ROLE OF LOW-COST GRAPHENE ON THE PROPERTIES OF POLYDIMETHYLSILOXANE (PDMS) FOR SENSING APPLICATIONS

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ABSTRACT

Polydimethylsiloxane (PDMS), classified as silicon, has been widely researched for flexible sensors due to its non-toxicity, biocompatibility, mechanical (200% elongation) and optical (95% transparency) properties. Despite having several attractive properties, it has some limitations as well, for instance poor conductivity, low tear resistance. The objective of this study is to use a low-cost graphene and investigate the effect of low loadings (0.1 to 3 wt%) of graphene on properties of the PDMS nanocomposites. Graphene has potential to enhance the properties of the PDMS owing to its large surface area, remarkable conductivity, good thermal, electrical, and mechanical properties. In the present study, Graphene filled PDMS nanocomposites were prepared by solvent casting method. Different concentrations of graphene were used to investigate the effect of low amount of graphene on the thermal and electrical properties of the PMDS. Dispersion of nonreinforcements plays a vital role on the properties of the polymer matrix. Therefore, dispersion of graphene into PDMS was studied using optical microscopy (OM) as depicted in the Figure1. Thermal stability of the PDMS and their nanocomposites with graphene was evaluated via thermogravimetric analysis (TGA). The curing behaviour of the PDMS-Graphene nanocomposites were investigated by differential scanning calorimetry (DSC). It has been observed that graphene improved the thermal stability of the PDMS-GP composites. It has been noticed from DSC results that exothermic peak shifted toward higher temperature with increasing the graphene loading. Furthermore, electrical tests of the PDMS nanocomposites were carried out. It has been observed that well-dispersed graphene has influenced the electrical properties of the PDMS and consequently increased the electrical conductivity of neat PDMS from 3×10^{-13} S/m to 8×10^{-7} S/m (PDMS-0.3GP).

1 INTRODUCTION

Flexible materials have attracted great attention and emerging as one of the most promising materials because of its wide range of potential applications for instance, smart electronic devices, wearable sensors, a flexible flat panel, and human-machine interface applications [1-3]. In this context, Polydimethylsiloxane (PDMS), a silicone-based elastomer is extensively researched due to its excellent properties such as high flexibility, biocompatibility, thermal stability, optical transparency, low permeability, low or non-toxicity, and easy in micropatterning owing to low glass transition temperature [4]. However, due to its limiting electrical properties including poor conductivity and dielectric constant and low mechanical durability such as poor tear strength limits its application as a sensing material for fabrication of wearable sensors [5].

Several approaches have been opted by researchers to improve these limitations of the PDMS. Among them, the most promising approach is the addition of nanomaterials as a reinforcing material that can enhance the properties of the polymer composites with respect to the pristine PDMS [6]. Graphene has potential to overcome the limitations of PDMS because of its excellent properties such as large surface area (2630 m^2/g) [7], high thermal conductivity in the order of 5000 W/mK [8], high electron mobility at room temperature (250,000 $cm^2/V/s$) [9], good mechanical properties such as high elastic modulus (1 TPa) [10, 11] and excellent electrical conductivity (1738 siemens/m) [12].

Attempts have been made to prepare PDMS-graphene nanocomposites and effect on the properties of PDMS nanocomposites. For instance, Choi et al., have fabricated a graphene filled PDMS nanocomposites for a strain sensor and observed an improvement in performance of PDMS due to the presence of graphene in the nanocomposites [13]. Wang et al., reported a graphene-added PDMS nanocomposites, which has high tensile properties and good light transmittance suitable for detecting human movement [14]. A highly transparent (around 70% transmittance), stretchable, and touch responsive sensor was prepared by Ponnamma et al., using graphene and PDMS [15]. Sheshkhar et al., manufactured a graphene embedded PDMS nanocomposites using in-situ polymerization and investigated the effect of different graphene loading (2.5% to 20%) on the thermal and mechanical properties of the nanocomposites [16]. The thermal conductivity, thermal diffusivity, and specific heat of PDMS nanocomposites were around 82%, 505% and 1040% respectively, which was higher than that of pristine PDMS. The mechanical properties of the nanocomposites varied linearly with the increased graphite content percentage filler [16]. Recently, Bosque et al., developed a wearable sensor based on graphene reinforced PDMS nanocomposites. An increase in the electrical conductivity of the PDMS nanocomposites has been observed and values ranged from around 10^{-3} S/m to 1 S/m with 5 and 11 wt% loading of graphene [17].

