Bubble-templated Construction of Three-dimensional Ceramic Network for Enhanced Thermal Conductivity of Silicone Rubber Composites

Shou-Jun Li\textsuperscript{a,†}, Jing-Chao Li\textsuperscript{a,b,†}, Pei-Zhi Ji\textsuperscript{a}, Wen-Feng Zhang\textsuperscript{a}, Yong-Lai Lu\textsuperscript{a,c,d,*}, and Li-Qun Zhang\textsuperscript{a,c,d}

\textsuperscript{a} State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
\textsuperscript{b} Beijing Key Laboratory of Wood Science and Engineering & MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing 100083, China
\textsuperscript{c} Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China
\textsuperscript{d} Engineering Research Center of Elastomer Materials Energy Conservation and Resources, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

Abstract With the continuous development of the electronics industry, the energy density of modern electronic devices increases constantly, thus releasing a lot of heat during operation. Modern electronic devices take higher and higher request to the thermal interface materials. Achieving high thermal conductivity needs to establish an interconnecting thermal conductivity network in the matrix. For this purpose, the suspension of Al\textsubscript{2}O\textsubscript{3} and curdlan was first foamed to construct a bubble-templated continuous ceramic framework. Owing to the rapid gelation property of curdlan, we can easily remove moisture by hot air drying. Finally, the high thermally conductive composites are prepared by vacuum impregnation of silicone rubber. The result showed that composites prepared by our method have higher thermal conductivity than the samples obtained by traditional method. The thermal conductivity of the prepared composite material reached 1.253 W·m\textsuperscript{−1}·K\textsuperscript{−1} when the alumina content was 69.6 wt%. This facile method is expected to be applied to the preparation of high-performance thermal interface materials.

Keywords Thermally conductive network; Alumina; Curdlan; Thermal conductivity

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INTRODUCTION

With the continuous development of the electronics industry towards high power consumption, integration and miniaturization, the energy density of modern electronic devices has increased significantly, thus releasing a lot of heat during operation. The heat should be removed to avoid local overheating. Otherwise, it often results in the reduction of operating stability and the service life.\textsuperscript{[1−3]} Thermal interface materials play a very important role in thermal management. It is usually filled in the gap between the main heating part and the radiator to eliminate the existing air and increase the effective heat transfer area, thereby increasing the efficiency of the heat transfer.\textsuperscript{[4,5]} Polymer materials, with unique merits such as light weight, electrical insulation, easy processing, and corrosion resistance, are widely applied as thermal interface materials.\textsuperscript{[6]} However, most of the polymer materials, whose thermal conductivities are usually below 0.3 W·m\textsuperscript{−1}·K\textsuperscript{−1}, cannot meet the requirements of the thermal interface materials. Therefore, the design of polymer materials with high thermal conductivity is urgently required.\textsuperscript{[7,8]}

Adding high thermal conducting fillers to the polymer matrix is an effective way to improve the thermal conductivity.\textsuperscript{[9]} Alumina (Al\textsubscript{2}O\textsubscript{3}), boron nitride (BN) and beryllium oxide (BeO) are considered to be suitable fillers for achieving high thermal conductivity and electrical insulation, and are widely used in the preparation of high thermally conductive polymer-based composites.\textsuperscript{[10−12]} However, it has still been a challenge to form an effective thermally conductive path under a low filling loading.\textsuperscript{[10,11]} At present, it is generally believed that the construction of interconnected filler network in polymer matrix is a very effective method for preparing the composites with high thermal conductivity.\textsuperscript{[14−16]} For example, Li \textit{et al.} prepared graphene/alumina-NR rubber composites via a graphene-assisted gel method.\textsuperscript{[17,18]} The GO@Al\textsubscript{2}O\textsubscript{3} hybrid filler was prepared by electrostatic self-assembly, and then the GO is gelled by reduction reaction to form hydrogel. Finally, the natural rubber-based composites were obtained after hot air drying, compression molding, and vulcanization. The thermal conductivity reaches 0.514 W·m\textsuperscript{−1}·K\textsuperscript{−1} at a filler loading of 18 vol%. Song \textit{et al.} constructed porous Al\textsubscript{2}O\textsubscript{3}/SR...
frameworks by chemical foaming method, and then soaked the framework to obtain the composites.\[16\] Firstly, ammonium bicarbonate, alumina and silicone rubber were mixed and stirred together. Then, the decomposition of ammonium bicarbonate was prompt by high temperature to generate foam during solidification. After solidification, a porous framework structure was obtained. When the alumina loading is 32.6 wt%, the composite shows a thermal conductivity of 0.747 W·m⁻¹·K⁻¹ and extremely high electrical insulation performance. Thermal conductive fillers can form thermal conductive paths by the above methods, but there are still some limitations. The filler frameworks constructed by graphene gelation will cause the loss of electrical insulation because of the use of graphene. In the method of the construction of thermal conductive path by foaming of silicone and filler, the filler still has a certain disorder in the framework. Based on the above two methods, we constructed a more orderly filler distribution and obtained better electrical insulation with a low filler loading.

