Effects of silanized nanodiamond on the mechanical and dynamic-mechanical properties of poly(dimethyl siloxane) nanocomposites

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Abstract

Nanodiamond (ND) was successfully functionalized by silanization process using vinyltrimethoxysilane to enhance interfacial bonding with poly(dimethylsiloxane) (PDMS) silicone rubber. The effects of silanized ND (sND) and untreated ND (uND) on the mechanical and dynamic-mechanical properties of PDMS/ND nanocomposites were investigated. It was revealed that sND is much more effective than uND in improving the tensile properties of PDMS due to the achievement of stronger interfacial interaction. The results exhibited that the Young's modulus and tensile strength of PDMS enhanced 25% and 70%, respectively, by adding 0.2 wt% sND. Moreover, the addition of both uND and sND to PDMS exhibited a substantial increase in storage modulus in the glassy region.

1. Introduction

Poly(dimethylsiloxane) (PDMS) is an organosilicon polymer containing a repeating [$SiO(CH_3)_2$] unit that exhibits very low glass transition temperature (less than -120 ºC [1]. Moreover, it possesses interesting properties such as high thermal, UV and oxidative stability, hydrophobicity, high dielectric strength, low surface energy, high gas permeability and biocompatibility [2-4]. However, due to the weak intermolecular forces between PDMS chains, it demonstrates low mechanical properties, which limits its potential applications [2].

Recently, the addition of carbon-based nanoparticles such as multi-walled carbon nanotubes (MWNTs) into PDMS matrix is highly regarded since it can enhance electrical, thermal and mechanical properties of PDMS. Furthermore, the efficacy of surface treatment of nanoparticles in such cases has been proved [1, 5-7].

Nanodiamond (ND) is well known for its prominent hardness, Young's modulus, thermal conductivity, variable surface chemistry, biocompatibility and resistance to harsh environments [8-10]. ND has a large specific surface area (greater than 200 m^2/g) with tailorable functional groups providing great surface

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reactivity [11, 12]. Consequently, ND is a promising reinforcement for the fabrication of nanocomposites [13]. However, its reinforcing capability has been limited due to its tendency to form agglomerates in polymer matrices [14]. Recently, several approaches for surface functionalization of ND have been used which not only contribute to deagglomeration but also improving interfacial bonding between ND and polymer matrix [15].

Here we report on the silanization of ND which can be efficient functional groups to interact with PDMS [7]. Literature shows a few report on the silanization of ND which are mostly based on demanding methods such as the reduction of ND and milling method [16, 17]. Moreover, the silanization of other carbon nanoparticles such as carbon nanofiber (CNF) and multiwall carbon nanotube (MWCNTs) have been reported earlier [18, 19].

In the present study, vinyltrimethoxysilane (VTS) was used to silanize ND surface by means of a straightforward method based on the esterification of hydrolyzed silane in an alcoholic solution. The merit of the aforementioned method is its simplicity to acquire silanized ND, referred as sND, avoiding complicated processes such as ND reduction which have already been used to obtain sND. The effects of sND and untreated ND (uND) on the mechanical and dynamic properties of PDMS/ND composites were investigated. The silane functionalization of ND which is used in the present investigation is expected to increase the compatibility of ND with PDMS because silane functional groups can create local silicon environment at ND surface. Using rheological investigation, Gavrilov et al [20] reported that uND can alter the conformation of PDMS and consequently, it can improve the mechanical properties of PDMS/ND composite. Furthermore, Shenderova et al. [21] reported a 15% increase in thermal conductivity of PDMS by adding 2 wt.% of uND. To the best of our knowledge, the research work on the PDMS/sND composite is very spares.

2. Experiment

2.1. Materials

Detonated ND with a primary particle average diameter of 4-6 nm, purity of 98-99% and SSA of 282 m^2/g was purchased from NaBond Technologies Co., China. PDMS (Sylgard 184 Silicone Elastomer, Dow Corning, USA) was supplied in liquid form consisted of a base elastomer (Part A) and a curing agent (Part B). Vinyltrimethoxysilane (VTS) with the purity of 97% from Merck was used for silane functionalization of ND. The following materials were used without further purification: ethanol (99.8% Sigma Aldrich), acetone (99% Merck), and acetic acid (99.85% Sigma Aldrich).

2.2. Silanization of ND

Surface modification of ND was first carried out by applying thermal oxidation of ND at 425 ℃ for 4 hours in order to increase the surface carboxyl content [11]. Then, the oxidized NDs were reacted with hydrolyzed VTS by esterification method [19]. To this aim, 80 ml solution of distilled water/ethanol (20:80 v/v) was prepared and its pH adjusted to 3.5-4.5 by adding acetic acid. Next, 1.5 ml of VTS added to the solution followed by stirring at ambient temperature for 30 minutes. This process leads to silane hydrolysis. Then, 0.3 g of oxidized ND was added to the solution and dispersed by ultrasonic bath (120 W, 28 kHz) for an hour. Next, the mixture was stirred for 4 hours at 65 ℃ using a hot plate. The

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suspension was then placed in an oven at 120 ℃ for 4 hours developing the esterification of silanol groups on ND surface and evaporation of water/ethanol solution. Finally, the sND was washed out sequentially with acetone, distilled water and dried in an oven at 120 ℃ for around 12 hours.

