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Influence of interfacial modification on the thermal conductivity of polymer composites

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Abstract In this study, the influence of modifying ZnO filler with surface-treating agents on the thermal conductivity of the ethylene-vinyl acetate copolymer (EVA) composites was reported. Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) were applied to analyze the surface modification of ZnO filler and the fractured surface morphology of the EVA–ZnO composites. The test results indicated that surface-treating ZnO filler with the valid modifying agents (stearic acid, OL-AT16, KH-560, or NDZ-132) at right dosage and treating temperature, the thermal conductivity of the EVA–ZnO composites can be enhanced effectively on account of reducing the interfacial phonon scattering; while the dosage of modifying agents exceed a right amount, the thermal conductivity of EVA–ZnO composites modified with the small-molecule treating agents (F-1, *n*-Octylic acid, or stearic acid) descend more evidently with the dosage increase.

Introduction

Thermally conductive polymer composites are being developed rapidly with the increase in applications. Most polymer resins are thermally insulating; typical thermal conductivity values for polymer resins are 0.1–0.3 $\mathrm{Wm^{-1}\ K^{-1}}$. Increasing the thermal conductivity of polymer resins opens large and new markets. The advantages of thermally conductive polymer composites as compared to metals (typically used) include improved corrosion resistance, lighter weight, and the ability to adapt the electrical and the thermal conductivity properties to suit the application needs [1, 2]. The use of thermally conductive polymer composites for heat dissipation has been increasing drastically, especially in the field of electronic packaging [3–6]. We also had reported the influence of increasing the thermal conductivity of the EVA-encapsulated rear layer on the temperature and photovoltaic transform efficiency of the solar cell [7].

In general, heat-conducting polymer material with a thermal conductivity above approximately 1 $\mathrm{Wm^{-1}\ K^{-1}}$ can be used in heat-sink applications [8–10]. One effective and convenient approach to improve the thermal conductivity of a polymer material is through the addition of some heat-conducting filler material, such as metal, graphite, carbon, and ceramic particles/fibers, etc. [9, 10]. The thermal and electrical properties of the polymer composites depend on the properties of the heat-conducting filler and the polymer resin, the volume content of the filler, the shape and size of the filler, the preparation process of the polymer composites and so on [1, 9].

The former studies concerned mainly on the kinds of the heat-conducting fillers and the resin matrix, the thermal conductivity of composites vary with the volume content of the heat-conducting filler, and the prediction model of the thermal conductivity of composites [1–18]. There were only few studies concerning the effect of interfacial modification, particularly different type surface-treating agents, on the thermal conductivity of polymer composites. However, interfacial modification has an important effect on the

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mechanics properties, the processing behavior and also the thermal properties of polymer composites [1, 9, 16, 19, 20]. Therefore, it is essential to investigate further the influence of interfacial modification on the thermal conductivity of polymer composites.

In this study, the thermally conductive EVA composites filled with zinc oxide (ZnO) were prepared. The effects of the kind of surface-treating agents, the dose of couplers and treatment process on the thermal conductivity of EVA composites were investigated. This is quite helpful in understanding the effect of interface on the thermal conductivity of polymer composites. By characterizing the modified fillers and the morphology of the composites, the mechanism of the effect of interfacial modification on the thermal conductivity of the composites was discussed.

Experiment

Materials

The ethylene-vinyl acetate copolymer (EVA), Elvax-220 W, with a melt flow index of 150 g/10 min, vinyl acetate content of 28%, density of 0.951 g/cm^3, and thermal conductivity of 0.25 Wm^{-1} K^{-1}, supplied by DuPont chemical company was used in this study. Zinc oxide (ZnO), with average size of about 1 µm, thermal conductivity of 34 Wm^{-1} K^{-1}, density of 5.62 g/cm^3, and shape of random grain, was obtained from Shanghai Jinghua Chemical Co., Ltd. The silane coupling agents of glycidoxypropyl trimethoxysilane KH-560 (correspond to SLANE Z-6040) and aminopropyl triethoxysilane KH-550 (correspond to SLANE A-1100) were obtained from Shanghai Yaohua chemical Co., Ltd. Stearic acid, *n*-Octylic acid, and di(2-ethylhexyl) phosphate F-1 were obtained from Shanghai chemical reagent Co., Ltd. Maleic anhydride graft polypropylene (MPP), with a melt flow index of 100 ± 5 g/10 min, maleic anhydride content of 1.8%, was obtained from Shanghai Sunny Co., Ltd. Aluminum and titanium complex coupling agent OL-AT16 was obtained from Shanxi Institute of Chemical Industry. Titanate coupling agent NDZ-132 was obtained from Nanjing Shuguang Chemical Co., Ltd.

