Effect of β-Silicon Carbide Size and Shape on the Properties and Microstructure of PMMA Matrix Nanocomposites

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ABSTRACT

The objective of this research is to fabricate and characterize PMMA matrix β-SiC nanocomposites with three types of SiC: nano-sized, micron-sized, and whiskers. The composites were fabricated via mechanical blending and compression molding at 170°C for 15 minutes at 10kN. The samples were then polished and imaged using an optical microscope. Next, electrodes were placed on via silver sputtering. Finally, the nanocomposites were tested using impedance spectroscopy. The samples were scanned from 10 MHz – 100 Hz using an AC voltage of 500 mV. The nanoparticle SiC reached percolation at 2 phr, while the micron-sized SiC and SiC_w reached percolation at 7.5 and 10 phr respectively. This trend corresponds with a more defined microstructure in the nanoparticle composite than the other two. These results suggest that the nanoparticles are able to segregate to the faces of the PMMA more easily than the larger particles.

Keywords: β-SiC, whisker, nanocomposite, PMMA, percolation

1 INTRODUCTION

Silicon carbide is often used as a filler in polymer and ceramic matrix composites to improve their electrical and mechanical properties. Silicon carbide whiskers (SiC_w) dispersed in an alumina (Al_2O_3) matrix have been used to make grills and flat stones for microwave heating[1]. While there has been research into such composites[2-4], there is a need for exploration of how to make a coating that could serve the same purpose and could be applied to other materials while costing less to make. The properties of ultra-pure beta (cubic) SiC single crystals, which Advanced Composite Materials, LLC(ACM) has developed[5] have excellent microwave heating properties and are the driving force for this research.

There has been some initial work done into the creation of electrically conductive bulk glass matrix composites with the beta SiC whiskers[6], following some successful work done with antimony doped tin oxide (ATO)[7] and tin doped indium oxide (ITO)[8]. However, working with ceramic glasses is challenging and expensive. Since poly(methylmethacrylate) (PMMA) has been used to make similar nanocomposites with ATO and ITO[9,10], it was decided to first evaluate the effect of changing the size and shape of the β–SiC on the resultant properties and microstructure using PMMA as the matrix in order to develop a better understanding of the interplay between the size of the matrix and the fillers. Earlier work focused on graphitic nanomaterials which do not change as much in size as the beta-SiC materials do[11,12].

In this paper, the percolation threshold of PMMA/ β-SiC as nanoparticles, micron-sized particles, and whiskers will be determined and the microstructures analyzed.

2 METHODOLOGY

This work will entail creation of PMMA nanocomposites that contain a network of β-SiC nano-particulates: nano-sized, micron-sized, and whiskers. The conductivity and microstructure of the samples will be analyzed with the change concentration of the SiC.

1.1 Fabrication and Characterization

The PMMA was polydisperse and obtained from Buehler Ltd. (Transoptic powder). The particle size was in the range of 10−100 μm. The nanoparticle, micron-sized, and whisker β-SiC were from US Research Nanomaterials, Inc., Alfa Aesar, and Advanced Composite Materials, respectively. The nano-SiC particles were imaged by TEM (Hitachi HT 7700 at 120 kV), and the micron- and whisker SiC were imaged in a Celestron PentaView LCD Digital Microscope. The particle size ranges of the nano- and micron-sized β-SiC are about 10-70 nm and 1-2 μm, respectively. The whisker SiC has a length range of about 10 - 50 μm and a diameter of about 1 μm. More precise imaging will be done at a later date.

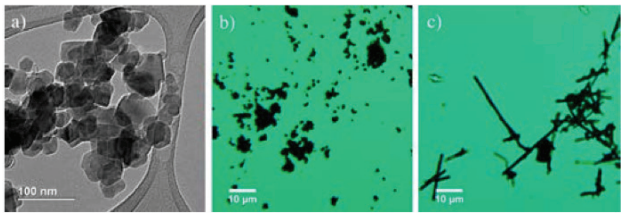

Figure 1: a) nano-sized b) micron-sized and c) whisker β-SiC

The SiC and PMMA were mechanically blended for 10-15 minutes in a blender at room temperature until fully mixed. This method uniformly distributes the nanoparticles throughout the PMMA. The blender will produce heat over time; therefore it was run in approximately 30 second intervals. If this care was not taken, the heat could partially liquefy the PMMA and decrease the connectivity of the

network. The composition of the SiC/PMMA composites was varied between 0.1 and12 phr, as shown in Table 1.

