Thermal conductivity and stability of nano size carbon black filled PDMS: Fuel cell perspective

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Abstract:

Carbon black filled Polydimethylsiloxane (PDMS) was considered as a prospective bipolar plate material candidate for a Fuel Cell. In this perspective, thermal conductivity and stability of the composites were investigated. Samples with filler weight fractions from 10% to 25% were prepared. The Thermal Gravimetric Analysis (TGA) study under oxygen atmosphere has shown good thermal stability of the composite up to 300 ℃. Thermal conductivity as a function of temperature and filler fraction was measured. Results have shown excellent improvement in the PDMS thermal conductivity with carbon black fillers (an order of magnitude, as compared to the pure PDMS). We found that PDMS-CB composites with lesser CB loading (10 wt %) achieve thermal conductivity on par with the reported values in literature of epoxy resin-CB composites (with 70wt% loading).

Keywords: Polydimethylsiloxane (PDMS); Polymer nanocomposite, Carbon black; Thermal conductivity; Thermal stability; Fuel cell

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1 Introduction

Graphite and metal based materials are routinely used as structural materials for fuel cell fabrication. Utilization of polymer based materials shall cut down weight and shall be more economically profitable when mass produced. If one considers polymer composites as an alternative replacement for Graphite and metallic materials, one has to improve the electrical and thermal conductivity properties of these polymer composites. Here we consider PDMS composites as possible structural material for fuel cell fabrication. Already PDMS is widely used in the microfabrication technology particularly in microfluidics. One can borrow soft lithography and other simple techniques developed for PDMS based microfabrication technology to generate the desired flow fields etc on PDMS composite based bipolar plates for a fuel cell. PDMS based conducting polymers have also been studied intensively [1-5]. The fabrication of the mentioned PDMS conducting polymer are mostly done by introduce a conductive fill such as Carbon Black (CB), metal powders or Carbon Nano Tubes(CNT) into PDMS polymer matrix.

However, in a fuel cell bipolar plate as well as structural material perspective, the thermal properties of PDMS composite are as much important as its electrical property simply because large amount of heat is generated during the operation of the fuel cell. Hence the PDMS composite as the structural bipolar plate material has to be able to dissipate the heat efficiently and be thermally stable. It was found that there is a lack of literature available on the thermal stability and thermal conductivity of the Carbon Black filled PDMS composite. Hence in this paper, we report on the detailed thermal stability and thermal conductivity measurements of the CB-PDMS composites in a fuel cell bipolar plate perspective. PDMS composite samples with specific wt %(10-25%) of Carbon black loadings were prepared. This range was chosen to study because these composites have shown good electrical conductivities in this particular range [1]. We

then compare these thermal properties with those of other polymer composites in the literature

2 Experimental

2.1 Materials

The conductive fillers are nano sized carbon black (20-40nm, Carbon black, Vulcan XC72) obtained from Cabot Corporation. The polymer matrix is PDMS (Sylgard 184 Silicone Elastomer) from Dow Corning.

2.2 Sample preparation

The pellet shape carbon black was first dispersed in methanol then ultrasonicated for 30 min to get nano size carbon black dispersion and then mixed with the PDMS, a in house designed mechanical mixer was used to mix the blends for 24 hours to obtain homogenous dispersion, then the crosslinker was add. Methanol totally evaporated during the ultrasonication and vigorous mixing. A vacuum degassicator was used to remove the bubbles caused by the mixing process. The blend was casted in the mold and oven baked for 8 hours at 60 ℃ to cure properly. A disk shape mold with diameter of 25mm and thickness of 1mm was designed for the specific requirement of the thermal conductivity measurement.

2.3 Characterization

Thermal Gravimetric Analysis (TGA) for thermal stability/degradation was performed using a TA Instrument TGA Q500 under air atmosphere. The heating rate was 10 ℃/min and the flow rate for oxygen and nitrogen are 5ml/min and 30 ml/min respectively. All experiments were conducted in the temperature range 30 ℃ to 800 ℃.

A widely used Cut-Bar technique (ASTM E 1225-87 methodology) was used for thermal conductivity measurement for samples with varied CB loading, as well as thermal conductivity dependence on temperature with the temperature range of 50 ℃ to 200 ℃.

