A poly(vinylidene fluoride) composite with added self-passivated microaluminum and nanoaluminum particles for enhanced thermal conductivity

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A polymer composite was prepared by embedding fillers made of self-passivated aluminum particles in two kind of sizes, micrometer size and nanometer size with different volume proportions into polyvinylidene fluoride matrix. The thermal conductivity and dielectric properties of the composite were studied. The results showed that the thermal conductivity of composites was significantly increased to 3.258 W/mK when the volume proportion of micrometer size Al particles to nanometer size Al particles is at 20:1, also the relative permittivity was about 75.8 at 1 MHz. The effective simulation model values were in good accordance with experimental results. © 2011 American Institute of Physics. [doi:10.1063/1.3580588]

With the development of integrated circuit chips toward higher density and higher frequency, more and more waste heat must be removed to make the chips work stable.¹ These substrate packaging materials must possess optimum relative permittivity and low dielectric loss to reduce the signal propagation delay, which in turn provides better device performance. They should also have good thermal properties such as high thermal conductivity to dissipate the heat generated and lower matching thermal expansion coefficient with silicon.² Thus there is a growing demand for highly conductive packaging materials. Polymer composites with high thermal conductivity and low dielectric constant are highly desirable for use in various branches of application, such as electric stress control,³ electromagnetic shielding,⁴ and higher storage capability of the electric energy.⁵ The process ability and other physicochemical properties of the polymer matrix are more advantageous for practical applications compared to ceramic materials.^{6,7} Recently, polymer composites filled with metal nanoparticles have invoked much interest due to their high dielectric constant.^{8–11} However, it should be noted that, although several polymer/metal nanocomposites with very high dielectric constant have been prepared, high dielectric loss is also achieved that is a disadvantage to practical applications. Our interest is to understand how to prepare the polymer composites not only with the expectable high thermal conductivity but also with optimum dielectric behavior.

In this work, we choose self-passivated micrometer and nanometer size aluminum particles (denoted as Al*) at ten different volume proportions as fillers to fabricate the polymer/metal self-passivated composites with improved thermal conductivity and relative permittivity while keeping low dielectric loss.

The microaluminum particles with an average diameter 2 μm were supplied by Tianjin Chemistry Materials Co. (Tianjin, China), while the nanoaluminum particles with an

average diameter 200 nm were supplied by Beijing Nachen Nanomaterials Co. (Beijing, China). Poly(vinylidene fluoride) (PVDF) powder was purchased from 3F Co. (Shanghai, China) and was used as the dielectric matrix of composites due to its superior ferroelectric nature with relative higher permittivity among the polymer families. First, two kinds of aluminum powders were dried at 120 °C for 24 h in oven so that they were passivated adequately to form alumina layers coating on the aluminum particles. The micrometer size Al* and nanometer size Al* were mixed at ten different volume proportions. (denote as $Y = V_{\text{micro}} : V_{\text{nano}} = 5:1, 10:1, 16:1, 18:1, 19:1, 20:1, 21:1, 22:1, 24:1$, and $30:1$, separately) Then the Al* fillers in ten different size ratios were separately dispersed into the PVDF matrix with the filler volume fraction of 50% to form ten composites. Finally, the ten different Al*/PVDF composites were treated by a rheometer at 180 °C and 20 min and then molded by hot pressing at about 200 °C under uniaxial pressure of 50 MPa for 25min. The

FIG. 1. SEM micrographs of the Al*/PVDF composite with $Y=20:1$ and TEM micrographs (the inset of Fig. 1) of the passivation layer thickness of microsize Al* particle.

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FIG. 2. (Color) The thermal conductivity and schematic particle distributions of Al*/PVDF composites as a function of the volume proportion of micrometer size and nanometer size Al* filler measured at room temperature.

final samples were made to be disks with 12 mm in diameter and 1 mm in thickness for dielectric measurement, and $\varnothing 20 \times 6$ mm for thermal conductivity. For comparison, the Al*/PVDF composites making of pure micrometer size and nanometer size aluminum particles separately at Y=20:1 were prepared.

Transmitted electron microscopy (TEM) (JEOL JEM-1230, Tokyo, Japan) was used to observe the nanoparticle dispersion in the composite samples. The dielectric properties were measured using an impedance analyzer (Agilent 4980A, USA) with 16034B dielectric test fixture in the frequency range of 100 to 1 MHz. The thermal conductivity (λ , W/mK) was measured using a thermal constant analyzer (HOT DISK TPS-2500s).

Figure 1 shows the scanning electron microscopy (SEM) and the TEM (the inset of Fig. 1) photos of the Al*/PVDF composite with Y=20:1. As seen in the figure, the micrometer size and nanometer size Al* are highly dispersed in PVDF polymer and the oxide thickness of microsize Al* particle is about 12 nm. With the compact microstructures, the value of thermal conductivity is significantly increased, and a well mechanical tightness is also achieved.