One of the challenges in producing large scale PDMS nanocomposites using graphene is the price of the graphene. Unfortunately, cost of commercially available graphene is still expensive. Price of a research-grade graphene powder range from 300-800$/kg. So far very high filler loading of graphene has been reported that led to poor mechanical properties of the composite and flexibility of the composite are also being compromised. Therefore, using a very low amount of graphene loading can resolve this problem. More research needs to be carried out to explore the effect of low loading on the electrical and mechanical properties of the PDMS-graphene nanocomposites.

In this work, a commercial, low-cost (20$/kg) , a very low amount (%) of graphene has been used to fabricate PDMS-graphene [18]. The objective of this project was to prepare a PDMS-graphene composites using solvent casting technique and investigate the effect of various loadings of low-cost graphene on the properties of the PDMS nanocomposites. The structural, thermal, and electrical properties of the PDMS-graphene composites have been evaluated for the sensing applications. Dispersion of graphene in PDMS was evaluated using optical microscopy (OM). Thermal properties of the PDMS and graphene filled-PDMS nanocomposites was investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Sensing properties of the prepared nanocomposites were studied using Keithley instruments. We expect that this low-cost graphene filled PMDS nanocomposites would pave a path for potential application in flexible sensors.

2 MATERIALS AND METHODS

PDMS (GELEST® GEL D200) used as a polymer matrix in this research work was purchased from Gelest, Inc., USA. Graphene (Black ™, 3X) employed as a reinforcing material was kindly provided by NanoXplore Inc., Montreal, Canada. PDMS comes as a colorless liquid and it is manufactured from two components: part (A), the base monomer and part (B), the curing agent. The monomer and curing agent were used in a ratio of 10:1 wt%. The base polymer and curing agent react via a platinum catalyzed hydrosilylation. Molecular structure of the PDMS and graphene sheet is depicted in the Figure 1. Chloroform used as dispersing media for graphene was purchased from Sigma Aldrich.

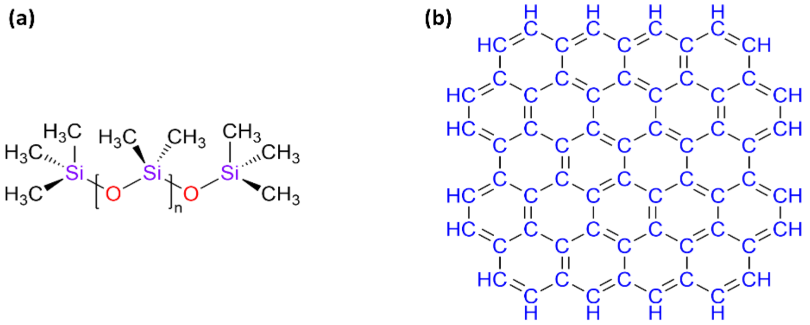

Figure 1. Schematic representation of molecular structure of (a) PDMS and (b) Graphene sheets

The nanocomposites of graphene filled PDMS were prepared by solvent casting. First graphene was dispersed in chloroform under bath sonication for 90 minutes and then this suspension was mixed with PDMS. The PDMS-Graphene mixture was further mixed using mechanical mixer at 800 rpm for 30 minutes. After that, the curing agent was added to this PDMS-Graphene suspension. Samples were cured at 130 °C for 30 minutes. The prepared nanocomposites were named according to the graphene concentration used in PDMS. Schematic of the sample preparation and the coding of samples are presented in Figure 2 and Table 1.

Table 1. Sample codes based on composition of Graphene-PDMS nanocomposites

No.	Code of material	PDMS (wt%)	Graphene (wt%)
1	Neat PDMS	100	0
2	PDMS-0.10GP	90.9	0.1
3	PDMS-0.30GP	90.7	0.3
4	PDMS-1GP	99.0	1.0
5	PDMS-3GP	97.0	3.0

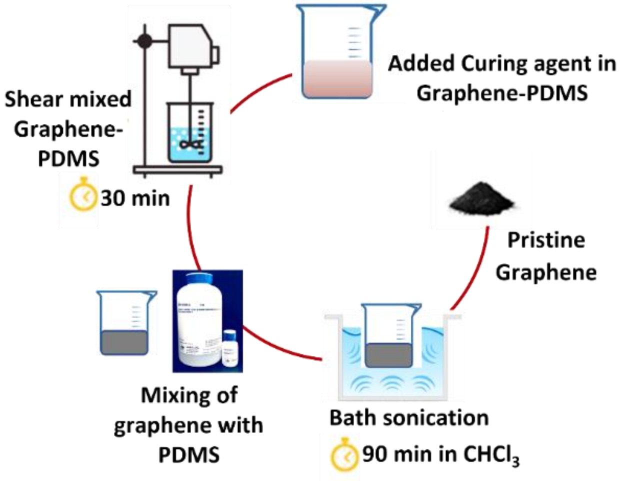

Figure 2. Schematic representation of preparation of Graphene-PDMS nanocomposites.

