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SPECIAL TOPIC — 80th Anniversary of Northwestern Polytechnical University (NPU)

Effects of filler loading and surface modification on electrical and thermal properties of epoxy/montmorillonite composite*

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Epoxy-based composites containing montmorillonite (MMT) modified by silylation reaction with γ-aminopropyltriethoxysilane (γ-APTES) and 3-(glycidyloxypropyl) trimethoxysilane (GPTMS) are successfully prepared. The effects of filler loading and surface modification on the electrical and thermal properties of the epoxy/MMT composites are investigated. Compared with the pure epoxy resin, the epoxy/MMT composite, whether MMT is surface-treated or not, shows low dielectric permittivity, low dielectric loss, and enhanced dielectric strength. The MMT in the epoxy/MMT composite also influences the thermal properties of the composite by improving the thermal conductivity and stability. Surface functionalization of MMT not only conduces to the better dispersion of the nanoparticles, but also significantly affects the electric and thermal properties of the hybrid by influencing the interfaces between MMT and epoxy resin. Improved interfaces are good for enhancing the electric and thermal properties of nanocomposites. What is more, the MMT modified with GPTMS rather than γ-APTES is found to have greater influence on improving the interface between the MMT filler and polymer matrices, thus resulting in lower dielectric loss, lower electric conductivity, higher breakdown strength, lower thermal conductivity, and higher thermal stability.

Keywords: modified epoxy resin, surface modification, electric property, thermal property

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1. Introduction

Significant development has been achieved in tailoring the thermal, mechanical, electrical, and other properties of polymer nanocomposites by introducing adequate fillers into polymer over recent years.[1–8] Inspired by the great improvements achieved in this field, growing interest has focused on developing polymer nanocomposites for electrical insulation application.[9–12] Various insulating particles such as alumina, titania, silica, and clay are frequently considered as promising fillers to improve the electrical performance of the polymer.[13–16]

Among the investigated fillers, clay nanosheets stand out as a key focus due to their favorable structure and physical properties associated with two-dimensional (2D) nanosheets.[17] As a member of clay family, montmorillonite (MMT) is particularly attractive due to its large surface area (~ 800 m^2/g) and large aspect ratio,[18] which makes it easy to be connected into three-dimensional (3D) network structures in a polymer matrix.[19] It has been demonstrated in many polymer systems that the combination of polymer–MMT nanocomposites is superior in strength, stiffness, fracture toughness, barrier properties, dimensional stability, and fire resistance of the polymeric matrices.[20,21] Besides, the nanocomposites with MMT are extremely attractive because of the light weight, thermal inertness, cost few, and eco-friendly.[22] Epoxy resin is a commonly available thermosetting polymer, which can be used as an electrical insulation material due to its good mechanical, thermal, and electrical properties as well as low thermal expansion coefficient.[23]

However, the intrinsic hydrophilicity of clay makes it difficult to disperse homogeneously in epoxy matrix, which leads to an imbalance in the distribution of electrical field in the material and inferior electrical performance of nanomaterials.[24] Clay can be usually modified through an ion exchange reaction to make it organophilic, which facilitates the polymer molecules to penetrate between the clay galleries.[25] How-

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ever, the organic moieties as modifiers of the MMT silicates can cause some problems, including reducing the degree of polymer crosslinking and weakening the interfacial adhesion between the filler and epoxy matrix.[26] In order to improve this interfacial interaction, silane grafting has been proposed as an effective approach to functionalizing MMT.[27,28]

Chu *et al.*[29] tried to improve the volume resistivity of epoxy composites by surface-modified silica nanoparticles. They found that the surface modification may affect the ρ_v values of the epoxy in two ways, one is to offer the nanoparticles different levels of water absorption, the other is to influence the polarization behaviors of the composites. Gao *et al.*[30] studied the relationship between the dielectric properties and nanoparticle dispersion of nano-SiO_2/epoxy composite. By applying surface modification, modified nano-SiO_2 has good dispersion in the composite, superior breakdown strength and corona-resistance. Essabir *et al.*[31] used the treated oil-palm fiber/clay to reinforce HLPE. It was noticed that the hybrid composites exhibit higher thermal stability. Therefore, it is easy to conclude that the electric and thermal properties of nanocomposites can be tuned by using surface modification of nanofillers.

