Surface iodination: A simple and efficient protocol to improve the isotropically thermal conductivity of silver-epoxy pastes

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A B S T R A C T

Heat dissipation is a critical issue in many areas such as the high-performance electronic devices. The present work gives a detailed investigation regarding a simple and efficient surface modification method, which can remarkably improve the thermal conductivity of the isotropically thermally conductive adhesives (TCAs). Herein we demonstrate that the thermal conductivity of TCAs based on micron-sized silver fillers can be improved to near eightfold merely through simple surface chemistry treatment of the fillers, without changing the conventional epoxy resin (adhesive) processing conditions. Experimental results show that the thermal conductivity of a TCA sample with iodine modified silver fillers (85 wt%, size 1–2 μm, near-spherical particles) achieved 13.5 $Wm^{-1}K^{-1}$ when cured at 150 °C. Compared to the unmodified silver-based TCAs, only 1.7 $Wm^{-1}K^{-1}$ was achieved when cured in the same condition. This work suggests that through modulating the filler interface of a TCA, the thermal conductivity of a TCA can be drastically improved. These TCAs with superior isotropic thermal conductivity may find many heat dissipation applications e.g. surface mounted devices (SMDs) and high power (printed circuit) motherboards.

1. Introduction

Effective heat dissipation from high-power electronic devices, e.g. ultra-fast computer chip modules and high-power light emitting diodes (LEDs), has become an urgent and complex problem. Due to the increased power density of such electronic devices, the heat generated from the core components increases the working temperature of the devices, drastically degrading their reliability and shortening their lifespan. Moreover, the accumulated heat often induces thermal fatigue and chemical reactions which also shorten the service life of these devices [1,2].

Thermally conductive adhesives (TCAs) are a good candidate for solving the above technical problems. As a composite material, thermally conductive fillers can couple with polymer resins to give excellent thermal property as well as the needed mechanical integrity and adhesion strength. The resin dispersants, e.g. silicones and epoxy resins, can provide mechanical integrity and adequate adhesion strength, bonding the electronic components tightly together; moreover, available filler materials, e.g. metal [3–6], carbon [7–9], and ceramics [2,10–13], can provide thermally conductive channels

for the TCAs. For example, carbon nanotube ($\sim$3000 $Wm^{-1}K^{-1}$), graphene ($\sim$5300 $Wm^{-1}K^{-1}$), boron nitride ($\sim$600 $Wm^{-1}K^{-1}$) and silver (427 $Wm^{-1}K^{-1}$) have been intensively investigated as the filler materials for a TCA recently, and have been applied in various heat dissipating applications.

As a bulk material, silver has the highest thermal conductivity (427 $Wm^{-1}K^{-1}$) and is rather oxidation-resistant ($E_o^{red} \sim 0.8$ V). Compared to carbon and ceramic, silver can be sintered at a temperature much lower than its melting point (962 °C) and form excellent ohmic conductance. Although silver does not have a comparable thermal conductivity rather than carbon or boron nitride, the weak lattice scatting as well as the electron transfer ability still provides it a relatively low contact resistance to serve as fillers in TCA. As list in Table 1, the silver-based TCAs exhibit a thermal conductivity around 4–27 $Wm^{-1}K^{-1}$. However, the TCAs based on carbon or boron nitride only show very humble thermal conductivity (e.g. 1–4 $Wm^{-1}K^{-1}$), because of the highly interfacial resistance. Therefore, silver may be the considerable materials for TCA fillers, rather than carbon or boron nitride.

For the available methods which are able to effectively enhance the thermal conductivity of a TCA, people tend to choose the following two options (Scheme 1): (1) *Increasing the filler concentration.* The increased filler content can build up more

Table 1
Thermal conductivity of most recently reported TCAs.

