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Enhancing thermal conductivity of epoxy with a binary filler system of h-BN platelets and Al_2O_3 nanoparticles

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A R T I C L E I N F O

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A B S T R A C T

Epoxy resin is a common adhesive bonding material used to join dissimilar materials, especially in the electronics and aerospace industries. However, its low thermal conductivity and high coefficient of thermal expansion limit the direct use of epoxy in practical applications. In order to improve thermo-mechanical properties, we have prepared a series of epoxy composites using a binary system of hexagonal-boron nitride (h-BN) and aluminum oxide (Al_2O_3) fillers and analyzed the effect of the ratio of these fillers on the thermal conductivity of composites. While h-BN platelets form the main thermal conductive network, Al_2O_3 nanoparticles bridge the separated h-BN platelets to build more thermal conductive pathways. We proposed the improving of thermal conductivity as well as the mechanical properties of the epoxy matrix by incorporating h-BN and Al_2O_3 fillers at an optimum ratio.

1. Introduction

Epoxy-based adhesives are being used in various industries effectively to join dissimilar materials and composites offering different advantages compared to mechanical joints [1]. Unfortunately, low thermal conductivity (~0.1 W/m K) and a high coefficient of thermal expansion of these epoxy-based adhesives limit their use in practical and special applications [2,3]. The durability and stability of electronic and mechanical devices depend on the operation temperature and the response to temperature variation. Therefore, developing an epoxy-based adhesive with high thermal conductivity is crucial. In recent studies, basically, two methods have commonly been used to improve the thermal conductivity. In the first group, electrically conductive materials such as graphite, graphene and carbon nanotube, etc., have been used at low filling content [4,5]. However, the dielectric breakdown strength of the composites decreases dramatically after the addition of the fillers. Moreover, these fillers certainly cause the composite to be electrically conductive [6]. In the second group electrically nonconductive fillers such as aluminum oxide (Al_2O_3) [7], zinc oxide (ZnO) [8], aluminum nitride (AlN) [9], boron nitride (BN) [2], and titanium dioxide (TiO_2) [10] are widely preferred. Additionally, the addition of these fillers enhances the physical properties of the epoxy resin (matrix) by increasing its thermal conductivity and lowering the coefficient of thermal expansion (CTE) [11]. In order to achieve a highly thermal conductive network, thermal conductivity, aspect ratio, size and loading content of the filler are crucial parameters.

Hexagonal boron nitride (h-BN) is considered to be an ideal choice thanks to its relatively high thermal conductivity (~300 W/m.K), low coefficient of thermal expansion, stable crystal structure, relatively low dielectric constant, high electrical resistivity, and nontoxicity [12]. It does not disturb the electrical properties of epoxy resins either [13,14]. However, in order to achieve high thermal conductivity (by forming a thermally conductive path) a high filler loading (>60 vol%) is needed. This situation causes a significant increase in the viscosity of the precursor mixture (filler and matrix), which hinders the homogeneous dispersion of fillers in the matrix. Recently, some studies have shown that Al_2O_3 nanoparticles can be loaded into h-BN incorporated epoxy matrix to build up thermal conductive pathways between h-BN platelets without increasing the viscosity of the epoxy matrix [13,15]. The formation of random bridges of networks between fillers improves the thermal conductivity of the composite [16,17]. However, the ratio between fillers and epoxy is a crucial parameter to achieve a high thermal conductivity.

