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Effect of coupling agents on the thermal conductivity of aluminum particle/epoxy resin composites

Wenying Zhou

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Abstract In this study, four kinds of coupling agents (CA), i.e., γ-aminopropyltriethoxysilane (KH-550), (3-glycidyloxypropyl)trimethoxysilane (KH-560), isopropyl tri(di(2-ethylhexyl)pyrophosphate)titanate (NDZ-201), isopropyl tri(di(2-ethylhexyl)phosphate)titanate (NDZ-102), were used to investigate their influences on the thermal conductivity and morphology of aluminum (Al) particle reinforced epoxy composite. The results indicate that the thermal conductivity of the composites increases with increasing Al particles concentration up to 48 vol.%; the surface modification of Al particles has an appreciable effect on the thermal conductivity. The thermal conductivities of the composite containing 48 vol.% Al particles treated with the KH-550, KH-560, NDZ-201, and NDZ-102 couplers, are 1.29, 1.48, 1.27, and 1.36 W/m K, respectively, corresponding to 1.03 W/m K of that without surface treatment. Furthermore, the concentration of CA has an influence on the thermal conductivity of the composites.

Introduction

The continuous integrated circuit (IC) miniaturization trend calls for replacing discrete passive components (capacitors, resistors, and inductors) with embedded passives [1–4]. Among passive components, special interest is focused on embedded capacitors because of their various functions, such as decoupling, bypassing, filtering, and timing. Additionally, they are also capable of enhancing the electrical performance and reducing the size and cost of an electronic system [5–9]. Until now, extensive attentions have been paid to the preparation of polymeric composites with a high dielectric constant but a low dielectric loss for the application in embedded capacitors [10–15], whereas, the thermal conductivity of these dielectric materials is rather low which might restrict their serviceable range [16]. It is essentially crucial for the heat generated and accumulated from the embedded capacitors or resistors to be dissipated as quickly and effectively as possible to maintain the operating temperatures at a desired level, otherwise, the thermal breakdown may occur due to the low-thermal conductivity of the polymeric dielectric materials [17–19]. So, the search and development of polymeric dielectrics possessing a high thermal conductivity and a high dielectric constant but a low dielectric loss poses an important influence on facilitating prolonging the lifespan of an embedded capacitor or resistor [20]. Significant progress has been achieved in developing the polymer composites with a high thermal conductivity, as well as a low dielectric constant and loss, for applications in electronic packaging and substrate [21–28].

The surface-passivated aluminum (Al) particle/epoxy possesses a high dielectric constant but a low dielectric loss, accompanied with a high thermal conductivity. The dielectric properties of the Al/epoxy had been reported [3, 6, 17], whereas, the thermal conductivity has not been studied in these literature reported. So, the objective of the present work is to investigate the influence of Al particles content and different coupling agents with varying concentration on the thermal conductivity and morphology of the Al/epoxy composite. To increase the thermal conductivity, in this work four kinds of coupling agents were used to modify the surface of Al particles and, to improve the

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W. Zhou (✉)
School of Chemistry and Chemical Engineering, Xi'an
University of Science & Technology, Xi'an 710054,
People's Republic of China
e-mail: wyzhou2004@163.com

interfacial adhesion strength between fillers and polymer, preferably via chemical bonds.

Experimental

Materials

The polymer matrix used in this study was a diglycidyl ether of bisphenol A-type epoxy resin (D.E.R.-331, Dow Corp.) with an epoxy value of 0.52–0.54. A flexible epoxy resin with low viscosity (Long chain polyglycol di-epoxide liquid resin, D E R-732, Dow Corp.) was used as a reactive toughening agent to overcome the brittleness and decrease the viscosity of the matrix. The curing agent was methyl hexahydrophthalic anhydride (MeHHPA) from Shanghai Shengyuan Co., China, and the cure accelerator was 2,4, 6-tri (dimethylaminomethyl) phenol (DMP-30) from Shanghai Haitai Co., China. The aluminum particle, with an average diameter of 2 µm, was purchased from Xi'an Sunwards Aerospace Aluminum Co., Shaanxi. The structures of the silane and titanate couplers used are shown in Table 1, which are from Nanjing Shuguang Chemical Co., China. Other chemical agents such as ethanol, dimethyl benzene, oxalic acid, etc., are all available from market.