2.3. Preparation and characterization of ND/PDMS nanocomposites

Nanocomposites containing uND (0.2, 0.5, 0.7, 1 and 1.5 wt%) and sND (0.2, 0.5, 0.7 wt%) with respect to the PDMS were prepared by first mechanical stirring of ND in Part A-PDMS for 4 hours (1000 rpm) and then by applying ultrasonic bath for 20 minutes to obtain uniform dispersion. Part B-curing agent was then added to the ND/Part-A mixture at a ratio of 10:1 (Part A: Part B). Next, the mixture was mechanically stirred again for 10 minutes. Then, the mixture was poured into the mold followed by degassing under vacuum for 1 hour. Subsequently, the mold was kept in an oven and the mixture was cured at 100 ℃ for 2 hours. Neat PDMS was also prepared in the same way for comparison.

The cured samples were cut with ISO 37:2005 die cutter type 2 in dumbbell shaped which tension strip section was 25 mm × 4 mm × 1mm. Tensile tests were conducted by using a HIWA 2126 universal testing machine (HIWA Engineering Co., Iran) equipped with a 50 kg_f load cell at ambient temperature and deformation rate of 50 mm/min. Five samples for each nanocomposite were tested by the tensile machine to acquire reliable results.

The temperature-dependent storage modulus and tan d of the nanocomposites were measured by dynamic mechanical analysis (DMA) Tritec 2000 (Triton Technology Ltd.) at a rate of 5 ℃/min and a frequency of 1Hz for rectangular samples with size of 10 mm × 10 mm × 1 mm.

3. Results and discussion

3.1. Tensile properties of PDMS/ND composites

Figure 1 displays the tensile strength and Young's modulus of PDMS filled with uND and sND. The tensile strength of PDMS/uND composites is highest at 1 wt.% loading indicating the optimum uND loading within the range of compositions studied here. In fact, further addition of uND led to a decrease in tensile strength for PDMS/uND composites. The extent of enhancement in tensile strength is highest for sND(0.2 wt%) among other samples which confirms the efficacy of surface functionalization in interaction and stress transferring between filler and PDMS matrix [22].

Young's modulus behavior is similar to tensile strength. Actually, the incorporation of 1 wt.% uND leads to an increase in Young modulus and tensile strength equivalent to 10% and 45%, respectively. Such an enhancement in the mechanical properties is in an accordance with literature data for PDMS/MWCNTs composites, where tensile strength increased 10.38% by adding 1 wt.% MWCNTs [6]. However, Young's modulus and tensile strength of PDMS/sND composites enhanced 25% and 70%, respectively when 0.2 wt.% sND added into PDMS followed by relative decrease at higher concentration. Actually, high filler concentrations lead to the formation of agglomerates, which substantially weakens the composites [6, 22].

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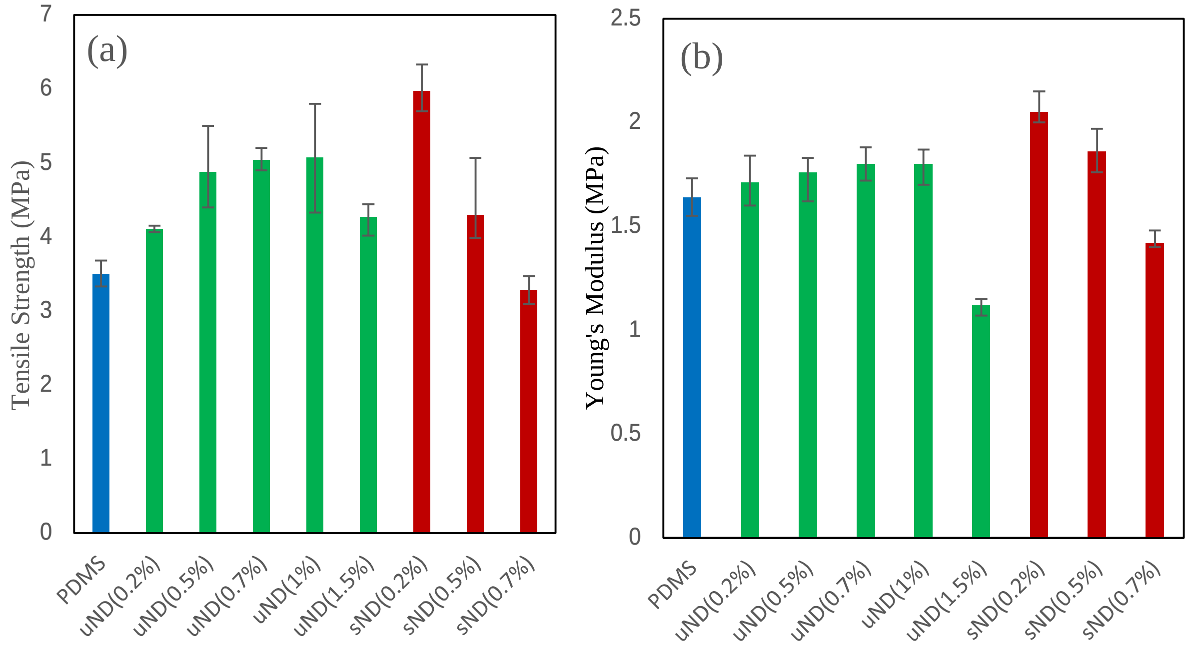

