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Study on Thermomechanical Properties and Morphology of an Epoxy Resin Thermally Conductive Adhesive under Different Curing Conditions

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Cite This: ACS Omega 2024, 9, 11637−11645

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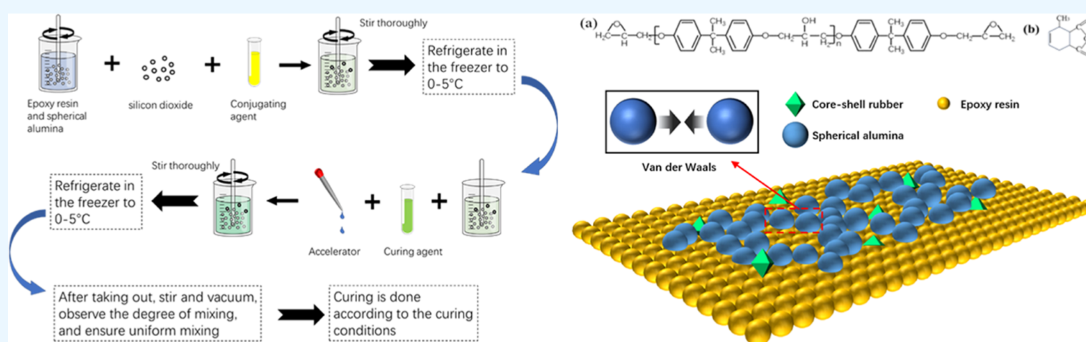

ABSTRACT: An epoxy resin thermally conductive adhesive is a type of thermosetting polymer encapsulation material that exhibits comprehensive performance, and the thermomechanical properties of this adhesive vary significantly under different curing conditions. In this paper, spherical alumina was used as a filler for thermal conductivity to prepare an epoxy resin thermal conductivity adhesive using a multistage freezing mixing method. The effects of various curing conditions on the thermal−mechanical properties and fracture morphology of the epoxy resin thermal conductivity adhesive were studied. The results showed that the curing condition of 150 °C/2.5 h significantly improved the performance of the epoxy resin thermally conductive adhesive. Through the shear test of the composite material, the influence of the curing agent on the adhesion of the thermally conductive adhesive under fixed conditions was explored. It was found that the curing agent with a superbranched structure exhibited latent properties and greatly enhanced the toughness of the cured epoxy resin product. Altering the curing conditions increases the shear strength by up to 307%. With the increase in curing temperature and the extension of curing temperature, the glass transition temperature gradually increased from 103.9 to 159.8 °C. The initial decomposition temperature T_{IDT} gradually increased from 295.4 to 310.1 °C, and the temperature at which the fastest decomposition rate occurs (T_{max}) gradually increased from 312.48 to 330.33 °C. The thermal stability of the substance increased with both temperature and time. The curing time and curing temperature were increased, and the morphology of the fracture of the epoxy resin thermally conductive adhesive cured sample gradually showed a ductile fracture from a typical brittle fracture. The research results reveal the influence of curing conditions on the thermal conductivity and thermal stability of the epoxy resin thermally conductive adhesive, which has a specific reference value for improving the performance of the epoxy resin thermally conductive adhesive, optimizing its usage conditions, and improving production efficiency.

1. INTRODUCTION

With the increasing demand for the integration of electronic devices in the semiconductor industry, traditional heat dissipation materials have been difficult to meet the packaging needs of electronic devices, and epoxy resin-based high-conductivity polymers are more and more widely used in heat dissipation applications because of their excellent insulation, good corrosion resistance, good mechanical strength, and low cost.[1−5] However, the geothermal conductivity of epoxy resin is very low,[6,7] which once limited its application in heat dissipation. In response to this shortcoming, predecessors made an epoxy resin thermally conductive adhesive by adding various thermally

Received: November 9, 2023
Revised: February 6, 2024
Accepted: February 12, 2024
Published: February 27, 2024

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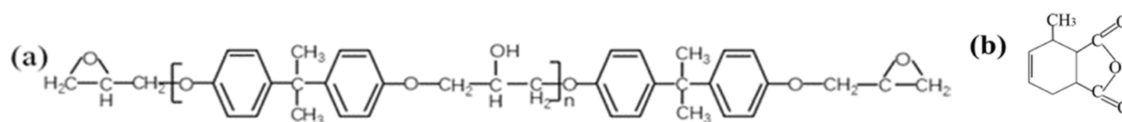

Figure 1. Chemical structure of the epoxy resin (a) and curing agent (b).