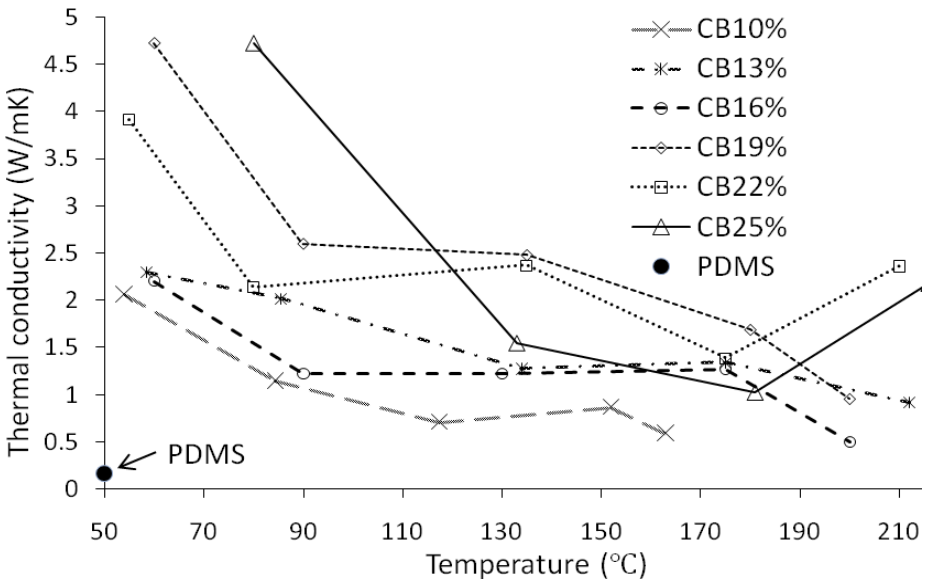
3 Results and Discussion

3.1 Thermal conductivity

Thermal conductivity (*k)* of the test specimens is measured using a cut-bar test facility under steady state conditions. The system is assumed to have attained steady state conditions when all the temperature sensors (thermocouples) indicate a constant value with a variation of less than $\pm 0.5^0$C. Variation of thermal conductivity as a function of mean bulk temperature is determined. Complete details of experimental procedure are described elsewhere [6]. Fig.1 shows the variation of thermal conductivity k as a function temperature for PDMS composites filled with carbon black with different filler fraction ranging from 10-25 wt %. The measurements of the thermal conductivity are made in the temperature range of 50-200^{0}C. The general trends have shown that the thermal conductivity decreases with temperature for all the specimens considered in the present investigation up to about 90^{0}C. However, thermal conductivity remained constant with minor variations up to the temperature of 180^{0}C. For the specimens with 22 wt % and 25wt % carbon black, thermal conductivity appears to increase beyond 180^{0}C and up to

200^0C. The experiments were terminated at 200^0C due to possible degradation of the samples. When compared to pure PDMS, there is a remarkable enhancement (an order of magnitude) in thermal conductivity of PDMS loaded with carbon black nano-particles in varying proportions. For example specimens with 10 wt % carbon black, the PDMS acquired thermal conductivity of 2.07 $Wm^{-1}K^{-1}$ as against 0.17 $Wm^{-1}K^{-1}$ for PDMS without carbon black (see ref. [7]). The experimental results also showed that the thermal conductivity of the samples increased in general with the percentage (10-25%) of carbon black present in the composite. This is attributed to the increase in conductive pathway and network density with increased number of filler particles [8].

Figure 1 Thermal conductivity VS Temperature for carbon black filled PDMS composites with different filler fractions (10-25wt %). The solid dot represents pure PDMS thermal conductivity value, taken from ref.{{68 Yamamoto, T. 2002}}



The thermal conductivity data of the present experimental investigation is more promising when compared to the investigations carried out earlier by other researchers. For example, the thermal conductivity of epoxy resin with 70wt% carbon black nano filler is 1.8 $Wm^{-1}K^{-1}$ [9]. Where as in our present experimental investigation, we found that a thermal conductivity value of 2.07 $Wm^{-1}K^{-1}$ can be achieved with a 10 wt % of carbon black in PDMS. This means, one needs a less wt% (almost seven times) carbon black in the case of PDMS as compared to epoxy resin to achieve same or a little higher values of thermal conductivity. Carbon black as a nano filler in PDMS is more effective in improving thermal conductivity than in epoxy resin.

