MECHANICAL REINFORCEMENT OF CROSSLINKED CYCLOSILOXANE BASED POLYMER NETWORK WITH BASAL-PLANE FUNCTIONALIZED GRAPHENE AT EXTREMELY LOW LOADING

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Abstract

Graphene was successfully incorporated into an extremely crosslinked cyclosiloxane based polymer network and the toughening effects were investigated. The graphene oxide (GO) was basally modified by allylamine to achieve better dispersion and incorporated into the cyclosiloxane rein via in situ polymerization. Mechanical reinforcement were observed at extremently low loading of graphene, and the covalent bonds between graphene nanosheets played an important role in mechanical reinforment of cyclosiloxane hybrid materials.

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1. Introduction

Polysiloxane is categorized as organic-inorganic hybrid material since it possesses both organic (Organic groups attached to Si atoms) and inorganic parts (-Si-O-Si-).[1] Organic-inorganic hybrid materials take the advantages of properties of inorganic materials and organic materials, so it has high hardness and heat resistance from inorganic parts as well as elasticity and flexibility from organic parts. Its unique material nature makes it as one of the promising candidates to be widely used in aerospace, electrical devices, automotives, biomedical fields and other possible areas.[2-4] Methods such as incorporateing fumed silica, carbon fiber, carbon nanotubes and graphene aiming to improve the mechanical properties has been done and possible functionality was desired.[4-11] However, all these studies were focused on polydimethylsiloxane (PDMS) based silicone rubber or related elastomers, which failed to function where higher Tg is desired. A recent publication on extremely hard but elastic cyclosiloxane based polymer network[12] (Denoted as cyclosiloxane hybrid matrix) synthesized via solventless process and its liquid state cyclosiloxane monomers draw our attention. However, the practical applications of this highly crosslinked network structure are hindered by the intrinsically brittle nature.

Among all the possible fillers to reinforce polymer matrix, graphene emerged as an superior choice in terms of the high specific area, the extended two-dimensional geometry, and the wrinkled surface which is critical for enhancing interfacial interaction enhancement between the fillers and matrix.[16] Various studies have been done to study the reinforcing mechanism of graphene inside ceramics [17-20] and polymers [13, 16, 21-27]. Several reinforcing mechanism were proposed.

Graphene based nanocomposites, benefiting from the high aspect ratio of graphene and other functional properties imparting by graphene towards polymer matrix, are regarded as one of the most promising smart materials of next generation. Recently, graphene was used to toughen brittle thermoset polymers and various toughening mechanisms have been proposed to explain the toughening effects of graphene nanosheets.[23-25] Furthermore, due to the high cost of graphene for industrial applications, low loading of graphene inside nanocomposites (within 0.5 wt%) is desired.[16, 26, 27] Nevertheless, most of the researches were based on epoxy systems, and very few papers talked about reinforcing of silicone resins. To the best of our knowledge, no report has been published on reinforcing of this cyclosiloxane based polymer with the incorporation of low loading of graphene nanosheets.

Motivated by the discussion above, we sought to investigate the reinforcing effects of graphene nanosheets in cyclosiloxane hybrid matrix. The content of graphene in nanocomposites was kept within 0.1 wt%. Graphene oxide (GO) was chemically modified via a facile method and both of them were incorporation into cyclosiloxane hybrid matrix via solventless process. The enhanced mechanical properties were observed and possible reinforcing mechanisms were investigated. This work paves the way to the practical applications of cyclosiloxane based hybrid.

2. Methods

2.1. Materials

2,4,6,8-Tetramethylcyclotetrasiloxane (D_4^H , Alfa Aesar), 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (D_4^V, Alfa Aesar), Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst, 3.2wt% Pt, Alfa Aesar), Allylamine (Alfa Aesar), natural graphite powder LBG8010 (Superior Graphite Company), sulfuric acid (A. R. 95-98 wt%, Sigma-Aldrich), nitric acid (A. R. 67 wt%, Sigma-Aldrich), potassium permanganate (Alfa Aesar), hydrogen peroxide (30%, VMR),and N,N-dimethylformamide (DMF, Sigma-Aldrich) were used as received.

