Three-Phase Percolative Silver–BaTiO₃–Epoxy Nanocomposites with High Dielectric Constants

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ABSTRACT: A three-phase epoxy-based composite with randomly distributed silver nanoparticles and BaTiO₃ particles was synthesized. By the incorporation of silver nanoparticles into the epoxy resin, the dielectric properties of the resin were significantly enhanced, and this provided an ideal host for further mixing with BaTiO₃ to prepare high-dielectric-constant, polymer-based dielectrics with high dielectric strength. The devices that adopted these composites demonstrated high relative dielectric constants of approximately 450, 110 times higher than that of the epoxy matrix, with a dielectric strength of 5 kV/mm at room temperature. These nanocomposites were found to be potentially useful for embedded capacitor applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 967–971, 2006

Key words: composites; dielectric properties; inorganic materials; nanocomposites

INTRODUCTION

Increasing needs for higher functionality and higher performance in future electrical devices are driving printed-wiring-board (PWB) technology toward electrically functionalizing the inner space of PWBs.[1,2] Embedded capacitors are specially printed portions within the PWB laminations that provide the charge-storing function without using precious surface space of the boards. With the passives (capacitors, resistors, and inductors) embedded into PWBs, significant reductions of parasitic impedance,[3] assembly cost,[1] and device size[2] become possible. One major challenge for implementing embedded capacitor technology is the development of new dielectric materials that possess good dielectric and mechanical properties. Particulate-filled (0 = dispersed particles; 1 = fibers; 2 = films or layers; 3 = solids; 0–3 = particles in solids), polymer-based composites provide an ideal solution, combining the mechanical properties of polymers and the electrical properties of fillers.

Much research has been carried out on ceramic–polymer systems that adopt traditional dielectric ceramic particles as fillers, such as BaTiO₃[4] and lead magnesium niobate/lead titanate.[5,6] However, in most cases, polymer composites with ceramic fillers suffer a low relative dielectric constant (ε_r; lt;100) even with a high filler loading (>50 vol %). This is, according to the mixing rule,[7] due to the low ε_r value of the polymer matrix (<10). Recently, two-component[8–12] and three-component[12–15] percolative composites, which contain randomly distributed conductive fillers within an insulator matrix, have demonstrated substantially higher ε_r values. The ε_r values of these composites follow a scaling equation:[16,17]

$$\varepsilon_r = \varepsilon_0 \left| (f_c - f)/f_c \right|^{-q} \tag{1}$$

where $\varepsilon_0, f_c, f,$ and q are the relative dielectric constant of the matrix, the percolation threshold, the filler volume fraction, and the critical exponent, respectively. Adopted conductive fillers include metals,[8,10–13] conductive polymers,[9,14] and carbon nanotubes.[15] Among them, composites with conductive polymers as fillers show a relatively high dielectric loss (tan δ; >0.2) and high frequency dependence,[9,14] which are undesirable for capacitor applications. Also, because of the cost, carbon nanotubes are currently impractically expensive to be fabricated on a large scale. Composites with metal fillers,[10–13] therefore, exhibit useful dielectric properties and easy manufacturing requirements.

In this article, we report the synthesis of an epoxy-based composite containing randomly distributed silver nanoparticles (40 nm) and BaTiO₃ fillers. By the incorporation of various amounts of silver nanoparticles, the dielectric properties of the epoxy matrix are

significantly enhanced without notable deterioration of the mechanical properties. This silver–epoxy composite, in turn, serves as a high-dielectric-constant host for mixing with BaTiO$_3$ to further improve ε_r without raising the risk of percolation (failure) and high loss.