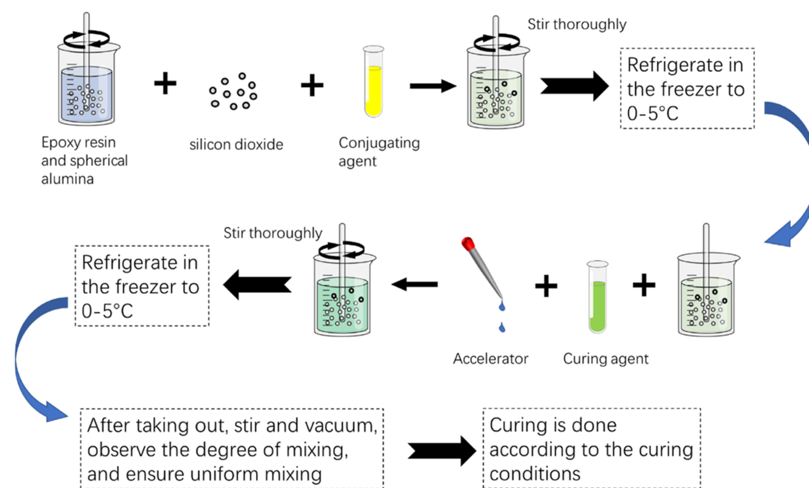

Figure 2. Flowchart of the epoxy resin thermally conductive adhesive prepared by the multistage freeze mixing method.

conductive fillers.[8,9] The addition of a thermally conductive filler should be based on enhancing the thermal conductivity effect and improving the overall performance of the composite material. Thermally conductive fillers can be roughly divided into metal fillers based on Cu, Al, Zn, and alloys;[10,11] inorganic ceramic fillers mainly based on Al_2O_3, ZnO, BN, and SiC;[12−15] carbon fillers based on graphene, carbon nanotubes, carbon nanometers;[16] and some composite fillers.[17,18] As a new type of thermal management material, the epoxy resin thermally conductive adhesive has been widely used in the heat dissipation process of electronic components.[19−22] It has superior thermal conductivity, which can effectively reduce the internal temperature of electronic components and improve the work efficiency and reliability of electronic components. However, while the thermal conductivity increases, the mechanical properties deteriorate due to the high amount of thermally conductive materials.[23] Therefore, adjusting the mechanical properties of epoxy resin thermal adhesives by other means is crucial.

The influence of curing conditions on the mechanical properties of epoxy resin thermally conductive adhesives is one of the less-studied problems. However, the properties of epoxy resin thermal adhesives are greatly affected by curing conditions.[24,25] The curing conditions affect the hardness and glass transition temperature of the epoxy resin thermally conductive adhesive, affecting its thermal conductivity. Therefore, the curing temperature and curing time are quantified,[26,27] and the influence of different curing conditions on the properties of epoxy resin thermally conductive adhesives is studied to guide the thermal management design and manufacture of electronic components.

This paper aims to explore the influence of different curing conditions on the properties of epoxy resin thermally conductive adhesives through experimental research. In the research of previous scholars, the following three experimental ideas are summarized: First, a series of shear tests and dynamic mechanical analysis (DMA) tests are carried out on epoxy resin thermally conductive adhesive samples under different curing conditions, and the mechanical properties of the samples under each curing condition are tested; second, the thermal conductivity and thermal stability of the samples under each curing condition were analyzed by the transient plate heat source method and thermogravimetric (TG) test. Finally, scanning electron microscopy (SEM) analyzes whether the fracture surface is ductile or brittle. Combined with the analysis of thermal conductivity and mechanical properties, the influence mechanism of different curing conditions on the properties of epoxy resin thermally conductive adhesives is revealed, and the thermal management design and manufacture of electronic components are guided. The results of this paper can provide a reference for work on thermal management.

2. SAMPLE PREPARATION AND TESTING

2.1. Sample Materials. Alicyclic epoxy resin 2021P (Nanjing Qiangshan New Materials Co., Ltd.), epoxy resin core−shell rubber toughening agent (Jongyuan, Japan), KBM-403 coupling agent (Shin-Etsu, Japan), pyrogenic silica (Wacker Chemie (China) Co., Ltd.), modified spherical alumina powder (50 μm) (Guangdong Jinge New Materials Co., Ltd.), heat-curing anhydride curing agent (Guangzhou Yihun Sheng Chemical Co., Ltd.), and methyltetrahydrophthalic anhydride latent epoxy curing agent (used as a promoter; Ajinomoto Corporation of Japan) were used. The chemical structures of the epoxy resin and curing agent are shown in Figure 1.

2.2. Sample Preparation. The composite sample preparation process is illustrated in Figure 2. The material was prepared, the resin was rewarmed, the crystals were dissolved, different cycloaliphatic epoxy resin 2021P proportions were weighed, and the toughening agent was mixed. The mixture was manually mixed with a squeegee knife, then modified spherical alumina powder (50 μm) was added, and KBM-403 coupling agent and fumed silica were added. The mixture was put in a blender, stirred evenly, and refrigerated in a freezer to 0−5 °C. After that, a high-temperature curing agent and accelerator were added, and the mixture was refrigerated in a freezer to 0−5 °C. After

https://doi.org/10.1021/acsomega.3c08950
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taking it out, the mixture was stirred under vacuum to observe the degree of mixing and ensure uniform mixing.

The sample was molded and cured under different curing conditions to study how different curing conditions affect the thermomechanical properties and morphology of the thermally conductive adhesive. The prepared samples were molded in an aluminum mold with a diameter of 2.5 mm and a capacity of 5 mL and placed flat in an oven at 100 °C, 2/2.5/3 h; 100 + 150 °C, 2/2.5/3 h; 150 °C, 2/2.5/3 h; and 180 °C, 2/2.5/3 h curing conditions to complete the curing. After taking it out, it was allowed to stand at room temperature, and the sample was demolded for testing.