2.2. Modification of GO by allylamine

GO was prepared according to a modified Hummer's method and dried by vacuum oven overnight, before modification by allylamine. Dried GO (100 mg) was suspended in DMF (100 ml), and the mixture was probe sonicated for 20 minutes to form a stable suspension. Allylamine (10 ml) was added into GO suspension and the obtained mixture was heated up to 50 ℃ for 48 hours under continuous stirring. The solid product was separated by vacuum filtration and washed with sufficient amount of ethanol and DI water to remove DMF and residual allylamine. After dehydration by freeze drying, the fluffy GO-AA was stored in a desiccator for further use.

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2.3. Nanocomposites preparation.

The synthesis route of cylcosiloxane hybrids and nanocomposites thereof is shown in Figure 1. Desired amount of GO or GO-AA was suspended in D_4^V by ultrasonic exfoliation. The mixtures were subjected to magnetic stirring to maintain well dispersion. Karstedt's catalyst (0.1 wt%) was added into the mixtures, followed by addition of D_4^H (Mass ratio of D_4^H : D_4^V 1:1). The resultant mixtures were stirred at room temperature until proper viscosity was reached before transferred into Teflon molds and cured at room temperature in vacuum. After partially cured at 80 ℃ for 4 h, the samples (~1 mm thick) were cut into appropriate dimensions for further characterizations. The cut samples were further cured at 150 ℃ for 24 h.

2.4. Characterization

Fourier transform-infrared (FTIR) spectroscopy was carried out using a Frontier model with ATR accessory (Perkin Elmer). 16 scans were recorded with resolution of 4 cm-1. 3-point bending test was carried out using Tensile Tester Instron 5567 with a 500 N load cell. The sample thickness was about 1 mm and the width was about 10 mm. All the samples were carefully polished before bending tests at a sample span of 16 mm with a 2 mm/min crosshead speed. 4-6 samples were tested for each system. Relative toughness was calculated by the following equation:

$$T = \frac{\int_0^{\varepsilon f} \sigma d\varepsilon}{\int_0^{\varepsilon fn} \sigma n d\varepsilon} \qquad (1)$$

Where T is relative toughness, σ is flexural stress, ε is flexural strain and εf is final flexural strain (σn and εfn stand for flexural stress and final flexural strain of neat cyclosiloxane matrix without graphene nanosheets). Scanning electron microscope (SEM) images were taken by FESEM 6340F (JEOL) and the samples were coated with palatium before being put into SEM chamber.

3 Results

3.1. Modification of GO

Figure 2 shows the FTIR results of GO and GO-AA, these FTIR spectra of GO and GO-AA are comparable. The disappearance of epoxy group (1058 cm^{-1}) as well as the appearance of –N-H (1573 cm^{-1}), C-N (1431 cm^{-1}) and C-OH (1214 cm^{-1}) indicated that allyamine reacted with GO and the appearance of C=C (932 cm^{-1}) furthur verified the successful grafting of double bonds onto graphene surfaces.

