Effect of the Filler Structure of Carbon Nanomaterials on the Electrical, Thermal, and Rheological Properties of Epoxy Composites

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ABSTRACT: Carbon nanotubes (CNTs) and graphene nanosheets (GNSs) were used as fillers in epoxy composites with the aim of increasing the electrical and thermal conductivities of the composites. The filling of pristine CNTs produced the highest electrical conductivity (σ), whereas a high CNT functionalization and the two-dimensional planar structure of GNSs were promising for improving the thermal conductivity. A combination of CNTs and GNSs exploited the advantages of both. When the CNT fraction was larger than 50 wt %, a higher σ was obtained. When a small amount of functionalized CNTs was added to the GNSs, the thermal conductivity was also increased. The rheological measurements revealed the lowest complex viscosity for the GNS filling and showed the exciting advantages of an easy processing. As a result, the mixed filling also exhibited a much lower viscosity than the pure CNT fillings. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3366–3372, 2013

INTRODUCTION

For decades, carbon-based fillers, such as carbon black, nanofibers, carbon nanotubes (CNTs), graphite, and graphene nanosheets (GNSs), have been used to impart electrical or thermal conductivity into the polymer matrix, which is usually an insulator for electrons and heat. Among these fillers, carbon nanomaterials, especially CNTs and GNSs, have the merit of a low percolation threshold because of their large aspect ratio and surface area. For the electrical properties of composites, the percolated pathways of conductive fillers play the most important role. CNTs are thus widely used because of their high abilities to conduct electrons.[1,2] However, the thermal conductivity is mainly affected by the interfacial resistance between the filler and the polymer matrix. Because of their planar structure, GNSs show a remarkable improvement in their thermal conductivity at low loadings, much more than that of CNTs.[3,4]

To achieve superior performance in composites filled with carbon nanomaterials, one might run into problems with regard to the dispersion of nanofillers in the polymer matrix and the interaction between them. These two issues are strongly related to the filler structure[2,5,6] and have different influences on the mechanical, electrical, and thermal properties. For the CNT fillings, there have been plenty of studies on the structural effects

of the tube diameter, wall thickness, tube length, and surface modification. However, another important issue, the rheological properties concerned with the processing,[7–10] has not been widely studied. Recently, a synergistic effect caused by the combination of CNTs and GNSs was reported;[11,12] this effect was ascribed to the bridging of CNTs across adjacent GNSs. Such a combination obviously also has structural effects from the two components and might have different influences on the electrical and thermal properties. For example, at a large loading of 10 wt %, although the thermal conductivity was improved because of the synergistic effect of single-walled carbon nanotubes (SWCNTs) and GNSs, the electrical properties were damaged because of the Schottky barrier, particularly between the GNSs and the semiconducting SWCNTs.[11] At a low loading of 1 wt %, unfortunately, it is still not known how the synergistic effect influences the electrical conductivity (σ).[12] In another study, where multiwalled carbon nanotubes (MWCNTs) and carbon black were filled at low loadings, an enhanced σ was observed as the carbon blacks filled the gaps between CNTs.[13]

In this article, we present a systematic study on the electrical, thermal, and rheological properties of epoxy composites filled with carbon nanomaterials at low loadings (<2 wt %). Single fillings of two types of pristine MWCNTs, —COOH-

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functionalized multiwalled carbon nanotubes (MWCNT–COOH) and GNSs, produced different σs, thermal conductivities, and complex viscosities. A high level of CNT functionalization decreased the CNT aggregation and, therefore, the viscosity. It was also promising that it reduced the thermal resistance as more phonons could be exchanged at the modified CNT–matrix interface. However, to improve σ, one should avoid functionalization. For the two-dimensional GNSs, although they cannot increase σ as high as the pristine CNTs, its planar structure allows a stronger interaction with the matrix to reduce the packing phenomenon and thus the viscosity and provides a more efficient interfacial thermal exchange. When a CNT–GNS network is formed in epoxy composites, both the electrical and thermal conductivities can be improved with the improvement depending on the total loading, type of CNTs, and CNT–GNS mass ratio. Furthermore, GNS is very important for reducing the viscosity, a parameter determining the difficulty of processing, for both its pure loading and the mixed one with CNTs.