2.3. Characterization.

2.3.1. Hardness Value. A D-type shore hardness tester was used to test the hardness of the cured samples completed under each curing condition.

2.3.2. Shear Strength. The shear test was performed on an electronic tensile testing machine of the HANDPI model. At a speed of 30 mm/min, the samples of aluminum plates coated with the epoxy thermally conductive adhesive under different curing conditions were tested by displacement control. To improve the measurement accuracy, four samples were tested for each curing condition. When no significant difference existed, the average value was taken as the shear strength under these curing conditions.

2.3.3. Dynamic Mechanical Properties (DMA). The dynamic mechanical properties were carried out on a dynamic thermomechanical analyzer of the DMA 242 E (NETZSCH, Germany) model. Temperature scanning ranged from room temperature to 220 °C, using three-point bending, a heating rate of 5 °C/min, and a frequency of 1 HZ. The sample size was 10 × 10 × 2 (thickness) mm^3.

2.3.4. Thermal Conductivity. The thermal conductivity reflects the thermal conductivity of the substance, and its value can directly reflect the thermal conductivity of the thermally conductive adhesive after curing, which is an essential index for judging the performance of the thermally conductive adhesive. The thermal conductivity test was performed on a Hot Disk TPS 2500S thermal conductivity meter (Hot Disk, Sweden). A curing block with a diameter of $D \geq 2.5$ mm and a thickness of ≥2 mm was prepared. To ensure the accuracy of the experiment, 4 test samples were prepared under each curing condition, and when there was no obvious difference, the average value was taken as the thermal conductivity under the curing condition.

2.3.5. Thermogravimetric Analysis. The thermogravimetric analysis of epoxy resin thermal adhesives was performed by an STA 449 F3 Jupiter synchronous TG-differential scanning calorimetry (TG-DSC) thermal analyzer (NETZSCH, Germany) at a thermal rate of 10 °C/min with a nitrogen stream of 50 mL/min. The solidified block was ground into a powder of 200−250 mesh, and thermal pretreatment was used to remove the thermal history of the sample.

2.3.6. Topography Analysis. The cured sample was frozen in liquid nitrogen for 5 min, taken out, and instantly brittle. The cross section was bonded vertically upward and fixed, a layer of gold powder was evenly sprayed at the fracture, and the fracture morphology of the solidified sample was observed by a Phenom pro benchtop scanning electron microscope (Phenom pro, Netherlands) at room temperature.

3. RESULTS AND DISCUSSION

3.1. Hardness Testing.

Hardness reflects the ability of the material to resist elastoplastic deformation and is a comprehensive index of the material's mechanical properties. The hardness test was carried out six times for each specimen, and the average value was taken as the hardness value of the sample. The results shown in Figure 3 show that the curing hardness of

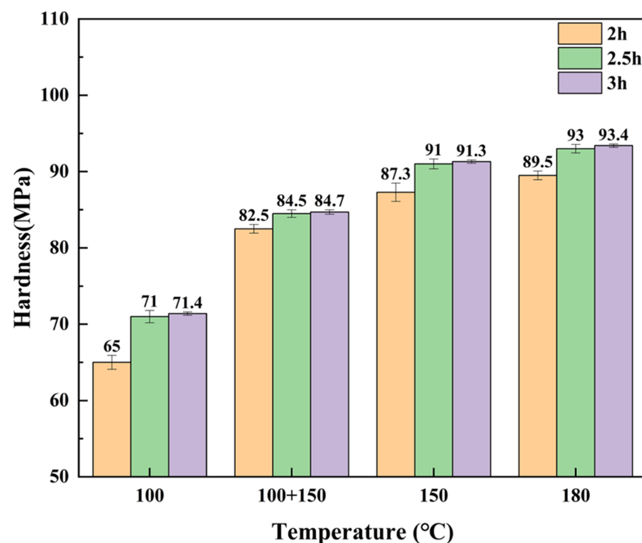

Figure 3. Hardness value of the epoxy resin thermally conductive adhesive under different curing conditions.

the epoxy thermally conductive adhesive is positively correlated with the curing time and curing temperature at the time of curing, and the hardness value of the sample increases with the increase of curing temperature and the extension of curing time. This is related to the degree of epoxy resin cross-linking.[28] The higher the degree of cross-linking of epoxy resin, the denser the internal structure, and the higher the hardness value. Among them, 100 + 150 °C, as one of the commonly used curing temperatures in commercial production, also satisfies this rule, because the heat obtained during the curing process is between 100 and 150 °C alone. This also shows that increasing the heat during the curing process can increase the cross-linking density of the epoxy resin, which, in turn, increases the hardness.

