

Thermal Conductivity of Epoxy Composites Modified by Microspheric Molybdenum Disulfide

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Research Article

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Abstract

In order to improve the thermal conductivity of epoxy resins (EP) without reducing their dielectric properties, a kind of molybdenum disulfide with microspheres structure (S-MoS₂) was prepared via surfactant promoting hydrothermal process based on the sodium molybdate, thiosemicarbazide, and sodium dodecyl sulfate. The S-MoS₂ was then used as modifiers to add into EP matrix to prepare a new kind of S-MoS₂/EP composites. The morphology of the prepared S-MoS₂ was observed by X-ray diffraction (XRD) scanning electron microscopy (SEM), while the influence of different S-MoS₂ loading on the dielectric properties, thermal conductivity and thermal resistance of S-MoS₂/EP composites was also researched. The results suggested that the reasonable content of S-MoS₂ can highly improve the thermal conductivity of S-MoS₂/EP, which can be attributed to the excellent thermal resistant and uniform dispersion of S-MoS₂ in EP matrix.

1. Introduction

Epoxy resin (EP) is a kind of commonly used materials with high mechanical properties, low creep tendency, excellent resistance to chemical corrosion and thermal deformation [1–2], thus it has been widely used in electronic and electrical materials. However, the traditional EP exhibits the poor thermal conductivity, it could not transfer heat in time when used as a micro-electronic component, which is easy to cause damage to the material itself. Therefore, it needs to be further modified [3–4]. Modification of epoxy resin can be divided into chemical method and physical method [5–6]. The chemical method is to introduce heteroatoms or functional groups into the EP molecular chain segment to improve its thermal conductivity [7], and the physical method is to add a variety of other thermal conductivity fillers or additives into the EP matrix [8]. Among which, the preparation of filled thermal conductivity EP composites has the advantages of flexible material selection, simple process and obvious improvement of thermal conductivity [9]. Commonly used thermal conductive fillers are boron nitride and aluminum nitride, carbon fiber, steel fiber, etc [10]. Although these packing add significantly can improve the thermal conductivity of EP resin, they also affect the mechanical properties and other performance of EP to a certain extent [11]. Therefore, how to reduce the additional damage of thermal conductive filler to EP resin in the maximum extent, the selection and modification of thermal conductive fillers should be further studied.

Molybdenum disulfide (MoS₂) has attracted extensive attention because of its unique three-layer structure (Mo atoms sandwiched between two layers of S atoms) [12], and its electronic, optical and mechanical properties are comparable to those of graphene [13]. In addition, as a transition metal disulfide compound, MoS₂ also has the characteristics of high electron mobility, valley polarization, strong orbital coupling, strong mechanical strength, excellent thermal conductivity, etc. [14–15], which can be used as an improver for electronic devices. Furthermore, MoS₂ with apparent closed structure (spherical or tubular) not only has the chemical structure and physical properties of traditional MoS₂, but

also has high chemical stability and thermal resistance, so it can be widely used in catalysts, supercapacitors, lithium ion batteries, solid nano lubricants and other fields [16].

From what has been discussed above, a new kind of MoS₂ particles with microspheres structure (S-MoS₂) was prepared via a hydrothermal process in this article. The surface-active agent sodium dodecyl sulfate was used as promoting additive, the TiO₂ were used as carries, while the sodium molybdate, thiosemicarbazide were used as raw materials to prepare the S-MoS₂. The S-MoS₂ was then added into EP as modifiers to prepare S-MoS₂/EP composites. The dielectric properties, thermal conductivity and thermal resistant properties of the S-MoS₂/EP composites were measured to study the effect of S-MoS₂ on the EP resins. This study is aiming to provide a new method for the development of a high thermal conductive resin that can be used in microelectronic component fields.

2. Experimental Methods

2.1 Materials

The EP resin (the purity of > 95 wt%) were purchased from Nantong Xingchen Synthetic Material Co. Ltd. The isophorone diamine (analytical pure) was purchased from Shanghai McLean Biochemical Technology Co., Ltd. The raw materials to prepare S-MoS₂ are sodium molybdate and ammonium thiourea (the purity was > 98%, purchased from Jingzhou fine chemical co., Ltd). The TiO₂ powder was purchased laboratory-made via hydrothermal method. The other reagents and solvents used in the experiments including: sodium dodecyl sulfate, hydrazine hydrate, chlorhydric acid, ethanol, and acetic acid, which were supplied by Tianjin Fuchen Chemical Reagents Factory without further purification.