Based on the above knowledge, the aim of this work is to discuss the effect of filler loading and surface modification on the morphology, electrical and thermal properties of the epoxy/MMT composites. Epoxy/MMT composites are prepared by the polymer blending method. Two different kinds of silane coupling agents, i.e., γ-aminopropyltriethoxysilane (γ-APTES) and 3-(glycidyloxypropyl) trimethoxysilane (GPTMS), are used for the surface treatment of clay nanoparticles. Then the dielectric response, electrical conductivity, breakdown strength as well as thermal conductivity of the modified epoxy composites are studied.

2. Experiment

2.1. Materials

Diglycidyl ether of bisphenol A (EPON-828) was used as epoxy prepolymer, cured with methyl tetrahydrophthalic anhydride (MeTHPA). The cure accelerator was benzyldimethylamine (BDMA). These materials were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Commercial grade montmorillonite, Nanomer I28E, was purchased from Nanocor Company (United States). Two types of silane coupling agents, i.e., γ-APTES and GPTMS, procured in Nanjing Shuguang Chemical Co., China, were used. The other reagents such as acetone were analytical pure and purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

2.2. Surface treatment for MMT

Surface modification of MMT using γ-APTES and GPTMS was carried out by using a wet method, which was reported by Peng.[32] Briefly, silane coupling agent was mixed with acetone for 10 min. Then, certain amount of MMT was added into the solution and sonicated for 1 h. The resulting slurry was reacted for 1 h at 130 °C before cooling to room temperature. The modified MMT was obtained after drying under vacuum at 110 °C for 2 h.

2.3. Preparation of epoxy/MMT nanocomposites

The epoxy/MMT nanocomposite was prepared by polymer blending method. Pure epoxy resin was also prepared for comparison. The procedure of preparation was as follows. Firstly, MMT powders were dispersed with acetone by ultrasonication for 5 min. Then epoxy resin was added into the acetone-clay slurry followed by ultrasonication for 30 min under ice bath conditions. Secondly, the mixture was placed into a vacuum oven at 50 °C/24 h to remove the solvent. Afterwards, curing agent and accelerant were added into the mixture. Then the system was mixed by using a rotation mixer (Thinky Co., Japan) with a rotation speed of 200 rpm for 1.5 min. After the mixing, the system was left under vacuum at 50 °C for 1 h until the bubbles and acetone in the resin were gradually dissipated. Finally, it was cured at 100 °C for 2 h and 150 °C for 10 h respectively. The compositions of the prepared samples were listed in Table 1.

Table 1. Sample compositions and designation.

Sample designation	MMT/wt.%	Surface treatment
blank	0	/
NC1	1	/
NC2	2	/
NC3	3	/
NC4	4	/
NC4-S1	4	γ-APTES
NC4-S2	4	GPTMS

2.4. Characterization

The dispersion state, the surface morphology, and the fractured morphology of the composites were observed with field emission scanning electron microscopy (FESEM, Hitachi SU660, Japan). The dielectric response of the nanocomposites was recorded by a broadband dielectric spectrometer (Novocontrol Ltd., Concept 80). The electrical conductivity of the samples was measured under 500 V at room temperature (24 °C) by using Keithley's 6517B electrometer and the 8009 resistivity test chamber. The dielectric breakdown strength was measured with spherical electrode systems (25 mm in diameter). The tested sample of 0.3 mm was sufficiently held between two copper balls, and the whole system was immersed in transformer oil. The applied voltage was set to rise at a

speed of 2 kV/s until the occurrence of breakdown. For each specimen, more than 10 measurements were carried out, while the average of these values was considered. Thermal conductivity measurement was conducted by the laser flash method (LFA-467, Netzsch, Selb, Germany) in a temperature range of 25–200 °C. Q600SDT simultaneous DSC/TGA analyzer was used to evaluate the thermal stability of epoxy nanocomposites. The modified epoxy composites were tested from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

3. Results and discussion

3.1. SEM of epoxy/MMT composite

The surface morphology and the fracture morphology of the modified epoxy composites with different MMT contents are shown in Fig. 1. The SEM images in Figs. 1(a) and 1(d) show that the fracture surface of the pure epoxy resin system is typical of the fracture surface of crosslinked thermoset and brittle fracture. However, NC4-S2 has a rather rougher fracture surface with several pores left by pulling out the MMT (Fig. 1(e)). Further observing the high-magnification image (Fig. 1(f)), the lamellar structure of MMT as well as the clear interfaces between the MMT and the matrix can be observed, which suggests a moderate interfacial adhesion between MMT and the polymer matrix.

