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ScienceDirect

Ceramics International 41 (2015) 2187–2195

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fabrication of silicon carbonitride-covered boron nitride/Nylon 6, 6 composite for enhanced thermal conductivity by melt process

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Received 16 September 2014; received in revised form 29 September 2014; accepted 2 October 2014

Available online 12 October 2014

Abstract

The surface-treated boron nitride (BN) particles are prepared with polysilazane (PSZ) by using a dip-coating method to fabricate a thermally conductive interface material. PSZ-BN particles are generated by crosslinking of PSZ on BN and heat treatment of the formed PSZ-BN at 700 °C to convert PSZ-BN to SiCNO-BN. The SiCNO-BN particles are fabricated with Nylon 6,6 by using an extruder and injection molding method. The interfacial adhesion between the BN particles and the Nylon 6,6 matrix is enhanced by surface treatment of the BN particles. The surface-treated BN/Nylon 6,6 composites exhibit thermal conductivity ranging from 0.3270 to 0.4230 W/m K (through-plane) and 1.6510 to 4.960 W/m K (in-plane), which is higher than that in the case of loading with pristine BN/Nylon 6,6 composites at the same weight fraction. The tensile strength and tensile modulus increase from 59.13 and 1.67 GPa with the use of pristine BN to 69.15 and 2.10 GPa with incorporation of SiCNO-BN into the Nylon 6,6 composite.

Keywords: A. Extrusion; B. Composites; C. Thermal conductivity; D. Nitrides; Surface treatment

1. Introduction

Recent advances in the field of electronics have resulted in the miniaturization of devices, facilitating integration of more components in a small volume, which in turn leads to higher device performance. Despite the advancements in the development of electronic devices, heat dissipation limitations still hamper the performance of electronic device components [1,2]. It is well known that the reliability of an electronic device is exponentially dependent on the operating temperature of the junction, whereby a small difference in the operating temperature (10–15 °C) can result in a two-fold reduction in the lifespan of a device [3]. Therefore, rapid dissipation of the heat generated in the device is crucial for maintaining the optimum operating temperature in the device. These problems have emphasized the need for improved thermal interface materials (TIMs) for use in chip packaging [4,5]. Thermal interface materials are thermally conductive materials that are used to reduce interfacial thermal resistance across jointed solid surfaces, such as between microprocessors and heat sinks, in order to increase the thermal transfer efficiency. Thermal interface materials are better conductors of heat than air in the device, and thus reduce the resistance to heat transfer caused by air voids. Generally, to enhance the thermal conductivity of TIMs, many kinds of particles such as boron nitride (BN), aluminum nitride (AlN), silicon nitride (SiN), alumina (Al_2O_3), silicon carbide (SiC), and silica (SiO_2) are introduced into a polymer matrix [6–9]. Among these various thermally conducting fillers, boron nitride (BN) is a widely used ceramic material that is considered an attractive candidate as a filler for TIMs based on the attractive properties such as high thermal conductivity, low coefficient of thermal expansion, and high electrical resistivity over a wide temperature range [10]. BN is also chemically stable with respect to most molten metals and glasses, organic solvents, and polymers, even at high temperature.

However, BN has very good chemical stability, which can be considered a drawback to its use as a filler. As it will not form chemical bonds easily, poor compatibility occurs between polymer matrix and boron nitride particle. Inhomogeneous

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http://dx.doi.org/10.1016/j.ceramint.2014.10.018

0272-8842/

dispersion of fillers in the polymer matrix can cause high resistance to thermal conduction at the interface, thereby reducing the thermal conductivity. Therefore further surface treatment is necessary to make reaction sites available on the particle surface to increase dispersion of BN particles. Kim et al. reported a surface-modified boron nitride/ETDS composite to increase the dispersion of the boron particles with a thermal conductivity of 2.85 W/m K, which is 1.44 times higher than that of the pristine BN/ETDS composite [11]. Gu et al. achieved a five-fold increase in the thermal conductivity by using epoxy filled with silane-modified BN (1.052 W/m K) relative to that of native EP (0.202 W/m K) [12]. Teng et al. reported a 743% increase in the thermal conductivity (1.913 W/m K) using multi-walled carbon nanotubes and boron nitride hybrid composites [13].

