FUNCTIONAL COMPOSITES WITH CORE-SHELL FILLER FOR THERMAL MANAGEMENT OF ELECTRICAL DEVICES

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Abstract
A novel core-shell materials have been manufactured in order to enhance the thermal conductivity of the epoxy based composites. Polymer derived ceramics technique has been used to produce fillers which core made of standard material was covered with high thermal conductivity shell. The synthesized fillers were characterized by infra-red spectroscopy, X-ray diffraction, scanning electron microscopy coupled with energy dispersive analysis. The measurements confirmed formation of the core-shell structure. Composites samples based on epoxy resin filled with the advanced core-shell fillers have been investigated in order to determine the effective thermal conductivity. Obtained composite samples exhibited improvement in thermal conductivity.

1. Introduction

Filled epoxy composites are well known and extensively used as insulating materials in power product applications. However heat management in such devices is a crucial issue for their proper operation. The effective heat dissipation needs to be improved in such devices to prevent from malfunction [1,2]. The addition of filler particles into epoxy resin can result in a significant improvement in the thermal, electrical or mechanical properties of the obtained composite [3].

Generally thermal properties of the composite are related to size and content of the filler grains and thermal conductivity of matrix and used filler [3]. However very important are characteristics of the filler-epoxy matrix interface due to strong phonon scattering processes and occurring interface resistance [4,5]. To increase thermal conductivity in epoxy composite materials the conductive paths must be maximized and thermal contact resistance decreased. The promising approach to obtain composite with higher effective thermal conductivity is the modification of filler particles [6]. Polymer derived ceramics technique which is frequently used to obtain core-shell structure [7,8,9], has been applied to produce filler which core is composed of silica flour, covered by boron nitride and silicon nitride shell.

The aim of the work is to check a possibility of increasing the thermal conductivity of the filled epoxy resin systems by using core-shell filler structure, with the core made of standard

material as SiO_2, and the coating made of high-thermal-conductivity (HTC) material, namely boron nitride (BN) or silicon nitride (Si_3N_4). Addition of the modified filler can significantly increase effective thermal conductivity of composite. Filler materials were synthesized by means of carbothermal reduction and nitridation process. Obtained filler materials were investigated by means of infra-red spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and also characterized by scanning electron microscopy (SEM) coupled with energy dispersive analysis (EDS). A representative set of epoxy matrix samples filled with core-shell material has been prepared and compared with the reference samples. The thermal conductivity measurements have been performed on these samples at the room temperature.

2. Experimental Procedure of filler preparation

2.1. Core-shell filler preparation

Silica coated by boron nitride was obtained according to procedure, where the boric acid (H_3BO_3), was chosen as boron source. A 1M solution of boric acid in methanol was prepared at room temperature, then silica Millisil W12 (derived by Quarzwerke) was added and stirred. The resulting suspension was left at room temperature under a hood until methanol is totally evaporated. Then dry powder was heated to 1000°C at a rate of 10°C/min and held for 2h under a flowing ammonia atmosphere. The flow was replaced by a nitrogen flow during cooling to room temperature.

The second material, silica coated Si_3N_4, was prepared using commercially available Perhydropolysilazane (PHPS). Silica Millisil W12 was added into the solution. In the next step solution was left under a hood to dry. Then the dry sample was heated to 1000°C at a rate of 5°C/min and held for 2h under a flowing nitrogen atmosphere. A part of this powder was then heat-treated at 1400°C in order to obtain crystallized nitride phase.

2.1. Composites preparation and thermal conductivity measurements technique

Epoxy derived from bisphenol A (DGEBA) CY 228 hardened with HY918 (derived by Huntsman) was used. Samples were prepared using designed fillers with 31% and 45% filler volume content (vol.%) by conventional vacuum casting method with the use of typical curing profile found in producer data sheet.

Thermal conductivity was investigated with steady-state method of thermal transport option of a PPMS device (Physical Property Measurement System) manufactured by Quantum Design Inc. Small cylindrical specimens, with the diameter of 6 mm and height ranging from 3 mm to 6 mm, were cut. Heat pulses were applied by a heater connected to the copper electrode glued to the sample with an epoxy binder having both high thermal and electrical conductivity. Also a thermometer was connected to this electrode and another thermometer was connected to the electrode glued to the opposite side of the sample. The thermal conductivity measurements have been performed in the high vacuum conditions at room temperature. A special algorithm of software was used to optimize measurements parameters, such as heat pulse duration, heater current and frequency.