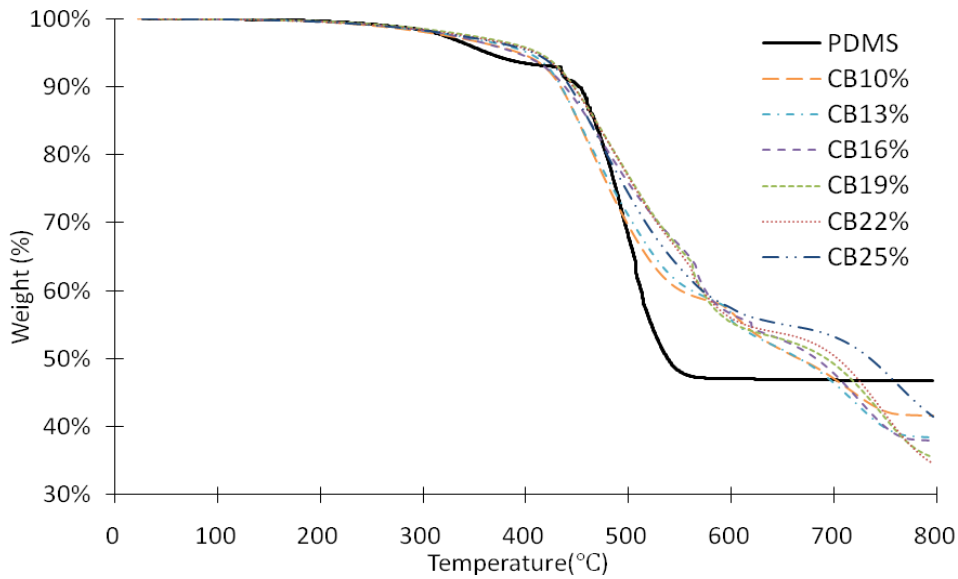
Further, it is to be noted from the data published by Liu et al [10] that both carbon nano tubes and carbon black at equal loading in PDMS equally improves thermal conductivity in a comparable way. Thus there is no significant difference in thermal conductivity values between carbon nano tube and carbon black filled PDMS in their experiments. However, carbon black is much less expensive when compared to the carbon nano tubes. Thus our choice of carbon black as nano filler in PDMS would be a better choice in the context of mass production of the CB-PDMS based fuel cells.

3.2 Thermal stability (TGA)

It is vital that the composite material maintains thermally stability at the high operating temperature of fuel cells. Therefore, the thermal stability/degradation of carbon black filled PDMS composites with various filler fractions were analysed by TGA in oxygen atmosphere. Pure PDMS was also tested for comparison. Results of TGA data are illustrated in Figure 2. Previous work has been done on same composites in nitrogen atmosphere [11]. TGA experiment was carried out in oxygen atmosphere in this work due to the specific application of these composites in the fuel cell perspective with oxidative environment.

Results show that all composites and pure PDMS start to degrade at 300 ℃ with 1.5% weight loss. First apparent weight loss for PDMS occurred between 300 ℃ and 400 ℃ and a rapid weight loss was found around 500 ℃, then 47% of residual PDMS appeared to be stable up to 800 ℃. However, for the samples with carbon filler, the first weight loss peaks were only observed in the range of 450 ℃ to 550 ℃. TGA measurements carried out under nitrogen atmosphere in these samples show similar results in weight loss [11]. Furthermore, second weight loss peaks arose above 700 ℃ in all CB filled PDMS samples.

Figure 2 Thermal conductivity VS Temperature for carbon black filled PDMS composites with different filler fractions (10-25wt %)



Furthermore, Figure 3 shows the weight loss and its derivative for 25wt% filled PDMS composite under oxygen and nitrogen atmosphere. From the figure, one can clearly see two major weight losses for the sample under oxygen, corresponding exothermic peaks can be found on the DTA curve at 475 ℃ and 761 ℃ respectively. The first weight loss