Materials	Methods	Thermal conductivity ($Wm^{-1}K^{-1}$)	Fraction	Binder	References
Carbon nanotube	Morphology control	0.43	1 vol%	PSS/PE/EGMA	[14]
	Using aligned carbon nanotube	4.87	16.7 vol%	Epoxy	[15]
Graphene	Non-covalent functionalization	1.53	10 wt%	Epoxy	[16]
	Multilayer graphene composing	5.40	10 vol%	Epoxy	[17]
	Roll milling	3.15	25 wt%	Silicon	[18]
Boron nitride	POSS-boron nitride nanotube	2.77	30 wt%	Epoxy	[19]
	Cold plasma modification	2.40	55 vol%	Silicon	[20]
	High mixing speed and temperature	1.97	28 vol%	Epoxy	[21]
Aluminum nitride	Solution blending	2.02	66.7 wt%	LCP	[22]
Silver-graphene	Silver and graphene hybrid	9.90		Epoxy	[23]
Silver spheres	Employing 15 wt% nanoparticles	6.00–7.00	85 wt%	Epoxy	[24]
Silver flakes	Employing 15 wt% nanoparticle	~27.00 (in-plane) & ~4.00 (vertical)	85 wt%	Epoxy	[24]
	Employing diluents	~27.00 (in-plane) & ~5.00 (vertical)	85 wt%	Epoxy-diluents	[25]
Silver particles	Sintering the nanoparticles	27.00	45 vol%	Epoxy	[26]
	Surface modification by iodine	13.50 (isotropic)	85 wt% (~35 vol%)	Epoxy	Present work
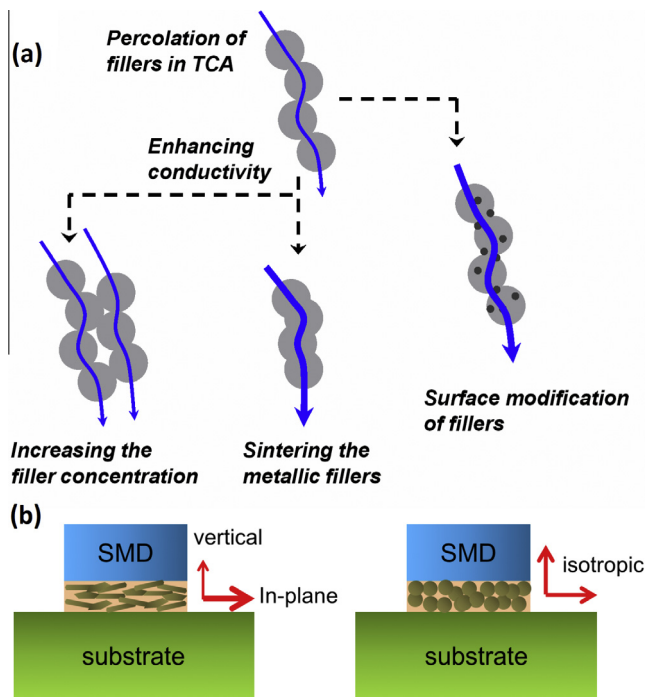
Scheme 1. (a) Methods for thermal conductivity enhancement (Both the increasing filler concentration and sintering fillers are the conventional methods. As compared, the surface modification of fillers is herein described in details). (b) A schematic comparison of the heat dissipation efficiency for the silver-flake based TCA (left) and the silver-particle based TCA (right).

electron percolation channels and thus improve thermal conductance. Yet a high filler concentration results in the increase of the viscosity of the paste and may cause processing problems such as a low printing resolution. Then solvents or diluents are often introduced to the paste to modulate its rheological properties [27]. However, evaporation of the diluents may cause the formation of voids, which harms the thermal conductivity and reliability of TCAs. Even though there are available reactive diluents, which can react with resin and do not release during the thermal curing process, the mechanical properties and reliability are often to some extent compromised. (2) *Sinter the metallic fillers with higher temperatures.* The sintering of silver substantially decreases the contact resistance of the fillers, thereby reducing the scattering of electrons and phonons [28]. However, the sintering of metal usually involves

a high-temperature curing process [25], which may be harmful to many temperature-sensitive electronic components. Although introducing some nano-silver can reduce the sintering temperature of the silver fillers and thus improve electrical conductivity of the whole composite [24,26], the involvement of smaller sized fillers also increases viscosity due to the increase of the area at the filler-resin interface. Considering the fact that silver is over 100 times more expensive than the resin and a high filler loading would deteriorate the mechanical strength of the resin-based composite. In addition, it is noted that the employment of anisotropic fillers, i.e. silver micro-flakes, is able to export a relatively high in-plane thermal conductivity of $\sim$27 $Wm^{-1}K^{-1}$ due to shear alignment effect and gravity [25]. Yet it has not a significant contribution to the property in vertical direction. Sometimes the shear alignment of silver flakes may to some extent depreciate the conductivity in vertical direction since the contact resistance along the stacked silver flakes could be enhanced. Considering the fact that for the surface mounting devices (SMDs), vertical thermal conductance is even more important than that for the in-plan direction, this method is not feasible in many applications.

Like many other composite materials, interface is a critical factor in determining the properties of composites. Generally, the physicochemical properties of the interface are closely associated with the surface chemistry of fillers. Recently, Yang et al. [29] reported a method by which silver flakes were surface – modified with a small amount of iodine prior to mixing them with the resin binder. This process results in the formation of some nano-islands containing both Ag^0 clusters and nonstoichiometric silver iodide. Those nano-islands on the surface of the micro-flakes are unstable during the silver paste curing process and are able to modulate the interface among the silver fillers, thus helping to reduce their contact resistance. In this way, the electrical percolation threshold of silver fillers was reduced to 27.5 wt% as compared with over 70 wt% of the control sample [29].