The rationale for adopting nanometer-size metal fillers in our work is the consideration of the filler size effect on the usefulness of these composites. In a classic 0–3 model,[16–18] the randomly distributed conductive fillers form clusters, that is, conductive networks, within the matrix. When the size of the largest cluster approaches the physical size of the matrix, discharge between electrodes, that is, percolation, will occur. On the basis of a random distribution, the cluster volume (V_{cluster}) is proportional to the product of the number of filler particles in the cluster (N_{filler}) and the average volume of fillers (V_{filler}):

$$V_{\text{cluster}} \propto N_{\text{filler}} \times V_{\text{filler}} \qquad (2)$$

On the basis of eq. (2), at the threshold concentration, we find

$$\bar{N}_{\text{filler}} \propto \bar{V}_{\text{cluster}}/V_{\text{filler}} \qquad (3)$$

where $\bar{N}_{\text{filler}}$ and $\bar{V}_{\text{cluster}}$ are the threshold filler number and threshold cluster volume, respectively. N_{filler} in a fixed volume is also proportional to the threshold filler concentration ($\bar{C}_{\text{filler}}$):

$$\bar{N}_{\text{filler}} \propto \bar{C}_{\text{filler}}. \qquad (4)$$

For a specific system, at any given filler concentration below the threshold, the percolation probability (P_{pcl}) is proportional to the filler concentration but inversely proportional to C_{filler}:

$$P_{pcl} \propto 1/\bar{C}_{\text{filler}}. \qquad (5)$$

Therefore

$$P_{pcl} \propto V_{\text{filler}}/\bar{V}_{\text{cluster}} = (D_{\text{filler}}/\bar{D}_{\text{cluster}})^3, \qquad (6)$$

where D_{filler} and D_{cluster} are the diameters of the filler and threshold cluster, respectively. In practical cases, D_{cluster} is a value close to the matrix thickness. This means that P_{pcl} depends not only on the filler concentration but also on the filler size and the size ratio of the filler to the matrix. For example, when the filler size is increased from 1 to 2 μm, P_{pcl} increases eightfold at the same concentration. In the case of a classic model for bulk samples,[16–18] the insulating matrix can be considered a three-dimensional infinity in comparison with the fillers. Therefore, the influence of the size ratio on P_{pcl} is negligible. However, in practical capac-

itors, dielectric materials need to be fabricated into thin layers of a typical thickness of 20–100 μm to increase the volumetric packaging density.[2] In this situation, the three-dimensional infinity assumption is no longer valid (instead, it is the 0–2 connectivity), especially when the filler size is in a micrometer range, which is comparable to the thickness of the dielectric layer. P_{pcl} will be much higher. Therefore, for capacitor applications, the size of the metal fillers in a percolative metal–polymer composite has to be in a nanometer range to lower P_{pcl}. However, previously reported studies on metal–polymer composites adopted micrometer-size metal powders[10,13] or even metal flakes.[11] In this work, an epoxy-based composite with randomly dispersed silver nanoparticles[12] 40 nm in diameter and submicrometer BaTiO$_3$ particles is developed. The highest dielectric constant that has been achieved is about 450, which is 110 times higher than that of the epoxy matrix. The resultant composites remain flexible and have good material processibility.

EXPERIMENTAL

The silver nanoparticles were synthesized by a redox reaction[18,19] with mercaptosuccinic acid (MSA) as a capping agent. The BaTiO$_3$ that was adopted was a commercial hydrothermal powder 240 nm in diameter (BT08, Cabot Inc.). The epoxy resin/hardener combination consisted of bisphenol A diglycidyl ether (D.E.R. 332; Aldrich) and 4-methyl-1,2-cyclohexanedicarboxylic anhydride (Aldrich), respectively. Imidazole (1 mol %) was used as a catalyst. After the synthesis and washing, silver nanoparticles were dispersed in acetonitrile under ultrasonication. Then, predetermined amounts of the epoxy resin and BaTiO$_3$ powders were added under magnetic stirring. Finally, the hardener and catalyst were added. Prototype capacitors were fabricated by the spin coating of the prepared silver–BaTiO$_3$–epoxy slurry onto a gold-coated aluminum substrate. A two-step drying–curing treatment was performed at 65 and 160°C, respectively. A thin layer of gold was deposited via sputtering as the top electrode. After trimming, the dielectric properties were measured with an HP 4194A impedance analyzer.