EXPERIMENTAL

Three different types of CNTs were used, namely, MWCNT-I (pristine, purity > 95%, diameter = 20–30 nm, length $\approx$ 20 μm), MWCNT-II (pristine, purity > 95%, diameter = 30–50 nm, length $\approx$ 20 μm), and MWCNT–COOH (functionalized, diameter = 30–50 nm, length $\approx$ 20 μm). MWCNT-I was purchased from CNano Technology, Ltd. (Beijing, China), and MWCNT-II and MWCNT–COOH were purchased from Organic Chemicals Co., Ltd. (Chengdu, China). The GNSs, purchased from Plan Nano Technology Co., Ltd. (Tianjing, China), were had four to eight layers (>85%) with a thickness of 2–4 nm and a lateral size ranging from hundreds of nanometers to tens of micrometers. The epoxy resin (CYD-128) was purchased from Baling Petrochemical Co., Ltd. (Yueyang, China). The curing agent, methyl tetrahydrophthalic anhydride, was purchased from Orient Chemical Factory (Jiaxing, China). The accelerating agent tris(dimethylaminomethyl) phenol was purchased from Tianhe Resin Co. Ltd. (Nantong, China).

The mixture of CNTs and GNSs was dispersed at a desired mass fraction in the epoxy resins by an EXAKT 50 three-roll mill (EXAKT Vertriebs GmbH, Norderstedt, Germany). The roller gap was 5 μm, and the rotation speed was 270 rpm. The dispersion process was repeated five times. After the curing and accelerating agents were added to the resins, with an epoxy–methyl tetrahydrophthalic anhydride–tris(dimethylaminomethyl) phenol mass ratio of 100 : 85:3, the resins were degassed at 80°C *in vacuo* for 20 min and then transferred into a prepreg. The curing was performed at 90°C for 2 h, 120°C for 2 h, and finally, 150°C for 4 h. Notice that in the whole study, we used the mass fraction of filler in epoxy resins to define the magnitude of loading without considering the masses of the two agents. That is, the final mass fraction should be scaled by division by a factor of 1.88.

The σ of the cured composite was measured from the current–voltage characteristics with a CHI-660C electrochemical workstation (Chenhua Instrument Co., Ltd., Shanghai, China). The thermal conductivity was measured with a DRL-III thermal conductivity meter, Xiangtan Instrument & Meter Co., Ltd. (Xiangtan, China). The rheological measurements were carried

out in an oscillatory mode on a Bohlin Gemini 200 rheometer (Malvern Instruments, Worcestershire, United Kingdom) for the epoxy resins before the curing and accelerating agents were added. A temperature ramp rate of 5°C/min and a frequency of 1 Hz were used.

RESULTS AND DISCUSSION

Carbon Nanomaterials

MWCNT-I and MWCNT-II were different mainly in their tube diameters, whereas MWCNT–COOH could be considered to be —COOH-functionalized MWCNT-II. As the aspect ratio of these CNTs was sufficiently large, of 400–1000, we found that the level of CNT functionalization might have played a more important role than the tube diameter because the level of structural imperfection, for example, the functionalization and defects, significantly determined the electrical and thermal properties of the CNTs. Figure 1 provides the Raman spectra for the CNTs and GNS. By calculating the ratio between the intensities of the D and G peaks (I_D:I_G), a quantity reflecting the level of imperfection, we found that MWCNT-I had the most perfect cylindrical structure, with I_D:I_G = 1.54. The ratio was still high because of sidewall defects. Although an annealing treatment could have improved the crystallinity by removing the sidewall defects,[14] all of the CNTs were used as received to study the influences from different levels of imperfection. For MWCNT-II and MWCNT–COOH, I_D:I_G became higher, up to 1.72 and 2.22, respectively. Therefore, it became possible to compare the structural dependence on single fillers and, furthermore, the effect of mixed filling with different combinations of CNTs and GNSs.