3.2. Shear Strength.

Figure 4 shows the shear strength of the epoxy resin thermally conductive adhesive under different curing conditions. Under the same curing time conditions, the shear strength of the epoxy resin thermally conductive adhesive under different curing conditions increases with the increase in curing temperature, and the amplitude of improvement varies greatly. Under the same curing temperature conditions, the shear strength of 100, 100 + 150, and 150 °C increased with time, but the shear strength of 180 °C became a downward trend. This trend can be attributed to the latent nature of curing agents in epoxy thermally conductive adhesives. At low temperatures, the activity of the curing agent is low.[29] The curing agent fails to function fully, resulting in a poor cross-linking reaction of epoxy resin and low cross-linking density, and with the increase of temperature and time, the curing degree becomes more and more complete,[30] and the shear strength becomes an upward trend.

The reason why the shear strength of the samples cured for 2.5 and 3 h at 180 °C is lower than that of the samples cured for 2 h can be attributed to the large difference between the internal temperature and the external temperature heating rate. When the samples are cured at a higher temperature, the thermal internal stress produced by the nonuniform temperature field is

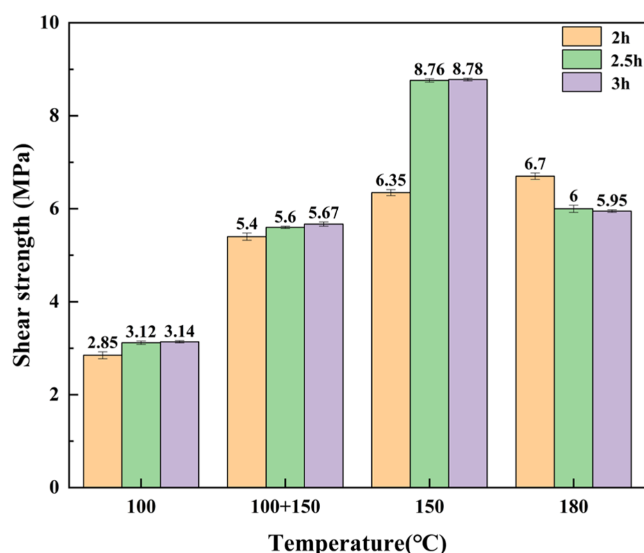

Figure 4. Shear strength of the epoxy resin thermally conductive adhesive under different curing conditions.

much larger than that of the samples under other curing conditions. As shown in Figure 5, the coefficient of linear expansion (αt = 45−55 × 10^{-6} â°C) of epoxy is very different from that of spherical alumina (αt = 45−55 × 10^{-6}/°C) at temperatures of (αt = 7−8 × 10^{-6}/°C) during the use of the temperature changes between the two due to the expansion and contraction of the uneven increase in the production of internal stress.[31] As a result, the shear strength of the sample cured for 2.5 and 3 h is lower than that of the sample cured for 2 h. Therefore, increasing the curing temperature and prolonging the curing time can improve the shear strength of the epoxy. Still, the high temperature will lead to high thermal stress in the sample and reduce the shear strength.

To sum up, increasing the curing temperature helps improve the shear strength, but the effect of this increase will worsen as the temperature increases. Increasing curing time can also increase the shear strength, but the internal stress caused by high-temperature curing will affect the material's toughness and reduce the shear strength.[32−34] Based on the above analysis, the subsequent further study used samples with a 2 and 2.5 h curing time for comparative analysis. Therefore, the production needs to select the appropriate curing time and temperature.

3.3. Dynamic Mechanical Properties. The viscoelastic behavior of the epoxy adhesive can be characterized by measuring the relationship between the loss factor and the curing conditions. The dynamic characteristics reflect the energy dissipation of the epoxy during the strain process. The temperature dependence of the loss factor measured by a dynamic thermomechanical analyzer[35−37] is shown in Figure 6.

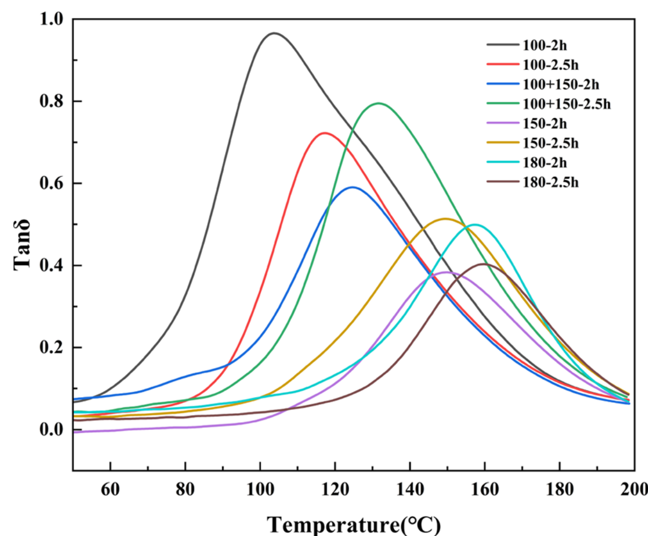

Figure 6. Relationship between loss factor and temperature of the epoxy resin thermally conductive adhesive under different curing conditions.