3. Results and discussion

3.1 FTIR characterization of powders

The BN coated SiO_2 obtained powder was investigated by Fourier Transform Infrared spectroscopy (Attenuated Total Reflectance FTIR Nicolet 380, Thermo Scientific), in order to find the bonding character of boron and nitrogen.
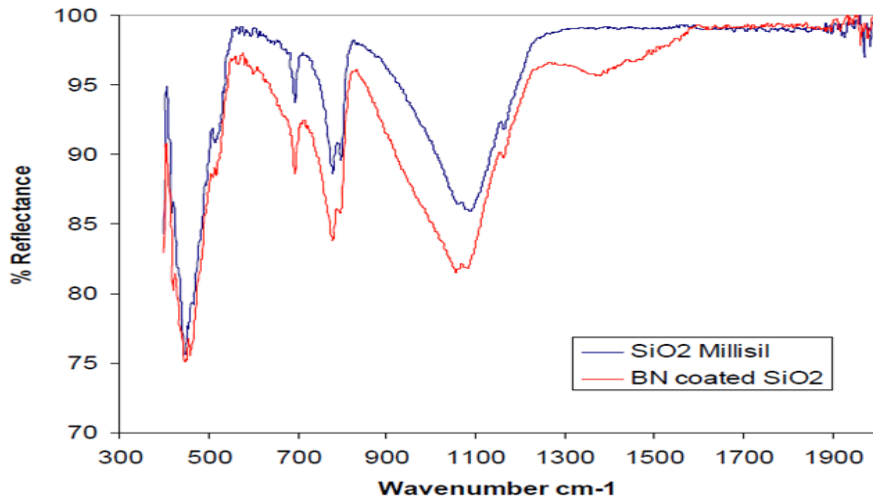

Figure 1. IR spectra of SiO_2 Millisil and coated SiO_2.

The IR spectra of pure and BN coated SiO_2 are shown in Figure 1. The positions and intensities of SiO_2 bands are almost the same but difference is observed at 1380 cm^{-1} (broad band), where BN absorption is expected. Indeed, pure BN has two characteristic bands: a strong band at 1373 cm^{-1} attributed to B-N stretching vibrations, and a weaker band at 816 cm^{-1} attributed to B-N-B bending vibrations [10].
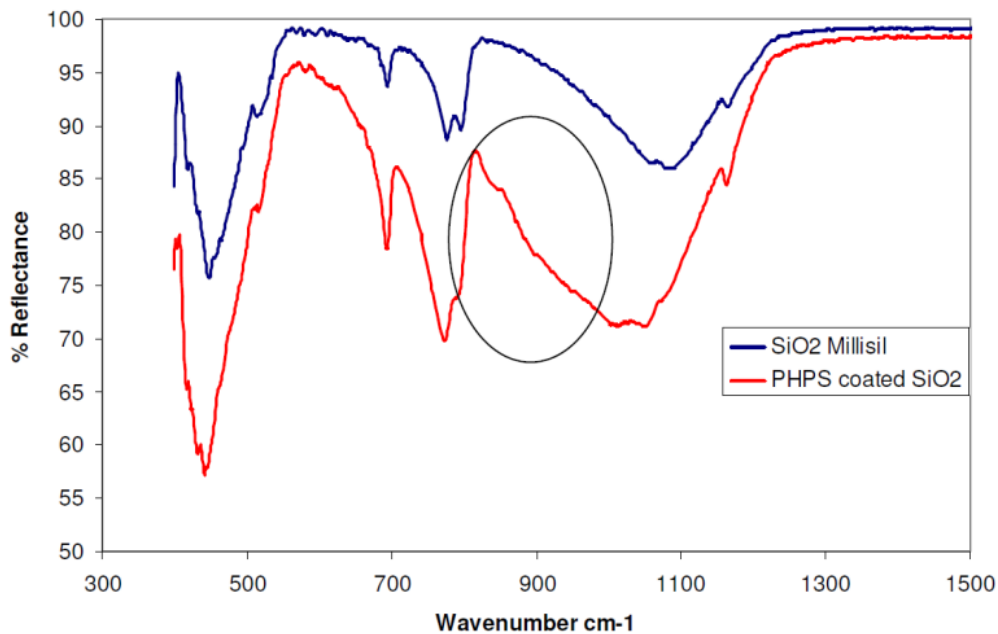

Figure 2. IR spectra of SiO_2 Millisil and PHPS-coated SiO_2.

