



Synthesis and gas permeability of highly elastic poly(dimethylsiloxane)/graphene oxide composite elastomers using telechelic polymers



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ABSTRACT

This study illustrates that amine functional groups on the ends of telechelic poly(dimethylsiloxane) (PDMS) can undergo post-processing reactions with surface epoxy groups on graphene oxide (GO) to form a robust elastomer during simple heating. In these materials, GO acts both as a nanofiller which reinforces the mechanical properties and participates as a multifunctional crosslinker, thereby promoting elastic properties. Experiments indicate that the telechelic PDMS/GO elastomer is highly crosslinked (e.g., more than 75 wt % is a non-dissolving crosslinked gel) but highly flexible such that it can be stretched up to 300% of its original length. Finally, the PDMS/GO elastomer was tested as a single gas barrier membrane and gas permeability was decreased ~45% by incorporating 1 wt % (0.43 vol %) of GO, thereby highlighting its potential use in practical applications.

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1. Introduction

In recent years, flexible polymers have become increasingly important for many applications that impact daily life, including wearable devices [1–3], flexible displays [4–6], and devices for monitoring physiological signals [7–9], to name a few. These high-end applications typically require the use of an elastomer or rubber, such as crosslinked poly(dimethylsiloxane) (PDMS), to impart flexibility and mechanical robustness in addition to comfort; all are important features for interfacing with the human body. While there exist commercial choices for PDMS elastomer precursors, such PDMS precursors are generally high in viscosity, limited to several grades and the recipe for preparing the final elastomer can be complex [10–12]. Therefore, the development of new methods for forming elastomers with only a few simple components which exhibit unique combinations of properties (e.g., electrically conductive but flexible and mechanically robust, etc.) could be very useful.

Herein, we report a simple process for creating a strong and flexible elastomer from a reactive mixture of graphene oxide (GO)

and functional telechelic (i.e., both ends functionalized) PDMS. The resulting composite has excellent mechanical properties but also serves as an effective and potentially economical gas barrier membrane for industrial use. For context, materials presenting a high barrier to oxygen permeation are typically very important for the applications listed above because flexible devices often contain organic components to promote flexibility that can be particularly susceptible to oxidative degradation.

For a number of reasons, the telechelic PDMS/GO composite elastomer described in this study can be considered to be unique when compared alongside other crosslinked PDMS materials. For instance, a distinguishing characteristic of the present elastomer is that it not only possesses the traditional properties of crosslinked PDMS materials, such as flexibility and good mechanical integrity, but it can also be made by simple and scalable methods using two low-cost materials: graphite and telechelic polymer. In contrast, conventionally crosslinked PDMS elastomers are typically synthesized by one of three methods: platinum-catalyzed addition, vinyl-peroxide, or condensation curing [13]. All of these methods require a catalyst to perform the reaction, accompanied with a range of several different chemical additives, sometimes including fillers such as silica [11,12]. Many prior studies have investigated the tuning of physical properties, including mechanical, electrical, and

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dielectric properties, of PDMS materials by adjusting the crosslink density [14], adding fillers such as silica [15], clays [16], carbon nanotubes [17], graphene derivatives [18] or other polymers [19]. Generally, these additional additives are most commonly physically intermixed with PDMS with no chemical bonding between the PDMS and additives. In contrast, the preparation of telechelic PDMS/GO composite elastomers in this study incorporates a GO filler that also participates as a multi-functional crosslinker, which facilitates formation of the final covalently bonded macromolecular network.

While neat PDMS is highly gas permeable, the addition of impermeable platelet-like fillers such as GO can dramatically inhibit gas permeation. Recent studies of gas barrier membranes using different graphene derivatives have focused on coating the surface of flexible substrates (such as PDMS films or sheets) with a thin layer of graphene or GO that is typically weakly bound by noncovalent adhesion forces [6,20,21]. Graphene coated membranes could be susceptible to sections of the coating delaminating from the flexible substrate after repeated stress, bending or upstream/downstream pressure cycles [6,20,22]. Other potential sources of damage from environmental exposure of the active graphene or GO coating layer, such as irreversible adsorption of undesired contaminants during prolonged use, could be possible. In contrast to this coating approach, the elastomer described herein forms a covalent macromolecular network between the flexible component (PDMS) and the gas impermeable component (GO) producing a dense and homogeneous barrier membrane. In summary, from a membrane engineering perspective, we believe this composite provides for the possibility of a cost-effective, high performance gas barrier membrane.