RESULTS AND DISCUSSION

Figure 1(a,b) presents micrographs of the cross section and surface of fabricated composite layers with a composition of 10 vol % silver and 40 vol % BaTiO$_3$. Figure 1(c) is an enlarged view of Figure 1(b), in which BaTiO$_3$ particles of 240 nm can be distinguished from the background. Figure 1(d,e) presents a transmission electron microscopy (TEM) micrograph and XRD results for the synthesized silver nanoparticles, respectively. The dielectric properties of the synthesized sil-
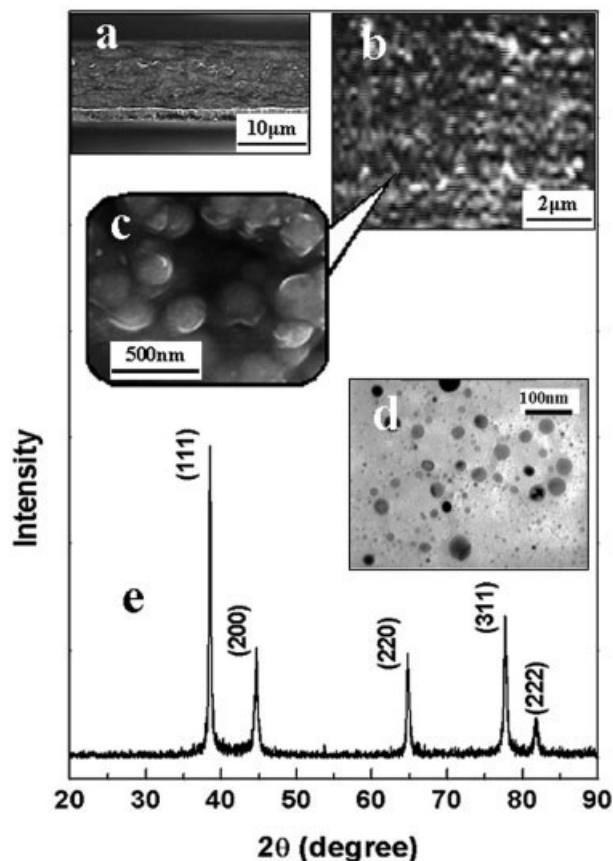
Figure 1 (a) Micrograph of the transection of a prototype capacitor with a silver–BaTiO₃–epoxy composite film that contained 10 vol % silver and 40 vol % BaTiO₃, (b) micrograph of the surface of a spin-coated silver–BaTiO₃–epoxy composite layer before gold coating, (c) enlarged view of part b [BaTiO₃ particles 240 nm in diameter (BT08, Cabbot) can be distinguished from the background], (d) TEM micrograph of the prepared silver nanoparticles with an average size of 40 nm (the silver nanoparticles were coated with a layer of MSA), and (e) X-ray diffraction pattern of the synthesized silver nanoparticles (indicating a well-crystallized cubic structure).

ver–epoxy nanocomposites are presented in Figure 2. ε_r of the composites increases from ~4 to above 300 with a silver concentration of 22 vol %, as shown in Figure 2(a). The variation of ε_r as a function of the silver concentration up to ~20 vol % shows good agreement with the scaling theory,[16] as shown in Figure 2(b). We have considered the Maxwell–Garnett,[18] Bruggeman,[20] and Skipetrov[21] models. There are many parameters in effect that are not considered in these models; for example, they do not simultaneously account for an assumption of a perfectly uniform distribution of the fillers, filler sizes and size distributions, shapes, agglomeration, surface chemistry, and impurities. However, the Maxwell–Garnett model fits our data best. The reduction of ε_r above 22 vol % does not follow the prediction by the equation, that is, a vertical drop of ε_r to nearly zero. However, ε_r of the

