples for AFM measurements were prepared by ultrasonic treatment of OMGO in chloroform for 1 h, followed by spin-coating OMGO suspensions in chloroform (0.03 mg $ml^{-1}$) on freshly cleaved mica surfaces at 2000 r.p.m. for 30 s and then drying under vacuum at room temperature.

The tensile properties were measured using an ESM-301 (MARK-10) tensile tester. The experiments were carried out at