The goal of this study is to present a systematic study on the effect of ratio between h-BN and Al_2O_3 fillers on the thermal and mechanical properties of an epoxy composite. Commercially available epoxy resin (Loctite 9412) was chosen as the matrix due to its extremely wide applications in the electronics, automotive and aerospace industries. We

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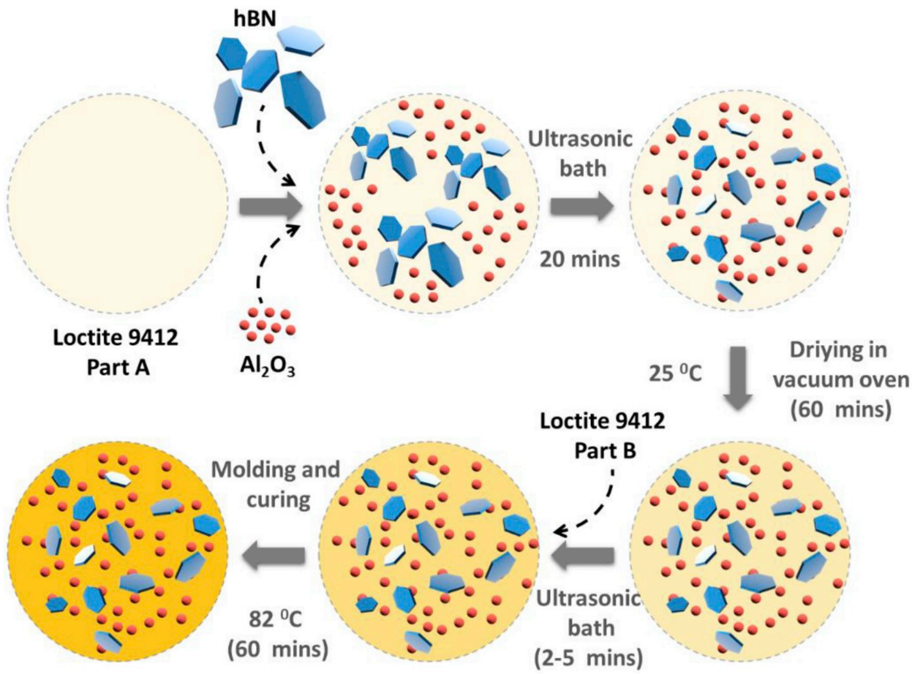

Fig. 1. Schematic flowchart of the synthesis processes of h-BN-Al_2O_3/Loctite composite.

used h-BN platelets to form the main thermal conductive network and Al_2O_3 nanoparticles for creating bridges (thermally conductive pathways) between h-BN platelets. We investigated the effect of both fillers in terms of thermo-mechanical properties by incorporating them into a commercially available epoxy matrix.

2. Experimental

Composites were prepared by a two-step process as shown in Fig. 1. First, Al_2O_3 (80 nm) and h-BN (65–75 nm) were dehumidified under 120 °C for 60 min. In the meantime, Loctite 9412 Part A was de-aired in a vacuum chamber (4.3 Torr). Then, the filler materials were cooled in air to room temperature. Since the cooling process takes a short time, re-humidification was not expected. Later, filler materials were added into the Loctite 9412 Part A (matrix) and mixed by hand to have a homogeneous mixture. Afterward, the mixture was placed into an ultrasonic cleaner for 20 min and degassed under vacuum (4.3 Torr) for 60 min. Then, Loctite 9412 Part B (curing agent) was added to the previous mixture by slowly mixing it to have homogeneous color. The final mixture was ultrasonicated for 2–5 min to promote a good dispersion and was then poured into testing molds. The molds were heated to 82 °C for 60 min in an oven to obtain full cure. Samples were labeled as 10 wt% Al_2O_3, 10 wt% h-BN, 20 wt% h-BN, 22.5 wt% h-BN+7.5 wt% Al_2O_3 and 24 wt% h-BN+7 wt% Al_2O_3 according to filler materials percentage in the composite.

Functional groups were identified by Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27) over the range 4000–600 cm^{-1} with an accuracy of 2 cm^{-1}. The surface morphology of the composites was studied by scanning electron microscopy (SEM, Supra55VP-Carl Zeiss). Differential scanning calorimetry (DSC, TA Instrument Q200) was performed at temperatures from 30 °C to 100 °C at a heating rate of 10 °C/min under a nitrogen atmosphere (25 mL/min) to study the glass transition temperature (Tg) of the composites. Dynamic mechanical analysis (DMA) was performed using a ARES G2 rheometer. The testing temperature was set as from room temperature to 100 °C a heating rate of 3 °C/min. The thermal conductivity value was measured with a guarded heat flow meter (TA Instrument DTC-300) under room conditions.