Table 1: Composition of SiC:PMMA nanocomposites

Powder Composition (SiC phr)	Powder Composition (SiC Vol%)
0.10	3.67×10^{-4}
0.50	1.83×10^{-3}
1.00	3.64×10^{-3}
2.00	7.21×10^{-3}
3.00	1.07×10^{-2}
7.50	2.56×10^{-2}
10.00	3.34×10^{-2}
12.00	3.94×10^{-2}
15.00	4.79×10^{-2}

The mixed powders were then compression molded in a Struers mounting press at 170 °C for 15 min. The pressure applied during molding was 10kN. The dimensions of the nanocomposites are 31.7 mm in diameter and about 2 mm in thickness.

Prior to electrical measurements, the samples were polished using 125, 70, 45, and 15 µm diamond disks and 3µm diamond paste. The samples were then imaged using a Celestron PentaView LCD Digital Microscope. Once imaged, a Denton Vacuum Desk II turbo sputter coater (Denton Vacuum, Moorestown, NJ) was used to coat the samples with Ag (nominal purity of 99.9%) as the contact electrodes.

A Solartron 1260 impedance analyzer was used together with a Solartron 1296 Dielectric Interface (Solartron Analytical, Farnborough, Hampshire, U.K.), for the electrical characterization of the nanocomposites. The samples were scanned from 10 MHz – 100 Hz using an AC voltage of 500 mV.

3 RESULTS AND DISCUSSION

Images of the microstructures of the SiC samples are shown in Figure 3. All of the 0.1 phr samples were partially transparent allowing for observation of the microstructures just below the surface. The nano-sized SiC shows a more defined microstructure than either the micron-sized or whisker SiC at both 0.1 phr and 7.5 phr. The hexagonal pattern with SiC along the faces and edges of the PMMA grains is maintained in all samples, however, as seen in Figure 3b, the micron-sized SiC did not segregate to the faces as much as the others. The whisker SiC in Figure 3c and f shows that the whiskers did not fully remain in the faces because of their length causing the microstructure to look less clean cut than the others.

