



Effect of pyrolysis atmospheres on the morphology of polymer-derived silicon oxynitrocarbide ceramic films coated aluminum nitride surface and the thermal conductivity of silicone rubber composites

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ARTICLE INFO

Article history:

Received 10 August 2013

Received in revised form

18 November 2013

Accepted 25 November 2013

Available online 1 December 2013

Keywords:

Surface modification

Aluminum nitride

Thermal conductivity

Polysilazane

Silicon oxynitrocarbide

Silicone rubber

ABSTRACT

Amorphous silicon oxycarbide (SiOC) and silicon oxynitrocarbide (SiONC) ceramic films coated aluminum nitride (AlN) were prepared by using preceramic-polysilazane (PSZ) with dip-coating method, followed by pyrolysis at 700 °C in different (air, Ar, N₂ and NH₃) atmospheres to converted PSZ into SiOC_{air} and SiONC_(Ar, N₂ and NH₃) ceramic. The existence of amorphous SiOC_{air} and SiONC_(Ar, N₂ and NH₃) ceramic films on AlN surface was characterized by FTIR, XRD and XPS. The interfacial adhesion between silicone rubber and AlN was significantly improved after the introduction of amorphous SiOC_{air} and SiONC_(Ar, N₂ and NH₃) ceramic films on AlN surface. It can be observed from AFM that the pyrolysis of PSZ at different atmosphere strongly affected to films morphology on AlN surface as SiOC_{air} and SiONC_{NH₃} ceramic films were more flat and smooth than SiONC_{N₂} and SiONC_{Ar} ceramic films. Besides, the enhancement of the thermal conductivity of silicone rubber composites was found to be related to the decrease in the surface roughness of SiOC_{air} and SiONC_(Ar, N₂ and NH₃) ceramic films on AlN surface. This present work provided an alternative surface modification of thermally conductive fillers to improve the thermal conductivity of silicone rubber composites by coating with amorphous SiOC_{air} and SiONC_(Ar, N₂ and NH₃) ceramic films.

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1. Introduction

Nowadays, thermally conductive polymer composites are very popular in the application needed electrically insulated property including packing or encapsulating materials [1] and thermal interface materials [2] in microelectronic devices and power equipments. Basically, thermally conductive polymer composites are made of polymer compounded with thermally conductive filler. Many efforts have been done to improve the thermal conductivity of the composites followed these strategies:

- (1) *Using high intrinsic thermal conductive filler*: the thermally conductive composites filled inorganic fillers such as boron nitride (BN) [3], aluminum nitride (AlN) [4] and silicon carbide (SiC) [5] provide higher thermal conductivity than the composites

filled inorganic fillers such as aluminum oxide (Al₂O₃) [2], silicon dioxide (SiO₂) [6] and zinc oxide (ZnO) [7] because of their higher intrinsic thermal conductivity.

- (2) *Using of hybrid fillers*: the synergistic effect of different shape fillers could provide a higher maximum packing fraction than the composites filled single filler, thus resulted in more efficient conductive pathways in the composites [8–11].
- (3) *The optimized processing conditions*: the effect of mixing speed, mixing time and mixing temperature impede the dispersion of filler and increase the agglomeration of filler particles, which result in the decrease in the thermal conductivity of the composites [12]. Moreover, the specimen fabricated by a method involving the use of solvent is considered to cause air bubbles to be trapped in the composites, thus decreased the thermal conductivity of the composites [13].

The alignment of fillers: some kind of fillers, such as boron nitride, possessed high thermal conductivity in the basal plane. Applying a magnetic or electric field would cause the fillers orient in the same direction, and result in the enhancement of

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the thermal conductivity of the composites in the aligned basal plane direction [14].

- (4) *Improving of the interfacial adhesion between filler and matrix:* the compatibility between filler and matrix was improved by surface modification of filler, hence enhance heat transfer at the filler-matrix interface [1,3–5,11,15].

However, the improvement of the interfacial adhesion between filler and matrix is one of the most effective ways to enhance the thermal conductivity of thermally conductive polymer composites. Polysilazane (PSZ) is an organosilicon polymer with NH_3 leaving group. Generally, it is widely used in coating applications since it provides high thermal stability, oxidation resistance and corrosion-resistant coating [16–18]. One of the unique and promising properties of PSZ is the conversion from preceramic-polymer into silicon oxynitride (SiONC) ceramics. Besides, many researches have been studied about the pyrolysis of PSZ in different atmospheres e.g.: air, argon (Ar), nitrogen (N_2), ammonia (NH_3), providing different chemical composition of SiONC ceramics [16,18–20].

In the previous work, it had been found that the introduction of polymer-derived amorphous SiOC ceramic film on AlN by pyrolysis of PSZ coated AlN under air atmosphere help improved the interfacial adhesion as well as the thermal conductivity of silicone rubber composites. Thus, in the present work, pyrolysis of PSZ coated AlN at 700°C in various atmospheres including air, Ar , N_2 and NH_3 was carried out in order to investigate the effect of pyrolysis atmosphere on the introduction of SiOC and SiONC ceramic films on AlN surface as well as the thermal conductivity of silicone rubber composites. SiONC coated AlN pyrolyzed at 700°C in Ar , N_2 and NH_3 atmospheres are abbreviated hereafter, as SiONC/ AlN_{Ar} , SiONC/ AlN_{N_2} and SiONC/ AlN_{NH_3} , respectively. Besides, SiOC coated AlN heated in air atmosphere is abbreviated as SiOC/ AlN_{air} . Then, surface characterization of SiOC/ AlN_{air} and SiONC/ $\text{AlN}_{(\text{Ar}, \text{N}_2 \text{ and } \text{NH}_3)}$ were also investigated and evaluated.