PHPS-coated silica sample was investigated by FTIR spectroscopy before heat treatment in order to find the bonding character of silicon and nitrogen. IR spectra of pure and coated SiO_2 are shown in Fig 2. The positions and intensities of SiO_2 bands are almost the same but the difference is observed in the range 850-1000 cm^{-1}, where the strongest Si-N absorption bands are expected [10]. It seems demonstrating that the sample contains PHPS before the furnace treatment.

3.2 SEM observations and EDS analysis

Scanning electron microscope (Hitachi S800) equipped with energy-dispersive spectroscopy analysis was used to analyze coated particles. Comparing the pure SiO_2 powders and material after BN deposition, EDS measurements clearly show the presence of BN in the batch with the 2 peaks around 0.2 and 0.4 keV. These results are presented in Figure 3.
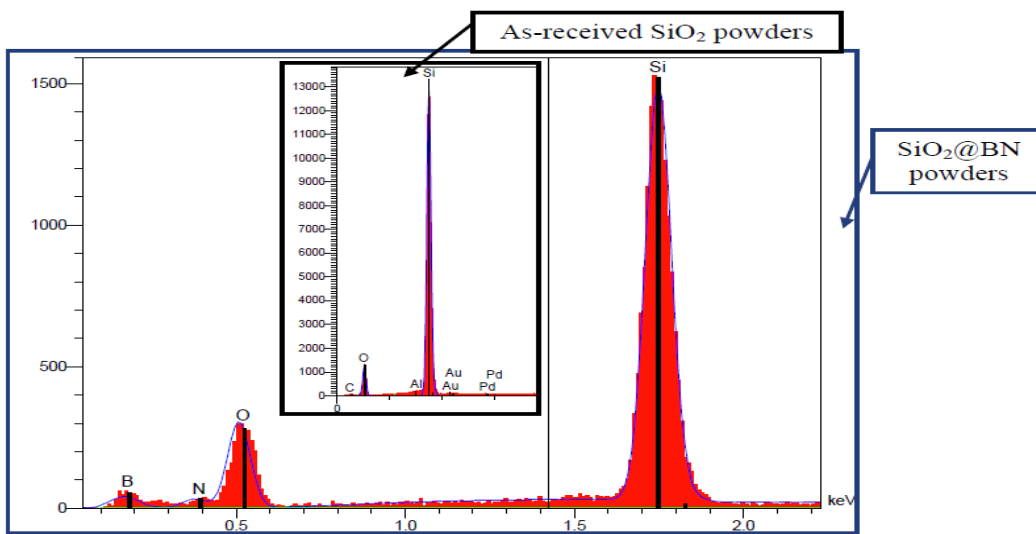

Figure 3. EDS measurements of SiO_2@BN powder..

The SEM pictures seem showing agglomerates which probably appear due to a high content of BN since the B/Si molar ratio was fixed at 20 in our process as presented in Figure 4 (left).
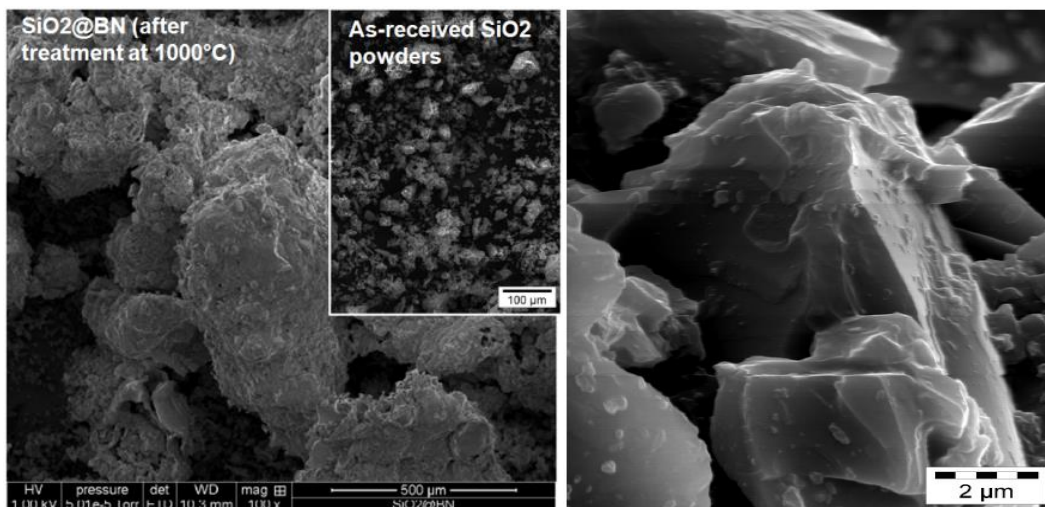

Figure 4. Left image: Grains of SiO_2@BN after treatment at 1000°C. Inset shows as-received SiO_2 powders. Right image: SEM picture of SiO_2@Si_3N_4 powders after treatment at 1000°C.