Dispersion plays a crucial role in preparation of nanocomposites; therefore, the dispersion of graphene in PDMS was confirmed by optical microscopy (OM) (Nikon LV100). The effect of graphene on thermal properties of the nanocomposites was characterized using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). DSC was performed to understand the cure kinetics of PDMS in presence of graphene. DSC measurements were performed on (DSCQ100, TA Instrument) under N_2 from -50 to 250°C at ramp of 10°C/min and TGA was done on TGA-Q500 (TA instruments) under N_2 from 30 to 900°C at ramp of 10°C/min. Furthermore, the electrical properties of the nanocomposites were characterized by Keithley (Model 8009) instrument. The specimens were placed in a resistivity test fixture as per ASTM D275. Current response of the materials was measured using a high resistance electrometer (Model 6517A, Keithley Instrument) by applying a DC voltage.

3 RESULTS AND DISCUSSIONS

Nanomaterials tend to agglomerate due to its large surface area. Therefore, in this work, graphene was well dispersed into the PDMS matrix using chloroform as a dispersing media. Figure 3 (a) shows the dispersion quality of 0.3 wt% graphene into the PDMS matrix. Brighter regions represent the matrix part, and dark or black part shows the graphene. Thermal stability of the materials is very important. Hence, thermal stability of the neat PDMS and PDMS-graphene nanocomposites with different graphene loadings (0.1 wt% to 3 wt%) were measured and TGA curves are shown in the Figure 3 (b) and results are tabulated in Table 2. It can be seen from the TGA curves that thermal stability of the nanocomposites were slightly improved in the presence of graphene except with 3 wt%, where the nanocomposites were slightly less stable at lower temperature. However, around 500 °C, the composites were stable. At T_d (5%) (temperature at 5% weight loss), thermal stability of the nanocomposites was slightly decreased with respect to neat PDMS. All the PDMS-GP nanocomposites were very much stable at T30%. It is noticeable that at T_d (30%) (temperature at 30% weight loss), almost in all nanocomposites, curve shifted to higher temperature and around 30 °C temperature increase observed as compared to the neat PDMS. Furthermore, the residual mass of the nanocomposites was relatively higher which again confirms the role of graphene on thermal stability of the nanocomposites.

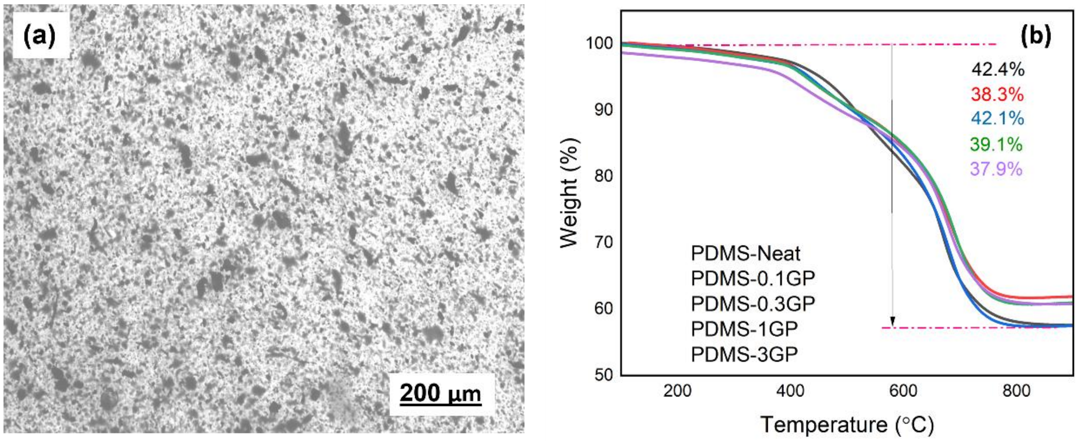

Figure 3. (a) Optical microscopy image of PDMS-0.3GP nanocomposites showing dispersion of 0.3 wt% graphene in PDMS (at 200 µm) and (b) TGA curves of neat PDMS and PDMS-graphene nanocomposites, vertical line indicates improvement in the thermal stability of the PDMS nanocomposites. The values in percentage shows weight loss of the materials (difference in upper and lower plateau represents weight loss of the materials in percentage)