Preparation of siliane and titanate couplers-modified Al particles

Surface treatment for Al particles using the silane couplers involved the following steps: (a) making an ethanol aqueous solution at a 95 wt% concentration; (b) adding the silane coupling agent with a set concentration to the solution and stirring for 15 min in a flask with reflux setting, adjusting the ethanol aqueous solution pH to 3–5 using diluted oxalic acid and stirring for 20 min; (c) adding Al particles to the solution made in (b) and stirring while ultrasonicating for 60 min; (d) heating to 80 °C and refluxing for 6 h while stirring and then cooling to room temperature, letting it set for 2 h; (e) rinsing with ethanol by filtration at least three times; and (f) drying the mixture at 110 °C for 10 h [20].

Surface modification of Al particles using the titanate couplers was carried out as follows: (a) a certain amount of the fillers and the titanate coupling agent was mixed in dimethyl benzene at 70 °C and stirred for 8 h; (b) the resulting mixture was filtered, and rinsed with dimethyl benzene at three times, and then vacuum dried at 120 °C for 10 h to remove the solvent.

Preparation of the Al/epoxy composites

The epoxy resin (D.E.R.-331) was blended with the flexible epoxy D.E.R.-732, the curing agent, Al particles, and

Table 1 Chemical structure of the coupling agents

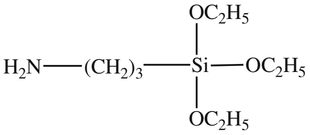
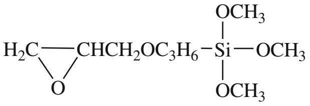
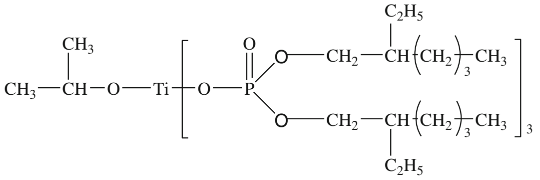
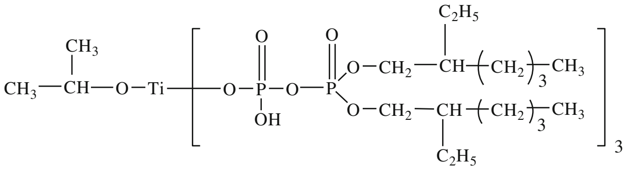
Material	Chemical structure
γ-Aminopropyltriethoxysilane (KH-550)	 $H_2N—(CH_2)_3—\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}—OC_2H_5$
(3-Glycidyloxypropyl)trimethoxysilane (KH-560)	
Isopropyl tri(di(2-ethylhexyl)phosphate)titanate (NDZ-102)	
Isopropyl tri(di(2-ethylhexyl)pyrophosphate)titanate (NDZ-201)	

Table 2 Formulation of Al/epoxy composites

Raw materials (g)	Content
Epoxy (D.E.R.-331)	70
Epoxy (D.E.R.-732)	30
MeHHPA	90
DMP-30	1
Al	Variant

accelerator according to the designed mass-fraction ratio (as shown in Table 2). Then, the blend was stirred vigorously for about 1 h, and the obtained homogeneous mixture was degassed for about 30 min in a vacuum to get rid of bubbles. After that, the liquid mixture was slowly poured into a clean glass plate mold kept at 80 °C, and was then cured in an oven at 100 °C for 1 h and 150 °C for 5 h. Afterwards, the cured sample was left to cool down to room temperature. Thus, the epoxy composites with Al powder concentrations ranging from 0 to 48 vol.% were prepared free of solvent.

Characterization

The surface chemistry of the Al particles was characterized by an FT-IR (Fourier transforms infrared) spectrometer (Perkin-Elmer, Paragon1000). The Al particles were first dried in an oven at 120 °C for 6 h, and then KBr pellets were prepared with the dried Al particles. The spectrum was collected in the range from 4000 to 400 cm^{-1}.