From Figs. 1(b) and 1(c), it can be seen that most of MMT sheets are uniformly dispersed in epoxy resin instead of agglomerated together in nanocomposites at such a high concentration (4 wt.% MMT). After the surface of the NC4-S2 system is carefully scratched, a series of MMT particles with diameters ranging from 161 nm to 278 nm can be observed clearly (Fig. 1(g)). As is well known, clay is easy to sedimentate in polymer matrix in the preparation process. In order to have a profound insight into the dispersion state of MMT, the fracture morphology of NC4-S2 is studied (Fig. 1(h)). No obvious differences can be observed between the upper and bottom sides. The MMT sheets are well-distributed in spite of some agglomerations. The absence of voids demonstrates the great efficiency of solvent evaporation in avoiding possible voids. These results indicate that a comparatively homogeneous dispersion state of epoxy/MMT nanocomposite can be obtained by an appropriate dispersion method and surface modification at high loadings.

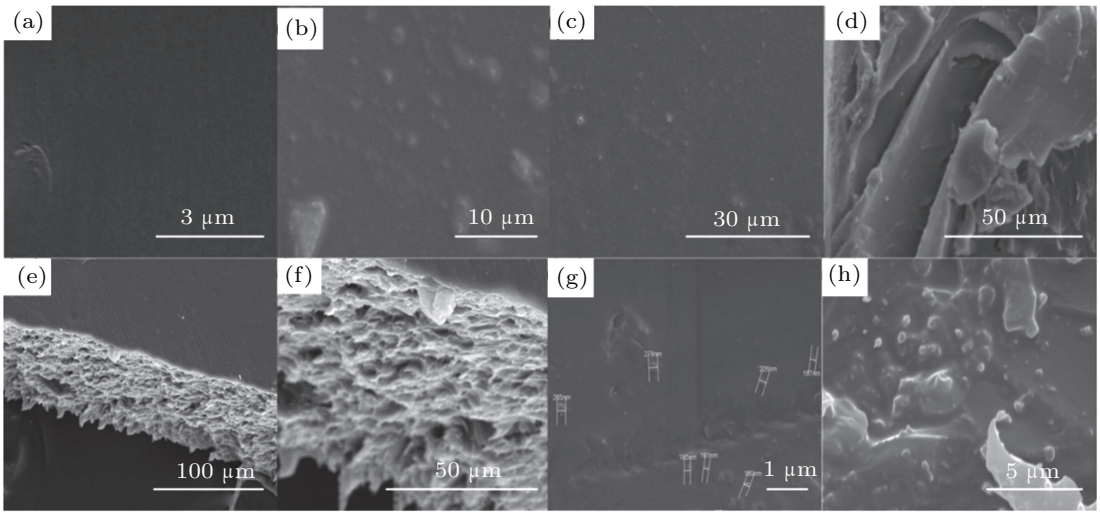


Fig. 1. SEM images of modified epoxy system: (a), (d) neat epoxy resin, (b) NC4-S1, and (c), (e)–(h) NC4-S2 at different magnifications.

3.2. Dielectric properties of epoxy/MMT composites

Figure 2(a) shows that the real part of permittivity (ε') for each of the modified epoxy composites decreases over the whole frequency after the addition of clay. The larger the concentration, the lower the value of ε'. The reason for the decrease of the composite can be attributed to the hindering of the polymer chains from moving because of the interfacial adhesion between MMT and epoxy resin. The polymer chains lose their freedom to relax under an external voltage, and are unable to contribute to the electrical polarization.[33] A similar result has been reported in polyurethane/clay nanocomposites[34] and epoxy nanocomposites containing TiO_2, Al_2O_3, ZnO, and clay fillers.[35–38] In the case of epoxy and surface-treated MMT nanocomposites, lower ε' is observed in the modified composites containing surface-treated clay. This can be explained by that the effect of silane coupling agent can improve the interfacial adhesion.[39] Silane coupling agent acts as a transient network in the system and it can lead to the further molecule restriction, which is harmful to polymer chain mobility.