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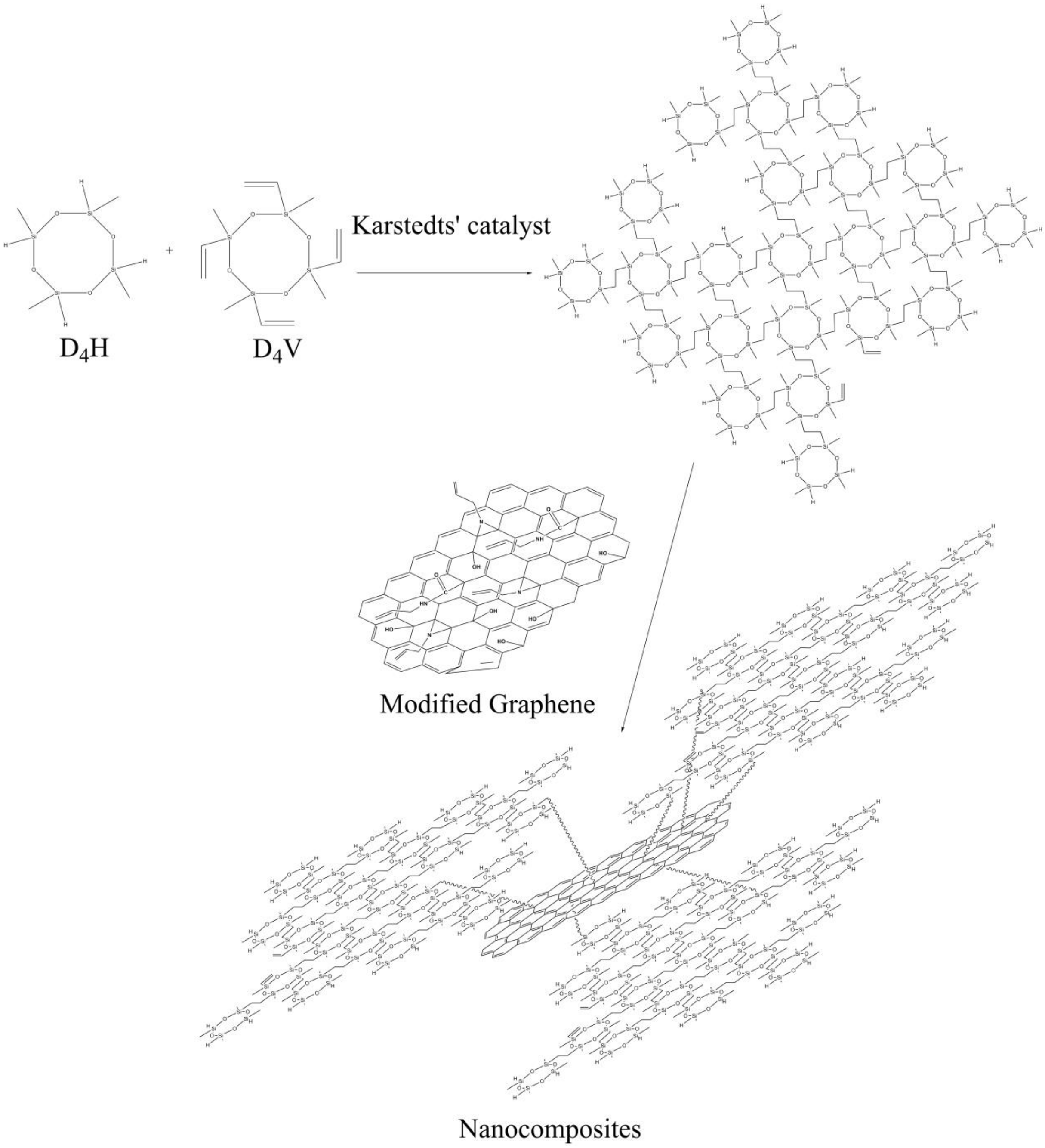

Figure 1. Fabraction of nanocomposites.

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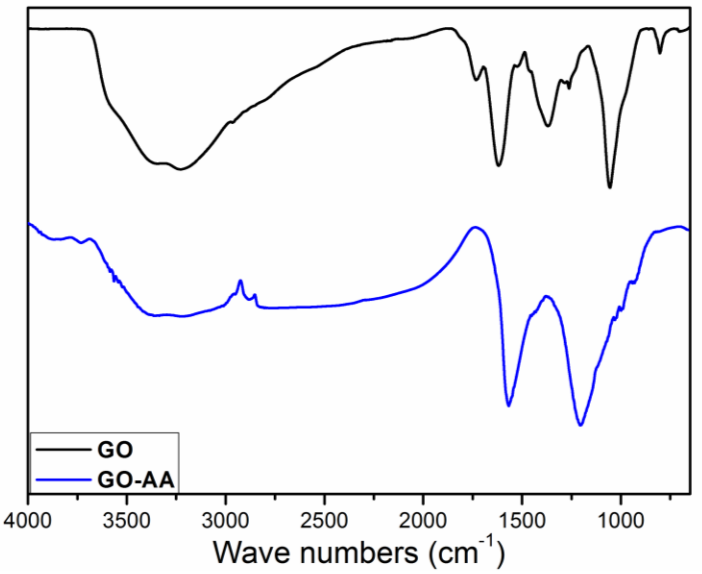

Figure 2. FTIR of GO and GO-AA.