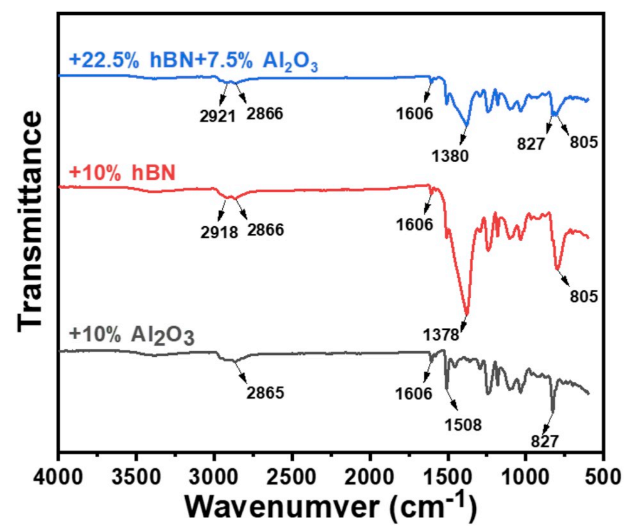

Fig. 2. FT-IR spectra of the composites at different filler adding (all percentages are given in wt%).

3. Results and discussion

FT-IR spectra of 10 wt% Al_2O_3, 10 wt% h-BN and 22.5 wt% h-BN+7.5 wt% Al_2O_3 composites are shown in Fig. 2. The broad absorption peak around 3400 cm^{-1} represents hydroxyl and amino groups at the edges of filler materials. The peaks at 2921 cm^{-1} and 2866 cm^{-1} are characteristic of asymmetric and symmetric C–H (-CH_2) stretching vibrations, respectively. The peaks at 1606 cm^{-1} and 1510 cm^{-1} can be assigned to amide C=O stretching. The strong absorption at 1380 cm^{-1} is due to B–N stretching and the peak at 1380 cm^{-1} is attributed to B–N bending [18,19].

The cross-sections of the prepared epoxy composites with different amounts of h-BN and Al_2O_3 fillers are presented in Fig. 3. It can be observed clearly that the h-BN and Al_2O_3 fillers were uniformly dispersed in the epoxy matrix (h-BN platelets and Al_2O_3 nanoparticles are shown by red and orange arrows, respectively). It is believed that

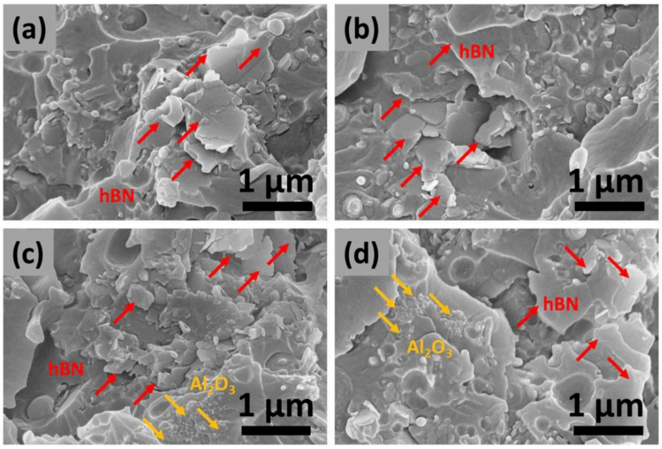

Fig. 3. SEM image of composite at **(a)** 10 wt% h-BN, **(b)** 20 wt% h-BN, **(c)** 22.5 wt% h-BN+7.5 wt% Al_2O_3 and **(d)** 24 wt% h-BN+6 wt% Al_2O_3 adding.