2.2 Preparation of the S-MoS₂/HNS

The S-MoS₂ was prepared by hydrothermal method. 0.484 g sodium molybdenate, and 0.364 g thiourea were added into the autoclave with polytetrafluoroethylene substrates, while 20 mL sodium dodecyl sulfate solution (which concentration is 0.016 mol/L) and 1g TiO₂ are also added into the autoclave. The autoclave was put into a high-pressure steam, 220°C for 24 h. The autoclave was then cool to room temperature, and the mixture was purred out. The mixture was cleaned by deionized water and anhydrous ethanol for 5 times, and the then dried at 50 °C for 12 h in a vacuum. The products S-MoS₂ were finally obtained after calcined at 500 °C.

2.3 Preparation of the S-MoS₂/EP composites

The S-MoS₂/EP composites were prepared via a casting method, and the preparation process is shown in figure 1. The EP were stirred in a glass beaker with isophorone diamine at 40 °C, and S-MoS₂ (the mass ratio is 0.0 wt%, 1.0 wt%, 2.0 wt%, 3.0 wt%, 4.0 wt%, and 5.0 wt%) were added into the EP, respectively. These mixtures were ultrasonic dispersed for 15 mins to obtain the well-dispersed matrix. The matrixes were then stirring under 40 °C until the pre-polymer completely dissolved, and the pre-polymer was

poured into a pre-heated mould with a release agent and degassed at 50 °C for about 30 mins in a vacuum drying oven. Finally, the mould with pre-polymer was put into a blast drying oven, and the cured process is 80 °C/1 h + 100 °C/1 h + 120 °C/2 h.

2.4 Measurements

The X-ray diffraction (XRD)

The X-ray diffraction (Bruker D8, Germany) was chosen to research the crystal structure of S-MoS₂ at room temperature.

Scanning electron microscopy (SEM)

The S-3400N scanning electron microscope (HITACHI, Japan) was chosen to observe the morphology of S-MoS₂, and the surface morphology of the fractured surface of the EP and S-MoS₂/EP samples at room temperature.

Dielectric properties

The dielectric properties of EP and S-MoS₂/EP samples were measured by dielectric constant dielectric loss tester (ZJD-A type, China Aviation Times Company).

Thermal conductivity

The thermal conductivity were measured by transient fast hot wire method of thermal conductivity tester (KDRX-Ⅱ, Xiangtan Xiangyi Instrument Co., Ltd, China).

Thermal resistant properties

The thermogravimetric analysis (TGA) was determined by a TGAQ50 in a nitrogen atmosphere, the heating rate is 20 °C min⁻¹.

The differential Scanning Calorimeter (DSC) was determined by a DSC-2910 in a nitrogen atmosphere, the heating rate is 15 °C min⁻¹.

3. Results And Discussion

3.1 Morphology structure of the S-MoS₂

The crystallographic structure of S-MoS₂ was studied by X-ray diffraction (XRD), the results are shown in Fig. 2. As can be observed from the Fig. 2, there are nine diffraction peaks appeared at $2\theta = 25.05^\circ$, 38.31° , 48.56° , 53.56° , 55.77° , 62.18° , 68.71° , 72.19° , 75.91° can be correspond to standard spectrum (21-1272) of anatase TiO₂ which is (101), (004), (200), (105), (211), (204), (116), (220) and (215), respectively,

indicating that there are some TiO_2 particles in the system. Meanwhile, there also the five different diffraction peaks appeared at $2\theta = 12.13^\circ, 29.12^\circ, 45.54^\circ, 52.17^\circ, 58.10^\circ$ are correspond to the lattice planes of the hexagonal structure molybdenite, which is (002), (100), (103), (105), and (110) respectively. These results confirmed that the S-MoS_2 has been formed in the system. However, the diffraction peak is not very smooth, and also exist some of messy peaks, indicating that the crystal state of S-MoS_2 is not very uniform. This phenomenon is due to the inhomogeneous structure of the synthesized S-MoS_2 system and the existence of a few impurities in the system.