Figure 3 shows 3-point bending data of GO and GO-AA nanocomposites and Table 1 shows the calculated relative toughness of them. flexural modulus of GO nanocomposites fluctuates as a function of graphene content while the flexural strength decreases with increasing graphene content. Compared with GO nanocomposites, the flexural modulus of GO-AA nanocomposites increased with graphene content, maximized at 0.04 wt% before decrease at higher loading. The flexural strength increases with graphene content, but less significant when graphene loading is lower than 0.04 wt%. The insignificant effect of GO on modulus is due to the weak graphene-matrix interfacial interaction resulting from their incompatibility. To the best of our knowledge, there is no reliable measurement of toughness of silicone resins including the cyclosiloxane hybrid matrix. The area under the stress-strain curves were used to represent the relative toughness (the toughness of hybrid matrix was normalized to 1 for intuitive understanding, equation 1) on comparative basis, to better demonstrate the impact of the addition of graphene nanosheets. For GO-AA nanocomposites, better dispersion and covalent bonds between graphene nanosheets and the hybrid matrix are the two main contributing factors for the increase of flexural modulus before it peaks at 0.04 wt% graphene loading, as well as for the increase of flexural strength with graphene loading from 0.02 wt% to 0.1 wt%. The subsequent decrease of flexural modulus might be due to poor dispersion above weight fraction of 0.04% which reduces the effective area for interaction.[21] the relative toughness of GO nanocomposites decreases while that of GO-AA nanocomposite increases with increasing graphene loading, reaching its highest value at 0.08 wt% GO-AA loading (153% increase in relative toughness). The increase in relative toughness is not only contributed by the increase of flexural modulus and strength but also the increase of flexural strain. Better dispersion improved the interfacial interaction between GO-AA and the hybrid matrix contributed by covalent bonds and wrinkled surface were responsible for the enhancement of mechanical properties. The covalent bonds, which can be regarded as bridges between graphene nanosheets and hybrid matrix, acted as anchors and provided better interfacial interaction and load transfer routes via graphene sheets.

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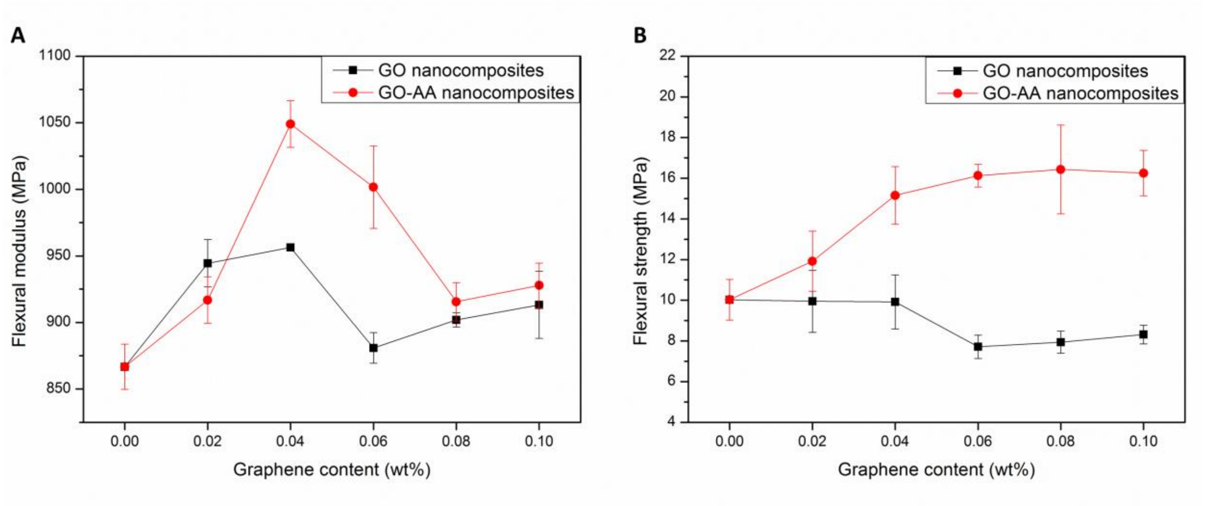

Figure 3. (A) Flexural modulus and (B) Flexural strength of GO and GO-AA nanocomposites

Table 1. Calculated relative toughness.

Specimen		Relative toughness
Cyclosiloxane hybrid		1.00
GO content(%)	0.02	0.92
	0.04	0.88
	0.06	0.57
	0.08	0.58
	0.10	0.55
GO-AA content(%)	0.02	1.35
	0.04	1.87
	0.06	2.17
	0.08	2.53
	0.10	2.36

3. Conclusions

Graphene was successfully incorporated into an extremely crosslinked cyclosiloxane based polymer network and the toughening effects were investigated. The graphene oxide (GO) was basally modified by allylamine to achieve better dispersion and incorporated into the cyclosiloxane rein via in situ polymerization. Mechanical reinforcement were observed at extremently low loading of graphene, 153% improvement in toughness were observed with only 0.08 wt% of graphenen nanosheets. This work may pave the way of pratical application of graphene nanocomposites.

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