Table 2. Thermal properties of PDMS and PDSM-Graphene nanocomposites

No.	Code of material	T_d (5%) *	T_d (30%) **
1	Neat PDMS	452.4	673.4
2	PDMS-0.10GP	430.1	698.1
3	PDMS-0.30GP	438.7	678.4
4	PDMS-1GP	426.9	696.8
5	PDMS-3GP	397.7	695.6

T_d (5%) *: is the temperature when weight loss of the sample reaches its 5%.
T_d (30%) **: is the temperature when weight loss of the sample reaches its 30%.

DSC was carried out to further analyze the effect of graphene on cure kinetics of the PDMS nanocomposites. First the neat PDMS was analyzed with three different heating rates (at 10 °C, 15 °C and 20 °C) and compared with PDMS-0.1GP. DSC curves of neat PDMS and PDMS-0.1GP are depicted in Figure 4 and data are summarized in Table 3. The typical exothermic peaks of the PDMS curing reactions occur in the range from 90 to 110 °C[19]. On increasing the rate of heating of PDMS, a shift of exothermic peak to higher temperature was observed and heat of reaction was also increased. It is interesting to note that in PDMS-0.1GP nanocomposites, the onset temperature, peak and end temperature values were increased as compared to the neat PDMS (almost 5-7 °C). Contrary, in PDMS-0.1 GP nanocomposites, a decrease in the heating of reaction values is observed. This behaviour is typically observed when filler inhibits the cross-linking process [19].

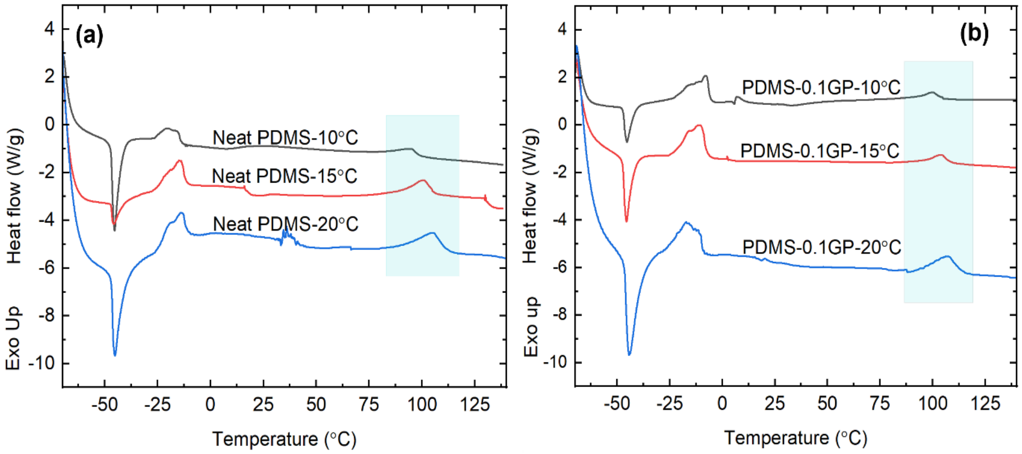

Figure 4. (a) DSC curves of neat PDMS with different heating rates and (b) DSC curves of PDMS-0.1GP with 10°C, 15°C and 20°C heating rates

Table 3. Thermal properties of PDMS and PDSM-0.1GP nanocomposites at three different heating rates

No.	Codes of materials	Onset Temp (°C)	Peak Temp (°C)	End Temp (°C)	Heat of reaction (J)
1	Neat PDMS-10°C	84.1	94.4	95.3	1.9
2	Neat PDMS-15°C	90.4	100.8	101.0	2.2
3	Neat PDMS-20°C	92.0	105.0	105.5	2.3
4	PDMS-0.10GP-10°C	91.7	100.0	100.1	2.5
5	PDMS-0.10GP-15°C	95.8	104.0	104.4	2.1
6	PDMS-0.10GP-20°C	95.9	106.6	107.7	1.9

As 10 °C/min heating rate is a typical heating rate used for the PDMS. Therefore, further DSC analysis of PDMS nanocomposites was carried out at same heating rate. Effect of graphene on exothermic peak of PDMS nanocomposites were analyzed and DSC curves of the PDMS nanocomposites are shown in Figure 5. It can be clearly seen from the Figure 5 that addition of graphene into PDMS matrix shifted the exothermic peak to higher temperature (3–7°C at most) with increase in are under curve. For neat PDMS, exothermic peak appears at 95 °C and in nanocomposites it is around 100-102°C. This shift in the exothermic peak is due to the presence of graphene in the nanocomposites which is affecting the cross-linking of the PDMS matrix.