Single Fillings

Rather than starting the discussion from the electrical and thermal properties of the epoxy composites, here we first put special focus on the rheological properties on the analysis of the structural effects of single fillers. This is because the physical properties of the composites filled with carbon nanomaterials strongly depended on the filler network formation, which is generally controlled by the thermorheological history and the processing conditions.
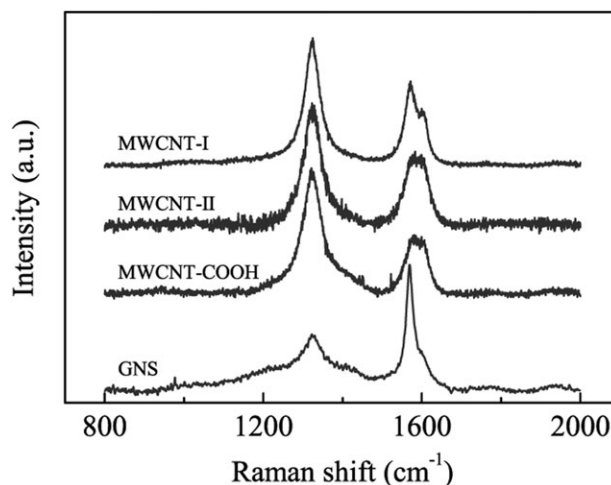

Figure 1. Raman spectra for MWCNT-I, MWCNT-II, MWCNT–COOH, and GNS.

Rheological Properties. Figure 2 shows the complex viscosity as a function of the temperature for the four different fillers at two loadings of 1 and 2 wt %. For each filler, the viscosity decreased upon heating in the beginning as the heating improved the movability of the epoxy resins. Then, the viscosity reached a plateau. This was because an increasing number of resins was cured as the temperature increased, and a further decrease in the viscosity was hindered. When the temperature was above 110°C, the curing started for all resins and made the viscosity increase sharply. For the point of view of processing, the lower the viscosity was at low temperature, the easier preparation of the resin–nanofiller mixture was. At the 1 wt % loading, the largest viscosity (at temperature < 60°C) was found for the MWCNT-I loading [see Figure 2(a)]. This was because these tubes had the most perfect cylindrical structure and increased the tendency to aggregate.[15] (In fact, the thinner tube diameter was another reason for the aggregation.) Figure 3(a) shows that a certain aggregation was observed in the final cured MWCNT-I/epoxy composite, even though the milling was repeated five times. For MWCNT-II and MWCNT–COOH, the viscosity was significantly decreased because the functionalized CNT surface allowed easier dispersion in matrix. For example, it became difficult to find aggregated CNTs in the MWCNT–COOH/epoxy composite [see Figure 3(b)]. For the planar structure of GNS, we suspect that the wide contact area allowed more polymer molecules to interact with the GNSs and thus lowered its movability. Therefore, the aggregation of GNSs was difficult. As shown in Figure 3(c), although there were many small pieces of GNS in a length scale of about 10 μm, these pieces did not pack together. However, despite the different magnitudes of viscosity, all of these carbon fillers induced an increase in the viscosity because of their large molecular sizes.

When the loading was increased up to 2 wt %, the viscosity became higher [see Figure 2(b)]. However, the increment was quite different for these nanofillers. For MWCNT-I, the viscosity increased by nearly six times, from about 7 Pa s up to

50–59 Pa s. According to the higher level of imperfection, MWCNT-II and MWCNT–COOH made smaller increments than MWCNT-I. For the GNSs, the viscosity was nearly unchanged and was still smaller than 1 Pa s; this indicated that its two-dimensional structure always allowed a much easier processing than the one-dimensional tube structure.

Notice that in this study we adopted the same curing process for all of the composites. However, this might have been influenced by the various nanofillers. Fortunately, the influence was negligible at low loadings of 2 wt % or lower because the difference in the final structure, as shown in Figure 3, had a relationship mainly with the different dispersion results and rheological properties.

Electrical Properties

Figure 4(a) shows the comparison of σ for different epoxy composites. The difference in conductivity indicated that the insulating nature of the matrix was not essential to the electronic transport properties, whereas the conducting fillers played a role.[16] The MWCNT-I/epoxy composite had the highest conductivity of 0.176 S/m, which was more than 11 orders of magnitude larger than that of the pure epoxy (1.2×10^{-12} S/m). When the level of functionalization was higher, the conductivity became about two and seven orders of magnitude smaller than those of MWCNT-II (0.001 S/m) and MWCNT–COOH (1.9×10^{-8} S/m), respectively. As the GNSs were highly reduced (indicated by the Raman spectrum in Figure 1), the measured conductivity of 0.0004 S/m was nearly the same as that of the MWCNT-II/epoxy composite. It was still much smaller compared to the MWCNT-I filling because the electron hoppings between the GNSs might have been suspended as more epoxy resins interacted with them.