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Figure 4 (right) presents a SEM picture of $SiO_2@Si_3N_4$ powders after treatment at 1000°C. One can distinguish a film on the powder surface which could correspond to the Si_3N_4 deposition already detected using FTIR technique. The particle size measured here are similar to those of the raw powder confirming that there is no significant modification of the particle size after deposition.

3.3 X-ray photoelectron spectroscopy

The XPS experiments were carried out on both batches: $SiO_2@BN$ and $SiO_2@Si_3N_4$. In both cases (see Figure 5) nitrogen element was detected, as well as boron for the boron containing-powder. The obtained values after quantification are presented in Table 1, with a higher content of nitrogen for the BN-containing batch, meaning that the BN film seems to be thicker than the Si_3N_4 one. The presence of carbon is due to the carbon tape on which the powders where deposited. These measurements were performed after grinding of the as-pyrolysed powders, implying that a part of the silicon detected could correspond to the silica. Moreover the coating is certainly not thick enough to avoid the electron beam to reach the silica grains, this explaining that a high content of Si was detected in the BN-coated material for instance.
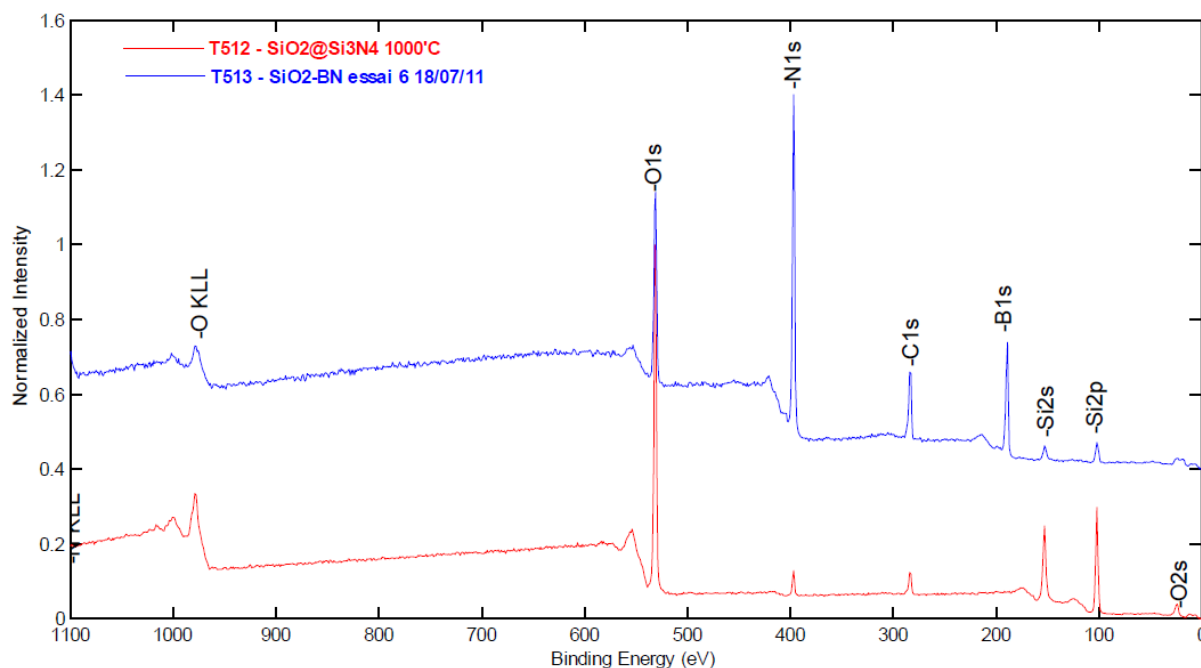
Figure 5. XPS spectra of $SiO_2@BN$ and $SiO_2@Si_3N_4$ batches (after treatment at 1000°C).

Content (wt.%)	B	N	C	O	Si
$SiO_2@BN$	34,3	33,9	13,4	15,2	3,3
$SiO_2@Si_3N_4$	0,0	5,2	9,7	56,3	28,8

Table 1. Composition determined after XPS analyses corresponding to spectra of Figure 5.