Since increasing filler concentration and sintering are not the ideal method for enhancing thermal conductivity of a TCA, and a surface modification method have been verified to enhance electrical conductivity, it is reasonable to pay more attention on TCAs based on the surface modified silver. Considering the fact that the electrical conductivity of silver fillers is around 10^{16}-fold higher than that of resin, and the ratio is only 10^3-fold for thermal conductivity, there is even no distinctive thermal percolation threshold for most TCAs [30]. In another word, once the filler concentration reaches the percolation threshold, an electrically conductivity network is formed in the composite and it shows ohmic

conductance behavior. However, it does not imply that there is a strictly proportional relationship for the enhancement of thermal conductivity because phonons also contribute to the thermal conductivity.

This study is aimed to provide a systematic study of the influence of interface modulation toward the thermal and mechanical properties of a typical silver based TCA. Instead of using silver micro-flakes, near-spherical silver micro-particles are employed as fillers, whose morphology avoids anisotropic conductivity due to shearing during the paste dispensing process, which is especially suitable for those SMDs, which are severely dependent on the vertical-directional heat dissipation. Surface iodination method is investigated due to the available data regarding the effectiveness in the improvement in electrical conductivity of the silver based composite [29]. Bisphenol-A type of epoxy (Shell Epon 828) is selected in this motif due to its wide applications in electronic packages, aerospace, and automotive industries. The surfaces of the silver microparticles were first treated by iodine and then the silver microparticles were mixed with epoxy resin with different loading ratios for preparing the TCAs. Through this study, an understanding of the interface effect on thermal properties of a TCA is obtained.

2. Experimental procedures

The silver microparticles fillers were purchased from Chengdu Banknot Printing Complex, China (SF-01C). The bisphenol A epoxy (Epon 828) and methyltetrahydrophthalic anhydride (MTHPA) which serve as the binder were provided by Shell and Nanya, China, and hexamethylenetetramine (99%), which acts as the catalyst of the resin dispersant, was obtained from Guangzhou Chemical Reagent Factory, China. Initially, the silver microparticles are dispersed in ethanol (99%, Sinopharm Chemical Reagent Co., Ltd.). Simultaneously a small amount of iodine was dissolved in ethanol. After turning clean, the solution was added in a drop-wise manner to the stirring silver–ethanol solution to modify the surface of the silver. All these processes were operated for around 1 h at ambient temperature. The epoxy binder was obtained by commixing the bisphenol A epoxy and MTHPA according to the equal epoxide equivalent weight (EEW) of the epoxy resin and the hydroxyl equivalent weight (HEW) of the hardener. A small amount of catalyst was added to the resin dispersant to accelerate crosslinking. After that, the silver particles were dispersed in the binder and they were commixed in a planetary rotary mixer (Hasai. Co., Shenzhan) at 1500 rpm for 16 min. Then the TCA samples were obtained after curing the mixture. Control samples using bare silver particles were also prepared for comparison.

The thermal conductivity of the cured TCAs in a through – plane mode was evaluated using a Netzsch Laser Flash Apparatus (LFA). Prior to the measurement, the TCA was prepared as small cylinders with diameter of 12.7 mm and height of 3.0 mm. At this macroscopic scale, the cylinders are assumed to be isotropic and homogeneous in conductivity. During the measurement, good transient signal matching from the LFA instrument was achieved (error under 10%). The thermal diffusivity (D) obtained was used to calculate the thermal conductivity (λ) by:

$$\lambda = D \times \rho \times C_p \tag{1}$$

where ρ and C_p are the density and thermal capacitance of the adhesive respectively.

The value of ρ was estimated by weighting the sample in the air and water, and then the mass values, m_{air} and m_{water} were obtained respectively. The density of the sample can be calculated as follows:

$$\rho_{sample} = \rho_{air} \times m_{air}/(m_{air} - m_{water}) \tag{2}$$

where ρ_{sample} and ρ_{air} represent the density of the sample and the air. The value of C_p was evaluated as:

$$C_p = a \times C_{Ag} + (1 - a) \times C_{epoxy} \tag{3}$$

where a is the ratio of silver by weight. C_{Ag} and C_{epoxy} are the specific heat capacity of silver ($0.24\,Jg^{-1}\,K^{-1}$) and epoxy ($1.2\,Jg^{-1}\,K^{-1}$) respectively. The average λ for each TCA cylinder was thus obtained. Any difference in λ among the tested samples was attributed solely to the surface treatment of the silver fillers.

The morphology of the silver microparticles was investigated using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). Differential scanning calorimetry (DSC) curves were recorded by a Netzsch 447 F3 thermogravimetry in nitrogen. The lap shear strength test was carried out using a MTS Universal Testing Machine (SUNS – 6104). Prior to the test, the TCA samples were filled in the gap between two PET films ($40 \times 10 \times 0.05$ mm), and their size is controlled within $30 \times 10 \times 0.056$ mm by the tapes. Then two PET films were stretched in the opposite direction until fracturing the TCA.

