Thermochimica Acta 529 (2012) 68–73

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal conductivity enhancement of BN/silicone composites cured under electric field: Stacking of shape, thermal conductivity, and particle packing structure anisotropies

Yuwang Han[a,*], Sumin Lv[a], Chanxi Hao[b], Fei Ding[a], Yi Zhang[a]

[a] College of Sciences, Nanjing University of Technology, No. 5 Xinmofan Road, Nanjing 210009, China
[b] College of Chemistry and Chemical Engineering, Nanjing University of Technology, China

ARTICLE INFO

Article history:
Received 28 July 2011
Received in revised form
11 November 2011
Accepted 22 November 2011
Available online 1 December 2011

Keywords:
Thermal interface material
Boron nitride
Electric field assisted structuring
Anisotropic thermal conductivity

ABSTRACT

We have prepared thermal conductive silicone rubbers filled with BN micro particles assisted with electric field assisted curing, and studied the electric field effect. The composites structure was characterized by XRD, SEM, and the results indicate that aligned conductive networks have formed between the electrodes under either AC or DC electric fields. Furthermore, the "*c*" axis of BN particles was found to orient along with the electric field and the orientation degree under AC was higher than that with DC. Upon increasing the filler volume fraction, the orientation decreases dramatically. In addition, we have investigated the thermal conductivity of BN/silicone composites with varying particle volume fractions and electric-field strengths. For example, under the AC electric field (50 Hz) of 11.0 kV/mm, the thermal-conductivity with 20% loading of BN increases by ca. 250% compared to that prepared without electric field. A two-level homogenization model was adopted to analyze and fit the thermal conductivity data.

1. Introduction

As heat dissipation is becoming a critical factor to the performance of miniaturized microelectronics [1], thermal interface materials (TIM) with high thermal conductivity and electrical insulation are desirable for a variety of applications. At a given filler composition, the apparent composite thermal conductivity depends on the particle shape, the orientation of particles to the thermal gradient, and the spatial relations among particles [2]. At a given particle loading, the thermal conductivity of composite can increase by means of maximizing conductive paths, minimizing the thermal resistance in each conductive path, and decreasing the thermal contact resistance at the filler–matrix interface [3].

The thermal conductivity is often enhanced by increasing the volume fraction of fillers so that an interconnected conductive network forms, i.e. a thermal conductivity of 32.5 W/mK was achieved, when boron nitride (BN) filled polybenzoxazine at its maximum filler loading of 78.5% by volume [4]. Mixing multiple sized particles can lead to high packing density and easy formation of conductive pathways [5]. For example, the powder mixture of BN and polyethylene particles has resulted in high density polyethylene (HDPE) composites with high thermal conductivity at low filler content, as compared to that made with melted mixing [6].

Under certain shear forces [7], magnetic [8–10] and electric fields [11–13], the filled particles can reorient to form a chain-like structure in the polymer matrix at a relatively low volume fraction. Applying a magnetic or electric field causes the dispersed particles to move and minimize their magnetostatic or electrostatic energy, which results in the formation of densely packed column structure [14,15]. Cho et al. have reported [16–18] that high DC or nanosecond-pulse electric field could induce the formation of BN nanosheet bridges in polysiloxane and the resulting thermal conductivity in the film thickness direction was significantly higher than others.

In this paper, we have applied both DC and 50 Hz AC electric fields to orient boron nitride pellets to form anisotropic thermal conductive BN/silicone composites that conduct heat more efficiently. Our results show that a column-like structure was formed with the BN basal plane aligned parallel to the electric field direction. The effective thermal conductivity of the composites has been significantly enhanced by the triple stacking of the particle shape, thermal conductivity and particle packing structure anisotropies.

2. Experimental work

2.1. Materials

Silicone rubber consisting of vinyl end blocked polymethylsiloxane (type: R657) was obtained from BiaoMei Fine Chemical

* Corresponding author.
E-mail address: hankeyi@sina.com (Y. Han).

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doi:10.1016/j.tca.2011.11.029

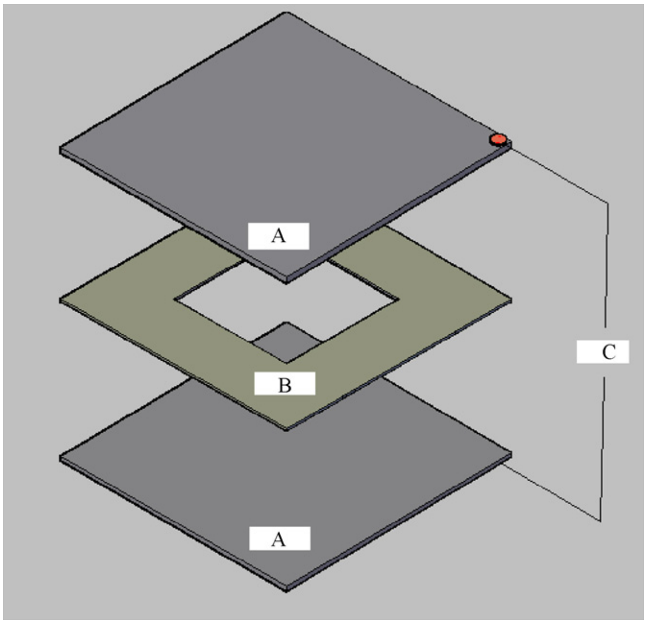

Fig. 1. Experimental modal (A: stainless steel sheet; B: rubber spacer; C: high-voltage source).