In the field of porous ceramics, surfactants, which can reduce the surface tension of the solution and stabilize the generated foam, are often used to foam inorganic particles.\[20,21\] Surfactants are chosen to foam the thermal conducting fillers to construct a spumescent 3D thermal conducting path, and fix the thermal conducting path through gelation of the curdlan. Curdlan is described as a natural polysaccharide fermented from Alcaligenes faecalis.\[22\] And gelation occurs after its suspension is heated and cooled, which can be achieved by methods such as the physical interaction of hydrogen bonds, etc.\[23,24\] With this characteristic, the foaming structure can be quickly fixed.

In this study, a simple foaming method for constructing 3D alumina thermal conducting paths was proposed, using the gelation of curdlan at heating condition to fix the path to prepare 3D alumina hydrogel. Then, a 3D alumina aerogel was prepared by the simple hot air drying. Finally, the 3D alumina rubber composite was prepared by vacuum assisted impregnation. SEM images confirmed the establishment of thermal conducting paths in the foaming structure. The resultant composite with 69.6 wt% of alumina loading achieved a thermal conductivity of 1.253 W·m⁻¹·K⁻¹, as well as a good electrical insulation performance.

**EXPERIMENTAL**

**Materials**

Alumina (70 μm) was purchased from Beijing JinruiLin Technology Development Co., Ltd (Beijing, China). Polydimethylsiloxane (PDMS) was purchased from Dow Chemical Company. Curdlan was purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Octyl decyl glucoside (APG-0810) was obtained from Shanghai Fine Chemical Co., Ltd. (Shanghai, China).

**Preparation of Alumina Framework Material**

100 mL of deionized water, 1.5 g of octyl decyl glucoside (APG-0810), 4 g of curdlan and a certain amount of alumina were put in the beaker and stirred at 450 r·min⁻¹ for 1.5 h. Heat the beaker containing the mixture at 80 °C, increase the rotate speed to 1200 r·min⁻¹, and wait 10 min for the reaction. The reaction mixture was quickly poured into the molds, and the alumina hydrogel was obtained after the temperature dropped to room temperature. The water-rich hydrogel was dried in a 70 °C drying oven for 2 h to obtain alumina aerogel framework. Put the frameworks into a tube furnace with N₂ and heat them at 500 °C for 30 min.

**Preparation of Al₂O₃ Gel Composite**

First, the solidified PDMS and the catalyst were mixed evenly in a ratio of 10:1. Then put the framework into the mixed PDMS glue solution, and impregnate for 6 h by assistance of vacuum. After impregnation, the framework was taken out and placed in a drying oven of 80 °C for 1.5 h to obtain the cured alumina silicone rubber composite. And alumina/PDMS random blend composites were prepared for comparison.

**Characterization**

The Hitachi S-4700 scanning electron microscope from Japan was used to observe the microstructure of alumina framework materials and alumina gel composites. The STARe SW 14.00 thermogravimetric analyzers from Switzerland were used to analyze the thermal stability of composites and the mass fraction of alumina. The thermal conductivity of the composite was measured by a DRL-II thermal conductivity tester from China. The volume resistivity of the composite was measured with a PC68 digital insulation resistance tester from China and a high resistance meter.