3. Results and discussion

As depicted in Fig. 1, the silver fillers immersed in ethanol with a small amount of iodine exhibit small islands on the surface. This is also confirmed in the SEM images in Fig. 2. After silver and resin are mixed homogeneously, TCA is obtained and then molded into a cylindrical shape. In order to simulate a situation for heat transfer in vertical direction, we used these specimens as the interconnecting material to transfer heat from a steady heat source (QILINBEIER GL-3250B electronic hot plate) to 10 mL of deionized water in a glass beaker overhead, and recorded the real-time temperature. A heating plate set at 80 °C was used as the heat source (Fig. 1d) to provide a steady heat source. The time-dependent temperature curves in the figure demonstrate that TCA with the modified silver undergoes a faster heat transfer process than the control sample, leading to a more rapidly temperature increase trend. This enhanced thermal transfer character correlates strongly with the surface structure of the fillers, whereas neither the DSC result nor the SEM images suggest a sintering phenomenon (Figs. 1c and 2). It is consequently deduced that the surface modification of the fillers effectively results in the improvement of the heat transfer efficiency in this experiment.

The morphology of the silver fillers of TCA is shown in Fig. 2. As shown in these SEM images, the fillers exhibit non-specific shape, indicating the isotropic characteristics. The size distribution of the grain is 1–2 μm. After the iodine modification, the surface of the particles presents many small islands with the size below 100 nm. This is demonstrated in Fig. 2b and d. This phenomenon is consistent with our previous study [29]. The presence of these small islands contains nonstoichiometric silver–silver iodide, which strongly correlates to the time-dependent self-evolution of the particles [31]. After a 180 °C treatment (15 min), the morphology of the modified silver does not change obviously. As can be seen in Fig 2e and f, no typical sintering phenomenon is observed. This is understandable because the silver particle is in micron-size and the surface energy is too low to depress the melting point. The cross-sections of the TCA with 85 wt% fillers are shown in Fig. 2g and h. The random distribution of the fillers in the resin dispersant indicates the isotropic property of the samples.

The thermally conductive performance of the TCA with bare silver and with iodine modified silver microparticles is presented in Fig. 3. Four different concentrations of silver content are used to investigate the thermal conductivity of the TCA samples. The increase of thermal conductivity of TCA and the slope of the increment become faster and larger as the silver concentration
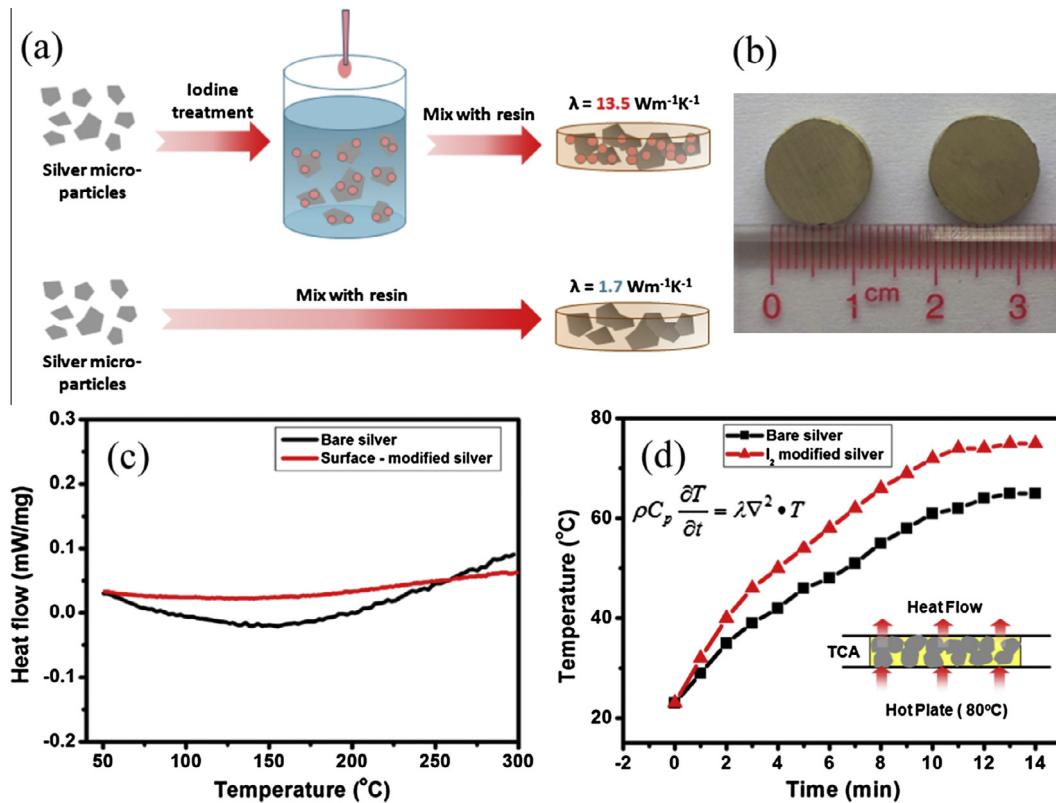
Fig. 1. (a) Surface modification of silver fillers. (b) Optical photograph of the specimen cylinders. (c) DSC curves of the silver particles. (d) Time-dependence temperature increasing curves of the heating water. (inset) Scheme of heat transfer from a plate to deionized water.