Surface modification

In order to ensure filler good dispersion and to improve the interface interaction between the filler and matrix, the surface-treating agents as described above were used for surface modification of the fillers. The surface modification was carried out as follows: (1) mixing the filler and the surface-treating agent of 0.5–4 wt% in terms of filler weight in a small amount of isopropyl alcohol or its aqueous solutions at 70 °C for 2 h, (2) vacuum drying to remove solvent at 80 °C for 12 h, (3) exposing the filler to ambient air for 8 h, (4) heat treating the filler at different temperature for 4 h. The treated fillers were stored in vacuum dryer.

Sample preparation

The EVA and fillers, which were weighed in terms of a certain volume content, were mixed on a two-roll mill (SK-160B, Shanghai Rubber Machine Company, China) at temperature of 95 ± 5 °C for 15 min; and then the molten compounds were transferred into the mold with the required dimension (50-mm diameter and 5–8-mm thickness for thermal conductivity). Pressure up to 10 Mpa was applied by hydraulic press (YX-25, Shanghai Ximaweili Rubber and Plastic Machine Company, China) and kept for 3 min at room temperature. The cylinder sample with 50-mm diameter and 5–8-mm thickness was released out of the mold. The samples were polished with sandpaper until surface become smooth.

Characterization

The thermal conductivity of composites was measured with an Anter thermal conductivity meter (Quickline-10B, American Anter Corporation) according to ASTM E 1530 (Guarded heat flow meter method). The testing error of the measurement is 0.02 Wm^{-1} K^{-1} (about ±0.01, <3%). There is not suitable means of direct charactering the interface thermal conductivity at present. So, it is helpful to analyze the interface with some other means. FTIR and SEM are extremely powerful techniques for studying modified filler surface and composites morphology [20, 21]. In order to observe the dispersion of filler particle in the matrix and the morphology of the composite, the surface of fractured specimen prepared by freezing in liquid nitrogen was observed with a scanning electron microscope (SEM) (JSM-6360LV, JEOL, Japan) after it was goldsputtered. The infrared spectra of raw ZnO filler and ZnO filler modified with coupling agents was obtained with FTIR (Magna-IR 550, THERMO NICOLET, USA).

Results and discussion

Effect of modifying agents on the thermal conductivity of EVA composites

Figures 1 and 2 show the effect of modifying agents on the thermal conductivity of EVA composites. In the case of the surface modification of ZnO filler, with the rising of modifying agents content, the thermal conductivity of composites increase at first, and then decline gradually

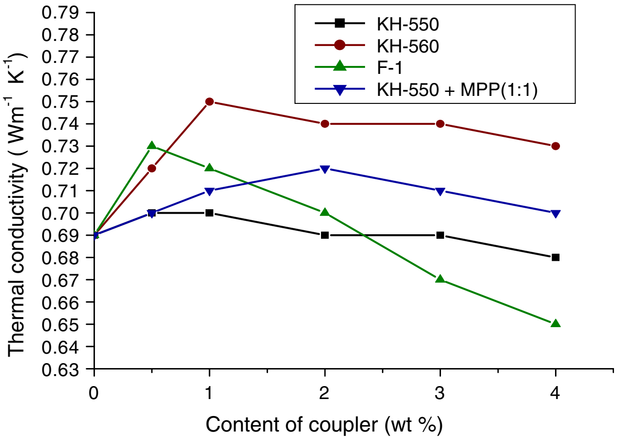


Fig. 1 Effect of modifying agents (KH550, KH560, F-1, or KH550/MPP) on the thermal conductivity of EVA–ZnO (27 vol.%) composites

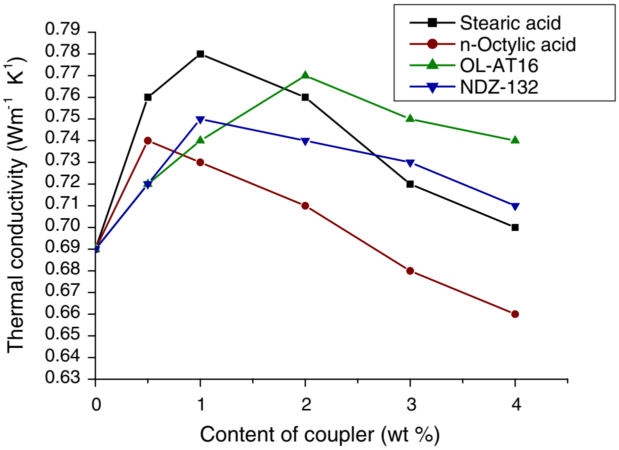


Fig. 2 Effect of modifying agents (stearic acid, *n*-Octylic acid, OL-AT16, or NDZ-132) on the thermal conductivity of EVA–ZnO (27 vol.%) composites

after reaching maximum. However, there are obvious differences in the thermal conductivities of EVA–ZnO composites treated with different modifying agents.