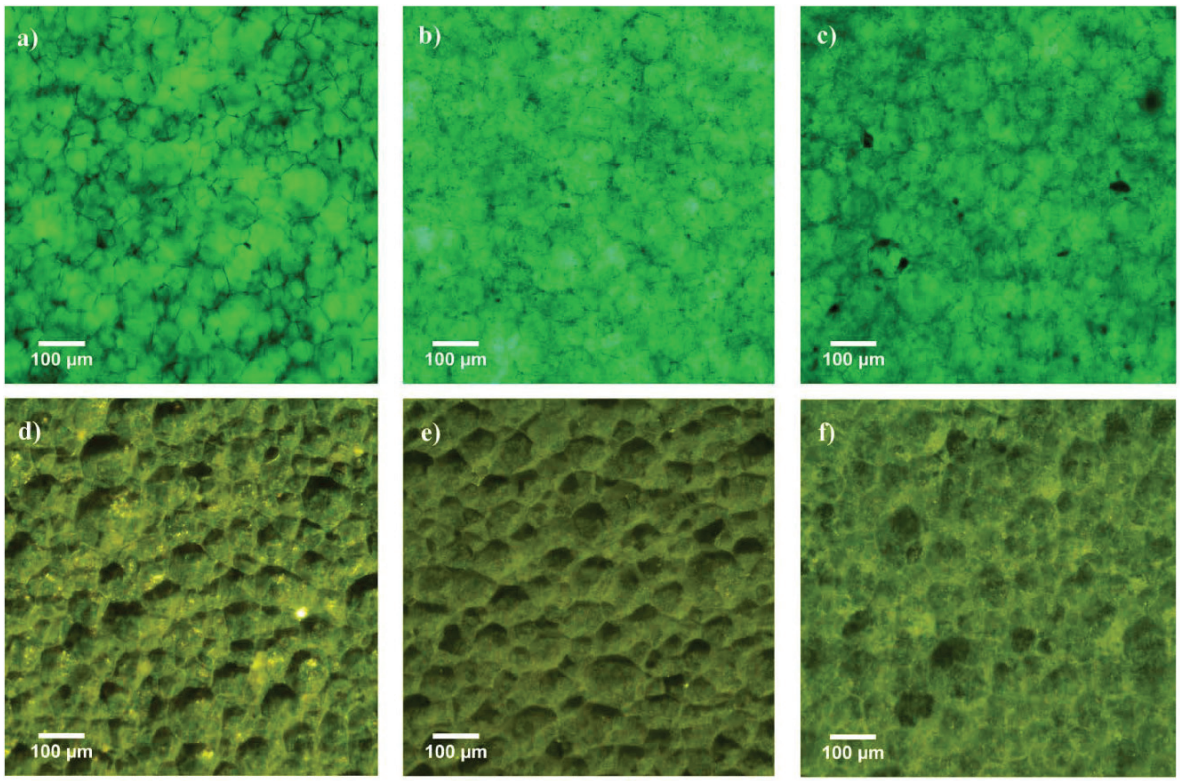

Figure 2: a) nano-sized, b) micron-sized, and c) whisker SiC PMMA nanocomposites containing 0.1 phr; d) nano-sized, e) micron-sized, and f) whisker containing 7.5 phr SiC.

The impedance measurements displayed in Figures 4-6 show the magnitude and the phase angle versus log frequency. Percolation is reached at 7.5, 2, and 10 phr for the micron-sized, nano-sized, and whisker SiC samples respectively. This is determined by looking at the phase angle graphs to see where a large change in phase angle occurs as a function of concentration. This result corresponds well with the observed microstructures. The nano-sized SiC had the most formed microstructure at 0.1 phr, and therefore would be expected to reach percolation at a lower phr. The nanoparticles would also be able to move within the composite to form the conducting paths more easily than larger particles. This is also exemplified by the whiskers which would have a more difficult time conforming to the faces of the PMMA and, as a consequence, formed a percolation last.It should be added that for the whisker composites made with borosilicate glass[3], a similar percolation threshold was also achieved. This is because those samples were made with glass particles of similar size to polymer particles used here.

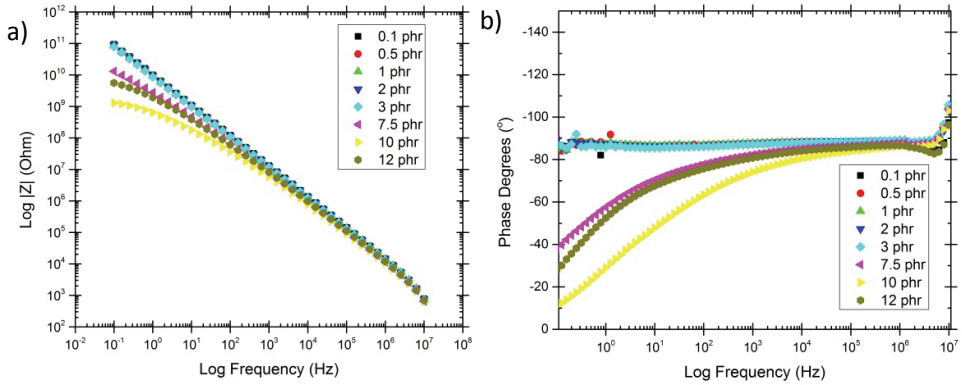

Figure 2: a) Log Impedance magnitude versus log frequency and b) phase angle versus log frequency for micron-sized SiC