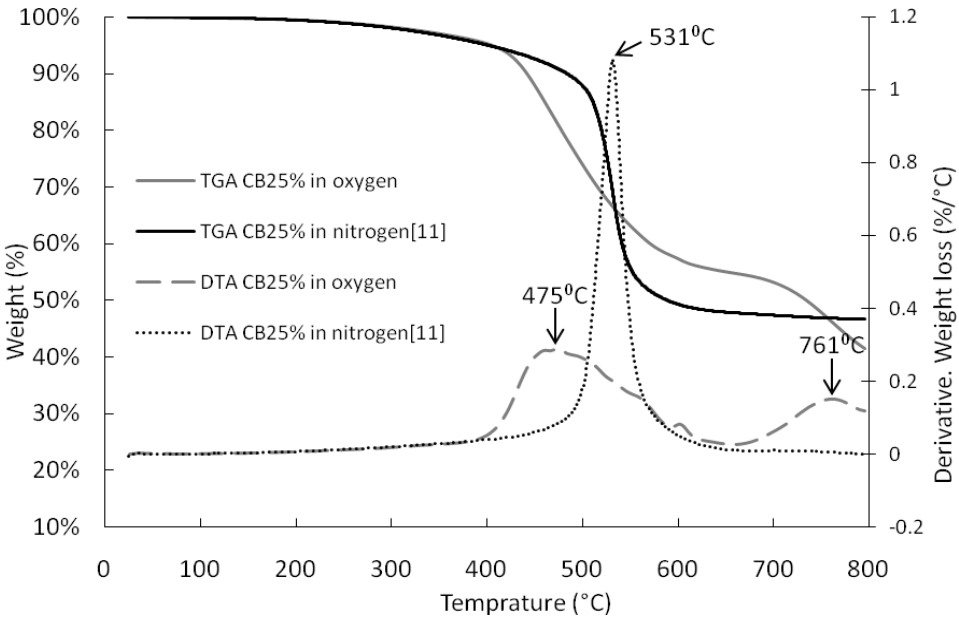
can be ascribed to be the degradation of PDMS polymer matrix with the catalysis of oxygen [12; 13]. According to Chhina et al [14], carbon black (Vulcan XC72) is thermal stable and does not oxidize until 700 ℃ in air, and the only weight loss peak was reported at 750 ℃. We can assume the second weight loss peak is due to the decomposition and oxidization of the carbon black filler. This also agrees with the TGA studies of carbon black (Vulcan XC72) in the literature [15-17].

Table 1 Temperatures (℃) at 50% Weight Loss of Samples

Sample	PDMS	CB10%	CB13%	CB16%	CB19%	CB22%	CB25%
Temperature(℃)	537.77	665.65	666.28	681.95	692.38	703.02	734.53

Characteristic temperatures at 50% weight loss of the samples are listed in Table 1, it is noticed that these temperatures are ascending with increasing filler fractions. This also indicated that the incorporation of carbon black filler in the PDMS polymer matrix has improved the thermal stability of the polymer composite [18-20].

Figure 3 Weight loss and its derivative as a function of temperature for 25wt% carbon black filled PDMS composite under oxygen and nitrogen atmosphere.



4 Conclusion

Thermal conductivity measurements were carried out on PDMS-CB composites as functions of temperature and as well as filler fraction. There is an order of magnitude of

increase of thermal conductivity of 10 wt% CB loaded PDMS-CB composite as compared to that of pure PDMS. Most importantly, as compared to other composites such as epoxy resin – CB, lesser CB loading for PDMS (only 10wt% for PDMS as compared to 70wt% for epoxy resin) is needed to achieve the same thermal conductivity of epoxy resin-CB composite. We found a general trend, namely, a plateau of thermal conductivities for all samples (different filler fractions) in the temperature range of 90^{o}C to 180^{o}C. This is a good region for operating the fuel cell, as the thermal conductivity is stable. Further we found that the thermal conductivity increases in general as the filling fraction is increased. However there are some irregularities which we attribute to sample homogeneity. The composites Blends have also shown synergistic improvement in thermal stability. The presence of carbon black filler in the PDMS polymer has resulted in retardment of the thermal decomposition of the composite. The mechanism of the retarded thermal degradation is not clear at this point and still need to be explored. Study of these composites with utilization in the fuel cell bipolar plate is still at the research and development stage. Further challenges remain to improve the electrical and mechanical properties.

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References

1 Niu, X., Peng, S., Liu, L., Wen, W. and Sheng, P. (2007) 'Characterizing and Patterning of PDMS-Based Conducting Composites*', *Advanced Materials*, Vol.19, pp. 2682-2686.

2 Chuang, H.S., Wereley, S., Cora, Ö.N., Usta, Y., Koç, M., Rana, S., Ortiz, P.M., Harris, A.J., Burdess, J.S. and McNeil, C.J. (2009) 'Design, fabrication and characterization of a conducting PDMS for microheaters and temperature sensors', *Journal of Micromechanics and Microengineering*, Vol.19, No.4, pp. 045010.