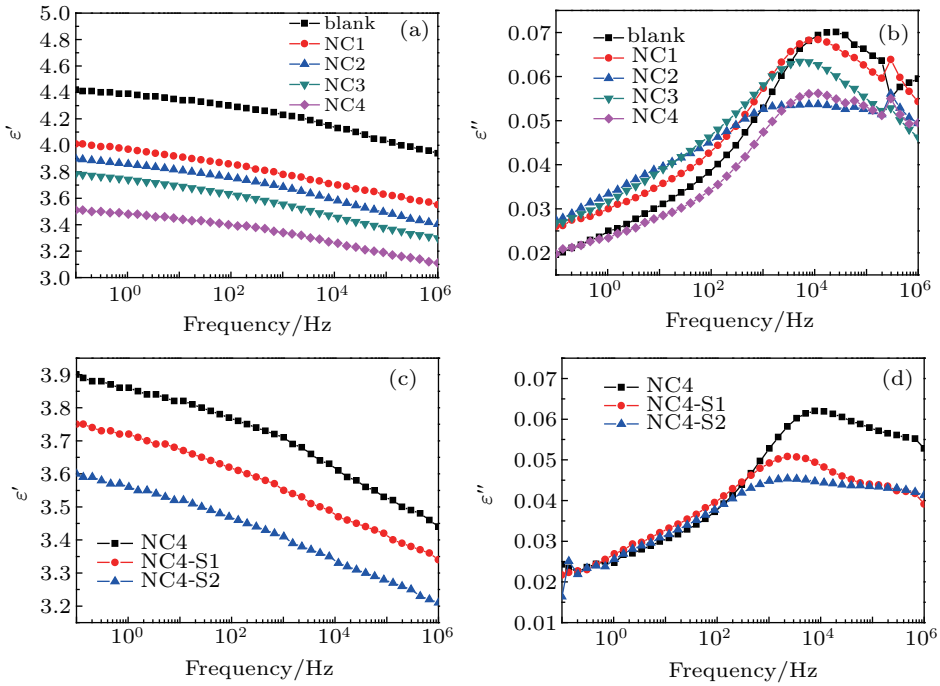


Fig. 2. (color online) Plots of dielectric response as a function of frequency with different MMT contents at −20 °C: (a), (c) real part of permittivity ε' and (b), (d) imaginary part of permittivity ε'' for different kinds of epoxy/MMT composites.

More interesting results emerge in the imaginary part of permittivity ε'' as a function of frequency. As can be seen in Fig. 2(b), the modified epoxy system shows a similar tendency with frequency increasing. When the frequency is low, the relaxation polarization can follow the change of frequency. The relaxation loss can be ignored and ε'' is very small. As the frequency increases, the relaxation loss continues to increase. The ε'' steadily increases and reaches to a peak around 10 kHz. Comparing with a neat epoxy system, the loss peak of the composite shifts toward the lower frequency accompanied with a reduced loss magnitude. The shift of the loss peak indicates that the addition of clay plays a role in increasing the relaxation time (τ) of relaxation polarization. The reduction of the loss magnitude is related to the restriction in charge transport in composites. The addition of MMT can affect the dielectric loss in two ways. The MMT nanoparticles can act as charge carriers, which can improve the dielectric loss of the modified epoxy system. Meanwhile, the introduction of MMT acts as the hindrance of charge carrier, resulting in the reduction of the dielectric loss. From the results, an explanation can be given that the effect of charge immobility is more important in the polymer blending modification. The rapid decrease in ε'' at high frequency indicates that the lower influence of relaxation polarization can fail to keep pace with the oscillating electric field.[40–45]

Further decreases of ε' and ε'' are obtained after surface modification of MMT (see in Figs. 2(c) and 2(d)). It can be ascribed to the effect of silane coupling agent. Silane coupling agent acts as a bridge in the system: the hydrophilic group of the agent interacts with a large number of hydroxyl groups on the surface of montmorillonite to form the strong Si–O bond at the interface; the hydrophobic group interacts with the molecular chain of epoxy resin. As a result, some epoxy molecules are connected chemically to the MMT, thus inducing further molecule restriction. A greater hydrogen bond is expected to form in NC4-S2 than in NC4-S1 because new hydroxyl functional groups would be introduced into the GPTMS by epoxy group. Therefore, it is not surprising that NC4-S2 has lower ε' and ε''. Especially, ε'' in epoxy nanomaterials containing modified MMT maintains a constant of 10^{-2} over the examined frequencies. It can be easily expected that with the proper loading of MMT and adequate surface modification, the dielectric loss of EP/MMT nanocomposites can be located in a desired range.