From Figs. 1 and 2, treating ZnO with stearic acid, OL-AT16, KH-560, or NDZ-132, the thermal conductivity of EVA–ZnO composites can be enhanced evidently. The thermal conductivity of EVA–ZnO composites increases, respectively, 13, 11.6, or 9.7% by treating ZnO with above-mentioned coupling agents in a right amount. However, treating ZnO with F-1 or KH550 + MPP, the thermal conductivity of EVA–ZnO composites increase slightly. Further, the thermal conductivity of EVA–ZnO composites modified with KH-550 even almost does not increase. Figures 1 and 2 also show that while the dosage of modifying agents exceed a right amount, the thermal conductivity of EVA–ZnO composites modified with F-1, *n*-Octylic acid, or stearic acid descend evidently with the dosage of modifying agents increase.

The varied effect of above modifying agents on the thermal conductivity of EVA–ZnO composites can be explained by the chemical property and structure of the modifying agents (show in Fig. 3).

A valid modifying agent can improve the practical adhesive bond of polymer to mineral. Fourier transform infrared spectroscopy is an extremely powerful technique for studying modifying agent–filler system; the structural changes of the modifying agents on the filler surface can be determined [20, 21]. The carboxylic group (–COOH) of stearic acid can reactively bond to ZnO (as show in Figs. 4, 5), and the long carbon chain of stearic acid can also entwine effectively with the macromolecule chain of EVA matrix. So, treating ZnO with a right dose of stearic acid can promote the compatibility and interface adhesive bond of EVA matrix to ZnO filler, reduce the faults such as tiny gaps and the interfacial phonon scattering, and enhance effectively the transfer ability of thermal vibration in EVA–ZnO composites [18, 22]. However, if the dosage of stearic acid exceeds a right amount, the excessive stearic acid small molecule will cause the multilayer molecule interface which can weaken the bond of EVA matrix to ZnO filler and increase the interfacial phonon scattering; besides, the excessive stearic acid small molecule may diffuse in EVA matrix and weaken the bond among EVA macromolecules. Therefore, while the dosage of stearic acid exceeds a right amount, the transfer ability of thermal vibration in EVA–ZnO composites (correspond to the thermal conductivity of EVA–ZnO composites) descend evidently with the dosage of stearic acid increase.

Figures 4 and 5 are the FTIR spectra of zinc stearate, stearic acid, ZnO, and ZnO treated with stearic acid. Figure 4 show the characteristic band of zinc stearate at about 1540 cm^{-1}, and the characteristic band of stearic acid at about 1700 cm^{-1}. Figure 5 shows there is only zinc stearate on the surface of ZnO filler treated with 1 wt% stearic acid; however, there is not only zinc stearate but also excessive stearic acid on the surface of ZnO filler treated with 4 wt% stearic acid. So, it was verified that excessive stearic acid on the surface of ZnO filler result in the thermal conductivity of EVA–ZnO composites modified with 4 wt% stearic acid lower evidently than that modified with 1 wt% stearic acid.

Although *n*-Octylic acid has the same carboxylic group (–COOH) as that of stearic acid, the carbon chain length of *n*-Octylic acid is shorter than a half of the carbon chain length of stearic acid. So, *n*-Octylic acid cannot entwine and bond so effectively to the macromolecule chain of EVA matrix as stearic acid does; the thermal conductivity of EVA–ZnO composites modified with *n*-Octylic acid also cannot be enhanced so evidently as that with stearic acid.

Di(2-ethylhexyl) phosphate F-1 also has a reactive phosphonic group (=PO–OH) which can bond to ZnO.