The lowest loading needed for the insulator–conductor transition in composites is defined as the *percolation threshold*. Here, we used a conductivity of 10^{-5} S/m as a criterion. The threshold was less than 0.2 wt % for the MWCNT-I filling, and it was
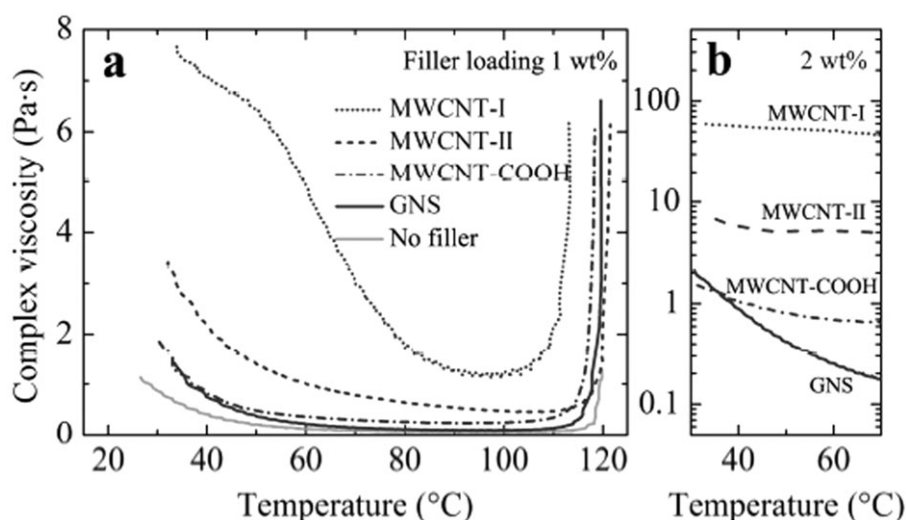

Figure 2. Complex viscosity as a function of the temperature, measured at a ramp rate of 5°C/min and a frequency of 1 Hz, with the loading different carbon nanofillers at loadings of (a) 1 and (b) 2 wt %. For a better comparison, the viscosity at 2 wt % was plotted in a log scale with temperatures of 30–70°C.
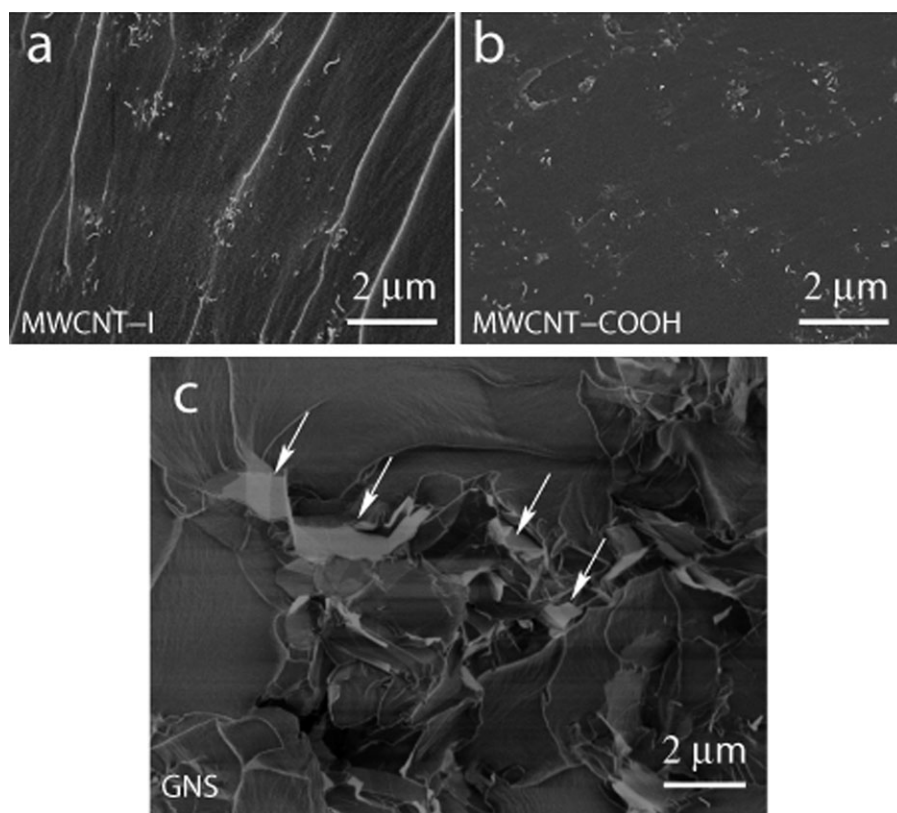
Figure 3. Scanning electron microscopy images of the epoxy composites filled with (a) MWCNT-I, (b) MWCNT–COOH, and (c) GNS with a filler loading of 1 wt %. The four selected places of GNS are marked by arrows.