To further research the morphology of S-MoS_2 , and scanning electron microscopy (SEM) was used and the result was shown as Fig. 3. As can be seen from Fig. 3A, the particle size of the powders is relatively uniform and presents the fluffy state, but there is still a small amount of S-MoS_2 agglomeration, which is caused by the hydroxyl group on the surface of the S-MoS_2 prepared by hydrothermal method. In addition, it can be observed that most of the particles show a relatively obvious spherical closed structure, indicating that the prepared S-MoS_2 is spherical structure. The remaining small amounts of particles with smaller particle size is carrier TiO_2 . In order to further observe the apparent morphology of the prepared S-MoS_2 , Fig. 2 shows the high-magnification SEM of Fig. 1. As can be seen from Fig. 2, S-MoS_2 has formed a good closed spherical structure, and its surface is relatively smooth, without load impurities. The above conclusions indicate that the prepared S-MoS_2 has a smooth and relatively uniform spherical structure

3.2 Dielectric properties of the materials

The dielectric constant of $\text{S-MoS}_2/\text{EP}$ composites with different content of S-MoS_2 . As can be seen from Fig. 4, with the increase of S-MoS_2 content, the dielectric constants of $\text{S-MoS}_2/\text{EP}$ composites exhibit the increasing trend. This is because as a metal sulfide, the dielectric constant of MoS_2 itself is higher than that of pure EP matrix, meanwhile, the addition of S-MoS_2 can affect the transport ability of the inner sub-chain segments of cyclic oxygen lipid, thus the polarization is easier to establish, leading to the increase of dielectric constant. In addition, it can also be observed that all of these $\text{S-MoS}_2/\text{EP}$ composites with different S-MoS_2 loading do not show obvious frequency dependence, indicating that that the polarization of the interface between S-MoS_2 and EP matrix can always keep up with the change rate of the applied electric field, which can be attributed to the unique spherical structure of S-MoS_2 and its good dispersion inside the EP matrix. Furthermore, although the dielectric constant of $\text{S-MoS}_2/\text{EP}$ composites have been improved to a certain extent, they still remain in a relative low range, which is owing to the independent state of S-MoS_2 with each other in the resin matrix, thus they do not form a leaky conductive path to become conductive materials. The relatively low dielectric constant of $\text{S-MoS}_2/\text{EP}$ composites can greatly meet the needs of their use in high frequency insulating electronic material.

By observing the curves of the dielectric loss of $\text{S-MoS}_2/\text{EP}$ composites changing with frequency (Fig. 5), it can be concluded that the dielectric loss of $\text{S-MoS}_2/\text{EP}$ composites has been greatly improved after the

addition of S-MoS₂. This is because the interface polarization of S-MoS₂ inside the EP resin increases their dielectric loss. In addition, the dielectric loss of both EP and S-MoS₂/EP composites increases with the increase of frequency, which is mainly because with the increase of frequency, the movement of polar molecules inside the S-MoS₂/EP composites gradually accelerates, and the heat generated by the friction between molecular chains increases. The interfacial polarization and internal molecular polarization also increase, which leads to the increase of dielectric loss of S-MoS₂/EP composites.

3.3 Thermal conductivities of the materials

As shown in Fig. 6, the influence of S-MoS₂ content on the thermal conductivity of S-MoS₂/EP composites is studied. As can be seen from the figure, the thermal conductivity of S-MoS₂/EP composites increases with the increase of the content of S-MoS₂. When the content of S-MoS₂ is 3.0 wt%, the thermal conductivity reaches the maximum of 0.3061 W/mk, which is 80.05 % higher than that of pure EP resin (0.1700 W/mk). These results suggesting that the thermal conductivity of EP can be significantly improved by adding S-MoS₂ appropriately. The enhancement of thermal conductivity of S-MoS₂/EP composites can be attributed to the excellent thermal conductivity of S-MoS₂ itself. However, when the content of S-MoS₂ continues to increase, the thermal conductivity of the S-MoS₂/EP composites does not further increase, and even slightly decreases. This is because when the content of S-MoS₂ is appropriate, it can be uniformly dispersed inside the EP resin, and its spherical surface can also provide a larger surface area for heat transfer, thus the thermal conductivity of the composite material increases. Whereas when the content of S-MoS₂ is too large, they are easy to agglomerate in the EP matrix and form a few voids, so their performance of thermal conductivity is greatly affected.