3.3. Electrical conductivity of epoxy/MMT composite

Figure 3 shows the electric conductivities of epoxy/MMT composites with different MMT contents. As shown in Fig. 3, the electrical conductivity of the epoxy/MMT composite seems to linearly increase with the growing content of MMT and has a maximum value of 1.2×10^{-14} S/m with 3 wt.% MMT. Such a rapid increase can be ascribed to the remarkable growth of charge carriers, which originates from foreign impurities, fillers, and electrodes under the influence of the applied field.[46] The use of MMT to obtain modified epoxy composite with controlled conductivity is a fascinating alternative because it can directly affect the mobility of cations while avoiding the mobility of counter anions. However, the conductivity of the NC4 system is found to be slightly lower than that of the NC3 system for the highly dense MMT

nanoparticles in the nanocomposites of the NC4 system, which act as barriers of the charge transfer and hamper of the movements of charge carriers, resulting in the decrease of conductance of NC4.

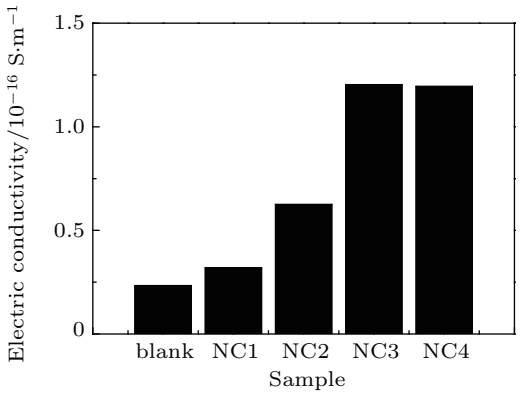


Fig. 3. Electric conductivity of epoxy/MMT composite subjected to DC voltage as a function of MMT content.

Figure 4 shows the electric conductivity of epoxy/MMT composite at 4 wt.% MMT content under the condition of direct current (DC) voltage. From Fig. 4, it can be seen that the conductivity of epoxy/MMT composite decreases dramatically after the MMT coupling treatment has been modified. Especially the NC4-S2 system is more pronounced (see in Fig. 4). The reason is that the surface modification is helpful in improving the compatibility between nanoparticles and epoxy, which can hinder charges from transferring, thus resulting in the reduction of electric conductivity. The result is in consistent with the decline in dielectric loss.

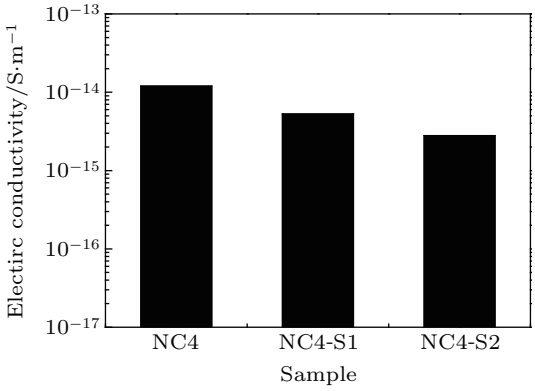


Fig. 4. Electric conductivities of epoxy/MMT composite samples with 4 wt.% MMT under the condition of DC voltage.

3.4. Dielectric breakdown strength of epoxy/MMT composite

Figure 5 shows the plots of breakdown strength and its Weibull distribution of the composites with different MMT contents. It is noticed that the breakdown strength of the epoxy/MMT composite at low loading is a little higher than that of the neat epoxy system. The improving dielectric strength of the epoxy/MMT composite by using clay is due to the increase of the interfacial area and scattering mechanism, which has been reported by many researches.[46–48] Scattered by the dispersed clay layers, the free charge carriers tend to lose their momentum and transfer the energy to the carriers nearby. Then the charge carriers cannot gain more energy to drift a long distance, thus it requires more energy obtained from the applied voltage to be involved in the process of breakdown.