0.3 wt % when then the GNSs were used [see Figure 5]. This difference was caused by the different filler structure (the difference was even >1 wt % when another matrix was changed[17]). For the former, the average tube length of about 20 μm could be well maintained with the three-roll mill.[18] This means that an efficient percolation network can be formed at a sufficiently low filler loading.[19,20] For the latter, as more matrix molecules might have interacted with the GNSs because of the large surface area, the probability of the formation of the GNS–GNS contact was reduced. Therefore, to form the connected network, more fillers needed to be loaded into the matrix. The situations for MWCNT-II and MWCNT–COOH were different yet generally showed a trend in which the surface modification increased the percolation threshold.[21,22] The threshold for MWCNT-II was nearly the same with the GNSs, whereas it could not be measured for MWCNT–COOH as the conductivity was still one order of magnitude smaller than the criterion even at a loading of 2 wt %.

Thermal Properties. Contrary to the electrical properties, where defect and functionalization degrade the conductivity, the higher the level of surface modification was, the more efficient the heat transfer at the filler–matrix interfaces was. Such a trend could easily be observed from different CNTs. The most perfect cylindrical structure of MWCNT-I induced the largest interfacial thermal resistance with the surrounding matrix.[23–26] Therefore, the improvement in the thermal conductivity was only 5% at the 1 wt % loading [see Figure 4(b)]. When there were more defects or functional groups on the CNT surfaces, such as in MWCNT-II

and MWCNT-COOH, the interfacial thermal exchange was enhanced, and this resulted in improvement of 7.6 and 14.6%, respectively. However, although the GNSs were nearly not functionalized (Figure 1), their planar structure significantly increased the interfacial contact area and connected more matrix polymers to interact with the GNSs. Therefore, it allowed more phonons to be exchanged at the GNS–matrix interfaces, decreased the interfacial thermal resistance, and thus helped the heat flow to pass more efficiently through fillers. As a result, the thermal conductivity was improved the most, by 17.4%.

It is important to point out that when functionalization is introduced to reduce the nanofiller–matrix interfacial thermal resistance, it also decreases the intrinsic conductivity of the nanofiller because of the reduction in phonon scattering length.[27] However, the decrease is still below one order of magnitude even at a high level of functionalization of 10 atom %[23] or just up to one-half in another recent study.[28] Therefore, the reduced conductivity is still much higher than that of the pure matrix, such as an epoxy; this indicates that a reduction in the interfacial resistance plays the most important role.