Morphological observation on the samples was performed using a scanning electron microscope (SEM) (model: JSM-7000F, JEOL, Japan). The fractured surfaces were prepared in liquid N_2, and were sputtered with gold in vacuum prior to observation. The observation was carried out on the cross-sections of samples to study fillers distribution.

The thermal conductivity of the samples was measured by a Hot Disk thermal analyzer (Hot Disk AB, Uppsala/Sweden) using the transient place source (TPS) method. A disk-shaped TPS sensor with a diameter of 7 mm and a thickness of 0.07 mm is placed between two circular sample pieces with diameters of 20 mm and thicknesses of ~2 mm. The upper surface and under surface were polished by fine sand paper prior to use.

Results and discussion

FT-IR characterization

Figure 1 shows the FT-IR spectra of both untreated and silane (1.0 wt% KH-550 and KH-560) and titanate (1.2 wt% NDZ-102 and NDZ-201) coupling agents treated Al particles. Figure 1a suggests that the absorption peak around 3673–3678 cm^{-1} is associated with vibration of the Si–OH group; the new adsorptions at 2696 and 2867 cm^{-1} are the characteristics for stretching vibration of the C–H bond of the silane, where the signal at 1246 cm^{-1} is assigned to vibration of C–O bond of the silane couplers, as compared to the untreated Al particles [3]. Figure 1b indicates that peaks around 2940 and 2880 cm^{-1} correspond to stretching vibration of the C–H bond of the titanate couplers compared with the without surface modification of Al particles.

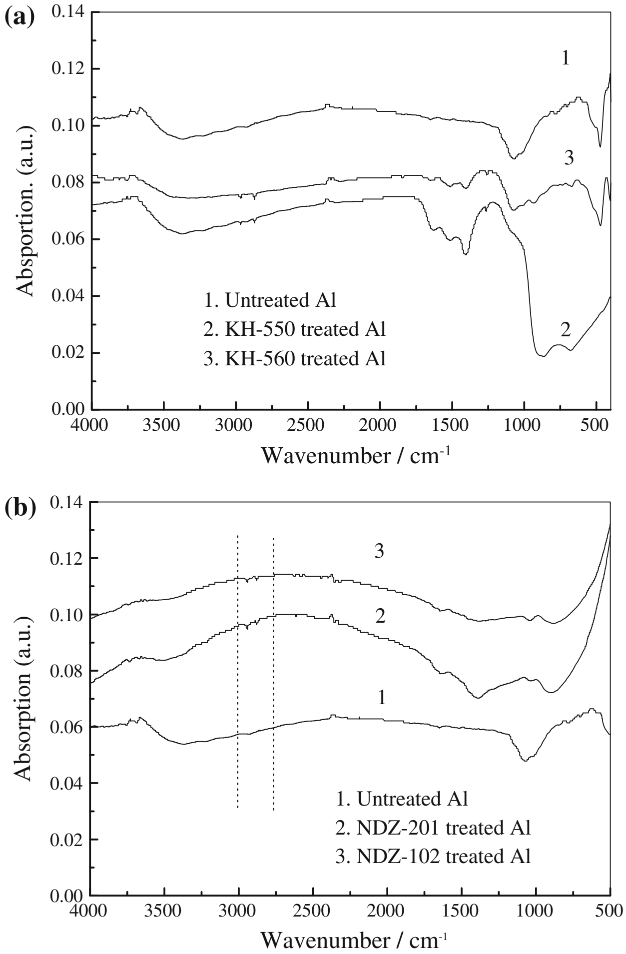


Fig. 1 FT-IR spectra of untreated and treated Al particles with couplers **a** silane, **b** titanate coupling agents

From the FT-IR spectrum of Fig. 1, we can speculate that the active chemical groups of coupling agent molecules had been chemically linked to the surface of Al particles. For example, a schematic showing the reaction mechanism of KH-560 silane coupler with the –OH groups on the oxide shell of an Al particles surface is illustrated in Fig. 2. The methoxyl groups of silane coupler were first hydrolyzed with water to form three silanol groups. And