increases. The thermal conductivity of the control sample increased from 0.6 to 1.7 $Wm^{-1}K^{-1}$ corresponding to the 50–85 wt% of silver loading. As compared, the samples with surface modified silver exhibited dramatically increased thermal conductivity from 1.1 to 13.5 $Wm^{-1}K^{-1}$ at the same filler loading. This increasing trend demonstrates that the surface modification for fillers enhances the thermal conductivity of TCA more rapidly when increasing the filler loading. A maximum enhancement of near 700% is observed and this value could be larger in accordance with such tendency. Our previous work suggests that this surface modification method substantially raises the electrical conductivity of the silver adhesive [29]. The improved interface is believed to be the major reason for the improvement of the thermal conductivity.

In order to evaluate the contribution of surface modified silver for the enhancement of the thermal conductivity of TCA, we prepared a series of samples based on the mixture of the iodine modified silver and bare silver in certain ratios. The ratio of the surface-modified silver to the total mass (Ag_I/Ag_{total}) is adjusted from 0.0 to 1.0 with 0.25 steps. The total weight ratio of silver is maintained constant, which is 66.7 wt% in the adhesive. As depicted in Fig. 3b, the thermal conductivity is enhanced from about 0.7–1.4 $Wm^{-1}K^{-1}$ with the increase of the Ag_I/Ag_{total} ratio. The increasing trend is strong in the range of 0.5–0.75 ratio. When Ag_I/Ag_{total} equals to 0.75, typically 2.7 g surface-modified silver and 0.9 g bare silver mix with 1.8 g epoxy binder, the TCA exhibits a thermal conductivity of 1.2 $Wm^{-1}K^{-1}$, which is approximately the same as that of the sample containing 60 wt% surface-modified filler (2.7 g modified and 1.8 g epoxy binder). It appears that 0.9 g bare silver does not make a significant contribution to the enhancement of thermal conductivity. The surface-modified silver contributes more than the bare one to the thermal conductivity of TCA.

To further investigate the mechanism of the enhanced thermal conductivity of the surface-modified silver in the TCAs, we measured the thermal conductivity of the samples with various curing temperatures and curing durations. The curing temperature dependence thermal conductivity for the samples with 80 and 85 wt% silver loading is shown in Fig. 4. As can be seen, when the curing temperatures vary from 110 to 190 °C, the thermal conductivities are around 1.4–1.5 and 1.6–2.0 $Wm^{-1}K^{-1}$ for the control sample. Only a small increment is observed, stemming from the shrinkage of the adhesive. As compared, the samples modified silver show linear increasing trends which are 5.4–7.3 and 11.6–18.7 $Wm^{-1}K^{-1}$ along with the curing temperature from 110 to 190 °C. The different increment may result from the different surface status of the fillers. This stronger enhancement demonstrates that the surface modification of the silver enhances the thermal conductivity of the TCA.

With prolonged curing duration, the thermal conductivity of TCA at first shows a rapidly increasing trend, followed by a steady state. As demonstrated in Fig. 4b and d, the thermal conductivity of the control samples of 80 and 85 wt% filler loading increases from 1.4 to 1.8 and from 1.7 to 1.9 $Wm^{-1}K^{-1}$, corresponding to the curing duration of 0.25–4 h, whereas the thermal conductivity of the TCAs with 80 and 85 wt% modified silver increases from 6.2 to 7.4 and from 13.5 to 15.0 $Wm^{-1}K^{-1}$, for the same condition. This finding implies that the surface modification of silver accelerates the increase in thermal conductivity of the TCA.