With the increase in curing temperature, the peak value of the loss factor decreases and the temperature corresponding to the peak value increases. The value of the loss factor represents the viscoelasticity of the material,[38,39] which is the ratio of the loss modulus G'' to the storage modulus G', namely, tan $\delta = G''/G'$. The maximum loss factor in Figure 6 does not exceed 1.0, indicating that the sample's viscosity gradually increases during heating. However, it is still in the form of an elastic solid. The peak value of the loss factor decreases with the increase of cure temperature, which indicates that the viscoelastic component ratio decreases, and the elastic component ratio increases when the glass state changes to a high elastic state. The peak value of the loss factor corresponds to the glass transition temperature of the sample,[40,41] and the peak value is shown in Table 1 With the

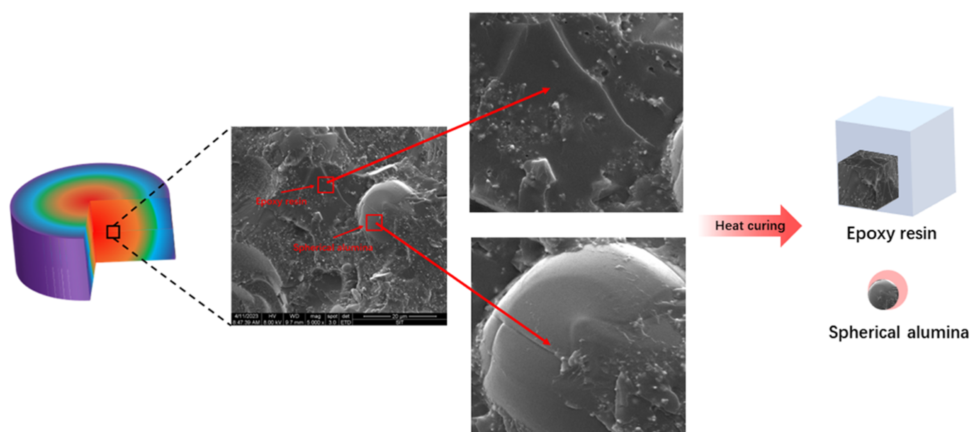

Figure 5. Schematic diagram of thermal internal stress generated by different coefficients of linear expansion.

https://doi.org/10.1021/acsomega.3c08950
ACS Omega 2024, 9, 11637−11645

Table 1. DMA Data of Epoxy Resin Thermal Adhesives under Different Curing Conditions

curing conditions	loss factor (tan δ)	the glass transition temperatures (T_g) (°C)
100 °C/2 h	0.966	103.7
100 °C/2.5 h	0.772	117.3
100 + 150 °C/2 h	0.590	124.7
100 + 150 °C/2.5 h	0.795	131.7
150 °C/2 h	0.383	149.5
150 °C/2.5 h	0.513	149.8
180 °C/2 h	0.499	157.3
180 °C/2.5 h	0.403	159.6

increase of curing temperature and the extension of curing time, it moves in the direction of high temperature. This is because the more heat the curing provides, the higher the cross-linking degree of the epoxy molecules, and the lower the free molecular volume, the movement of the molecular chain is blocked, and the glass transition temperature increases.[42−45]

3.4. Thermal Conductivity of the Epoxy Adhesive. The epoxy adhesive's thermal conductivity was studied using a thermal conductivity analyzer to measure the thermal conductivity. As shown in Figure 7, the thermal conductivity

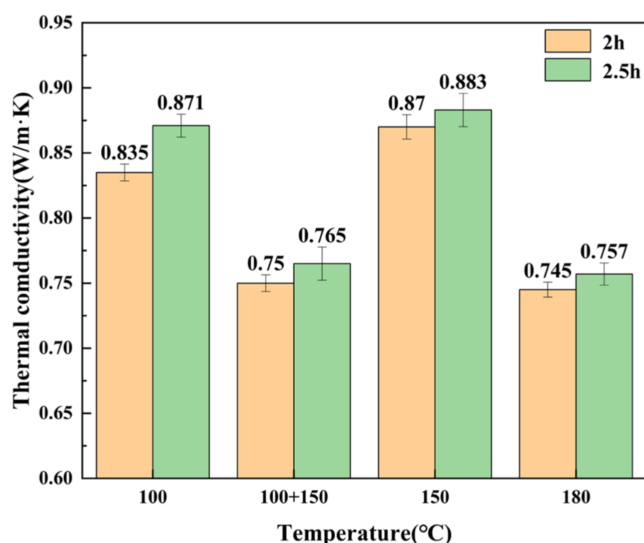

Figure 7. Thermal conductivity of the epoxy resin thermally conductive adhesive under different curing conditions.

of the cured samples prepared under different curing conditions was measured at room temperature. First, it can be intuitively concluded that increasing the curing time can improve the thermal conductivity of the epoxy-cured samples. As shown in Figure 8, because the spherical alumina particles in the epoxy heat-conducting adhesive form heat-conducting channels during the heat-curing process, the accumulation of heat-conducting channels makes the heat-conducting channels contact each other to form a heat-conducting grid, greatly improving the thermal conductivity of the epoxy adhesive.[46,47] The structure of the heat conduction grid will be more stable, and the heat conduction performance will be further improved with a prolongation of time.