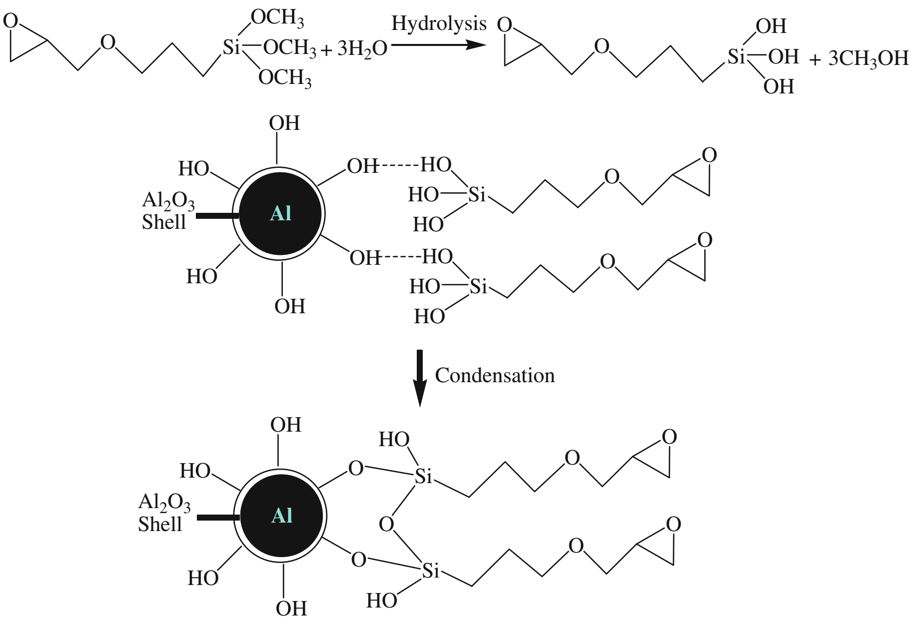


Fig. 2 Schematic showing the reactions of KH-560 silane coupler with Al particle surface

then, the silanol groups were condensed with the hydroxyl groups on the alumina shell of Al particles to form the Si–O–Al bond via acid-catalyzed reactions [3]. The KH-550 silane coupling agent has similar reaction mechanism with alumina shell of Al particles as KH-560.

Thermal conductivity

The influence of Al concentration and surface treatment on the thermal conductivity of Al/epoxy composites is presented in Fig. 3. It can be seen that the thermal conductivity always increases with increasing the volume fraction of Al up to 48%. The thermal conductivity of epoxy filled with 37 and 48 vol.% of Al particles reach 0.9 W/m K, and 1.03 versus 0.22 W/m K for the neat epoxy. The thermal conductivity increases rather slowly at low Al loading, i.e., less than 14 vol.%; after that, then increases quickly. This is because the heat-conductive Al particles surrounded or encapsulated by epoxy matrix can not touch one another at low loading, thus, leading to high thermal contact resistance. As the Al concentration increases further (greater than 14 vol.%), filler particles begin to touch one another and form particles clusters. The layer of epoxy resin between the adjacent Al particles becomes thinner and thinner, leading to a decreased thermal contact resistance [13]. Therefore, the thermal conductivity is enhanced obviously.

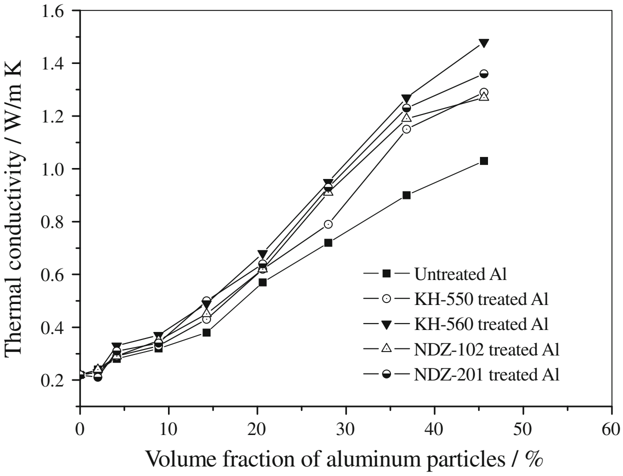


Fig. 3 Effect of surface modification of Al particles on the thermal conductivity of Al/epoxy composites at various filler concentration