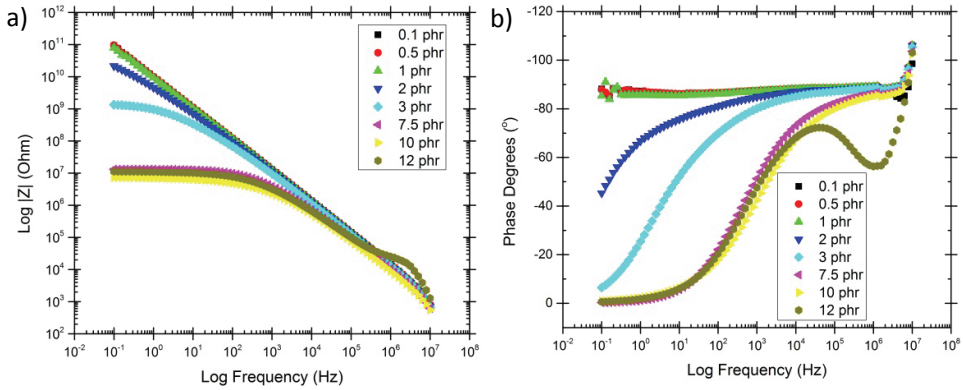

Figure 3: a) Log Impedance magnitude versus log frequency and b) phase angle versus log frequency for nano-sized SiC

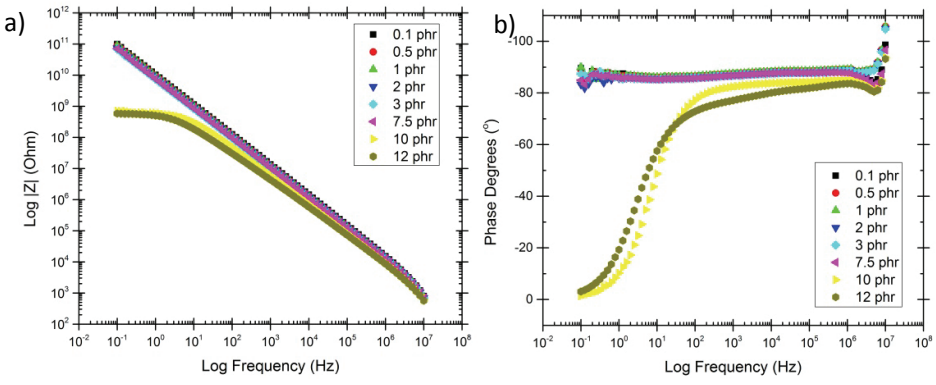

Figure 4: a) Log Impedance magnitude versus log frequency and b) phase angle versus log frequency for whisker SiC

The resistivity of all three sets of PMMA and SiC nanocomposites is shown in Figure 7. This figure shows that the nano-sized SiC containing composites are more conductive than the micron-sized or whisker SiC composites at essentially all concentrations evaluated and that the percolation thresholds agree with those estimated above. This is in part because the resistivity curves are obtained by taking the lowest frequency impedance to calculate the resistivity using the specimen dimensions.

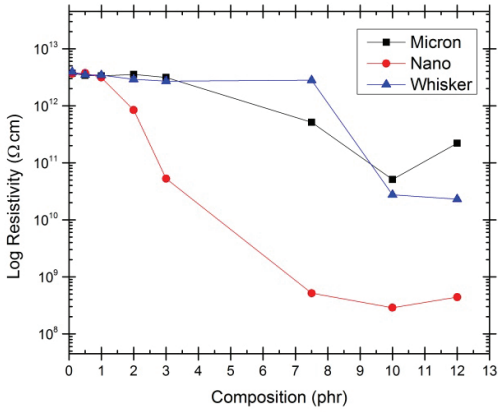

Figure 5: Resistivity of PMMA/SiC nanocomposites as a function of SiC content.

4 CONCLUSIONS

Nanoparticle, micron-sized, and whisker β-SiC/ PMMA matrix nanocomposites were fabricated and characterized. Mechanical blending and molding were used in the creation of the samples. The samples were then polished, imaged using an optical microscope, and silver sputtered. Impedance spectroscopy with a scan from 10 MHz– 100 Hz using an AC voltage of 500 mV was used to characterize the samples. The nanoparticles had both a more defined microstructure and the lowest percolation at 2 phr. The SiC_w had the least defined microstructure and the highest percolation at 10 phr, and the micron-sized SiC reached percolation at 7.5phr. Therefore, the results suggest that the smaller particles are able to segregate to the faces of the PMMA more easily than the larger particles during compression molding.

5 Acknowledgements

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