We also evaluated the temperature-humidity reliability of the TCA. Samples with 80 wt% fillers and cured in 150 °C for 15 min are examined. These samples are placed in a chamber with an 85 °C/85% relative humidity condition. As listed in Table 2, for the iodine treated TCA samples, there is a negligible change in thermal conductivity after 500 and 1000 h. Both samples show a slight increment in thermal conductivity, which may be related to the
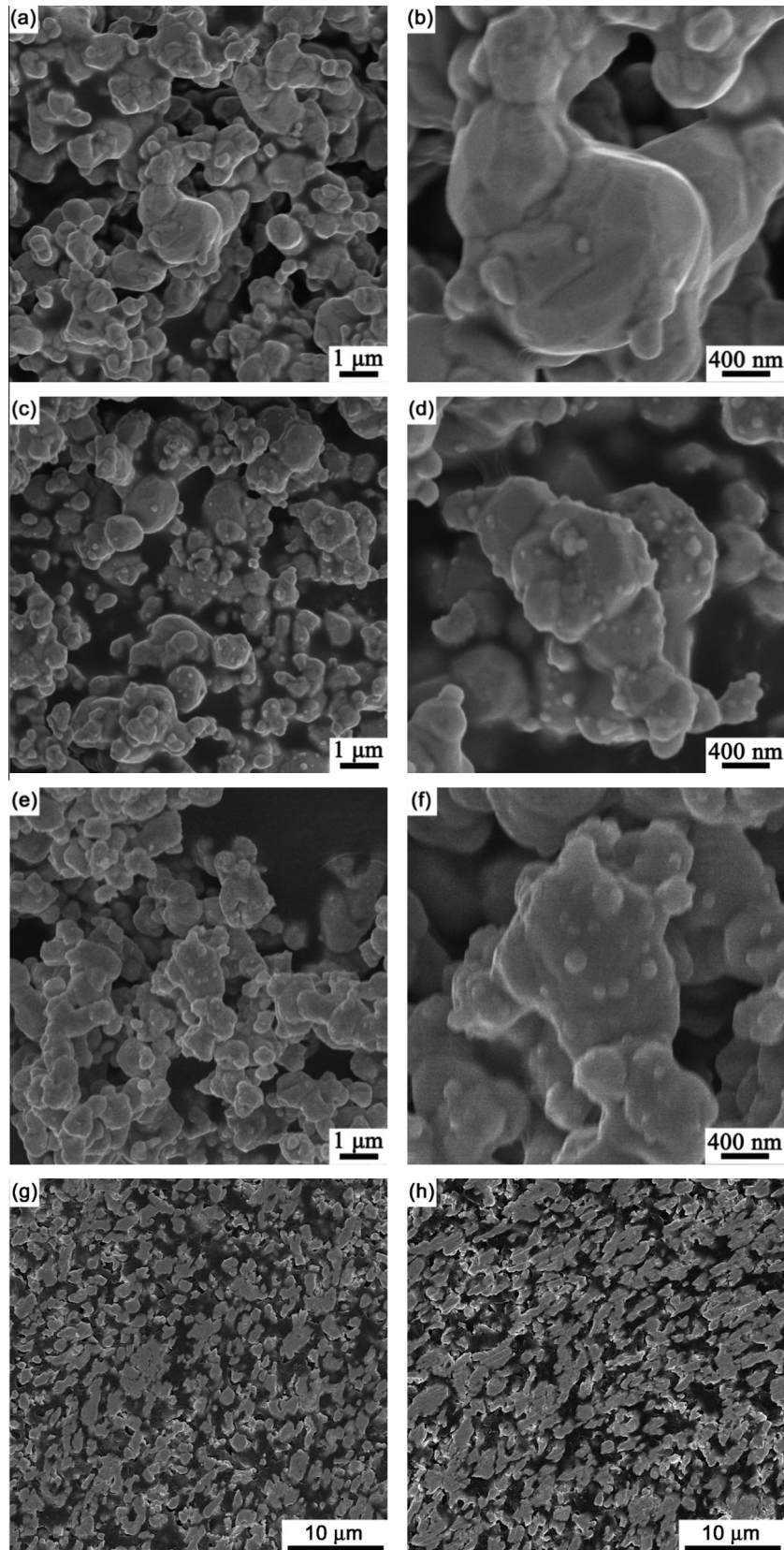
Fig. 2. SEM images of silver particles and cross-section of TCAs. (a) Untreated silver particles. (b) A zoom-in area in (a) which shows a smooth surface of the particles. (c) Surface-modified silver particles. (d) A zoom-in area in (c) which shows there are small islands on the particles. (e) Silver particles after 180 °C treatment. (f) A zoom-in area in (e) which shows small islands on the particles after 180 °C treatment. (g) The cross-sectional image of the TCA sample with bare silver particles. (h) The cross-sectional image of the TCA sample with surface-modified silver particles. After surface modification, small islands appeared on the surface of the silver particles. These islands are preserved after 180 °C treatment. These SEM images suggest that all silver fillers shows unnoticeable sintering phenomenon.