Figure 3 demonstrates that the use of coupling agents clearly improves the thermal conductivity of the composites at high Al content. As we know, various phonon-scattering processes cause thermal resistance, and the interfacial thermal barriers in composites are mainly due to phonons scattering as a result of an acoustic mismatch and the flaws associated with the matrix–filler interface. For the sake of environmental protection, no any inertia solvent such as acetone was employed in this study. So, the viscosity of the resulting mixture can only be reduced by means of the active diluter (D.E.R.-732) and liquid acid anhydride curing agent (MeHHPA). At high Al content it is difficult to get rid of bubbles trapped in the mixture during the processing, which results in the formation of the air holes reserved in the composites. Therefore, the thermal conductivity slightly increases at high filler content owing to the residual air voids in the cured epoxy [14].

It is well known that the four coupling agents used here have two different functional groups, one (i.e., amino,

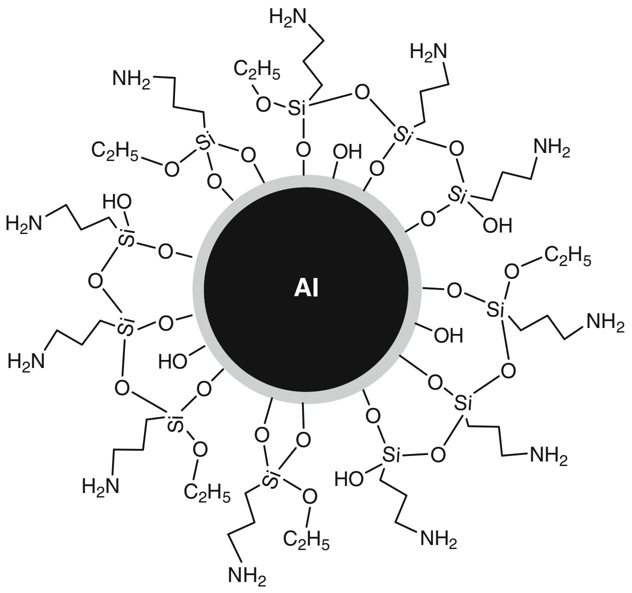


Fig. 4 Schematic representation of a surface treated Al particle with silane coupler KH-550

epoxide group, long carbon aliphatic chain, etc.) that is attracted to the epoxy resin, and the other that is reacted to the active chemical group (i.e., hydroxyl group) on the surface of Al [12]. After surface modification of Al particles, the coupling agent can be chemically grafted to the surface shell of Al particles. The schematic representation of a surface treated Al particle with KH-550 silane coupler is displayed in Fig. 4. Thus, the organic active groups (i.e., amino, epoxide groups) or long molecular chains on the surface of modified Al particles either reacts with the reactive groups of epoxy matrix, or entangles with it. Therefore, the addition of coupling agents to epoxy matrix improves the interface bonding between the Al particles and matrix, leading to an enhanced thermal conductivity [15]. For instance, as seen from Fig. 3 the thermal conductivities of the composite containing 37 vol.% Al particles treated with the KH-550 (1.5 wt%), KH-560 (1.5 wt%), NDZ-102 (1.2 wt%), and NDZ-201 (1.2 wt%) are 1.15, 1.27, 1.19, and 1.23 W/m K, respectively, corresponding to 0.90 W/m K of that without surface treatment; and at the same coupling agent content the thermal conductivities of the composite containing 48 vol.% Al particles treated with KH-550, KH-560, NDZ-102, and NDZ-201 are 1.29, 1.48, 1.27, and 1.36 W/m K, respectively, corresponding to 1.03 W/m K of that without surface treatment.