In order to further investigate the reasons for the improvement of S-MoS₂ on thermal conductivity of S-MoS₂/EP composites, the fracture morphology of EP resin and S-MoS₂/EP composites filled with 3.0 wt% S-MoS₂ was observed by SEM. As can be seen from Fig. 7, the fracture surface of EP is relatively smooth and there is no particulate matter, indicating that its heat conduction mainly depends on the crosslinking structure of epoxy resin. But for the S-MoS₂/EP composite, its fracture surface is very rough, with obvious bulges and some granular materials, which proves the existence of S-MoS₂ in the EP matrix. In addition, the distribution of these particles is relatively uniform, no obvious agglomeration phenomenon, indicating that at 3.0 wt % content, S-MoS₂ can be uniformly dispersed in the EP resin, so as to provide a good path for heat conduction (the thermal conductivity mechanism of EP and S-MoS₂/EP composites is shown in Fig. 8).

3.3 Thermal resistant of the materials

The thermogravimetric analysis (TGA) results of pure EP resin and S-MoS₂/EP composite resin with 3.0 wt% S-MoS₂ content are shown in Fig. 9. It can be seen from the figure that the initial decomposition temperature of the S-MoS₂/EP composite is 302°C, which is lower than that of pure EP resin (325°C) to a

certain extent, indicating that the addition of S-MoS₂ can promote the curing process of EP resin. At 800°C, the carbon residual rate of the S-MoS₂/EP composite is 20.53%, which is 271% higher than that of pure EP resin (5.52%). This high carbon residual rate indicates that the composite has higher thermal stability after the addition of S-MoS₂. This phenomenon can be attributed to the high heat resistance of S-MoS₂ itself and the spherical structure of S-MoS₂ which allows heat to transfer well within the EP resin. High heat resistance is also very beneficial to the improvement of its thermal conductivity, which can effectively reduce the damage of external heat to the material when it is subjected to heat.

The reciprocal TG results (DTG) of the above pure EP resin and the S-MoS₂/EP composite containing 3.0 wt % S-MoS₂ were calculated respectively, and the results were shown in Fig. 10. As can be seen from the figure, the trends of the two curves are similar, and there is only one obvious thermal decomposition peak in both curves. These results indicate that the addition of S-MoS₂ does not significantly change the thermal decomposition mechanism of EP resin, and there is only one main thermal decomposition reaction. In addition, the thermal decomposition temperature of EP is 383°C, while that of the S-MoS₂/EP composite is 318°C, indicating that S-MoS₂ can reduce the thermal decomposition temperature while improving the thermal resistance of the S-MoS₂/EP composite.

4. Conclusion

A kind of molybdenum disulfide with microspheres structure (S-MoS₂) was prepared via surfactant promoting hydrothermal process, and the S-MoS₂ was then used as modifiers to add into EP matrix to prepare a new kind of S-MoS₂/EP composites. The results show that the dielectric constant of the S-MoS₂/EP composite increases and the dielectric loss can be kept at a low level after adding appropriate S-MoS₂. In addition, when the amount of S-MoS₂ is 3.0 wt%, the thermal conductivity reaches the maximum of 0.3061 W/mk, which is 80.05 % higher than that of pure EP resin (0.1700 W/mk), and their thermal resistant are also increased. The enhancement of thermal conductivity on S-MoS₂/EP composites can be attributed to the high thermal conductivity of S-MoS₂, as well as its spherical structure to facilitate heat transfer, and the high heat resistance of S-MoS₂/EP composites is also very beneficial to the improvement of its thermal conductivity.