Second, the thermal conductivity increased by 4.3, 2, 1.5, and 1.1%, respectively, when the curing time was extended for half an hour. With the increase in curing temperature, the increase in thermal conductivity decreased but the overall increase was small. This can be attributed to the fact that the cross-linking reaction is carried out more thoroughly as the curing temperature increases. Hydrogen bonds are created between the hydroxyl group in the epoxy structure and the oxygen atoms on the surface of the alumina. It is related to van der Waals and mainly contributes to the heat conduction channel of the epoxy. The gap between the epoxy meshes was reduced during the cross-linking process, and the thermal conductivity was increased.[48,49] In the case of high cross-linking, the effect of heat conduction grid strengthening by extending the time will be reduced.

Finally, the thermal conductivity of the four groups of samples under curing conditions of 100 and 150 °C at corresponding temperatures was similar to that of the two groups of samples under curing conditions of 100 and 150 °C at corresponding temperatures. The thermal conductivity of the four groups of samples under curing conditions of 100 and 180 °C at corresponding temperatures was similar to that of the two groups of samples and lower than the curing conditions of 100 and 150 °C of the four groups of samples. This can happen for several reasons. The thermal conductivity of the samples solidified at 100 and 150 °C is similar, but that of the samples solidified at 100 and 180 °C is lower, which may be due to the thermal stress in the samples solidified at 100 °C; the internal thermal stress disturbs the formation of a heat conduction grid with the new heating environment of 150 °C, and the heat conduction channel with the two curing temperatures is disorderly, so a stable and effective thermal conductivity grid cannot be formed, which leads to low thermal conductivity. The low thermal conductivity of the cured sample at 180 °C may be because the formation of heat conduction channels is blocked by the exposure of core−shell rubber, which means that the density of heat conduction grids is poor under the condition of 180 °C curing and lower thermal conductivity.

In general, the appropriate curing temperature and curing time can significantly improve the performance of the epoxy. Still, when the curing time is too long, it will lead to excessive curing, which increases the brittleness of the cured material and reduces its toughness. Therefore, the production must be based on specific circumstances to select the appropriate curing time.

3.5. Thermal Stability of the Epoxy Adhesive. The epoxy's thermal stability and decomposition behavior were investigated by TGA and DTGA,[50,51] as shown in Figures 9 and 10. Thermal stability factors include the initial decomposition temperature (T_{IDT}) at 5% weightlessness, the temperature at 10% weightlessness ($T_{10\%}$), the residual weight read from the TGA curve, and the temperature at the maximum rate (T_{max}) in the DTGA curve, as shown in Table 2.

The results showed that the values of T_{IDT}, $T_{10\%}$, and T_{max} increased with the increase in curing temperature and curing time. This indicates that the thermal stability of the epoxy adhesive increases steadily with increasing curing temperature and curing time,[52−54] mainly because the cross-linking density of the epoxy network increases with increasing curing temperature and with the increase of curing time, and the increase of cross-linking density will directly affect the stability of the epoxy thermally conductive adhesive. The results showed that the residual weight of the decomposed epoxy was independent of the curing condition.

3.6. Fracture Morphology Analysis. After drying and spraying gold powder on the epoxy-cured samples after brittle fracture, the fracture morphology of the clean samples was

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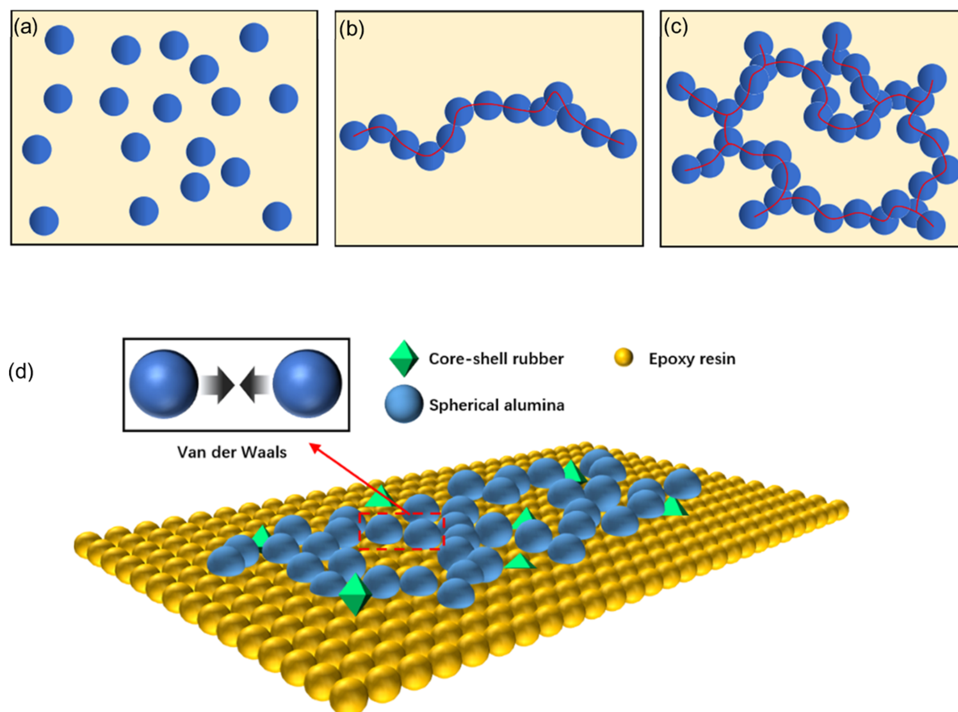

Figure 8. Schematic diagram of the thermal conductivity mechanism of the epoxy resin thermally conductive adhesive. (a) Dispersed thermally conductive filler; (b) thermal conduction channel; (c) thermally conductive grid; and (d) three-dimensional structure of a thermally conductive grid.