Fig. 3 The molecular structure of modifying agents

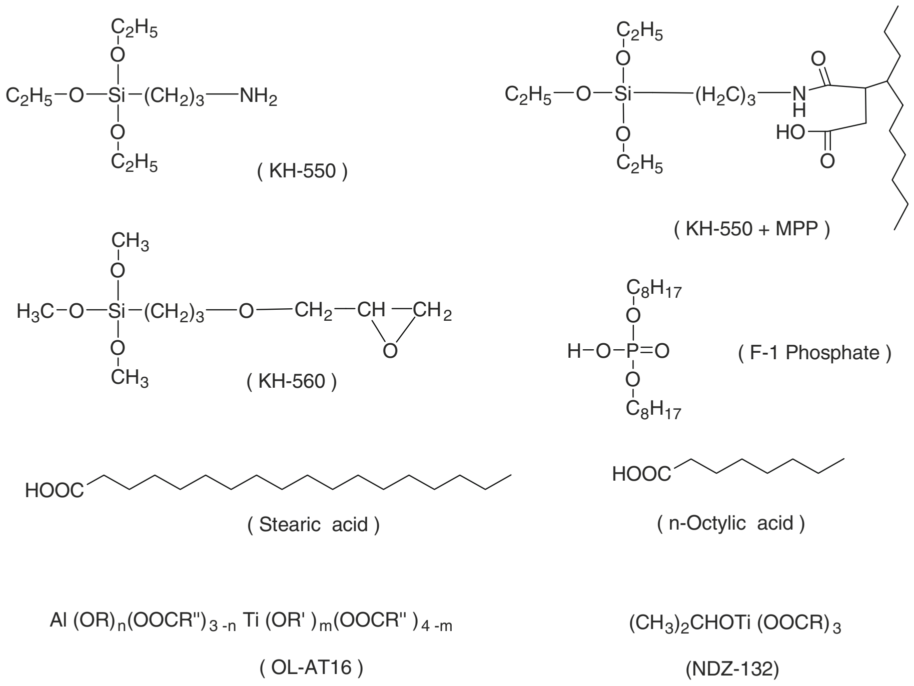


Fig. 4 The FTIR spectrums of ZnO treated with stearic acid, zinc stearate, and stearic acid

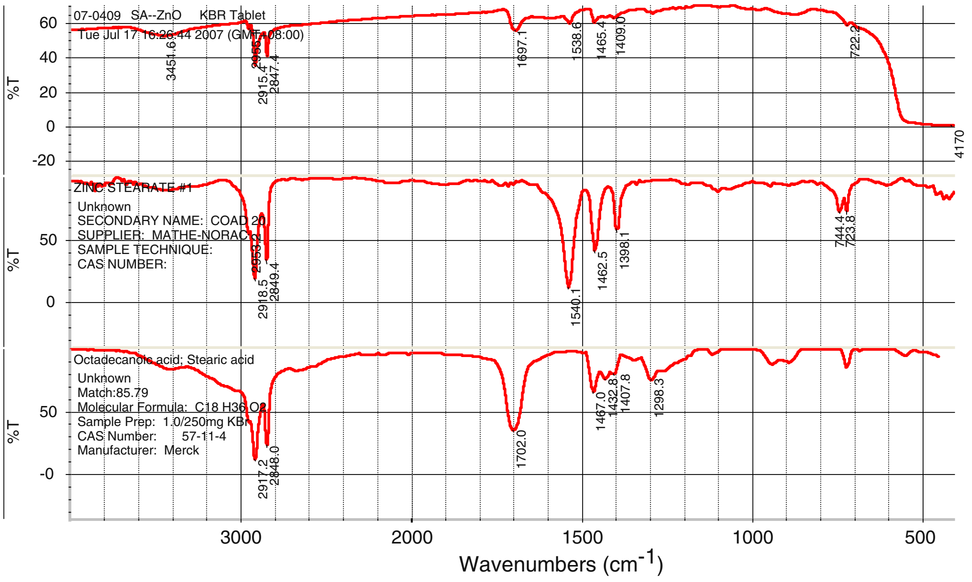


Figure 6 shows there appear the characteristic absorptive bands (at 1189 and 1101 cm^{-1}) of new functional group on the surface of ZnO filler treated with F-1. It indicates that di(2-ethylhexyl) phosphate F-1 has bonded to ZnO filler. However, ethylhexyl groups of F-1 are side branching chains, and too short to entwine and bond so effectively to the macromolecule chain of EVA matrix as stearic acid does. Similarly, treating ZnO with di(2-ethylhexyl) phosphate F-1 cannot promote so effectively the interface adhesive bond of EVA matrix to ZnO filler as that with stearic acid; the thermal conductivity of EVA–ZnO composites modified with F-1 only can be enhanced slightly.