Figure 2 shows the thermal conductivity of the composites with different volume fractions of Al* fillers measured at room temperature. It can be seen clearly that there is a sharp peak at Y=20:1 with the maximum value of the thermal conductivity of 3.258 W/mK, which is nearly 18 times of that of pure PVDF. The addition of micrometer size and nan-

ometer size Al* particles is very effective in improving thermal conductivity of polymer composites. There are mainly two reasons to explain this phenomenon. On one hand, it is the free electrons in metal aluminum that enhance the thermal conductivity of polymer composites. The immethodical movements of the free electrons can schlep much heat which results in more and more waste heat be removed. The alumina coating on aluminum particles has less influence on heat conducting due to its thin thickness. Because of the alumina coating, self-passivated aluminum can be regarded as ceramic filler, a low dielectric loss is also achieved. On the other hand, the compact microstructures have been obtained because of the close packing of big particles and small particles, which forms the effective conductive networks or pathways to enhance the thermal conductivity of polymer composites. As shown in the inset schematic particle distributions in Fig. 2, it is a schematic representation to depict the close packed structure that the nanometer size particles cover or surround micrometer size particles. When Y=20:1, an effective conductive network is formed, which is the best volume proportion. But when Y is smaller or bigger, the effective conductive networks or pathways are not well formed.

The frequency dependency of relative permittivity and dielectric loss of the composites with the different volume proportion of Al* filler in low frequency range (0.1 kHz–1 MHz) is shown in Figs. 3(a) and 3(b), respectively. As indicated in Fig. 3(a), the permittivities show slight decrease with the frequency increasing in the frequency range of 0.1 kHz–1 MHz. The maximum relative permittivity achieved is 75.8 at 1 MHz when Y=20:1 Al*/PVDF composite and the filler content of composites was 0.5. This remarkable enhancement in relative permittivity should be attributed to the space charge polarization in aluminum particles network formed by interparticle junctions and sample electrodes, as the interfaces of conductor and insulator increasing with the increasing of Al* content. It is shown in Fig. 3(b) that the dielectric loss gently increases initially then increases obviously after 10 kHz, and ten curves are almost superposed as one curve. The dielectric loss mainly includes polarization loss and conduction loss. The conduction loss is caused by the charge flow through the composites which depends on the electric conductivity of composites.

Furthermore, the comparison of relative permittivity and dielectric loss of the Y=20:1 Al*/PVDF, Al*(micrometer)/PVDF, and Al*(nano) composites are shown in Figs. 4(a) and 4(b), respectively. It is obvious that there is a sharp contrast between the nanosize and microsize mixed particles and pure monosize particles. The mixture of

FIG. 3. (Color) The frequency dependence of relative permittivity (a) and dielectric loss (b) of Al*/PVDF composites with different volume proportion.

FIG. 4. (Color) The comparison of relative permittivity (a) and dielectric loss (b) of the Y=20:1 Al*/PVDF, Al*(micrometer)/PVDF, and Al*(nano) composites.

microparticle and nanoparticle aluminum can significantly enhance the dielectric properties. The composite is a three-phase composite of aluminum, alumina coating layer and PVDF matrix.

Many theoretical and empirical models have been proposed to predict the effective thermal conductivity of polyphase mixtures. A review discussed the applicability of many of these models that appear to be more promising.¹² The effective thermal conductivity of a composite is strongly affected by its composition, structure, intrinsic thermal conductivities, filler particle size, shape, and interfacial thermal resistance, etc.

In this work, a conduction model as in the following is adopted.

$$\frac{1}{k_c} = \frac{\phi_1}{k_{s1}} + \frac{\phi_2}{k_{s2}} + \frac{\phi}{k_f}, \quad (1)$$

where k_{s1} , k_{s2} , and k_f are the thermal conductivities of the Al, PVDF matrix, and air, respectively, and ϕ_1 , ϕ_2 , and ϕ are the volume fraction of Al, PVDF matrix, and air in composites, respectively. The ϕ value can be obtained by ration of relative density to theoretical density.

Figure 5 shows a comparison of the experimental and modified model thermal conductivities of the Al*/PVDF composites. As seen from this figure, the model predicts the

FIG. 5. (Color) Comparison of the experimental and modified model values of the thermal conductivity from different volume fraction of the Al*/PVDF composites.

thermal conductivity values fairly well by an experiential constant 3.874 and a lower relative calculation error of 9.55% can be obtained. Because of so many affected factors of the effective thermal conductivity of a composite, there are few models getting the relative error under 10%. It can be seen clearly that there is a peak at Y=20:1 with the maximum value of the thermal conductivity. This is due to the presence of more connecting paths between the filler without the disturbing matrix.

In summary, the alumina filled PVDF polymer composites with mixed self-passivated micrometer size and nanometer size aluminum particles were prepared. The obtained Al*/PVDF (50% vf of fillers) composites show remarkably enhanced thermal conductivity and relative permittivity and display relative low loss tangent. The maximum value of the thermal conductivity of Al*/PVDF composites is 3.258 W/mK when $V_{\text{micro}}:V_{\text{nano}}=20:1$ and the relative permittivity is about 75.8 at 1 MHz. The results are owing to the free electrons transportation in the network of metal aluminum particles with the well-proportioned compact microstructure made of the mixture of microparticles and nanoparticles embedded into PVDF matrix.

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