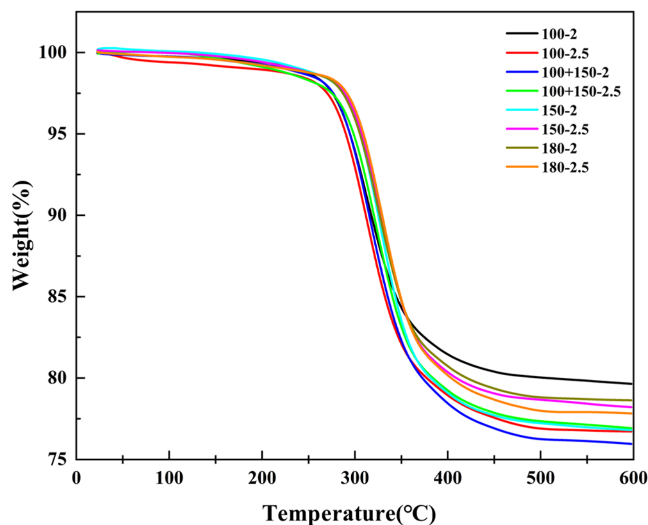

Figure 9. Thermogravimetric curves of epoxy resin thermal adhesives under different curing conditions.

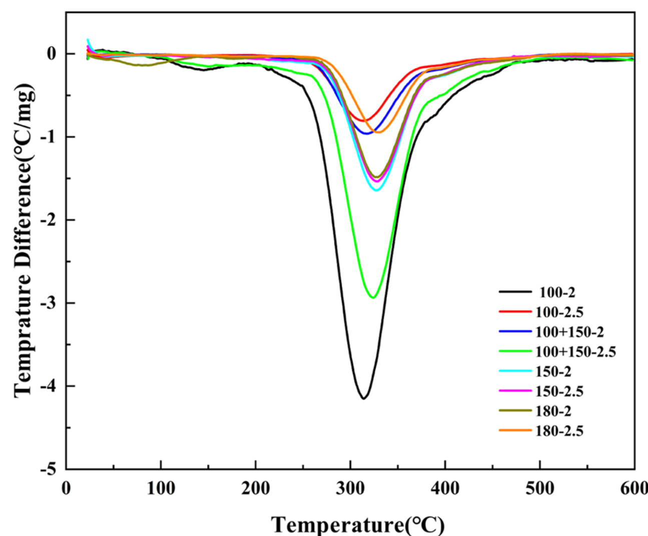

Figure 10. DTG curves of epoxy thermal adhesives under different curing conditions.

examined by SEM. Figure 11a,b shows that the fracture surface of the clean epoxy is smooth and the glass structure is obvious, which is a typical brittle fracture behavior of the epoxy. Figure 11c−h shows that the fracture surfaces of the epoxy thermally conductive adhesive samples show stick−slip and shear patterns. The surface of the fracture is less smooth, showing a multilayer stack, and the roughness increases with the curing temperature. The curing temperature at Figure 11e−h shows that the sample has a clear mirror fragmentation pattern, and the thickness of this multilayer stack pattern increases with the curing temperature.

The pattern of the sample under the same curing temperature and longer curing time has a multilayer and multiplane zigzag pattern. This means that the fracture of these samples requires

Table 2. Influencing Factors of Thermal Stability of the Epoxy Resin Thermally Conductive Adhesive under Different Curing Conditions

curing conditions	T_{IDT} (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	char yield (%)
100 °C/2 h	295.4	317.4	312.48	79.2
100 °C/2.5 h	291	311.8	313.8	76.72
100 + 150 °C/2 h	295.4	315.2	324.24	75.96
100 + 150 °C/2.5 h	299.3	320.7	325.47	76.9
150 °C/2 h	306.2	325.1	326.99	76.77
150 °C/2.5 h	308.4	328.3	327.76	78.21
180 °C/2 h	304.6	327.2	328.39	78.6
180 °C/2.5 h	310.1	329.6	330.33	77.83