Declarations

ACKNOWLEDGEMENTS

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Figures



Figure 1

The preparation process of S-MoS₂/EP composites

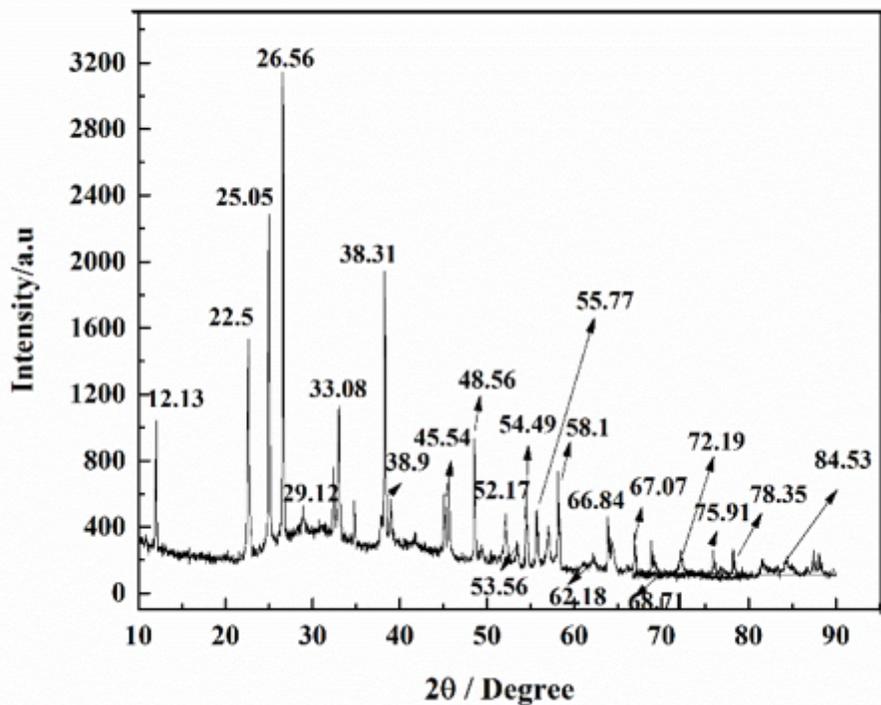


Figure 2

The XRD result of S-MoS₂

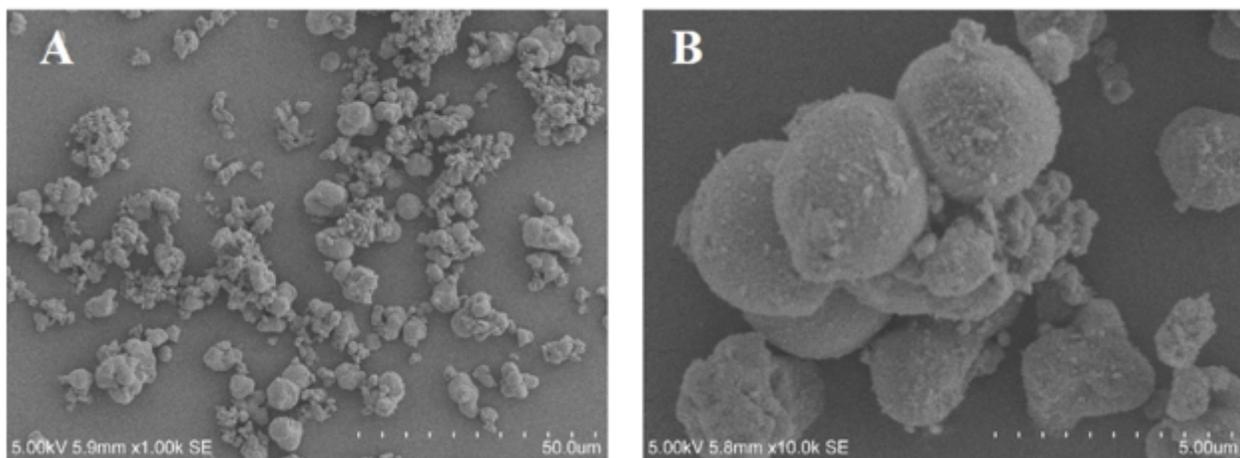


Figure 3