Mixed Fillings
Following the idea of combining the advantages of different fillers,[11,29,30] we added to the epoxy matrix a mixture of CNTs and GNSs with a designed mass ratio between them. Here, MWCNT-I and MWCNT–COOH were combined with the GNSs to optimize the electrical and thermal conductivities,
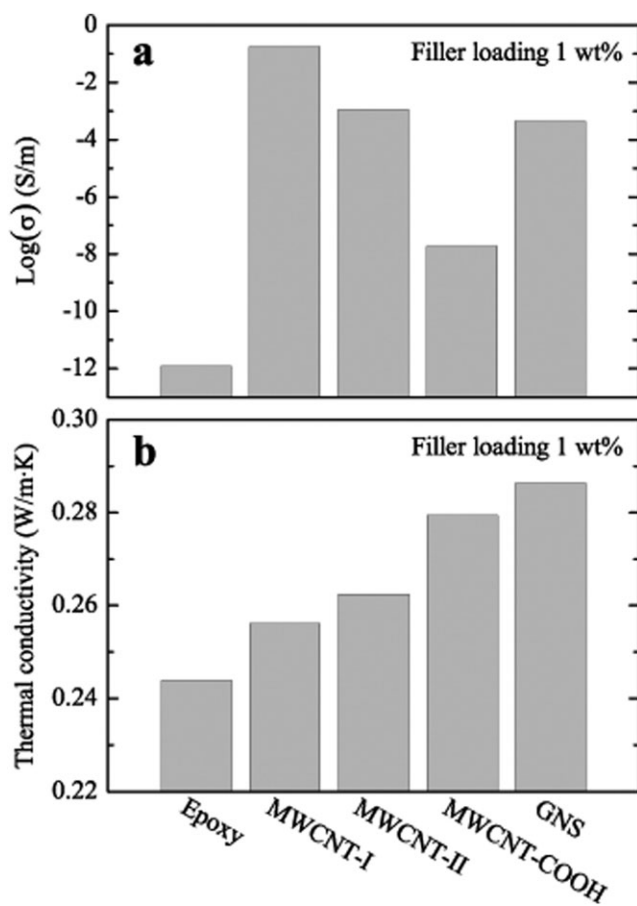
Figure 4. (a) σ and (b) thermal conductivity values of the pure epoxy and epoxy composites filled with 1 wt % MWCNT-I, MWCNT-II, MWCNT–COOH, and GNS.

Figure 5. (a) σ and (b) thermal conductivity values of the epoxy composites as functions of the filler loading.

respectively. Such combinations are typical to reveal the effect of a CNT–GNS network on the matrix. (Other combinations can be considered according to one's request; however, we found that it was always difficult to reach the highest electrical and thermal properties at the same time.) Figure 5(a,b) shows the results for our choices of combination.

Electrical Properties. Because of their different structures, the MWCNT-I filling required a lower percolation threshold than the GNSs to reach an σ of 10^{-5} S/m. With a further increase in the loading up to 2 wt %, the MWCNT-I/epoxy composite still exhibited a conductivity that was more than one order of magnitude larger than that filled with the same amount of GNSs. It seemed that when the CNTs were changed partly into GNSs, there should have been a decrease in σ. This was correct at high loadings. For example, at the same loading of 10 wt %, the SWCNT–GNS mixture decreased the conductivity by about two to four orders of magnitude compared with the two single fillings.[11] On the contrary, we observed an increase when 0.2–0.4 wt % mixed fillers were used. Figure 5(a) shows the results at the CNT–GNS mass ratio of 1 : 1. The conductivity at the 0.3 wt % mixed loading was 2.9×10^{-2} S/m, which was much higher than the values of 2.4×10^{-3} and 2.3×10^{-5} S/m for the MWCNT-I and GNS loadings, respectively. At the 0.4 wt
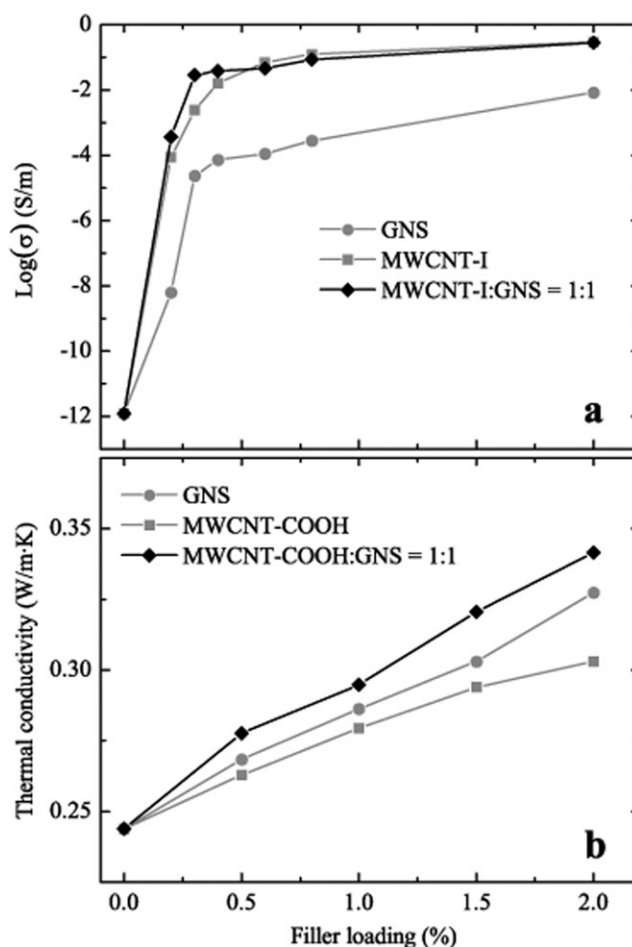
% loadings, the difference in the conductivity became smaller. Above 0.5 wt %, there were no differences between the CNT–GNS and pure CNT loadings. This indicated that around the percolation threshold, a certain amount of planar GNSs might have connected the CNTs separated as far as several micrometers along two different dimensions, much more than the one-dimensional bridging by individual CNTs. However, at high loadings, as all of the CNTs could be connected with themselves, the addition of GNSs provided little contribution to the conductivity or even might have destroyed the efficient CNT conducting pathways.[11]