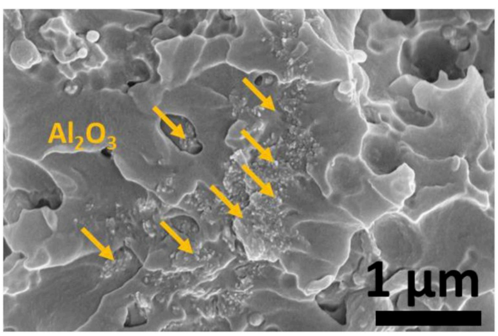

Fig. 4. SEM image of the composite at 10 wt% Al_2O_3 adding.

these two different morphologies (Fig. 3 a, b and Fig. 3 c, d) would provide different pathways for heat flow through the h-BN/Al_2O_3 particulate network to reduce thermal resistance in the composite structure. For comparison, the dispersion of Al_2O_3 nanoparticles in the epoxy matrix is shown in Fig. 4.

The temperature-dependent mechanical properties (storage modulus and loss factor) of the composites were analyzed by DMA as shown in Fig. 5. These properties are highly dependent on the amount of the h-BN and Al_2O_3 fillers in the epoxy matrix. Fig. 5a shows that the storage modulus increased after adding the h-BN and Al_2O_3 fillers into the epoxy matrix. Similarly, the peak position of loss factor ($\tan\delta = G'' / G'$ where G'' is the loss modulus that can be stated as the energy dissipation of

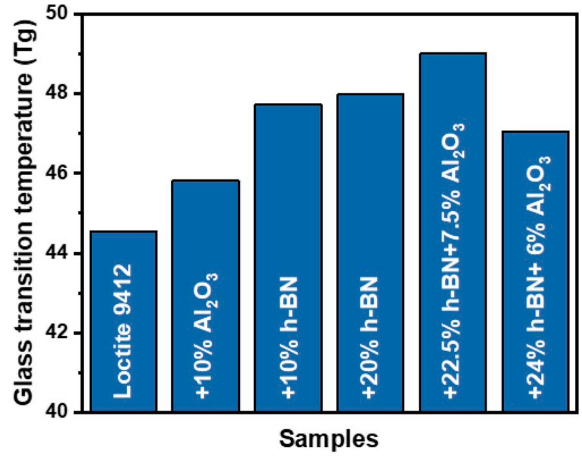

Fig. 6. The glass transition temperature (Tg) of epoxy and prepared filler(s)/epoxy composites (all percentages are given in wt%).

polymer chain motions and G' refers the elastic response of the polymer system) shifted to higher temperatures after adding filler as shown in Fig. 5b. The tan δ of composites gives an estimation of the damping effect of the polymer network.

The glass transition temperature (T_g) can be obtained from the peaks of the tan δ curves. It is well known that higher T_g values are preferred in the aerospace industry to widen the service temperatures of the structures. 22.5 wt% h-BN+ 7.5 wt% Al_2O_3 shows the highest T_g value (49.73 °C) which can be interpreted in terms of the addition of h-BN platelets and Al_2O_3 particles to the epoxy resin decreasing the free space in the epoxy matrix as given in Fig. 6.

The thermal conductivity (at different temperatures from −15 °C to 100 °C) of the Loctite 9412 (pure epoxy matrix) and the prepared composites are shown in Fig. 7a. As expected, the thermal conductivity increased with the increasing amount of the h-BN platelets and Al_2O_3 nanoparticles due to increased thermal conductive pathways and networks in the epoxy matrix. The thermal conductivity changed from 0.26 to 0.32 W/m.K at 100 °C while h-BN content was increased from 10 to 20 wt% (which is similar to the results of Gu et al. who showed a thermal conductivity of almost 0.30 W/m.K at 20 wt% BN) [20]. One can see that the thermal conductivity of the prepared composites is mainly provided by h-BN platelets. With the increase of h-BN concentration, the platelets started to contact and form the thermal conduction pathways as shown in Fig. 7b. This schematic diagram represents the possible heat flow pathways (red lines) between h-BN platelets interacting with each other. However, using only h-BN platelets may not be enough for an effective heat transfer through the composite structure due to the high thermal