Glycidoxypropyl trimethoxysilane KH-560(correspond to SLANE Z-6040) is capable of reacting with filler surface moisture to generate silanol groups which may form hydrogen bonds and reversible oxane bonds with the surface of ZnO filler [21]. Figure 7 shows there appear the characteristic absorptive bands of hydrogen bonds at about 3440 cm^{-1} and oxane bonds at about 858 cm^{-1} on the surface of ZnO filler treated with KH-560. Furthermore, the glycidoxypropyl group of KH-560 has good compatibility with EVA and can entwine effectively with the macromolecule chain of EVA matrix. So, modifying ZnO with a right dose of KH-560 also can promote the compatibility

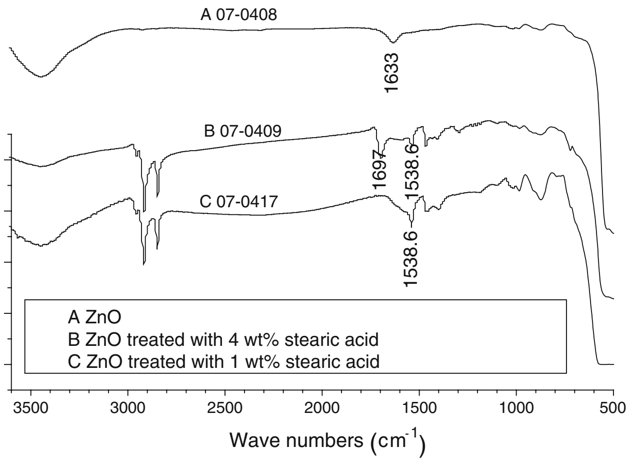


Fig. 5 The FTIR spectrums of ZnO and ZnO treated with stearic acid

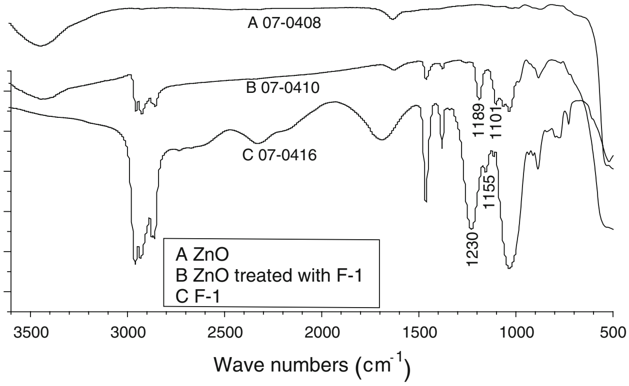


Fig. 6 The FTIR spectrums of ZnO, F-1, and ZnO treated with F-1

and interface adhesive bond of EVA matrix to ZnO filler, reduce the faults such as tiny gaps and the interfacial phonon scattering, and enhance effectively the thermal vibration transfer ability in EVA–ZnO composites.

Although, aminopropyl triethoxysilane KH-550 (correspond to SLANE A-1100) is also capable of reacting with filler surface moisture to generate silanol groups which may form hydrogen bonds and reversible oxane bonds with the surface of ZnO filler [21] (as shown in Fig. 8), the thermal conductivity of EVA–ZnO composites modified with KH-550 almost does not increase. The reason may be that the aminopropyl group of KH-550 is too short, and does not have good compatibility with EVA matrix; so, KH-550 cannot bond and entwine effectively with the macromolecule chain of EVA matrix. As a result, treating ZnO with KH-550 cannot promote the interface adhesive bond of EVA matrix to ZnO filler, and cannot enhance effectively the thermal vibration transfer ability in EVA–ZnO composites.

However, treating ZnO with KH550 + MPP, the thermal conductivity of EVA–ZnO composites can increase certainly. As shown in Scheme 1, reacting with KH-550, MPP can increase the chain length of the coupling agent [21, 23]. So, it can promote the coupler entwine with the macromolecule chain of EVA matrix and the thermal conductivity of EVA–ZnO composites increase.

While the dosage of KH-560 or KH-550 exceeds a right amount, with the dosage of coupling agents increase, the thermal conductivity of EVA–ZnO composites modified with KH-560, KH-550, or KH-550 + MPP descend more slightly than that with F-1, *n*-Octylic acid, or stearic acid. This may be because excessive KH-560 or KH-550 can polycondensate to form polysilicone which is similar in thermal conductivity to EVA matrix.