The change in the electrical properties depended on the CNT–GNS mass ratio. At the 0.4 wt % loading, where the difference was still measurable, the conductivities were 0.0162, 0.054, 0.0386, 9×10^{-4}, and 7.3×10^{-5} S/m with ratios of 1 : 0, 2 : 1, 1 : 1, 1 : 2, and 0 : 1, respectively. Clearly, the CNTs determined the electrical properties more greatly, whereas a small amount of GNSs could remarkably facilitate network formation at low filler loadings.

Thermal Properties. Rather than the pristine CNTs, we used the most MWCNT–COOH. Figure 5(b) shows the thermal conductivities as functions of the filler loading for GNSs,

MWCNT–COOH, and their mixture at a mass ratio of 1 : 1. Generally, a thermal threshold did not exist as the conductivity was monotonically increased with the amount of carbon nanofillers. Compared with MWCNT–COOH, the GNSs had a greater ability to improve the conductivity; this was mostly ascribed to the planar structure. For CNTs, even though the highly functionalized ones were used, their one-dimensional structure restricted the number of neighboring resins and heat exchange with the matrix. (Although it was not measured in this study, we believe that if the GNSs were also highly functionalized, the improvement in the thermal conductivity could have been even higher.) When the two structures were mixed, a synergistic enhancement was observed because of the bridging of the CNTs over nonneighboring GNSs, as shown in Figure 6(a), where two GNS layers were connected by the CNT network. At the 1 wt % loading, the GNSs, MWCNT–COOH, and their mixture (mass ratio = 1 : 1) improved the thermal conductivity of the epoxy matrix up to 0.286, 0.279, and 0.295 W m^{-1} K^{-1}, respectively. These values agreed very well in magnitude with a recent study (up to 0.321 W m^{-1} K^{-1}), where

a similar group of functionalized CNTs and GNSs was used.[12] However, because of the low loading, the difference of 0.009–0.016 W m^{-1} K^{-1} between the mixed and single fillings was much smaller than that at a high loading of 10 wt %.[11]

By changing the mass ratio for the CNT–GNS filler, we found that the greater the amount of GNSs was, the higher the thermal conductivity was. Also at the 1 wt % loading, when the ratios were 2 : 1 (more CNTs) and 1 : 2 (more GNSs), the conductivities were measured to be 0.291 and 0.299 W m^{-1} K^{-1}, respectively. It was an interesting result because, for the thermal conductivity, a small amount of CNTs might have played a bridging role between the nonneighboring GNSs, whereas when the CNT content was increased further, the larger CNT–matrix interfacial resistance drew back the overall performance. Notice that the optimal CNT–GNS ratio might have been even down to 1 : 9, depending on the filler structures.[12] Furthermore, with increasing loading, the CNT–GNS network showed a better ability to improve the thermal conductivity.