**RESULTS AND DISCUSSION**

**Microstructure of Al₂O₃ Gel Composites**

Fig. 1 shows the process of preparing alumina gel composites by foaming. First, the alumina and curdlan are mixed and stirred at a low speed to obtain a uniform suspension. Then, the suspension was placed in an 80 °C water bath and stirred at 1200 r·min⁻¹ for 10 min. When the suspension of curdlan is heated, gelation will occur with increasing temperature. The suspension will be converted to a reversible gel below 80 °C and to an irreversible gel at 80 °C or above. The hydrogen bonds among the three curdlan chains entangle each other to form a triple helical structure, and then each glucose residue in the helix binds two molecules of water. After the reaction, it was cooled to room temperature, and an alumina hydrogel was formed. Then, it is dried by heated air to obtain alumina aerogel. In this way, a complete 3D thermal conducting path is constructed through the foaming method and the heated air-drying method. The addition of surfactant reduces the surface tension of the suspension. Foam is generated at the gas-liquid interface by stirring. The surfactant stabilizes the generated foam. During stirring, alumina and curdlan are repelled into the foam. This foaming structure can be fixed due to the rapid gelation characteristics of the curdlan.

Figs. 2(a)–2(d) show SEM images of the frameworks with different alumina mass fractions. It can be seen that, as the mass fraction of alumina increases, the foaming structure is gradually improved, and there are fewer and fewer openings in the wall of foam. In other words, the thermal conducting path is gradually improving. The existence of openings is due to the fact that the foams are stabilized by surfactant rather than thermodynamics, and thus the merging and coarsening are likely to occur.\[15\] However, these openings provide con-
Fig. 1  Schematic diagram of 3D-Al₂O₃-PDMS preparation process.

Fig. 2  SEM images of alumina gels: (a−d) alumina gels with different alumina contents, (e, f) the cells on them, (g−i) alumina gels heated in nitrogen at 500 °C.

Convenience for the preparation of the alumina gel composites. Figs. 2(e) and 2(f) show SEM images of openings in the wall of foam. The figure shows the existence form of the curdlan and alumina, i.e., the alumina particles are attached to the curdlan. And the internal foaming structure can be observed through the openings. Figs. 2(g)−2(i) show SEM images of the alumina framework after burning in a nitrogen atmosphere at 500 °C, aiming to remove the curdlan and compare whether the existence of curdlan will affect the thermal conductivity after the composite is compared. It is obvious that after the treatment, the curdlan has disappeared, and the openings in the wall of foam have become larger. During the removal of curdlan, a part of the alumina should fall off, which may be a very small amount but may cause some damages to the thermal conducting path.

Then, the microstructure of the composites is discussed. Fig. 3(a) presents an element map of the cross section of the composite. The elements, such as silicon, aluminum and oxygen, were analyzed. The map shows that aluminum is distributed around the silicon, which means the distribution of the alumina framework is around the silica gel. This result proves that the PDMS is successfully injected into the framework through vacuum impregnation, and that there is no obvious defect between silica gel and alumina framework. Figs. 3(b)−3(d) show SEM images of the cross section of the alumina gel composite, among which Figs. 3(c) and 3(d) are
respectively the composite prepared by impregnating silica gel directly into the alumina framework and the composite by burning the alumina framework and then impregnating the silica gel. A regular shape can be seen in a cross-section of the silica gel from Fig. 3(c), while the shape of the silica gel cross section in Fig. 3(d) is not so. The comparison of the two gave a speculation that curdlan will support the alumina to some extent to help its adhesion to curdlan. And if the curdlan is removed, the strength of the framework material will be reduced partly. Due to the pressure or capillary force, some damages took place in the weak part of the framework during the impregnation process. But with those damages, the alumina framework still remains a continuous structure and can be used as a continuous thermal conducting path.

**Fig. 3**  3D-Al₂O₃-PDMS microstructure. (a−c) SEM images; (d) SEM image of 3D-Al₂O₃-PDMS and EDS mapping images of Si, Al and O.