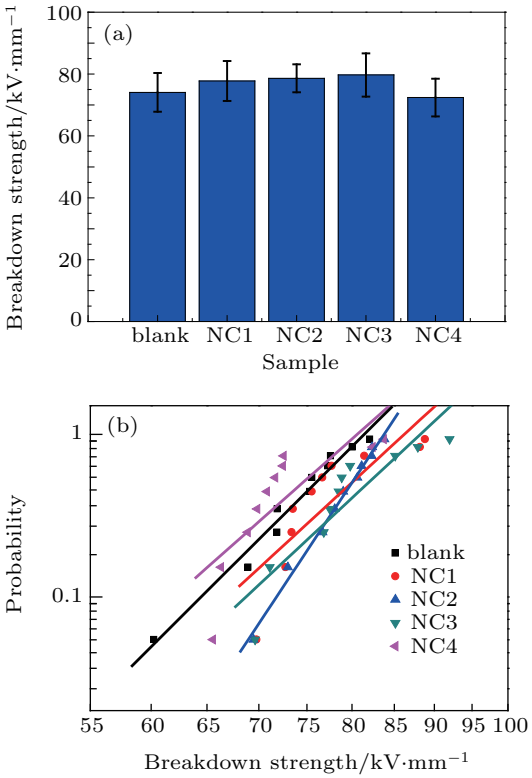


Fig. 5. (color online) Epoxy/MMT composites with different MMT contents subject to AC voltage: (a) breakdown strength, and (b) Weibull plots of breakdown data.

However, when the MMT content is 4 wt.%, the dielectric strength of the epoxy/MMT composite is a little lower than that of the pure epoxy. This phenomenon can be explained as that the presence of agglomerations, which makes it possible for the impurities and defects accumulation zone to be distributed in an interface region, leads to the decrease of the breakdown strength.

Figure 6 shows the breakdown strength and Weibull plots of breakdown data for the epoxy/MMT composites with various MMT coupling treatment subject to alternating current (AC) voltage. Compared with the NC4, the NC4-S1 fails to enhance the dielectric strength, while the NC4-S2 exhibits some increase. The enhancement of NC4-S2 can be explained by the influence of the interface between the epoxy resin and MMT nanoparticles on the space charge distribution and charge densities,[49] leading to a better distribution of the electrical stress.[50] The opposite effect of NC4-S1 can be ascribed to its relatively incompatible interface. Moreover, some

residual surface agents which do not have the interaction with MMT can act as the defects in the nanocomposite, giving rise to the reduction in breakdown strength.

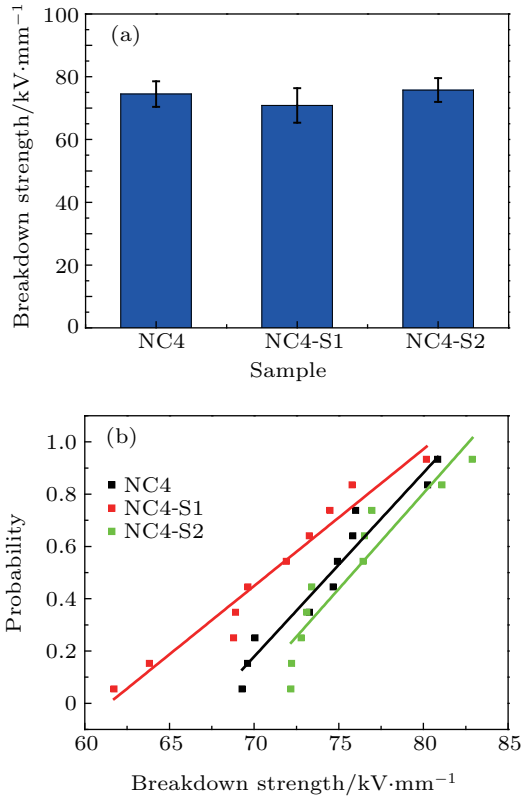


Fig. 6. (color online) (a) Breakdown strength and (b) Weibull plots of breakdown data for the epoxy/MMT composites with different MMT coupling treatment subject to AC voltage.

3.5. Thermal conductivity of epoxy/MMT composite

Polymer dielectric with a relatively high thermal conductivity has a major effect on facilitating the heat dissipation, avoiding the deterioration, and prolonging the lifespan of the insulation system.[51] The influence of MMT content on the thermal conductivity of epoxy/MMT composite is shown in Fig. 7. The thermal conductivity of pure epoxy system at 25 °C is 0.195 W/(m·K). When the applied temperature rises, the thermal conductivity of neat epoxy first increases gradually and reaches a peak of 0.241 W/(m·K) at 150 °C.