Rheological Properties. Although the loading of carbon nanofillers significantly improved the electrical and thermal properties, the increase in viscosity made the processing more difficult. MWCNT-I was the worst because, after the loading, the viscosity of epoxy at room temperature was increased by nearly seven times (Figure 2), whereas for the MWCNT–COOH and GNSs, the increases were very small. Thus, to achieve the highest thermal conductivity by a combination of the MWCNT–COOH and GNSs, there should have been no difference in the processing compared with the two single fillers. In fact, in results that were more exciting than we expected, a slight decrease in the viscosity was observed for the MWCNT–COOH–GNS filling. To show such a decrease more clearly, we preferred to compare the MWCNT-I–GNS loading with the corresponding single loadings [see Figure 6(b)]. At the same 1 wt % loading and at 30–40°C, the MWCNT-I and GNS increased the complex viscosity up to about 7 and 1.5 Pa s, respectively, whereas their mixture increased it up to about 4 Pa s. The viscosity seemed to be the sum of their components. For example, at a 2 wt % mixed loading, a viscosity of about 8 Pa s was also very close to the sum of their single loadings at 1 wt %. Therefore, more than the enhanced electrical and thermal conductivities, the mixed loading could make the processing more convenient, where the two-dimensional GNSs obviously played a key role.
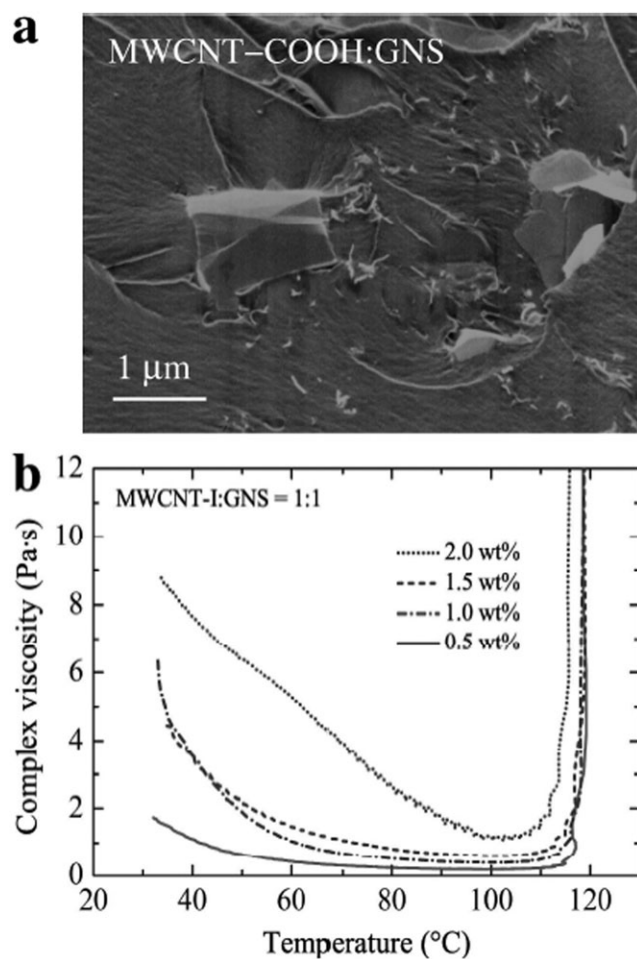
CONCLUSIONS

We studied the effects of single and mixed loadings of carbon nanofillers on the electrical, thermal, and rheological properties of epoxy composites. For the single loadings, the surface modification of the CNTs benefitted the thermal conductivity and composite processing but decreased σ. The two-dimensional GNSs were very promising for taking the place of CNTs because of their the ability to disperse well and their enhanced interfacial heat exchange. For the mixed loadings, there were two ways to design the fillers. On one hand, when a small amount of CNTs were replaced by GNSs, the planar structure helped to form a more efficient network for electron transfer within the matrix, especially around the percolation threshold. On the

Figure 6. (a) Scanning electron microscopy image showing the bridging effect. The filler loading was 1 wt %, and the MWCNT–COOH–GNS mass ratio was 1 : 1. (b) Complex viscosity as a function of the temperature at different total loadings of mixed filler with an MWCNT-I–GNS mass ratio of 1 : 1.

other hand, when the GNSs were mixed with a small amount of CNTs, the latter could bridge the nonneighboring GNSs to introduce more interfacial heat exchanges. Compared with the CNT loading, the mixed one also had an important advantage for processing, as reflected by the small rheological viscosity.

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