**Thermal Stability of Al₂O₃ Gel Composites**

The thermogravimetric curves of the composites are shown in Fig. 4. It is assumed that the alumina will not change in quality when heated to 800 °C. It is known that the residual value of pure PDMS at 800 °C is 26.7%. The formula is used to roughly estimate the mass fraction of alumina in the composite, in which x is the residual mass fraction of samples with different alumina addition amounts, and y is the calculated mass fraction of alumina in the corresponding composite. It is calculated that the mass fractions of alumina in the composites with initial addition amounts of 100, 200, 300 and 400 g are 22.5 wt%, 41.1 wt%, 64.0 wt% and 69.6 wt%, respectively. Several samples are named as 3D-Al₂O₃-PDMS-X, among which X are described as the mass fraction of each sample. The thermogravimetric curves tell that the thermal stability of several composites is higher than that of pure silica gel. Taking the temperature at which the mass fraction is lost by 5% as the decomposition temperature, the decomposition temperature of silica gel falls into 393.56 °C. And the decomposition temperatures of several composites elevated by 14.52, 41.45, 59.30 and 66.35 °C with the increase of alumina loading, showing that the establishment of 3D thermal conducting path can improve the thermal stability of the composites. According to the results of thermogravimetric analysis and calculation, the alumina composites prepared by random blending method are used as reference samples. Several samples are named as R-Al₂O₃-PDMS-X, among which X refers to the mass fraction of each sample.

**Fig. 4** Thermogravimetric curves of 3D-Al₂O₃-PDMS.

**Thermal Conductivity of Al₂O₃ Gel Composites**

Fig. 5(a) shows the thermal conductivity of the 3D-Al₂O₃-PDMS and random Al₂O₃-PDMS as a function of filler loading. The thermal conductivity of the composites prepared by the two methods gradually increased with the increase of alumina mass fraction. It is reasonable that the larger the mass fraction of the filler is, the more thermal conducting paths are formed in the matrix. The phonons are gradually changed from passing through the matrix and the filler alternately, to passing the connected filler network more. When the content of alumina is increased from 22.5 wt% to 69.6 wt%, the thermal conductivity of the composites prepared by simple blending method is raised from 0.34 W·m⁻¹·K⁻¹ to 0.97 W·m⁻¹·K⁻¹, while that of 3D-Al₂O₃-PDMS composite is from 0.39 W·m⁻¹·K⁻¹ to 1.25 W·m⁻¹·K⁻¹. In order to prove the certain advantages of our thermal conductive composites, some published studies on thermal conductive composites filled with alumina are listed in Table 1.

As shown in Table 1, compared with some published research results, our composites show better thermal conductivity. It indicates that the thermal conducting path constructed by our foaming method is effective. With the increase of the mass fraction of alumina, the thermal conductive paths are gradually constructed, thus greatly improving the thermal conductivity. The composite material prepared by the alumina framework without curdlan shows the same trend. The result revealed that the thermal conductivity can be affected a little by the removal of curdlan, but will be improved under a lower alumina loading. The reason for this phenomenon may be that, we speculated, the structure of the thermal conducting path itself is not perfect due to the low alumina loading rate. Therefore, the negative effects of removing the curdlan on the framework will not be particularly obvious. Moreover, a small amount of carbon may remain in the framework after the removal, which may be the cause for the positive effect.

The Agari model was used to analyze the data, which can
log\(\lambda\) = \(V\cdot C_2 \cdot \log\lambda_2 + (1 - V)\cdot \log(C_1 \cdot \lambda_1)\)  

(1)

where \(V\) is the volume fraction of filler, \(\lambda\), \(\lambda_1\), and \(\lambda_2\) represent the thermal conductivities of the composite, polymer matrix (PDMS, 0.25 W·m\(^{-1}\)·K\(^{-1}\)) and the filler (Al\(_2\)O\(_3\), 30 W·m\(^{-1}\)·K\(^{-1}\)), respectively. \(C_1\) is the factor that affects the crystal size of the polymer, and \(C_2\) is the freedom factor that forms the thermally conductive particle chain. The closer the value of \(C_2\) is to 1, the easier the filler particles form a thermal conducting path.\(^{[34,35]}\)

Taking 1 as the value of \(C_1\), we predicted the thermal conductivity of composites with different filler volume fractions with the Agari model. Fig. 6 shows that as the filler volume fraction increases, the predicted value becomes closer and closer to the actual value. The larger \(C_2\) value of the composites containing the 3D filler network indicates a better thermal conducting path.