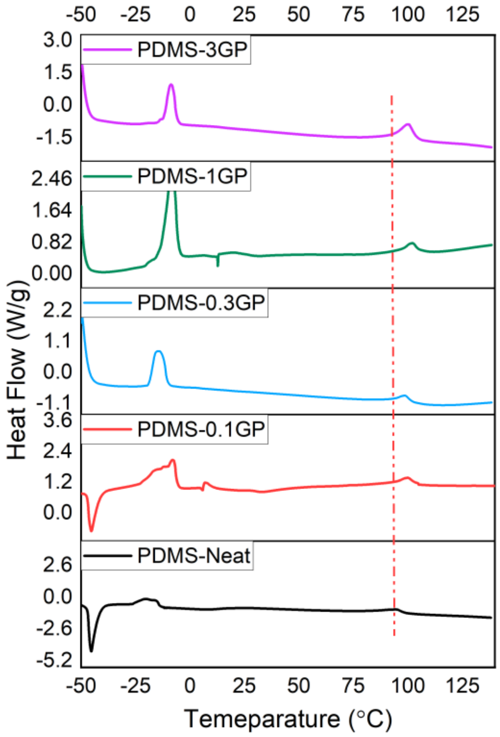

Figure 5. DSC curves of neat PDMS and PDMS nanocomposites at heating rate of 10°C/min, red line (dashed) showing a shift of exothermic peak towards higher temperature in nanocomposites due to the presence of graphene

The electrical properties of the PDMS-GP nanocomposites are highly dependent on the dispersion of graphene into the polymer matrix, aspect ratio of graphene and the interactions between the graphene and polymer matrix [20]. For neat PDMS the electrical conductivity comes around 3×10^{-13} S/m. The effect of different graphene loading on electrical conductivity of PDMS nanocomposites is shown in the Figure 6. It can be seen from the graph that on increasing the graphene content electrical conductivity of the PDMS nanocomposites is increasing. Addition of graphene in PDMS affected the electrical conductivity of the composite and a value of 8×10^{-7} S/m obtained for PDMS-0.3GP. This result evident the potential of low loading of graphene contents and can be used to improve the electrical properties of the PDMS nanocomposites. Prepared PMDS nanocomposites can be potentially used for a sensing application.

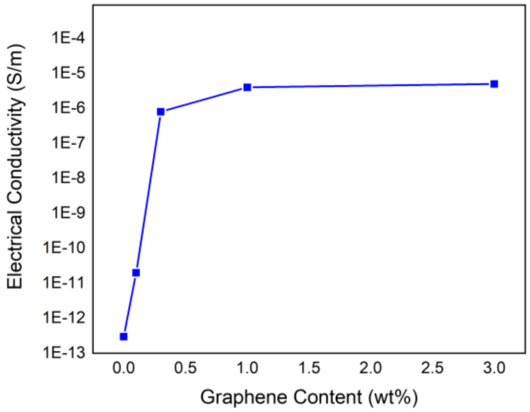

Figure 7. Electrical conductivity values for PDMS-Graphene nanocomposites as a function of graphene loadings

4 CONCLUSIONS

In summary, in this work, a low cost-graphene filled PDMS nanocomposites were prepared using solvent casting methods and effect of graphene on thermal and electrical properties of PDMS was evaluated. As dispersion of nanomaterials plays a crucial role, therefore, dispersion of graphene in PDMS was studied by optical microscopy. It has been observed from the TGA and DSC that thermal stability of the PDMS was slightly increased in the presence of graphene particularly with low amount of graphene (0.3 wt%). Furthermore, the electrical properties of the PDMS-GP nanocomposites: especially with 0.3 wt% of graphene was improved. This improvement in the properties of PDMS-GP nanocomposites can be because of the good dispersion of graphene into the PDMS. Our work provides a cost-effective way of preparing PDMS-graphene nanocomposites which have potential to be used for sensing applications.

5 ACKNOWLEDGMENTS

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