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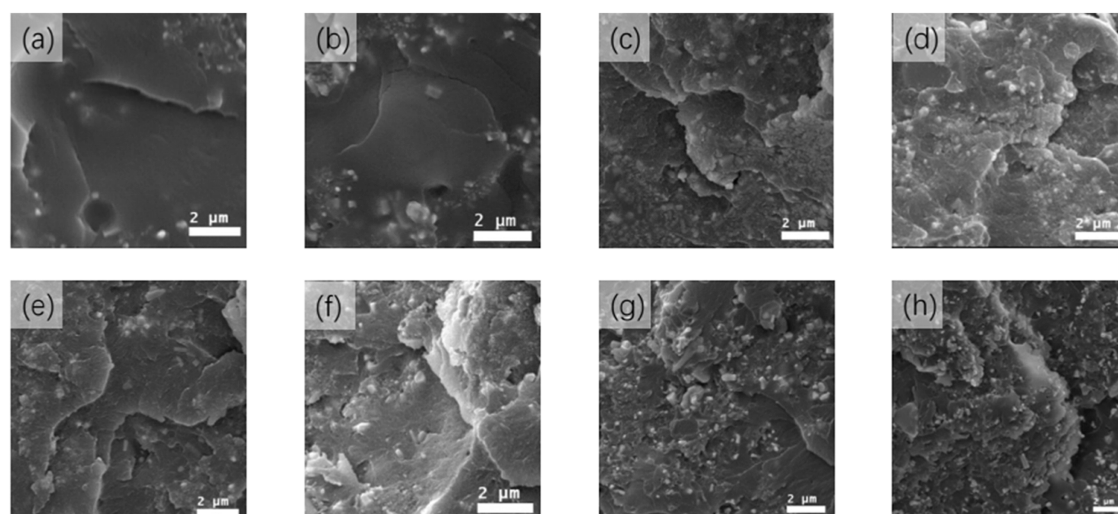

Figure 11. Fracture morphology and microstructure of the epoxy resin thermally conductive adhesive under different curing conditions: (a) 100 °C/2.5 h, (b) 100 °C/2.5 h, (c) 100 + 150 °C/2.5 h, (d) 100 + 150 °C/2.5 h, (e) 150 °C/2.5 h, (f) 150 °C/2.5 h, (g) 180 °C/2.5 h, and (h) 180 °C/2.5 h.

more energy, indicating that the increase in curing temperature and curing time has a toughening effect.[55,56] This toughening effect can be attributed to an increase in curing temperature, which increases the cross-linking density of the epoxy, and the stress of matrix fracture is hindered by more post-cross-linking epoxy, gradually deflecting the stress and changing the orientation. Due to a spherical alumina heat conduction grid, this orientation is mostly horizontal, thus resulting in a multiplanar sawtooth pattern.[57,58] Figure 11g,h shows that mirror fragmentation is most pronounced. There is no obvious multifaceted jagged structure because when the curing condition is high-temperature curing, the internal stress will be released at the same time as the brittle fracture. Its high energy will destroy the multilayer structure of the sample and present a more fractured irregular shape. At the same time, because of the high internal stress energy, the core−shell rubber is exposed. From Figure 3, it can be seen that the curing temperature is 180 °C because the core−shell rubber is extruded by internal stress. It exists in the cured sample in an uneven state, and its toughening effect is weaker than that of internal stress. Therefore, when the curing temperature is 180 °C, the shear strength decreases when the curing time is prolonged.

4. CONCLUSIONS

(1) From the mechanical properties of the epoxy, increasing the curing temperature and prolonging the curing time will make the hardness value of the cured samples higher and higher, and the glass transition temperature (TG) will gradually move toward high temperature, which is positively correlated with the degree of cross-linking of the epoxy. In the same way, the increase in curing temperature can increase the shear strength, but if the curing temperature is too high, the stress in the sample will be too high, and the shear strength will decrease.

(2) According to the thermal properties of epoxy resin thermally conductive adhesives, the thermal conductivity of the variable temperature curing is poor. This may be because the two different curing temperatures are the internal stress of the sample, which disturbed the formation of the internal heat conduction grid, affecting the heat conduction effect. The internal stress caused by high-temperature curing (180 °C) makes the core−shell rubber distribute unevenly in the sample, which blocks the formation of the heat conduction channel, weakens the density of the heat conduction grid, and affects the heat conduction effect. The increase in curing time can effectively improve the thermal conductivity, but the effect will decrease with the increase in curing temperature. With the increase in curing temperature and curing time, more heat was obtained in the curing process, the cross-linking density of the epoxy was higher, and the thermal properties of the cured samples were more stable.

(3) According to the fracture morphology of the epoxy adhesive, with the increase of curing temperature and curing time, the cross-linking density of the epoxy adhesive increases, and the toughness of the cured epoxy adhesive increases, the fracture morphology of the cured epoxy adhesive shows ductile fracture gradually from the typical brittle fracture, and the existence of thermally conductive grid makes the fracture stress diffuse along the horizontal direction, changing the original stress orientation, forming a multilayered, multiplanar jagged structure. After high-temperature curing and cooling, more internal stress is produced, and energy is released during brittle fracture, which destroys the fracture structure.

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https://doi.org/10.1021/acsomega.3c08950
ACS Omega 2024, 9, 11637−11645

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China [Grant No. 2021YFB3501700], the Shanghai Science and Technology Committee (STCSM) Science and Technology Innovation Program [Grant Nos. 22N21900400 and 23N21900100], the National Natural Science Foundation of China [Grant No. 12104311], the Science and Technology Talent Development Fund for Young and Middle-aged Teachers of Shanghai Institute of Technology [Grant No. ZQ2022-3], the Key R&D Program of Jiangsu Province (Grant No. BE2023048), the Haining Municipal Science and Technology Project (Grant No. 2022008), and the Shanghai Chenguang Program [Grant No. 22CGA74].

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