Table 3 Effect of coupling agent content on the thermal conductivity of Al/epoxy

Coupling agent	Coupling agent content (wt%)	Thermal conductivity (W/m K)	
		37 vol.% Al	48 vol.% Al
KH-550	1.0	1.08	1.14
	1.5	1.15	1.29
	2.0	1.12	1.21
KH-560	1.0	1.20	1.34
	1.5	1.27	1.48
	2.0	1.16	1.43
NDZ-102	0.8	1.08	1.19
	1.2	1.19	1.27
	1.8	1.13	1.24
NDZ-201	0.8	1.14	1.25
	1.2	1.23	1.36
	1.8	1.21	1.34

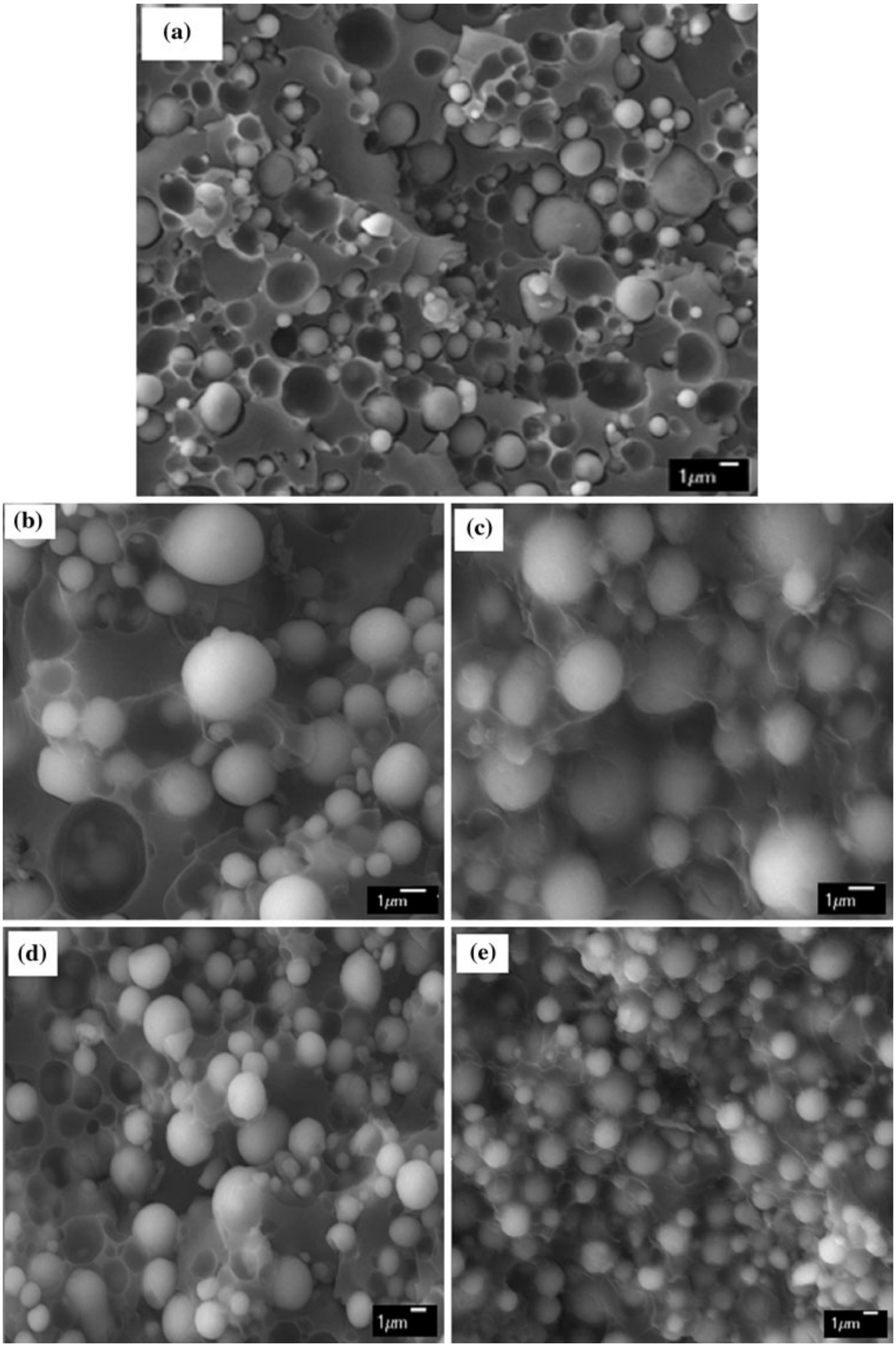
The concentration of coupling agent has an influence on the thermal conductivity of the Al/epoxy composites. The dependences of thermal conductivity of Al/epoxy on the concentration of coupler contents are summarized in Table 3. It can be observed from Table 3 that the thermal conductivity of the composites increases at a low concentration but decreases at a high concentration of the coupling agent used. The maximum thermal conductivity values appear at about a 1.5 wt% concentration for the KH-550 and KH-560 silane coupling agent, and about a 1.2 wt% concentration for the NDZ-102 and NDZ-201 titanate coupling agents for the composites containing Al loading at 37 and 48 vol.%, respectively.