2. Experimental section

2.1. Materials

In order to synthesize PDMS/GO elastomers, three components were combined: telechelic PDMS as the base material, GO as both a filler and multifunctional crosslinker, and tetrahydrofuran (THF; Fisher Chemical) as a solvent. Aminopropyl terminated telechelic PDMS with a viscosity of 1000 cSt ($M_n = 25,000$ g/mol, DMS-A31, henceforth referred to as N1000) and 2000 cSt ($M_n = 30,000$ g/mol, DMS-A32, henceforth referred to as N2000) were purchased from Gelest and used without any further purification. For comparison, silanol terminated PDMS with a viscosity of 1000 cSt ($M_n = 26,000$ g/mol, DMS-S31) and epoxypropoxypropyl terminated PDMS with a viscosity of 15 cSt ($M_n = 550$ g/mol, DMS-E11) were also purchased from Gelest and used as received. GOs were synthesized by the modified Hummer's method as described elsewhere [23], where sulfuric acid, potassium permanganate, hydrogen peroxide, and hydrochloric acid were purchased from Sigma–Aldrich and used as-received. Pre-oxidized graphite from Bay Carbon Inc. (SP-1) was used as the starting material to synthesize GOs. The nominal number average particle size of the SP-1 graphite was approximately 19.3 μm [24], and it has been reported by others that the GO sheet size reduces to an average value of 8.3 μm when this grade of graphite is oxidized using the modified Hummer's method with an oxidation temperature of 35 $^\circ\text{C}$ [25].

2.2. Fabrication of PDMS/GO elastomers

First, a known amount of telechelic PDMS (for 1 wt % GO composites, 990 mg) was dissolved in THF (6 ml) while stirring to ensure complete dissolution of the polymers. Then, dried GO (10 mg) was suspended in the solution with vigorous stirring, and a homogeneous dispersion of GO in this solution was promoted by

sonication using a 400 W probe sonicator (Branson Digital Sonifier 450) with 10% amplitude for 10 min (24 kJ) in an ice bath. It is noteworthy to point out that, although THF is not a good solvent for GOs, amine terminated telechelic PDMS can effectively act as a surfactant to assist in dispersing GOs homogeneously in THF through hydrogen bonding between amine ends and oxygen containing groups on GO surfaces. A good dispersion after sonication was confirmed by examining the residual liquid film in the vial while rolling the vial containing the solution and after pouring the majority of the solution into a PTFE dish for solution casting. In either case, the liquid film in the vial was essentially transparent (although brownish-black from the GO content) for all solution concentrations and no aggregates could be identified with the naked eye. This solution was immediately poured into a Teflon dish and covered in order to slowly evaporate the solvent thereby solution casting a film at room temperature. Solvent was evaporated for at least 2 days and then the sample was vacuum dried at room temperature for an additional day to make a homogenous PDMS/GO uncrosslinked liquid sol. In order to form a crosslinked elastomer, the sol precursor was heated to 160 $^\circ\text{C}$ in a vacuum oven for 24 h and cooled slowly to room temperature before use.

For one of the gas permeation tests, a reference sample (neat PDMS elastomer) was synthesized by reacting aminopropyl terminated telechelic PDMS and epoxypropoxypropyl terminated telechelic PDMS. A detailed explanation of how this freestanding, neat PDMS elastomer was synthesized is summarized in the supporting information.

2.3. Characterization of PDMS/GO elastomers

The chemical crosslinking reaction between PDMS and GOs was investigated using Fourier transform infrared spectroscopy (FTIR; Thermo Nicolett, 6700) with a scan size (resolution) of 2 cm^{-1} collected over 256 scans per sample. Solvent uptake and gel content of each composite elastomer were calculated using Equations (1) and (2) below where 'w' indicates weight, according to ASTM D2765 test method C. THF was used as the solvent to dissolve away unreacted soluble polymers.

$$\text{Solvent Uptake (\%)} = \frac{W_{\text{after swell}} - W_{\text{before swell}}}{W_{\text{before swell}}} \times 100 \quad (1)$$

$$\text{Gel Content (\%)} = \frac{W_{\text{after swell and dried in vacuum}}}{W_{\text{before swell}}} \times 100 \quad (2)$$

All rheological experiments were conducted on a shear rheometer (TA Instruments, AR-2000EX) using an 8 mm parallel upper plate and a Peltier lower plate fixture for temperature control with a gap of 500 μm . First, a strain sweep was conducted to identify the linear viscoelastic regime at 25 $^\circ\text{C}$ in the range of 0.01–10% strain at a frequency of 1 Hz. A frequency sweep was then conducted at 25 $^\circ\text{C}$ in the range of 0.01–10 Hz with 0.1% strain. Temperature sweeps were conducted from 25 $^\circ\text{C}$ to 100 $^\circ\text{C}$ with 5 $^\circ\text{C}$ step changes using both 0.1% strain and a frequency of 1 Hz. Stress relaxation tests were conducted by subjecting the sample to an initial strain of 10% and 20%. In order to measure the mechanical properties of the composite elastomers, microtensile specimens were prepared by solution casting on a mold (i.e., to produce a dog bone sample with a gauge length of 22 mm, width of 4.8 mm and thickness of about 0.7 mm) satisfying ASTM D1708-13 standards. An Instron (model 5966) equipped with a 1 kN load cell was used with a strain rate of 10 mm/min (i.e., at our gauge length this is a nominal strain rate equivalent to 50 mm/min for ASTM D638 standard samples, which is the recommended speed for rubber samples) and samples were tested in triplicate.

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