3 Rwei, S.P., Ku, F.H. and Cheng, K.C. (2002) 'Dispersion of carbon black in a continuous phase: Electrical, rheological, and morphological studies', *Colloid & Polymer Science*, Vol.280, No.12, pp. 1110-1115.

4 Cong, H. and Pan, T. (2008) 'Photopatternable conductive PDMS materials for microfabrication', *Advanced Functional Materials*, Vol.18, No.13, pp. 1912-1921.

5 Gong, X. and Wen, W. (2009) 'Polydimethylsiloxane-based conducting composites and their applications in microfluidic chip fabrication', *Biomicrofluidics*, Vol.3, pp. 012007.

6 Rao, V.V., Bapurao, K., Nagaraju, J. and Murthy, M.V. (2004) 'Instrumentation to measure thermal contact resistance', *Measurement Science and Technology*, Vol.15, No.1, pp. 275-278.

7 Yamamoto, T., Fujii, T. and Nojima, T. (2002) 'PDMS–glass hybrid microreactor array with embedded temperature control device. Application to cell-free protein synthesis', *Lab on a Chip*, Vol.2, No.4, pp. 197-202.

8 Burden, A.P., Guo, W. and Hutchison, J.L. (1998) 'Exploiting voltage contrast scanning electron microscopy to investigate conductive polymer composite resettable fuse devices', *Polymer,* Vol.39, No.18, pp. 4211-4217.

9 El-Tantawy, F., Kamada, K. and Ohnabe, H. (2002) 'In situ network structure, electrical and thermal properties of conductive epoxy resin–carbon black composites for electrical heater applications', *Materials Letters,* Vol.56, No.1-2, pp. 112-126.

10 Liu, C.H., Huang, H., Wu, Y. and Fan, S.S. (2004) 'Thermal conductivity improvement of silicone elastomer with carbon nanotube loading', *Applied Physics Letters,* Vol.84, No.21, pp. 4248-4250.

11 Chen, H., Botef, I., Guduri, B. and Srinivasu, V.V. (2010) 'Thermal and bonding properties of nano size carbon black filled PDMS', International Conference on Advanced Nanomaterials and Nanotechnology', Guwahati. India.

12 Camino, G., Lomakin, S.M. and Lazzari, M. (2001) 'Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects', *Polymer,* Vol.42, No.6, pp. 2395-2402.

13 Tiwari, A., Nema, A.K., Das, C.K. and Nema, S.K. (2004) 'Thermal analysis of polysiloxanes, aromatic polyimide and their blends', *Thermochimica Acta,* Vol.417, No.1, pp. 133-142.

14 Chhina, H., Campbell, S. and Kesler, O. (2006) 'An oxidation-resistant indium tin oxide catalyst support for proton exchange membrane fuel cells', *Journal of Power Sources,* Vol.161, No.2, pp. 893-900.

15 Baturina, O.A., Aubuchon, S.R. and Wynne, K.J. (2006) 'Thermal stability in air of Pt/C catalysts and PEM fuel cell catalyst layers', *Chemistry of Materials,* Vol.18, No.6, pp. 1498-1504.

16 Su, F., Zeng, J., Bao, X., Yu, Y., Lee, J.Y. and Zhao, X.S. (2005) 'Preparation and characterization of highly ordered graphitic mesoporous carbon as a Pt catalyst support for direct methanol fuel cells', *Chem.Mater,* Vol.17, No.15, pp. 3960-3967.

17 Su, F., Zhao, X., Wang, Y., Zeng, J., Zhou, Z. and Lee, J.Y. (2005) 'Synthesis of graphitic ordered macroporous carbon with a three-dimensional interconnected pore structure for electrochemical applications', *J.Phys.Chem.B,* Vol.109, No.43, pp. 20200-20206.

18 Jakab, E. and Omastová, M. (2005) 'Thermal decomposition of polyolefin/carbon black composites', *Journal of Analytical and Applied Pyrolysis,* Vol.74, No.1-2, pp. 204-214.

19 Omastova, M., Podhradska, S., Prokes, J., Janigova, I. and Stejskal, J. (2003) 'Thermal ageing of conducting polymeric composites', *Polymer Degradation and Stability,* Vol.82, No.2, pp. 251-256.

20 Zhang, J., Feng, S. and Ma, Q. (2003) 'Kinetics of the thermal degradation and thermal stability of conductive silicone rubber filled with conductive carbon black', *Journal of Applied Polymer Science,* Vol.89, No.6, pp. 1548-1554.