The SEM of S-MoS₂

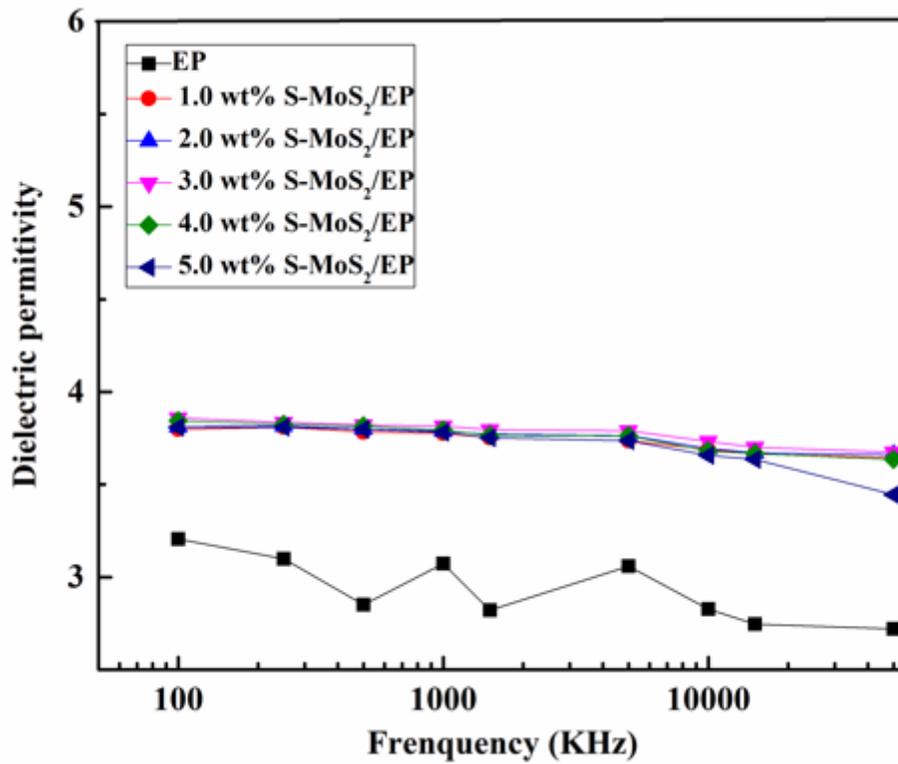


Figure 4

Theof S-MoS₂/EP with different content of S-MoS₂ varies by frequency

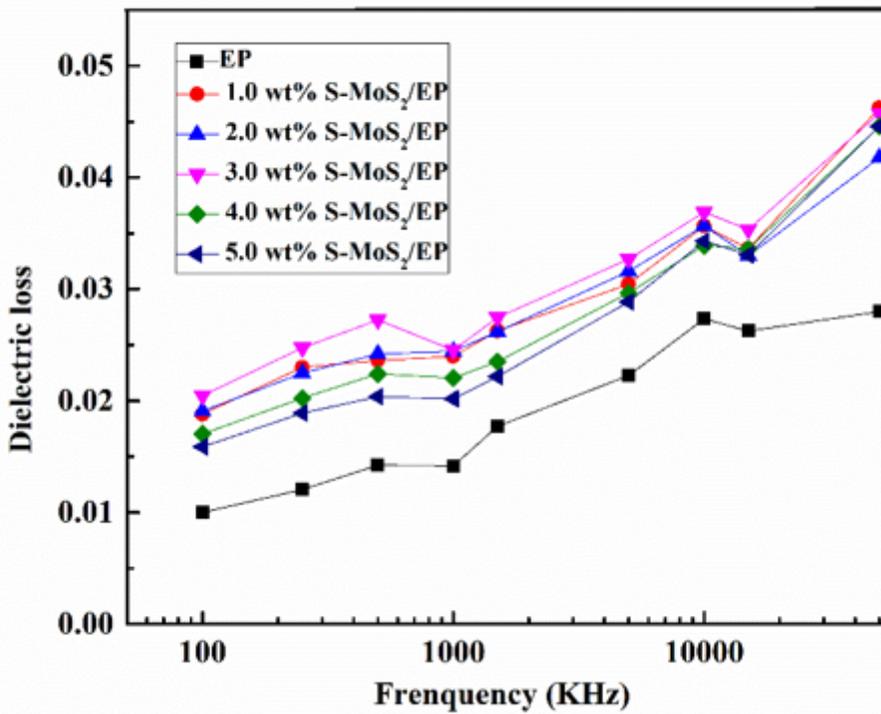


Figure 5

The dielectric loss of S-MoS₂/EP with different content of S-MoS₂ varies with frequency

