

# CERAMIFIABLE EPOXY COMPOSITES WITH ENHANCED THERMAL CONDUCTIVITY

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# ABSTRACT

Simultaneously improving the thermal conductivity and flame resistance of epoxy composite is still a challenge. Herein, a novel epoxy composite with high thermal conductivity and greatly enhanced flame retardancy was developed through constructing integrated three-dimensional (3D) network based on boron nitride (BN), talc, ammonium polyphosphate (APP). The thermal conductivity of the composite with filler network reached 3.04 Wm<sup>-1</sup>K<sup>-1</sup>, which was 15.2 and 3.1 times of those of pure epoxy and sample with random filler distribution. The LOI value of the composite with filler network reached 37.8%, which was 1.9 and 1.4 times of those of pure epoxy and sample with random filler distribution, the effects of various combinations of filler on the flame resistance of the epoxy composite was also evaluated. The prepared composite with filler network exhibited excellent shape stability and mechanical strength even after ablation at 1000 °C. The network structure constructed by BN had a positive effect on heat transfer, while APP led to the formation of phosphoric acid at high temperature, adhering to talc and other residues together. A ceramic-like residue was formed on the firing surface, which enhanced the barrier effect of char layer and flame resistance of the composite.

## **1 INTRODUCTION**

With the frequent occurrence of fire accidents in new energy transportation and electronic industry, there was an increasing demand on the reliability of thermally conductive and flame-retardant composites. Fire safety has attracted great attention from all walks of life, which is related to human personal safety and property safety. However, simultaneously improving the thermal conductivity and flame resistance of polymer composite is still a challenge. Therefore, new methods and strategies were needed for combating this issue. Furthermore, there is no uniform conclusion on the relationship between thermal conductivity and flame resistance, as it is complex. On the one hand, some researchers believe that high thermal conductivity was beneficial to the flame resistance of materials, which is based on the fact that materials with high thermal conductivity can transfer heat to the whole system in time to avoid excessive local position temperature, reducing the possibility of combustion and prolonging the ignition time <sup>[1-3]</sup>. On the other hand, some scholars argue that the high thermal conductivity of the material has not beneficial to flame resistance, which was mainly based on the fact that the high thermal conductivity caused the heat radiation easier and faster to transfer to the inside of the material, leading to the material with lower thermal decomposition temperature. Fewer reports focus on explicating the relationship between thermal conductivity and flame resistance along with the mechanism. Thus, a strategy to develop an efficient and simple preparation of high performance resinbased composites with advanced thermal conductivity and flame resistance is significant and necessary to disclose the relationship and mechanism of thermal conductivity and flame resistance.

Meanwhile, strategies to make polymer composite ceramifiable in the fire are reported, and they could be converted to ceramic-like residues when they are fired at high temperatures. Epoxy resin is one of the most versatile thermosetting polymeric materials. The construction of a continuous thermally conductive pathway to improve the utilization of fillers in epoxy has become an essential

issue in the preparation of high thermal conductivity composites<sup>[4]</sup>. In addition, the epoxy composites could have even wider applications if they also have good fire resistant property.

# **2 EXPERIMENTAL**

As indicated in Fig. 1a, BN, Talc, APP and NH<sub>4</sub>HCO<sub>3</sub> were first uniformly mixed in certain mass ratios and pressed into disks. Subsequently, the samples were heat treated in an oven at 80 °C for 12 h to create a BN/Talc/APP (3D-BTA) compound filler network. NH<sub>4</sub>HCO<sub>3</sub>, as a structural component substance, decomposed to gas at 80 °C. Then, the epoxy resin and MTHPA (epoxy resin:MTHPA=5:4, by weight ratio) was evenly mixed and the 3D-BTA network was cautiously immersed in the mixture and degassed for 40 min. The composite curing system was set at 90 °C for 1 hour and then at 140 °C for 4 hours. Finally, epoxy composites (3D-BTA/EP) with compound filler 3D-network structures were obtained.



Fig. 1: Schematic diagram of preparation of (a) 3D-BTA/EP composites and (b) R-BTA/EP composites

#### **3** RESULTS AND DISCUSSIONS

The structure of the filler network was of vital importance for the thermal transport of the composite. Fig. 2b-d display the microstructure of the cross-section of the compound filler (3D-BTA) networks. As can be seen, the filler network was a kind of 3D connected porous structure. As shown in Fig. 2e-g the normal distribution curve of the size and number of pores in the filler network, the peak relative frequency of the pores in the 3D-BTA1 filler network occurred at around 200  $\mu$ m, with the increase of the filler content, the size and number of pores in the filler network gradually decreased. It has to be noted that this continuous filler network could serve as an effective way for the heat dissipation of composites. The surface morphology of the sample before the release of NH4HCO3 by heat treatment was shown in Fig. 2a, and it already exhibited a continuous porous structure, which was due to the slow pyrolysis of NH4HCO3 at room temperature.

When this sample of porous filler structure was infiltrated by epoxy resin, the epoxy composites with 3D filler network were obtained as shown in Fig. 2B-D. The filler network was maintained as an integrated 3D structure, and this could contribute to the enhancement of the thermal conductivity of epoxy composites.