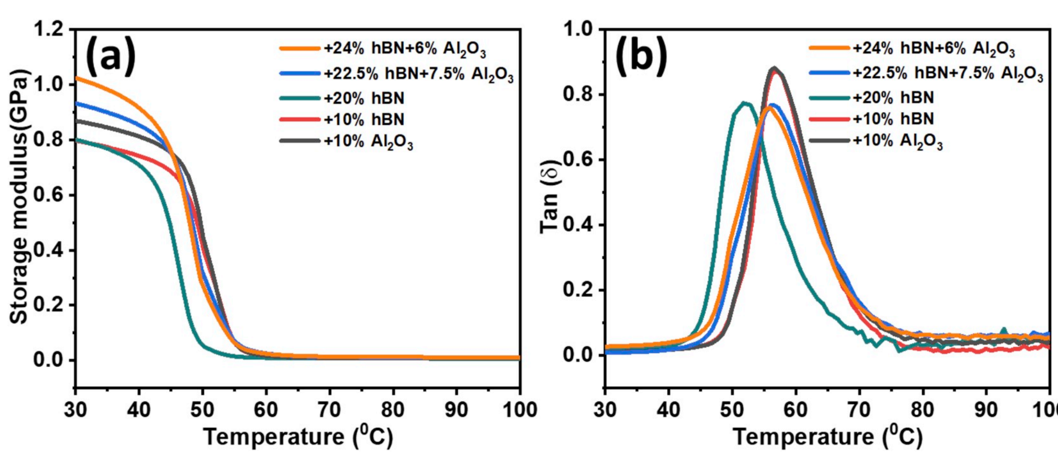

Fig. 5. **(a)** Storage modulus and **(b)** loss tangent versus temperature of prepared composites (all percentages are given in wt%).

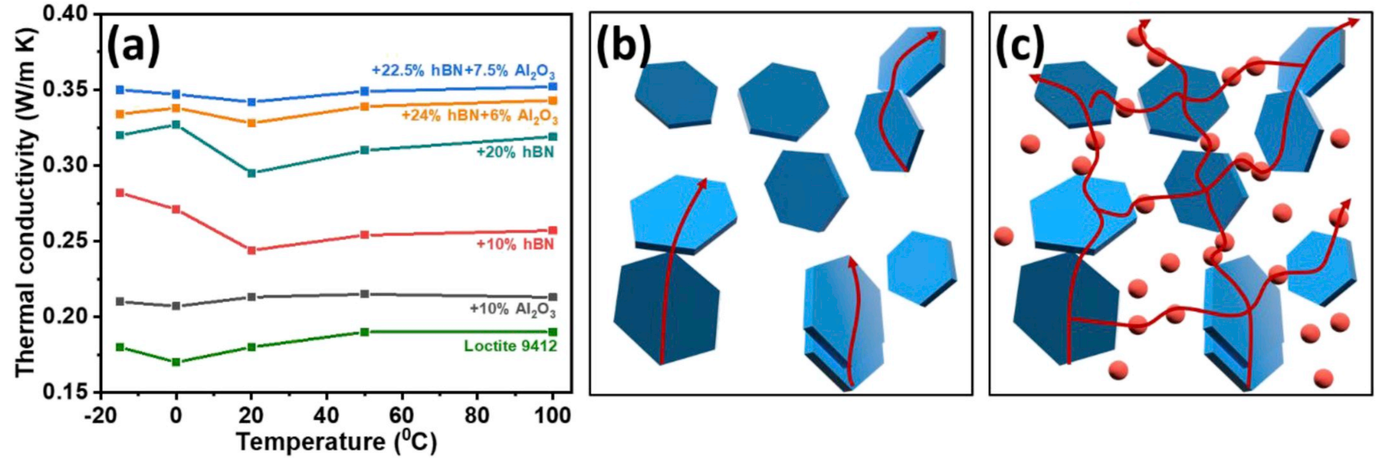

Fig. 7. (a) Effect of filler type and amount on the thermal conductivity of epoxy composites. Schematic description of thermal conductive paths in (b) h-BN platelets/epoxy and (c) h-BN + Al_2O_3/epoxy composites (all percentages are given in wt%).

resistance (gaps) between separated h-BN platelets.