Figure 1. Tensile properties of PDMS composites prepared in the present study; (a) Tensile strength, (b) Young’s modulus

3.2. DMA analysis of PDMS/ND composites

DMA was used to investigate the molecular mobility of PDMS matrix and interfacial interactions on PDMS/ND nanocomposites. Figure 2a and b show the storage modulus and tand versus temperature for neat PDMS and the composites, respectively. According to Figure 2a, the incorporation of both uND and sND in PDMS improve substantially the storage modulus in the glassy region. This can be explained by the high stiffness and proper dispersion of ND and appropriate interfacial interaction with PDMS matrix [23]. However, uND represents a little more improvement in storage modulus in the glassy region compared to sND. Silane condensation among silane molecules on the sND surface and subsequently formation and agglomeration of polysiloxane layers may develop regions with higher free volume around sND surface [19, 24].

According to Figure 2b, T_g (defined as the temperature at which maximum loss tand is reached) displays an increase for uND and sND, compared with neat PDMS, from -113.7 to -112.8 ℃. In literature, the higher T_g is ascribed to interfacial interaction between polymer and filler [24]. Therefore, sND exhibits an improved interfacial interaction with PDMS in comparison with uND. Furthermore, the addition of sND to the PDMS matrix results in the greatest tand peak. The similar observation was reported by Chua et al. [7] who worked on silanized MWCNTs in PDMS matrix. They ascribed such behavior to interactions

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between rubber chains and functional groups on the surface of filler which retard the motion of rubber segments and thus prolong the PDMS response time toward dynamic fields.

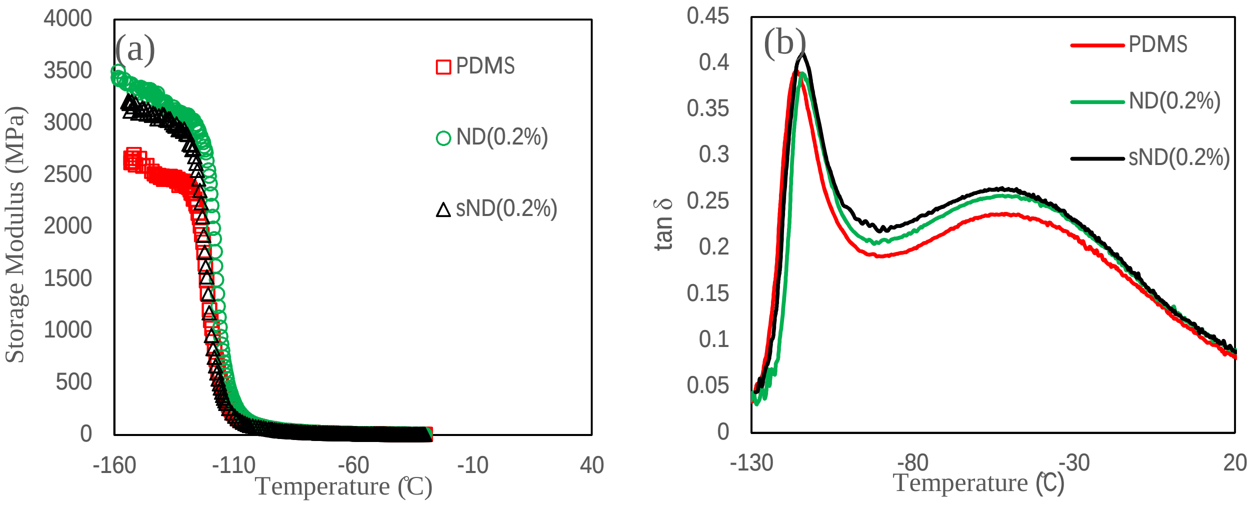

Figure 2. Thermo-dynamic mechanical properties of PDMS/ND nanocomposites.

4. Conclusions

In the present work, the effects of silanized nanodiamonds (sND), which were synthesized by esterification reaction, on mechanical and dynamic properties of PDMS/ND were investigated. Both untreated ND (uND) and sND were incorporated in PDMS to obtain PDMS/ND composites. It was found that sND provides a significant increment in the tensile strength and Young’s modulus of PDMS compared to uND, which indicates the effectiveness of surface functionalization in interaction and stress transferring between filler and PDMS matrix. Moreover, the composite containing sND exhibited higher glass transition in comparison to other samples implying an improved interfacial interaction with PDMS for sND.

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