Fig. 2: SEM images of (a) the BTA/NH4HCO3 sample and (b) 3D-BTA1, (c) 3D-BTA2 and (d) 3D-BTA3 filler networks without resin and their composites: (B) 3D-BTA1/EP, (C) 3D-BTA2/EP and (D) 3D-BTA3/EP and the normal distribution curve of the size and number of pores in the (e) 3D-BTA1, (f) 3D-BTA2 and (g) 3D-BTA3 network (Note: NOP represent number of pores)

Fig. 3a exhibited the thermal conductivity of the epoxy composites with various filler loading and distribution. The thermal conductivity of the composites increased with the increase of filler loading as expected. With the introduction of the filler network 3D-BTA, the thermal conductivity of the resin was remarkably enhanced, which was significantly higher than that of the composites (BTA/EP) with randomly distributed fillers. The thermal conductivity of 3D-BTA3/EP reached 3.08 Wm<sup>-1</sup>K<sup>-1</sup>, approximately 15 times higher than that of pure epoxy resin, and 3 times higher than that of BTA/EP composites with randomly distributed fillers.



Fig. 3: Comparison of thermal conductivity (a) of the 3D-BTA/EP and R-BTA/EP composites; IR images of EP, R-BTA/EP and 3D-BTA/EP during (b) heating processes and temperature changes during (c) heating and (d) cooling

The thermal transfer of the different composites during heating and cooling processes were also monitored by infrared thermography. Fig. 3b shows that the thermal response speed of the composites with a 3D filler network structure during heating was also faster than that of the composites with randomly distributed filler. Fig. 3c-d show the temperature change of the composites during heating and cooling. It can be found that the temperature of composite with integrated filler networks (3D-BTA3/EP) can rapidly rise from 29.8 °C to 78.3 °C within 150 s, which was much more efficient than that of samples with randomly distributed fillers (R-BTA3/EP), further reflecting the superiority of structural design. The thermal response of R-BTA3/EP sample was similar with that of 3D-BTA1/EP sample. Highly thermally conductive composites can be used in a wide range of applications, such as electronic, aerospace and other applications. The outstanding thermal conductivity enables the heat to be diffused in time, ensuring that the equipment remains within a safe temperature range and extending the life of the equipment.

EP, R-BTA/EP and 3D-BTA/EP samples were ignited by alcohol lamp to observe the ignition time and combustion state of samples. It can be found from Fig. 4a that pure EP burned within 20 s and continued to burn intensively even without ignition. In contrast, the ignition time of R-BTA3/EP was extended to 55 s (Fig.4d), which was attributed to the fact that the filler combination of BN, Talc and APP played a positive role in the flame retardancy of the composites, but self-extinguishing property could not achieve when the flame left. Interestingly, the flame retardancy of R-BTA3/EP sample was also similar with that of 3D-BTA1/EP sample, just like thermal response shown in Fig3. Good heat dissipation has been found to be essential in retarding the combustion of composites. When certain part of the composites was overheated, that part of heat can be dissipated in time to avoid excessive accumulation of local heat, leading to the retardation of combustion. Meanwhile, the ignition time of 3D-BTA2/EP and 3D-BTA3/EP was further extended to 64 s and 75 s, respectively, and selfextinguishing occurred after leaving the ignition source as shown in Fig. 4 f-g.



Fig. 4: Flammability test of (a) EP, (b, c, d) R-BTA/EP, and (e, f, g) 3D-BTA/EP

Aiming to assess the stability of residues, the 3D-BTA3/EP sample was ablated in a muffle furnace at 600, 700, 800, 900 and 1000 °C for 30 min. It can be found from Fig. 5a that the sample can maintain its original form without cracks under different ablation temperatures. The colour of the residue gradually turned white as the temperature increased, due to the oxidation of the carbon residue at high temperatures. Fig. 5b-c showed the volume shrinkage and compress strength of 3D-BTA3/EP composite at different temperatures. The degree of volume shrinkage decreased with increasing of ablation temperature, while the compress strength of the residues increased, which was attributed to the ceramifiable reaction. The ceramic skeleton was formed after ablation, which provided mechanical properties for the char layer, and further enhancing the flame resistance of the composite.



Fig. 5: (a) Surface morphology of 3D-BTA3/EP at different temperatures; (b) Volume shrinkage and (c) compress strength of 3D-BTA3/EP after ablation at different temperatures

## 4 CONCLUSIONS

Novel epoxy resin composites featuring high thermal conductivity and flame retardancy were fabricated. The effects of BN, Talc and APP on the heat dissipation, flame retardancy of the composites and fire resistance, shape stability and strength of ablation residues were evaluated. When a certain amount of heat was given to the surface of the composite, the composite with integrated filler network had excellent thermal conductivity, and it was possible to transport the heat on the plane and to the interior in time, avoiding excessive accumulation of local heat, leading to the retardation of combustion.

For sample 3D-BTA3/EP, its thermal conductivity and LOI value reached 3.04 Wm<sup>-1</sup>K<sup>-1</sup> and 37.8%, about 15.2 and 1.9 times of that of pure epoxy, respectively, as well as 3.1 times and 1.4 times of that of sample with random filler distribution. After ablation at 1000 °C, a ceramic-like residue was formed, which exhibited excellent shape stability and good mechanical strength. The mechanism analysis of heat conduction and flame retardancy showed that BN introduced into the network structure had a positive effect on heat transfer, and APP led to the formation of phosphoric acid at high temperature, which could adhere to talc and other residues together. The following ceramifiable reaction led to the generation of a ceramic-like residue, which improving the barrier effect of char layer and fire resistance of the system. This work provides new ideas and approaches for the preparation of epoxy composites with combined thermal conductive, flame-retardant and even fire proofing properties, which may have great applications in new energy transportation and electronic industries.

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