Ltd., Guangzhou, China. The thermal conductive filler used was a BN powder with a purity of 99.9% and average particle size of 20 μm, kindly provided by DENKA (Japan). The thermal conductivity of BN in "*c*" direction and perpendicular to "*c*" are 60 W/mK and 2 W/mK, respectively. $Al(OH)_3$ (H-WF-8SP) was obtained from Aluminum Corporation of China Limited (CHALCO) with D50 = 8 μm, and spherical alumina is DAW-05 (DENKA, Japan).

2.2. Specimen preparation

Silicone rubber R657B was mixed with certain amount of BN powders followed by the addition of R657A that has catalytic agent, which was further mixed for 15 min and degassed with a vacuum pump. The mixture was then transferred to a modal composed of a pair of stainless steel sheet and a rubber spacer (Fig. 1), in which the sheets were connected to a high-voltage source and cured for 30 min in an oven at 80 °C. PET films were used as the separation layer on both sides of the sample.

2.3. Characterization

The orientation of BN in the composites was characterized by X-ray diffraction (Thermo ARL X'TRA X-Ray Diffractometer) with Cu Kα radiation operated at 45 kV and 35 mA. Powder diffractograms were recorded over a 2θ range of 5–80° at a scanning speed of 10° min^{-1}. Surface perpendicular to the electric field direction was irradiated.

Table 1
The XRD data of BN's interplanar angles between the planes ($h\,k\,l$) and the basal plane ($0\,0\,l$) calculated on a unit cell of BN. $a = b = 2.173$ Å, $c = 6.657$ Å.

2θ	$h\,k\,l$	φ
26.7	0 0 2	0
41.5	1 0 0	90
43.7	1 0 1	82.86
50.1	1 0 2	75.9
55.1	0 0 4	0

The sample morphology at different treatment stage was observed in scanning electron microscopy (SEM) (S-4800, Hitachi). The thermal conductivity was measured with a LW-9091IR static state measurement apparatus (Longwin, Taiwan) that is designed based on ASTM D5470. The sample sheet was pressed between two cooper plates subjected to a heat flow. The heating source was adjusted to maintain the sample temperature at 80 °C (constant T_c mode).

2.4. Simulation

We have adopted a two-level homogenization model: Bruggeman method was used to calculate the effective conductivity of particle chains [19], followed by the determination of overall suspension conductivity with an effective-medium theory that is found to fit accurately the components of the thermal-conductivity tensor. With this procedure, we have determined the effective conductivity of the field-induced, BN-particle chains and the equivalent particle volume fraction within the chains.

3. Results and discussions

3.1. Structure and orientation

Fig. 2 and Table 1 show the main information of the BN crystal. Fig. 3 shows the XRD patterns of the composites prepared under DC and AC electric fields with different BN volume fraction (VF). The diffraction peak at $2\theta = 26.7°$ is ascribed to the face diffraction (0 0 2). The stronger the diffraction intensity of the (0 0 2) face is, the less the (0 0 2) faces are aligned. It is clear seen from Fig. 3 that diffraction intensity of (0 0 2) face increases with the increasing of volume fraction. That means the orientation degree is decreased with the increasing of BN volume fraction. This peak appears to be the strongest peak in all the samples prepared under DC electric field and its intensity increases with increasing the BN VF. But for

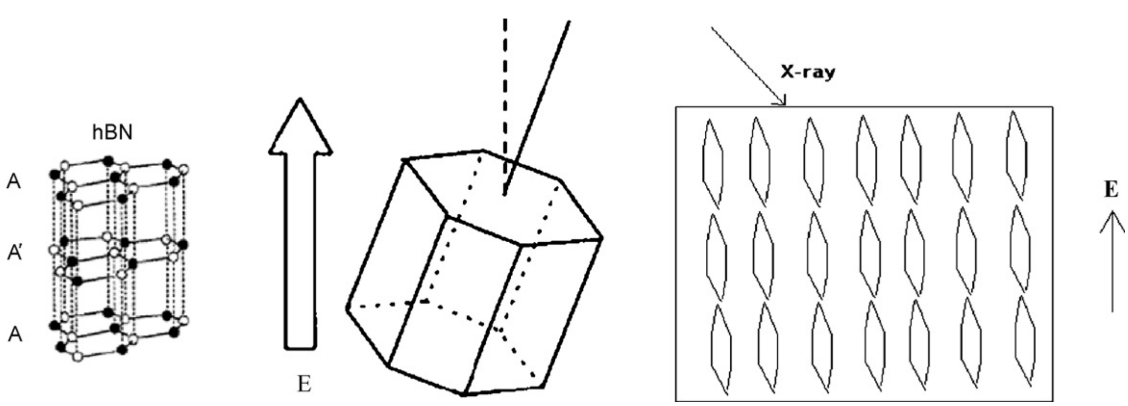

Fig. 2. Information of the BN crystal.