Aluminium and titanium complex coupling agent OL-AT16 and titanate coupling agent NDZ-132, not only can bond effectively with ZnO filler [23], but also have long carboxyl ester chains which have good compatibility with EVA matrix. Therefore, treating ZnO with OL-AT16 or

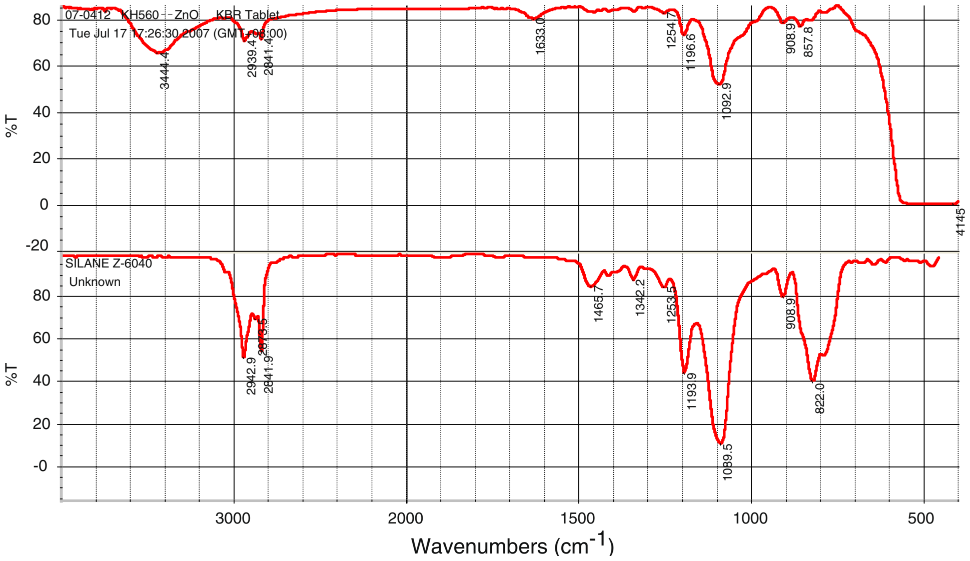


Fig. 7 The FTIR spectrums of Z-6040 (correspond to KH-560) and ZnO treated with KH-560

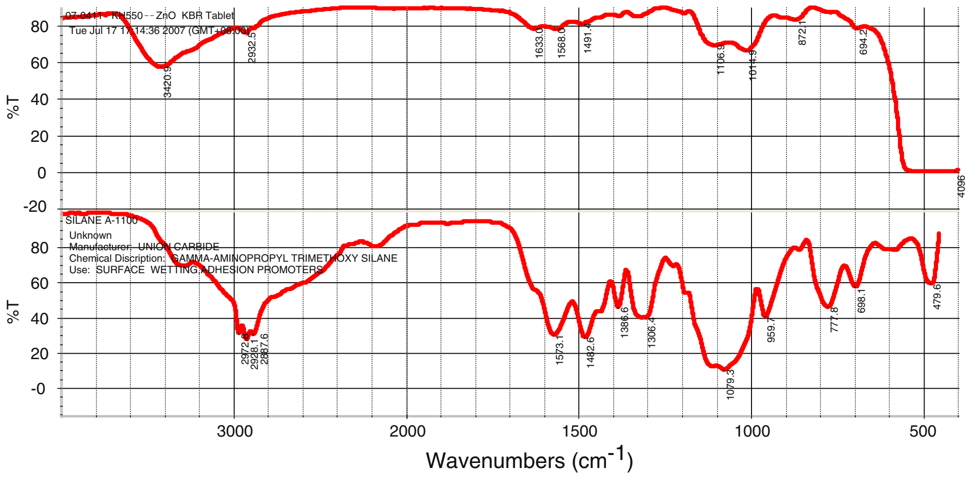
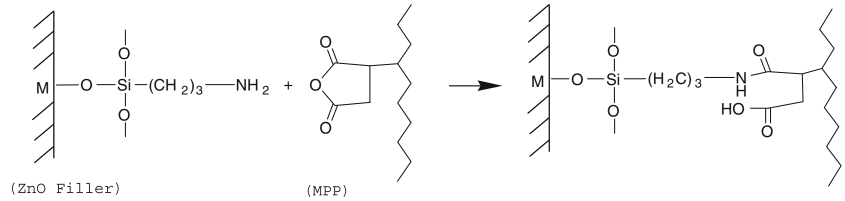


Fig. 8 The FTIR spectrums of A-1100 (correspond to KH-550) and ZnO treated with KH-550



Scheme 1 The reaction of MPP to KH-550

NDZ-132 also can promote the compatibility and interface adhesive bond of EVA matrix to ZnO filler, reduce the faults such as tiny gaps and the interfacial phonon scattering, and enhance effectively the thermal vibration transfer ability in EVA–ZnO composites (as shown in Fig. 2).