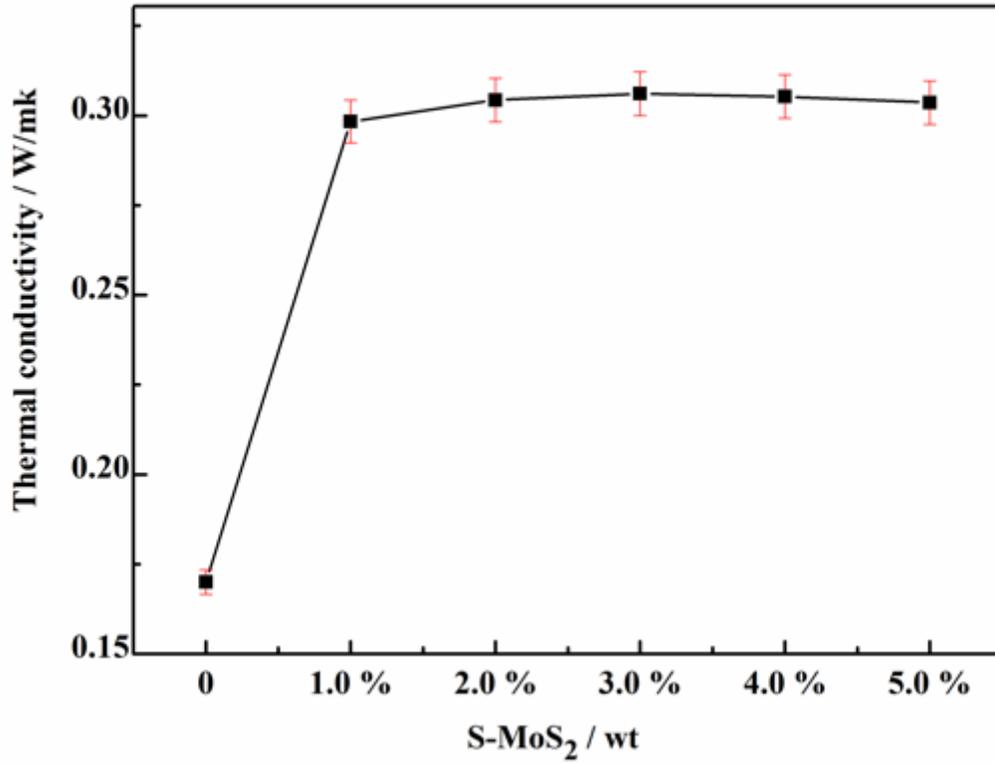


Figure 6

The thermal conductivities of S-MoS₂/EP with different content of S-MoS₂

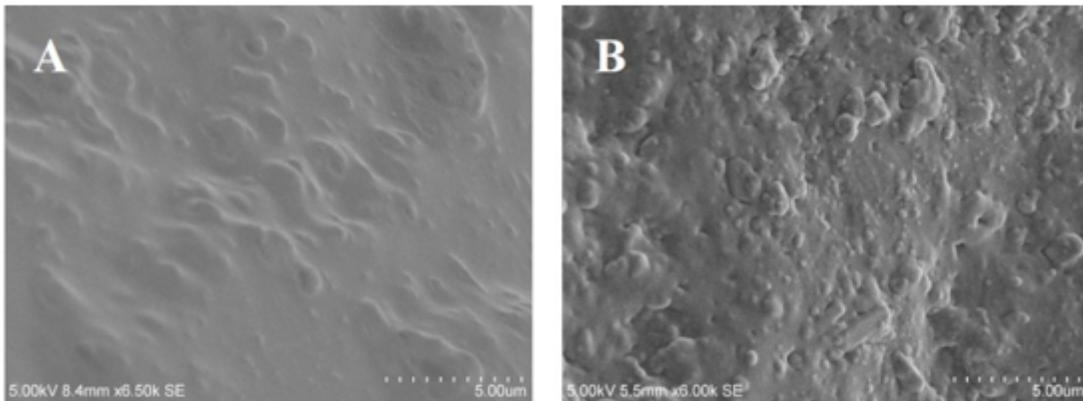


Figure 7

SEM of fracture surfaces taken from the resins (A: EP; B: S-MoS₂/EP composites with 4.0 wt% S-MoS₂)