3.4 X-ray diffraction

The powders were investigated by XRD (PANalytical MPD). In the case of BN coated filler the BN remains amorphous at temperatures lower than 1400°C. Therefore trial was done with increase of the temperature of a part of the SiO_2@BN sample up to 1400°C. However the XRD results highlighted only formation of Crystoballite instead of Quartz phase for SiO_2. The main BN crystalline phase peak (at $2\theta = 13°$) was still absent.

The XRD patterns of as-received SiO_2 Millisil and treated SiO_2 are compared in Figure 6. The crystalline phase of SiO_2 Millisil was pure Quartz. This phase was also observed on the sample after treatment 1400°C, but a second phase of SiO_2 (Cristobalite) was formed during the treatment. The circled diffraction peak (at positions 13° 2Θ) and shoulder (at 31° 2Θ) could be attributed to Si_3N_4. The insert presents a spectrum after intermediate treatment at 1000°C which brings out the absence of this signal. This is consistent with the fact that silicon nitride crystallizes more rapidly above 1200°C. It must be noticed that the high-temperature treatment was performed in order to point out the formation of crystalline Si_3N_4 but, obviously, this sample was subjected to a pyrolysis up to 1000°C in order to prevent the Quartz-to-Cristobalite transformation.
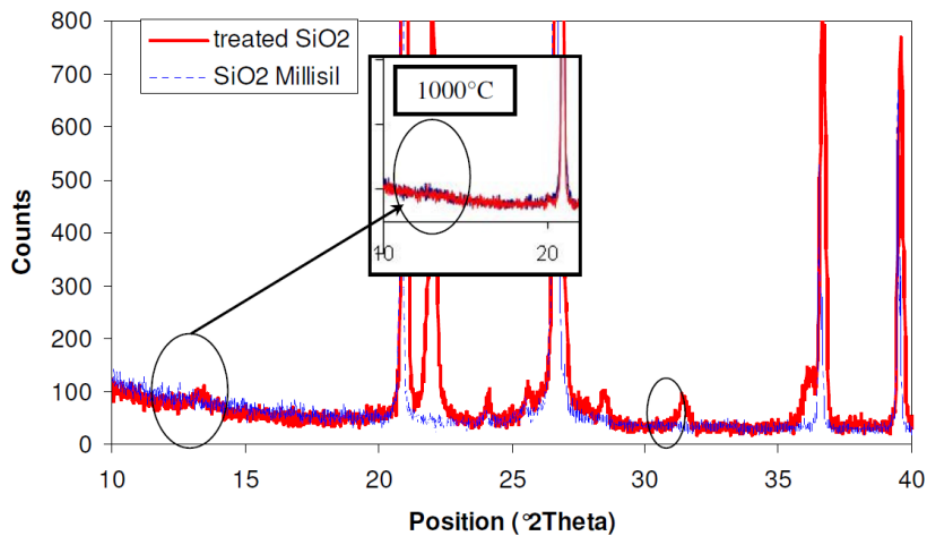
Figure 6. XRD patterns of SiO2 Millisil as-received and treated SiO2 at 1400°C (inset: treatment at 1000°C).

3.5 Thermal conductivity results

Sample	Filler content (vol.%)	Thermal conductivity (W/mK)	Relative increase (%)
SiO2	31	0.62	reference
	45	0.97	reference
SiO2@BN	31	0.67	8
	45	0.83	-14
SiO2@Si3N4	31	0.78	26
	45	1.02	5

Table 2. Thermal conductivity results obtained in 300K, for composites filled with designed fillers SiO_2@BN and SiO_2@Si_3N_4.

Thermal conductivity results measured for prepared composites were presented in Table 2. Effective thermal conductivity was enhanced by 8% in case of SiO_2@BN. In case of SiO_2@Si_3N_4 thermal conductivity increased by 26% although thicker layer of silicon nitride. The enhancement of thermal conductivity is especially visible for lower content of the filler (31 vol.%). For higher filler content enhancement was not effective.

4. Conclusions

A new type of core-shell fillers have been successfully prepared and characterized. Application of core-shell filler leads to enhancement of the epoxy composite thermal conductivity. Despite much thicker layer of high thermal conductivity coating in the case of SiO_2@Si_3N_4, the observed thermal conductivity is more enhanced in comparison to SiO_2@BN filler, for which thicker HTC coating was obtained. Such behavior can be explained by better filler-matrix interface leading to less scattering of phonons. The performed investigations indicate that low amount of high thermally conductive advanced material can open way for a more affordable epoxy composites which can be well applied for the heat management applications.

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