Effect of surface modification temperature of filler on the thermal conductivity of EVA–ZnO composites

Besides the kind and dosage of surface-treating agents, surface modification temperature of ZnO filler also has effect on the thermal conductivity of EVA–ZnO composites. The experiment results are shown in Fig. 9.

As shown in Fig. 9, there appear similar trend of thermal conductivities of the EVA–ZnO composites modified with different surface-treating agents. With the temperature of surface treating ZnO filler rising, the thermal conductivities of the EVA–ZnO composites modified with these surface-treating agents all increase at first, and then descend gradually. The data in Fig. 9 show that the thermal conductivities of the composites get a maximum as the temperature of surface treating ZnO filler are between 100 and 120 °C. It indicate that modifying ZnO filler at 100–120 °C, the interface adhesive bond of EVA matrix to ZnO filler can be promoted most effectively; so, the thermal vibration transfer ability in EVA–ZnO composites can reach a maximum.

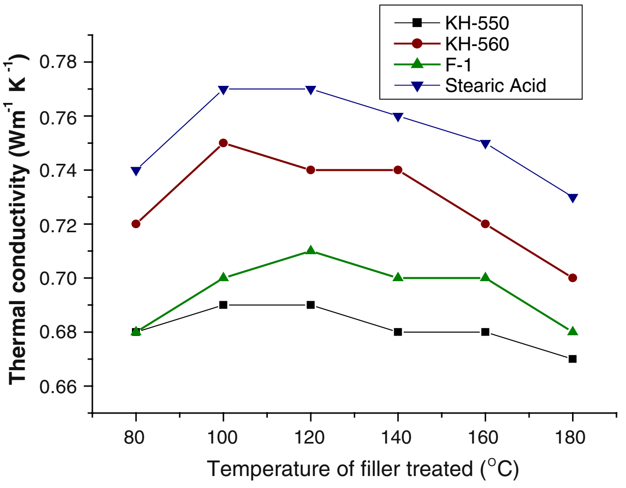


Fig. 9 The effect of filler-treated temperature on the thermal conductivity of EVA–ZnO (27 vol.%) composites

Influence of surface modification of filler on the morphology of EVA composites

Figures 10 and 11 are the fractured surface SEM morphology of the composites filled with untreated ZnO and ZnO treated with KH-560. There are obvious differences between Figs. 10 and 11. For the EVA composites filled with untreated ZnO, although the filler particles can be dispersed well, the interface adhesive bond of EVA matrix

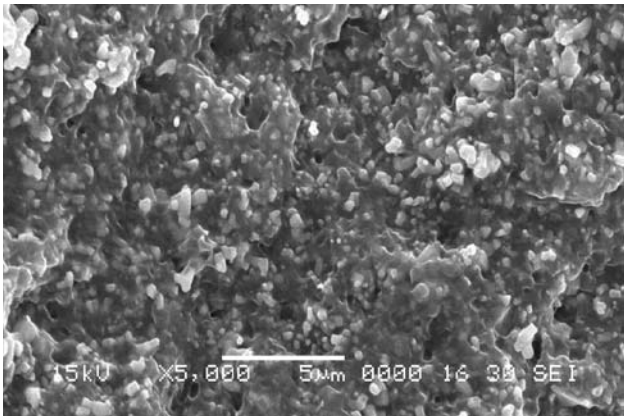


Fig. 10 The SEM image of the fractured surface morphology of EVA composites filled with untreated ZnO

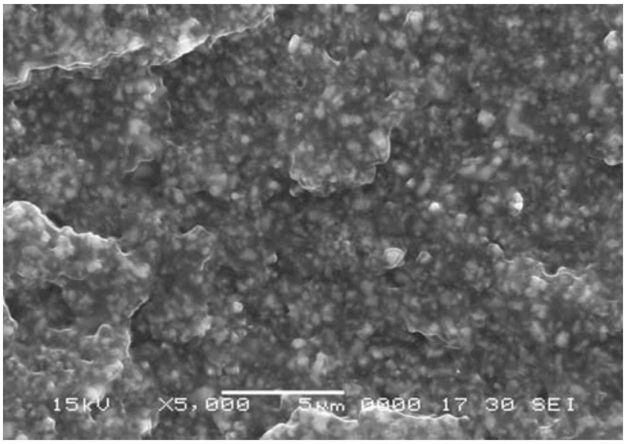


Fig. 11 The SEM image of the fractured surface morphology of EVA composites filled with KH-560 treated ZnO

to ZnO filler seems to be not firm. As shown in Fig. 10, lots of ZnO filler particles were directly pulled out of EVA matrix, and the surface of many ZnO filler particles is quite bare and not stuck by EVA matrix. Owing to the poor compatibility and adhesion, there are not only tiny gaps between ZnO filler and EVA matrix, but also many faults such as holes in the composites. These above are able to result in the decrease of the thermal conductibility of the composites on account of the phonon scattering.