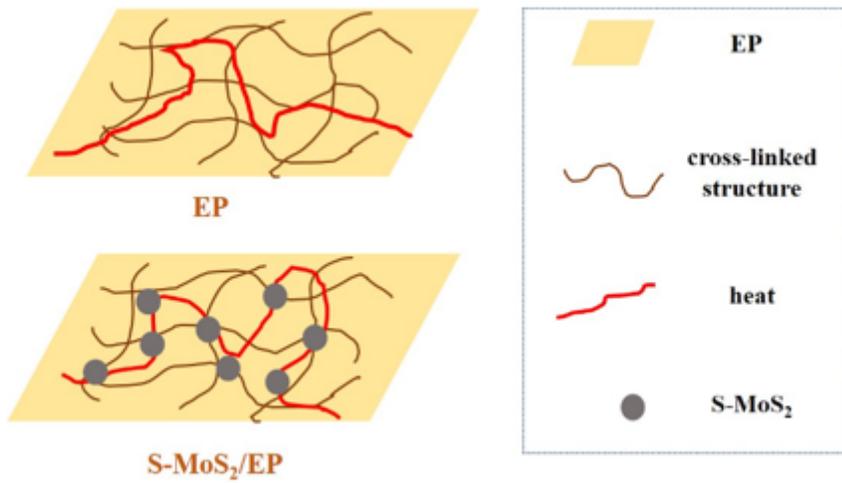


Figure 8

Schematic diagram of heat conduction mechanism

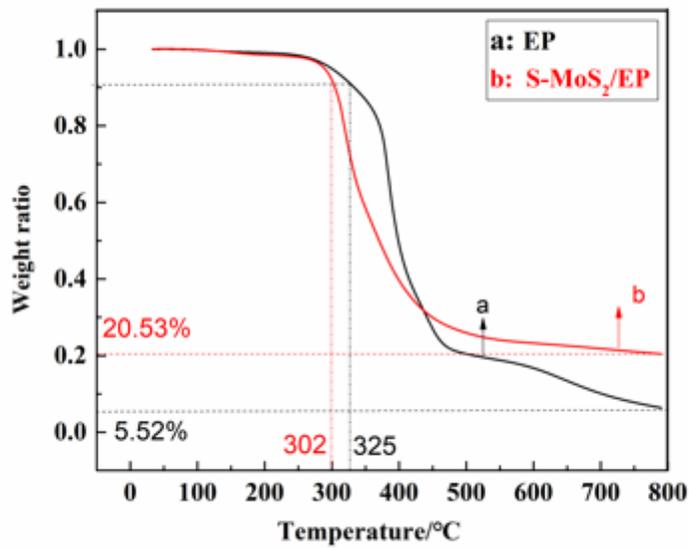


Figure 9

The TGA curve of the EP and S-MoS₂/EP composites with 3.0 wt% S-MoS₂

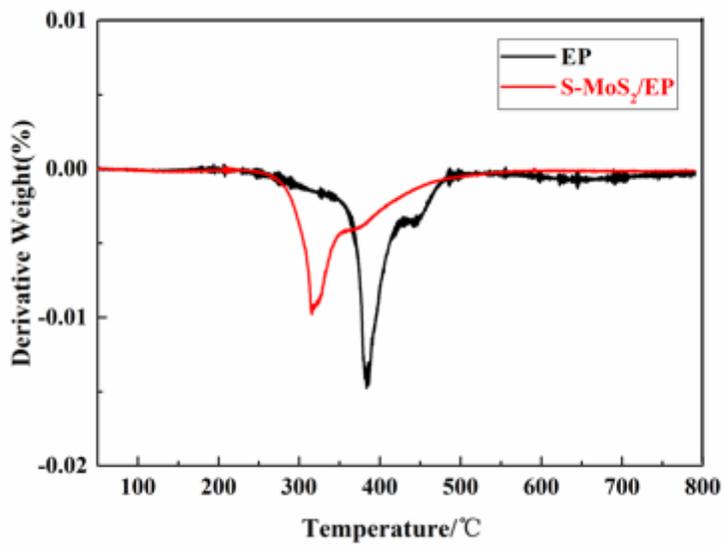


Figure 10

The DTG curve of the EP and S-MoS₂/EP composites with 3.0 wt% S-MoS₂