As the temperature further increases, the thermal conductivity of the epoxy/MMT composite drops gradually. When MMT is added into the epoxy resin, its influence on the thermal conductivity is not stable until the thermal conductivity in NC4 abruptly increases. The heat conduction mechanism is established based on phonon transfer (i.e., lattice vibrations). Various phonon scattering processes lead to attenuation of the thermal conductivity within a material because of an acoustic mismatch and the flaws which are associated with the interface between epoxy resin and MMT nanofillers.[52] In the NC1 system, the phonon scattering at the interface plays a dominant role in impeding the enhancement of thermal conductivity.[53] The obvious increase of thermal conductivity in the NC4 system indicates the formation of large-scale thermal networks under a relatively high loading due to the agglomerations of MMT nanoparticles in the composite.[54]

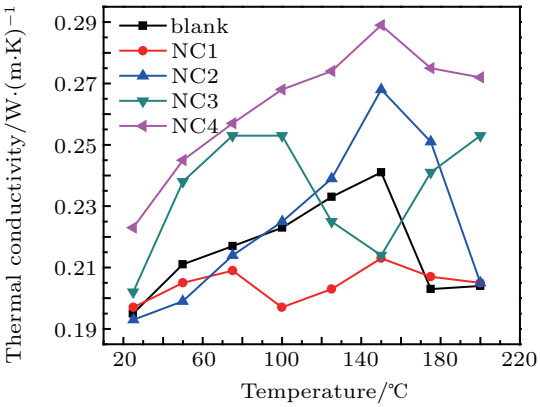


Fig. 7. (color online) The thermal conductivity versus temperature of epoxy/MMT composites with different MMT contents at various temperatures.

The thermal conductivities of epoxy/MMT composites with different coupling treatments at various temperatures are shown in Fig. 8. From Fig. 8, it can be found that the introduction of coupling agents treated MMT does not improve the thermal conductivity of the epoxy/MMT composite at 4 wt.% content. The reduction of thermal conductivity of NC4-S1 and NC4-S2 can be explained as that the excessive use of coupling agents makes the interface become a barrier to heat transfer, which gives rise to the reduced thermal conductivity of the composite.[55]

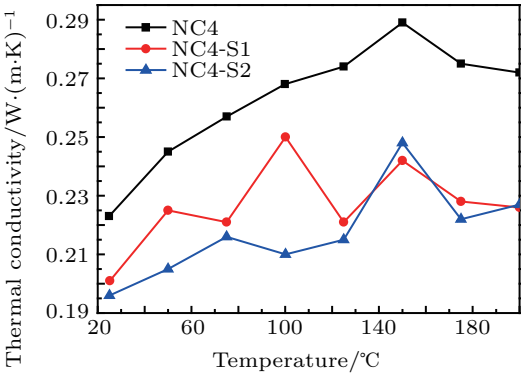


Fig. 8. (color online) The thermal conductivity versus temperature of epoxy/MMT composites with different coupling treatments.

3.6. TGA analysis of composites

To evaluate the thermal durability of the hybrid, TGA analysis is conducted and the results are shown in Figs. 9 and 10.

No obvious weight loss is observed for all samples before 300 °C (see in Fig. 9(a)) due to the good thermal stability of epoxy resin. With the rising of temperature, an abrupt weight loss can be observed around 400 °C because of the degradation

of the macromolecular chain. The TGA curves are analyzed by defining two parameters, namely, $T_{initial}$ (the temperature at which the degradation starts) and T_{max} (the temperature at which the degradation rate is maximum). The results of TGA analysis are shown in Table 2. As can be seen, the NC1 and NC2 have higher $T_{initial}$ and lower T_{max} than pure epoxy while NC3 and NC4 exhibit lower $T_{initial}$ and T_{max}.

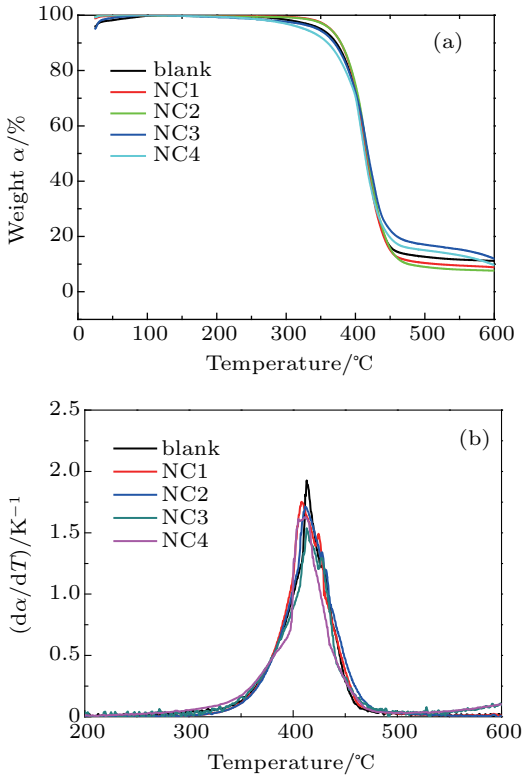


Fig. 9. (color online) Plots of (a) weight and (b) degradation rate versus temperature of nanocomposites for all five epoxy systems.