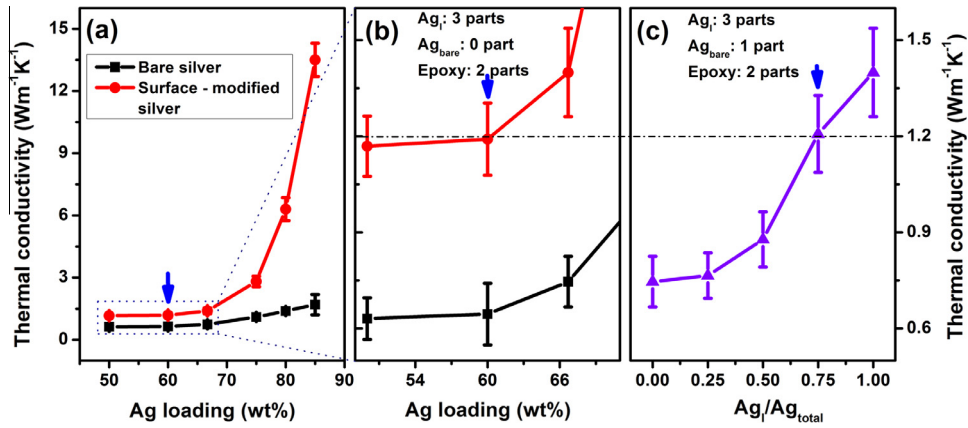
Fig. 3. (a) Thermal conductivity of the TCA samples vs. various silver filler loadings (b) A zoom-in area in (a) which shows the thermal conductivity of the TCA with 60 wt% silver loading (as pointed by the arrow) (c) Thermal conductivity of the TCA samples with different ratio of Ag_I to total filler concentration Ag_{total} (total filler concentration is maintained at 66.7 wt%). As can be seen, the two samples with the same Ag_I parts (by weight) in each formulations as indicated in (b) and (c) show analogous thermal conductivity (indicated by the arrows and the partition line), which suggests that without surface modification, the portion of bare silver fillers make negligible contribution to the thermal conductivity of the TCA. (The scales in *y*-axis in both (b) and (c) are the same.).
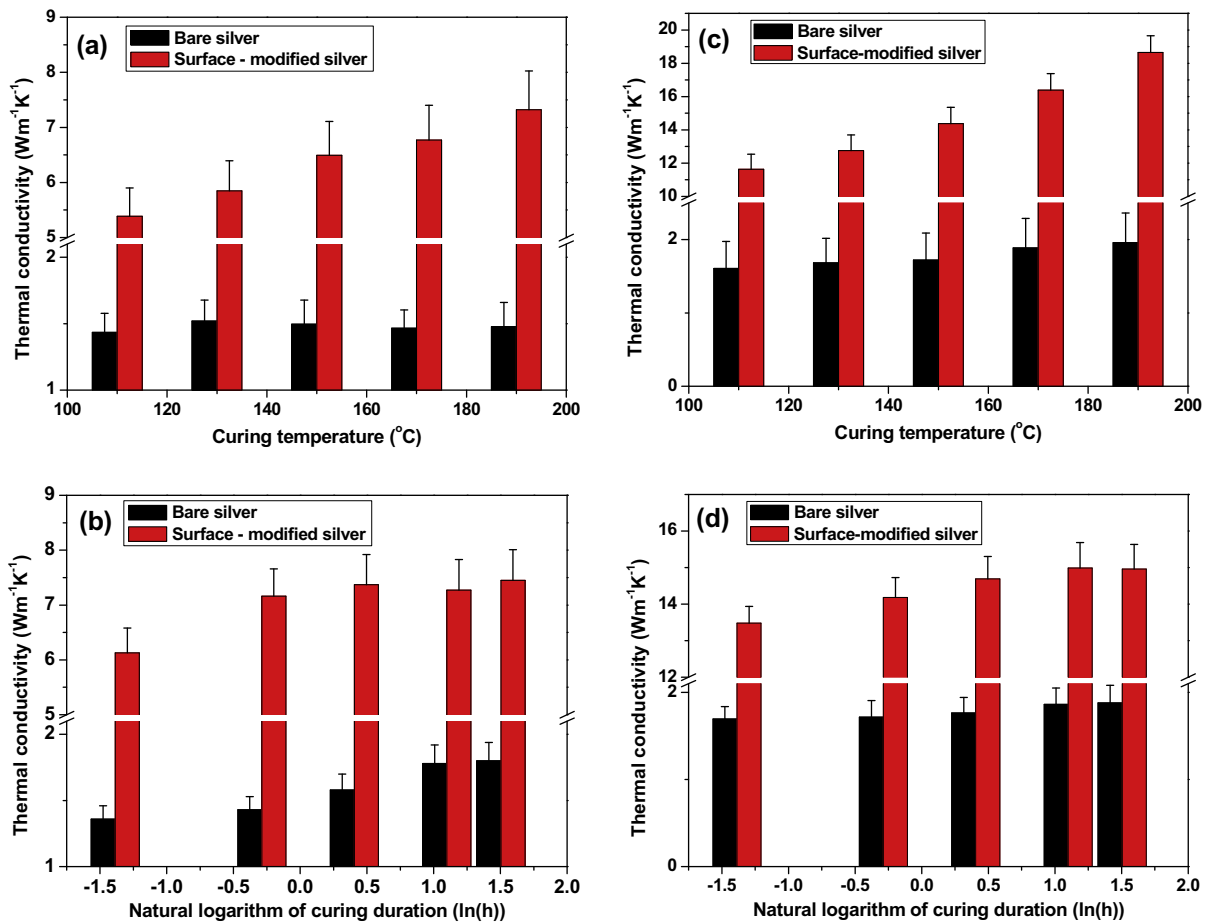
Fig. 4. (a) and (c) Thermal conductivity of the TCA samples (a and c represent 80 and 85 wt% TCA) at various curing temperatures in 15 min curing duration. (b) and (d) Thermal conductivity of TCA samples (b and d represent 80 and 85 wt% TCA) at 150 °C in various curing durations.