The use of coupling agents with adequate content to the composites improves the thermal conductivity, whereas, the thermal conductivity decreases with increasing the coupling agent concentration further. That is because too much coupling agent might disperse in the interface between the Al particles and matrix, as a kind of low-thermal conductivity material, the redundant coupling agent would cause phonon scattering and give rise to decreasing thermal conductivity of the composites [14]. Additionally, at low coupling agent content the lower thermal conductivity can be attributed to that the coupler used can not effectively improve the phase interface bonding between Al particles and matrix.

Morphology

SEM micrographs of transversally cut samples containing 48 vol.% Al particles without or with surface treatments (couplers content: 1.5 wt% KH-550, KH-560 silane; and 1.2 wt% NDZ-102, NDZ-201 titanate) are observed in Fig. 5. From Fig. 5a it can be seen clearly that the smooth rounded holes observed in the micrograph are related to the Al particles that were pulled out from the fractured surface, indicating that the phase interactions force between epoxy and Al particles is very weak. Furthermore, there is almost

Fig. 5 SEM micrographs of the epoxy composites containing 48 vol.% Al particles **a** untreated, **b** KH-550, **c** KH-560, **d** NDZ-201, **e** NDZ-102



no matrix resin observed on the surface of Al particles, suggesting only low energy is needed to pull out Al particles from the matrix. Figure 5b–e represents the morphologies of different coupling agents treated Al particles/epoxy composites. They show an enhanced homogeneous distribution of Al particles throughout the entire epoxy matrix compared to that without surface treatment as seen in Fig. 5a. From Fig. 5b–e we can observe appropriate wetting characteristics at the interface since there are little voids found at the fractured surface. Moreover, the phase interface is rather indistinct, and even some phase interface layer can be noticed from Fig. 5c–e. Additionally, the distortion, deformation or broken pieces of cured epoxy matrix are found at the fracture surface from which the Al particles were pulled off, which demonstrates a nicer interfacial adherence between the Al particles and epoxy matrix.

Figure 5 proves that the use of coupling agents effectively improves the homogeneous dispersion of Al particles in epoxy, eliminates the agglomerate of filler, and decreases the air voids ($k_{\mathrm{air}} = 0.0024$ W/m K) content and defects in the composites. Therefore, the thermal conductivity is enhanced evidently at the presence of four couplers employed in this work..

Conclusion

FT-IR analysis results confirm that the silane and titanate coupling agents used in this study were chemically grafted on the alumina shell of Al particles.

The thermal conductivity always increases with increasing Al concentration up to 48 vol.%. The surface modification of Al particles has an evident effect on the thermal conductivity. The thermal conductivities of the composite containing 48 vol.% Al particles treated with the KH-550, KH-560, NDZ-102, and NDZ-201 couplers are 1.29, 1.48, 1.27, and 1.36 W/m K, respectively, corresponding to 1.03 W/m K of that without surface treatment. The thermal conductivity of the composites increases at a low concentration but decreases at a high concentration of the coupling agent used. At an optimal coupling agent concentration the maximum thermal conductivity value can be obtained.

SEM observation reveals that the use of coupling agents improves the interfacial adherence between Al particles and epoxy resin, and decreases the voids and defects at the phase interfaces.

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