2. Experimental

2.1. Materials

Silicone rubber (K941-U), 2,5-dimethyl-2,5-bis(tertiarybutylperoxy) hexane (C-8) were obtained from Shin-Etsu silicone, Japan. PSZ based coating resin (KiON HTA 1500) was purchased from Clariant GmbH, Germany. AlN with average particle size of $5\text{ }\mu\text{m}$ was provided from Taiyen, Taiwan. AlN particle size of $5\text{ }\mu\text{m}$ abbreviated as AlN hereafter. All of chemicals were used as received.

2.2. Surface modification of AlN

PSZ was applied on AlN by using dip-coating method as shown in Scheme 1. First, AlN was dipped and stirred in PSZ solution ($\text{AlN}:\text{PSZ}=2:1$, w/w) at room temperature for 1 h. After that AlN dispersion was filtered to remove the exceed PSZ solution and the filtered-PSZ coated AlN was placed in an oven at 180°C for 24 h to allow crosslinking of PSZ on AlN surface (the first 3 h PSZ-coated AlN was gently grinded every 30 min to prevent the aggregation of the modified AlN). Then, the pyrolysis of PSZ-coated AlN in air, Ar , N_2 and NH_3 atmospheres was carried out by using tube furnace (STF54434C, Thermo Scientific, USA). These procedures were performed with the heating rate of 3°C per minute to the temperature of 700°C , then dwell of about 2 h, finally cooling with the rate of 10°C per minute to room temperature.

2.3. Preparation of silicone rubber filled SiOC/ AlN_{air} and SiONC/ $\text{AlN}_{(\text{Ar}, \text{N}_2 \text{ and } \text{NH}_3)}$

Silicone rubber was compounded with untreated AlN and the modified AlN at the content of 30 volume percent (vol%), followed by the addition of curing agent, both step were executed in the two roll mixing mill with the mixing time of 60 min. Then, the well-mixed silicone rubber-filler composites were compression molded at 160°C with a pressure of 10 MPa for 20 min in an automatic hot press machine (GF-50, You Found Hydraulics Industrial, Taiwan).

2.4. Characterization

Infrared (IR) spectra were recorded within the scanning range of $4000\text{--}400\text{ cm}^{-1}$ for KBr pellets of samples on an FTIR spectrometer (Nicolet, Nexus 670). Field emission-scanning electron microscopic (FE-SEM) and energy-dispersion X-ray (EDX) micro-analysis observation of AlN and the composites on carbon tapes were performed on a JEOL JSM-6500F operated at a voltage of 20 kV. Both filler particle and composites were doing platinum sputtered in order to enhance the electrical conductivity at the surface. For EDS analysis, the measurement were performed five different particles for each sample. Crystallinity of AlN was performed on X-ray diffractometer (XRD) (D2 phaser, Bruker AXS, USA) using a monochromatic $\text{Cu K}\alpha$ radiation with a wavelength ($\lambda/2$) of $1.54\text{ }\text{\AA}$. X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, VG Scientific, UK) was used to analyze elemental composition and chemical state of the elements. In XPS analysis, a monochromatic Al $\text{K}\alpha$ X-ray source was used at 1486.6 eV ($650\text{ }\mu\text{m}$ spot-size). Spectra were quantified and analyzed using XPSPEAK 4.1 software. Thermal conductivity of the composites was measured using a Hot Disk Thermal Analyzer (Hot Disk AB, Uppsala, Sweden). Each specimen size was $2\text{ cm} \times 2\text{ cm} \times 0.35\text{ cm}$ with a sensor diameter of 0.3 cm placed between two similar samples. The thermal conductivity of each sample was measured in triplicate. The sensor supplied a heat-pulse of 0.03 W for 10 s to the sample and the associated change in temperature was recorded. Atomic force microscopic (AFM) observation was performed in air using a Digital Instruments NanoScope III apparatus. Sapphire was used as a substrate. PSZ solution was dropped directly onto the $1\text{ cm} \times 1\text{ cm}$ sapphire substrates, and then the solution was spin-coated at 5000 rpm for 120 s. Finally, the substrate was allowed to moisture-crosslink and pyrolysis in various atmospheres following the same procedure as surface modification of AlN.

3. Results and discussion

3.1. Characterization of SiOC/ AlN_{air} and SiONC/ $\text{AlN}_{(\text{Ar}, \text{N}_2 \text{ and } \text{NH}_3)}$

SiOC_{air} and SiONC_(Ar, N₂ and NH₃) films were applied on AlN surface as shown in Scheme 1. The existence of SiOC_{air} and SiONC_(Ar, N₂ and NH₃) films on the surface of AlN after pyrolysis at 700°C under air, Ar , N_2 and NH_3 atmospheres was confirmed by IR absorption spectroscopy, as shown in Fig. 1. Untreated AlN revealed characteristic IR absorption bands of Al–N and Al–O bonds at $700\text{--}800$ and 600 cm^{-1} , respectively [21]. It was observed that SiOC/ AlN_{air} and SiONC/ $\text{AlN}_{(\text{Ar}, \text{N}_2 \text{ and } \text{NH}_3)}$ exhibited an absorption band of Si–O–Si bond of silicon dioxide and Si–C–Si bond of silicon carbide at around $1080\text{--}1060$ and $840\text{--}800\text{ cm}^{-1}$, respectively [22,23]. Moreover, SiONC/ $\text{AlN}_{(\text{Ar}, \text{N}_2 \text{ and } \text{NH}_3)}$ revealed Si–NH–Si bond at 1170 cm^{-1} . The appearance of Si–O–Si bond in PSZ was due to the moisture-crosslinking of PSZ under air atmosphere which were consequently introduced oxygen (O) into the backbone of PSZ network [16]. Typically, the ceramization of PSZ at high temperature was resulted from the condensation reactions

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