Treating ZnO filler with modifying agents such as KH-560 etc., the compatibility of ZnO filler with EVA matrix are able to be improved, the absorbed substance on the surface of ZnO filler will decrease, and the adhesion of EVA matrix to ZnO filler can also be promoted effectively. So, as shown in Fig. 11, there not only almost appear not bare ZnO filler particle which was directly pulled out of EVA matrix on the fractured surface of the composites sample, but also is few fault such as hole in the composites. Therefore, as a result of the phonon scattering being reduced, the thermal conductibility of the EVA composites filled with KH-560 modifying ZnO filler can be enhanced effectively.

Conclusions

Surface-treating ZnO filler with the valid modifying agents (stearic acid, OL-AT16, KH-560, or NDZ-132,) at right dosage and treating temperature, the thermal conductivity of the EVA–ZnO composites can be enhanced effectively. The valid modifying agent not only can bond to ZnO filler, but also have good compatibility with EVA and proper chain length to entwine effectively with the macromolecule chain of EVA matrix. While the dosage of modifying agents exceeds a right amount, with the dosage increase, the thermal conductivity of EVA–ZnO composites modified with the small-molecule treating agents (F-1, *n*-Octylic acid, or stearic acid) descend more evidently on account of forming the multilayer molecule weak interface. The right treating temperature is between 100 and 120 °C.

Surface-treating ZnO filler with the valid modifying agents can improve the compatibility of ZnO filler with EVA matrix, promote effectively the adhesion of EVA matrix to ZnO filler; and reduce the faults and tiny gap in the EVA–ZnO composites, finally, enhanced effectively the thermal conductibility of the EVA–ZnO composites on account of reducing the interfacial phonon scattering.

References

1. Bigg DM (1995) Adv Polym Sci 119:1
2. King JA, Tucker KW, Vogt BD, Weber EH, Quan CL (1999) Polym Compos 20:643
3. Devpura A, Phelan PE, Prasher RS (2001) Microscale Thermophys Eng 5:177
4. Procter P, Solc J (1991) IEEE Trans Compon Hybrids Manuf Technol 14:708
5. Bujard P, Kuhnlein G, Ino S, Shiobara T (1994) IEEE Trans Compon Hybrids Manuf Technol 17:527
6. Xu Y, Chung DDL, Mroz C (2001) Composites 32:1749
7. Lee B, Liu JZ, Sun B, Shen CY, Dai GC (2008) Express Polym Lett 2:357
8. Weber EH, Clingerman ML, King JA (2003) J Appl Polym Sci 88:112
9. Heiser JA, King JA (2004) Polym Compos 25:186
10. Bigg DM (1986) Polym Compos 7:125
11. Nielsen LE (1973) J Appl Polym Sci 17:3819
12. Agari Y, Uno T (1986) J Appl Polym Sci 32:5705
13. Dawson DM, Briggs A (1981) J Mater Sci 16:3346. doi: 10.1007/BF00586296
14. Ervin VJ, Klett JW, Mundt CM (1999) J Mater Sci 34:3545. doi: 10.1023/A:1004674308487
15. Dong QQ, Zheng Q, Zhang MQ (2006) J Mater Sci 41:3175. doi: 10.1007/s10853-006-6373-6
16. Privalko VP, Novikov VV (1995) Adv Polym Sci 119:31
17. Balagurov BYa, Vinogradov GA (2006) Composites 37:1805

18. Lee GW, Park M, Kim J, Lee JI, Yoon HG (2006) Composites 37:727
19. Chou TW (1993) Structure and properties of composites. VCH, Weinheim
20. Hatsuo I (1988) Interfaces in polymer, ceramic and metal matrix composites. Elsevier, New York
21. Plueddemann EP (1982) Silane coupling agents. Plenum Press, New York
22. Clancy TC, Gates TS (2006) Polymer 47:5990
23. Zhang LM, Dai GC (2007) Express Polym Lett 1:608