Compounding with fillers and a matrix, as well as blending and chemically modifying existing polymers are attractive methods of developing new materials with improved properties for specific applications. Polymer blends and compounds are commonly prepared by mechanical mixing of the components in the molten state. It is well known that by using different mixers, and by varying the mixing parameters, it becomes possible to control the phase morphology, and thus to improve the blend performance. Kuriger et al. reported improved thermal properties of polypropylene composites with aligned Pyrograf III$^{\text{TM}}$ that were prepared by an extrusion process [14]. Sui et al. synthesized reinforced polypropylene composites by using a twin-screw extruder [15]. Generally, ceramic-powder-reinforced polymers are fabricated by the extruder method based on consideration of the effects of the particulate reinforcements on the composite properties. The extruder method is widely utilized due to its simplicity and speed as a technique for mixing and designing moldable materials, as well as its solvent-free manufacturing protocol and high mixing efficiency. In addition, the extrusion process has been demonstrated to be an effective melt blending process for producing thermoplastic composites because the process provides uniform, high shear compounding, which results in zones that have better mechanical properties than those compounded in a two-roll mill or a high-speed mixer [16].

Polysilazanes (PSZ) are polymers whose backbones consist of alternating Si and N atoms with pendent carbon-containing groups, and are widely used in precursors, coating solutions, and blending applications [17,18]. PSZ coatings have good thermal stability, are electrically insulating, and provide oxidation and corrosion resistance. A unique and potentially exploitable property of PSZs is that they are pre-ceramic polymers and can be converted into SiCN ceramics via thermal treatment. Currently, there is no published research on the surface modification of inorganic fillers by coating polymer-derived ceramics onto the thermally conducting fillers as a method of improving the thermal and electrical properties of the composite system.

In this study, BN/Nylon 6,6 composites were fabricated using both raw BN and surface-treated BN particles, respectively. To enhance the dispersion and interfacial adhesion in polymer matrix the BN particles were coated with polysilazane (PSZ) via the dip-coating method. The PSZ-BN particles were further converted to SiCNO-BN by heat treatment at 700 °C and SiCNO-BN/Nylon 6,6 composite mixtures were compounded using an extruder. Moreover, the injection molding method was also used to fabricate the SiCNO-BN/Nylon 6,6 composite to achieve alignment of the SiCNO-BN particles in the injection direction. Measurement of the thermal conductivities of the BN composites and the relation of the thermal conductivity to the SiCNO-BN particle concentration are presented herein. In addition, the effect of the surface-treated BN particles on the mechanical properties of the composite is investigated based on dynamic mechanical analysis (DMA) and ultimate tensile stress (UTS) analysis.

2. Experimental methods

2.1. Materials

Boron nitride was supplied by LG Innotek (Seoul, Republic of Korea) and used after drying under vacuum at 80 °C. Commercially available Nylon 6,6 was supplied by LG Chemicals (Seoul, Republic of Korea). According to the supplier, the molecular weight (as determined by gel permeation chromatography (GPC) using polystyrene standards) was M_w=43,000 and M_n=22,000 g/mol. Polysilazane-based coating resin (KiON HTT-1800) was purchased from Clariant GmbH, Germany.

2.2. Surface treatment of BN particles with polysilazane

Boron nitride (BN) was used after thorough washing with ethanol and drying in a vacuum oven at 30 °C for 1 day. Polysilazane (PSZ) was coated unto the washed BN using the dip-coating method. BN particles were dipped and stirred in PSZ solution (BN:PSZ=1:1 w/w) at room temperature for 1 h. The BN dispersion solution was then filtered to remove any excess PSZ solution. The filtered PSZ-coated BN (PSZ-BN) was treated at 180 °C to allow moisture-crosslinking of PSZ on the BN surface. During drying, PSZ-coated BN was gently ground every 30 min for 2 h to prevent aggregation and was subsequently treated in an oven for 18 h. Finally, the PSZ-BN particles were treated at 700 °C in air for 2 h. This process was required to convert PSZ-BN into SiCNO-BN. The procedure for fabrication of SiCNO-BN is illustrated in Fig. 1.

2.3. Preparation of SiCNO-BN/Nylon 6,6 composites

Composites of SiCNO-BN and Nylon 6,6 were prepared by melt mixing. Both Nylon 6,6 and SiCNO-BN were dried at 80 °C for 24 h under vacuum prior to melt mixing. Melt mixing was performed in a twin extruder (model BA-11, L/D ratio = 40, Bau Technology, Seoul, Republic of Korea) in a specified temperature range. The temperature of the feeding zone, melting zone, mixing zone, and exit die were 265, 280, 280, and 270 °C, respectively. The feeding rate of materials and the extrusion speed were held constant at 100 g/min and 300 rpm, respectively. The melt-mixed composites were immediately quenched in a water bath after extrusion. The