Table 2
Parameters of reliability examination for 80 wt% samples (Wm^{-1} K^{-1}).

Samples	0 h	500 h	1000 h
With bare silver	1.7 ± 0.1	2.1 ± 0.1	2.2 ± 0.1
With surface-modified silver	13.5 ± 0.5	15.0 ± 0.6	15.4 ± 0.6

further shrinking of the TCA when it is placed at 85 °C for a long time [32]. This allows the approaching of fillers so that a slight increment of the conductivity is observed. The reliability of TCA is considerable for industry application.

In addition to thermal transportation, the TCA must also provide adequate mechanical support and interconnection function. In order to evaluate the influence of surface modification to the
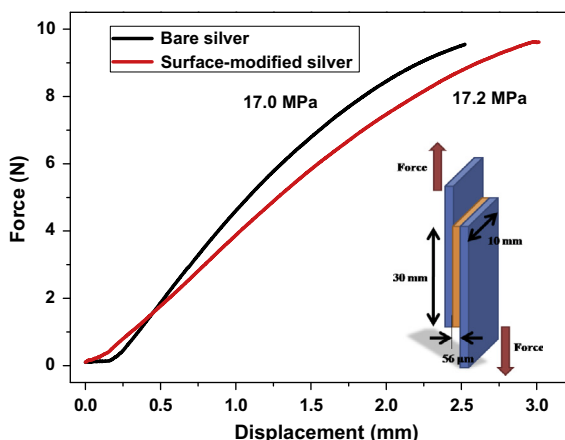
Fig. 5. Stress–strain curves of the lap shear test of the TCA samples (85 wt% silver concentration).

mechanical property of the TCAs, we performed the lap shear strength test for the samples on a universal tensile tester, and the results are shown in Fig. 5. As can be seen, the samples with bare silver and with surface modified silver present a similar force–displacement relationship. Both samples typically fail at 2.5–3.0 mm total displacement, corresponding to forces of 9.5 and 9.6 N. The mean nominal shear strengths for the samples are 17.0 and 17.2 MPa, respectively. In another word, the surface modification for silver fillers does not significantly alter the adhesion properties of the TCA.

In the present work, we prepared the TCA using micron-sized non-specific silver microparticles. Without employing nano-sized particles, anisotropic fillers or a high – temperature treatment, the thermal conductivity of the TCA is enhanced to near eightfold after simple surface modification of the filler. The previous research implies that the introduction of iodine is effective in promoting the spontaneous evolution of the species at the surface of small silver particles [31]. The enhanced electron transfer at the interface was observed by measuring the electrical conductivity of the adhesive, and the details implied that such enhancement is strongly associated with the surface status of the silver [29]. This indicates the spontaneous evolution at the surface of the particles could substantially improve the interfacial contact among the micro-fillers, and the improvement effectively enhances the thermal conductivity of the monolithic TCA sample. The reduction of contact resistance allows a high electrons and phonons transmission rate at the interface of silver microparticles. A high curing temperature may expedite this evolution, in agreement with the increasing trend of thermal conductivity in accordance with the increase of curing temperature. Potentially, the enhancement of thermal conductivity might further increase if spherical and larger filler is employed, since the small specific surface area might reduce the phonon-electron scattering and then allow more electrons to transfer at the boundary of the fillers. Nevertheless, to achieve an optimal comprehensive performance, appropriate resin species and silver content need also to be considered, so as to make a balance of thermal conductivity, mechanical strength and cost.

4. Concluding remarks

The present work introduces a surface modification method for the silver fillers of TCA. The thermal conductivity of TCA with such modified particles is drastically enhanced from 1.7 to 13.5 Wm^{-1} K^{-1} (about 700% improvements), which is the highest enhancement for the isotropic TCAs without sintering the metal fillers.

Meanwhile, the thermal conductivity of the samples with the modified fillers increases according to the curing temperature. Compared to those sintering-based processes, the advantage of the current method can avoid the nanoparticles and it is compatible with conventional epoxy resins, thus the thermal–mechanical property of the TCA can match with most of the fiber-reinforced polymer (FRP) circuit boards very well; This surface modification is very simple, effective and suitable to most current electronic packaging process. Since the silver micro-fillers are in near-spherical shape, and thus the TCA can provide isotropically thermally conductive behavior, which is suitable with general thermal dissipation applications. Moreover, the TCA preserves an excellent adhesion property which is around 17 MPa of the shear strength (with 85 wt% of silver) because the binder still occupies a large volume fraction. Considering all these advantages, we envisage broad applications of this technique in the packaging for heat radiation in high-density integrated electronic devices, aerospace, and automotive industries etc.

Acknowledgements

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