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Table 1  
Research results reported on thermal conductive composites filled with alumina.

| Filler          | Matrix | Loading | \(\lambda\) (W·m\(^{-1}\)·K\(^{-1}\)) | Ref.  |
|----------------|--------|---------|-------------------------------------|-------|
| Al\(_2\)O\(_3\)| Epoxy  | 70 wt%  | 0.447                               | [26]  |
| Al\(_2\)O\(_3\)| SR\(^a\) | 70 wt%  | 0.78                                | [27]  |
| Al\(_2\)O\(_3\)| Epoxy  | 75 wt%  | 1.19                                | [28]  |
| Al\(_2\)O\(_3\)| PR\(^b\) | 70 wt%  | 1.1                                 | [29]  |
| Al\(_2\)O\(_3\)| Epoxy  | 48 vol% | 1.03                                | [30]  |
| Al\(_2\)O\(_3\)+AgNP| Epoxy | 70 wt%  | 1.304                               | [1]   |
| Al\(_2\)O\(_3\)| PLA\(^c\) | 70 wt%  | 0.82                                | [31]  |
| Al\(_2\)O\(_3\)| Epoxy  | 35 vol% | 0.83                                | [32]  |
| Al\(_2\)O\(_3\)| PDMS   | 69.6 wt%| 1.253                               | This work |

\(^{a}\) Silicone rubber; \(^{b}\) Phenolic resin; \(^{c}\) Polylactic acid.

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Fig. 5  
(a) Thermal conductivities of 3D-Al\(_2\)O\(_3\)-PDMS and Al\(_2\)O\(_3\)-PDMS; (b, c) Surface temperature curves and thermal infrared imaging of 3D-Al\(_2\)O\(_3\)-PDMS, Al\(_2\)O\(_3\)-PDMS and PDMS.

Fig. 6  
Thermal conductivities of three composite materials and theoretical curve predicted by Agari model.

We heated the lower surfaces of alumina gel composites, random blending composites and pure silica gel samples separately of the same mass fraction, and monitored the temperature changes on the upper surfaces of them. As shown in Fig. 5(c), the thermal conductivity of the alumina gel composite has obvious advantages within the first 100 s compared to that of the simple blending composite, which indicates a faster temperature response of alumina gel composite. After 100 s, the temperature change tends to be stable, and the thermal conduction gradually reaches equilibrium.

**Finite Element Simulation**

The heat transfer processes of 3D-Al\(_2\)O\(_3\)-PDMS and Al\(_2\)O\(_3\)-PDMS can be simulated by finite element simulation. The two models
have the same alumina content of 36 vol%, and the same width. The left end of the two models was heated to the same temperature to simulate the heat transfer process. It can be seen from Figs. 7(a) and 7(b) that, at the same distance, the 3D-Al$_2$O$_3$-PDMS simulation diagram with 3D thermal conduction network shows a higher temperature, indicating a higher thermally conductive efficiency. As shown in the heat flow simulation diagram of the two models in Figs. 7(c) and 7(d), the heat flow in 3D-Al$_2$O$_3$-PDMS is more obvious than that in Al$_2$O$_3$-PDMS.

**Electrical Insulation Properties of Al$_2$O$_3$ Gel Composites**

For thermal management applications of most electrical devices, a high enough electrical resistivity is of significance for the thermally conductive composites. Generally speaking, electrical insulation refers to that the volume resistivity is greater than 10$^9$ Ω·cm. The result shows that the volume resistivity of our composites with 22.5 wt%, 41.4 wt%, 64.0 wt% and 69.6 wt% mass fraction are 1.09×10$^{11}$, 1.89×10$^{11}$, 2.97×10$^{11}$ and 5.87×10$^{11}$ Ω·cm, respectively. All the samples meet the requirements of electrical insulation.

**CONCLUSIONS**

In summary, we prepared the filler frameworks by a simple foaming method and successfully prepared a composite with high thermal conductivity. The reason for the increased thermal conductivity falls into the fact that the filler framework can act as a complete thermal conducting path in the matrix. The thermal conductivity of the prepared composites reached 1.253 W·m$^{-1}$·K$^{-1}$ when the alumina content was 69.6 wt%. This method may provide some ideas for the development of new thermal interface materials. This study, however, only focuses on a single filler. In the future, it may be possible to use hybrid fillers, which can achieve a higher thermal conductivity at a low filling amount.

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