Table 2. Characteristics of epoxy nanocomposites from TGA analysis.

Sample	$T_{initial}$/°C	T_{max}/°C
Blank	350.3	413.0
NC1	364.0	408.0
NC2	363.7	411.3
NC3	345.7	413.0
NC4	327.0	411.7

The plots of degradation rate versus temperature for all five epoxy systems are shown in Fig. 9(b). It shows that the epoxy/clay nanocomposite has a lower degradation rate at its T_{max} than pure epoxy. Such a reduction is attributed to the thermal barrier effect of clay on epoxy in reducing the oxygen uptake and the escape of volatile gases produced by polymer degradation.[56] Moderate $T_{initial}$, T_{max} and lower rate of degradation suggest that the best thermal stability is achieved for epoxy nanocomposites containing 2 wt.% clay.

As can be seen from Fig. 10 and Table 3, after surface modification, the NC4-S1 and NC4-S2 have lower $T_{initial}$ and higher T_{max} than NC4 and the degradation rates equal to that of NC4. The result indicates that the long-term thermal stability can be improved by using the surface modification. The enhanced thermal stability can be explained by the enhanced interfacial adhesion between the dispersed clay and epoxy resins.[57]

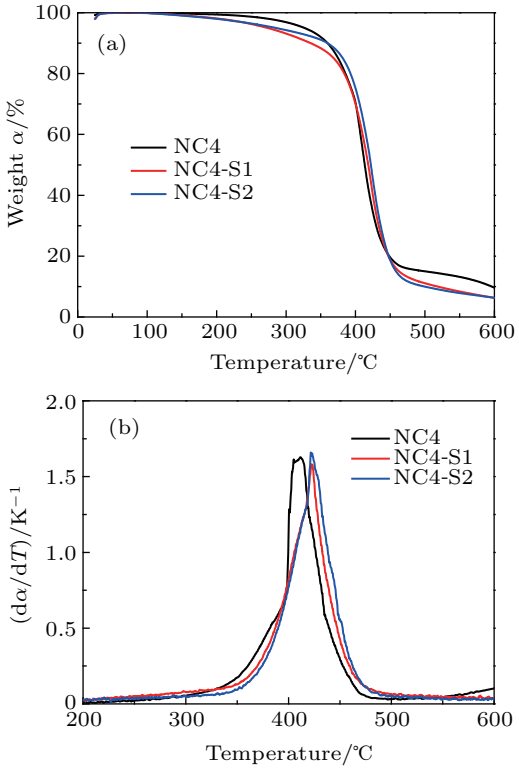


Fig. 10. (color online) Plots of (a) weight and (b) degradation rate versus temperature for nanocomposites with different coupling agents.

Table 3. Effect of coupling agent on the thermal stability of epoxy nanocomposites.

Sample	$T_{initial}$/°C	T_{max}/°C
NC4	327.0	411.7
NC4-S1	286.0	422.0
NC4-S2	276.0	421.7

4. Conclusions

Based on the results of the epoxy/MMT composite, it can be concluded that well dispersed epoxy/MMT composite is successfully synthesized. Compared with the pure epoxy resin, the epoxy/MMT composite, whether MMT is surface-treated or not, shows low dielectric permittivity, low dielectric loss, and enhanced dielectric strength. The MMT in the epoxy/MMT composite also affects the thermal properties of the composite, showing improved thermal conductivity and stability.

The surface functionalization of MMT not only conduces to better dispersion of the nanoparticles, but also significantly affects the electric and thermal properties of the hybrid by influencing the interfaces between MMT and epoxy resin. Improving interfaces are good for enhancing the electric and thermal properties of nanocomposites. What is more, the MMT

modified with GPTMS rather than γ-APTES is found to have a greater influence on improving the interface between the MMT filler and polymer matrices, thus resulting in lower dielectric loss, lower electric conductivity, higher breakdown strength, lower thermal conductivity, and higher thermal stability.

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