In order to increase the thermal conductivity, one should form contact between h-BN platelets. After adding Al_2O_3 nanoparticles to the h-BN/Loctite composite, Al_2O_3 particles filled the gaps between isolated h-BN platelets and acted as a "bridge" to promote the heat flow (red lines) as shown Fig. 7c. Therefore, the thermal conductivity of the 22 wt% h-BN-7.5 wt% Al_2O_3 composite reached 0.35 W/m K (which can be achieved by a BN content over 30 wt%) [20]. It can be seen that h-BN platelets play the major role on the thermal flow, and the amount of the Al_2O_3 particles is crucial to improve the overall thermal conductivity. When composite does not have enough Al_2O_3 nanoparticles to fill gaps between h-BN platelets (24 wt% h-BN-6 wt% Al_2O_3), an increasing amount of h-BN platelets seems not to be able to improve thermal flow by itself (0.34 W/m K). This situation explains why the 22 wt% h-BN-7.5 wt% Al_2O_3 composite showed better performance than the 24 wt% h-BN-6wt% Al_2O_3 system as shown in Fig. 7a.

Even though it is quite difficult to make a direct comparison of our results with others presented so far in the literature, it is important to analyze the outcome in a global sense. However, the information about the performance of synergetic mixture for different particles is restricted at the same time. A complimentary study about the performance of nano/nano mixtures is necessary. Considering studies in the literature, composite structures including micro-h-BN particles have nearly a 250% enhancement in thermal conductivity with 20 wt% particle: epoxy ratio (see e.g. Ref. [19]). Moreover, there is up to a 45% improvement in storage modulus of a composite adhesive (see e.g. Ref. [21]), where T_g values were also increased by 18%. In the case of Al_2O_3 nanoparticles (rather than T_g) a significant increase (by 20%) of the storage modulus was reported [22]. Also, an increase of the thermal conductivity of an organic matrix by 150% was shown by adding Al_2O_3 nanoparticles at 50 wt% [16]. There have also been studies which cover the use of micro h-BN and nano Al_2O_3 combined to enhance the thermal conductivity of insulating epoxy resins. It was reported that adding a mixture of h-BN and Al_2O_3 fillers at 30 wt% can enhance the thermal conductivity of the epoxy matrix by almost 700% [13]. On the contrary, the same effect is not observed in terms of glass transition temperature and corresponding mechanical properties. Moreover, most similar studies report only the use of microsized h-BN filler. Therefore, there is a strong need for more systematic studies to understand the synergetic effect of nanosized h-BN and Al_2O_3 fillers for designing future epoxy-based composite and adhesives.

4. Conclusions

In this study, a series of epoxy composites with a binary system of h-BN platelet and Al_2O_3 nanoparticle fillers have been prepared to identify the effect of filler ratio on thermal conductivity. h-BN platelets form the main thermally conductive networks in the composite and Al_2O_3 nanoparticles connect isolated h-BN platelets like a bridge to form thermal conductive pathways. The strength modulus and thermal conductivity of a 22.5 wt% h-BN+7.5 wt% Al_2O_3 composite were found to reach 0.94 GPa and 0.35 W/m.K, respectively. This shows that with a binary system of h-BN platelets and Al_2O_3 nanoparticles, thermal conductivity can be improved almost two times in comparison to the neat epoxy 0.19 W/m.K. The epoxy resin composite with higher thermal conductivity could be a potential epoxy-based adhesive in the electronic, automotive and aerospace industries.

Declaration of competing interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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