silver–epoxy composite decreases gradually with the further incorporation of silver above 20 vol % and exhibits a relatively broad peak. The absence of percolation is possibly due to the presence of a surfactant layer on each silver nanoparticle surface, which prevents particles from directly coming into contact with one another. The presence of a surfactant layer on silver nanoparticles prepared by this method was shown by Chen and Kimura.[22] The reduction of ε_r beyond 22 vol % is believed to be caused by the increase in the porosity. When the solid content increases, the glue (epoxy) content decreases gradually and becomes insufficient to occupy all the pores. Moreover, because of the strong polarity of the surfactant, hydrogen bonding will be formed between silver particles. Therefore, they form a relatively rigid frame. Larger porosity results, as can be observed in Figure 3. Figure 3(a–d) shows that with the silver content increasing from 10 to 40 vol %, the roughness and porosity of the composite increase. In any case, the absence of percolation is considered to be a signif-
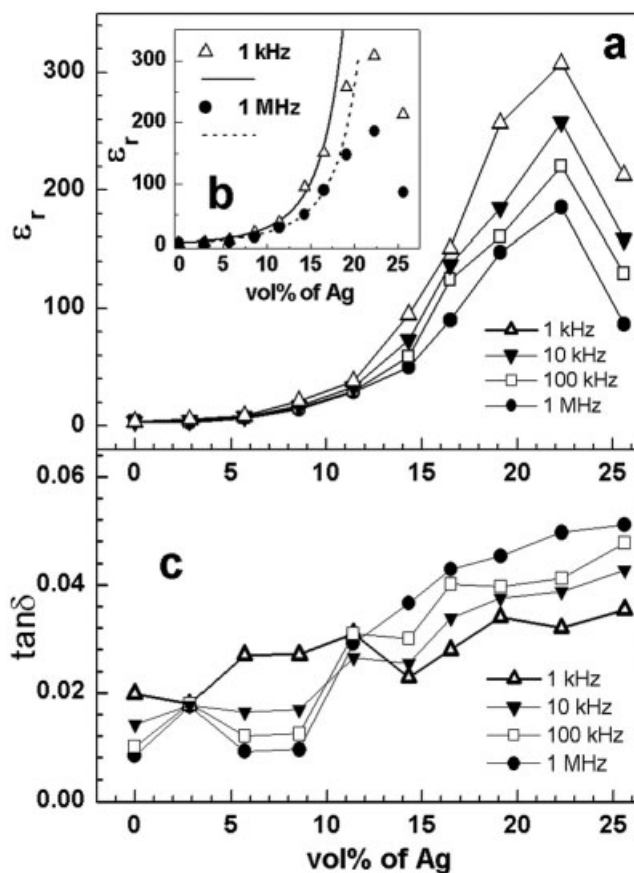

Figure 2 (a) Room-temperature ε_r values of the silver–epoxy composites as a function of the silver concentration, (b) best fit curves of the experimental ε_r data to the scaling equation[16] at 1 kHz and 1 MHz (with $\varepsilon_r = 3.84$, $f_c = 28$, and $q = 3.52$), and (c) room-temperature tan δ values of the silver–epoxy composites as a function of the silver concentration.
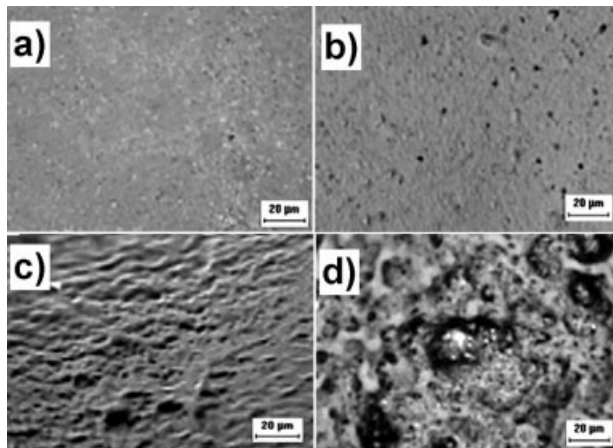
Figure 3 Micrographs of the silver–epoxy composites with (a) 10, (b) 20, (c) 30, and (d) 40 vol % silver. The roughness and porosity changes can be observed.

icant merit of this silver–epoxy composite for device applications. Figure 2(c) presents tan δ of the silver–epoxy composites as a function of the silver loading. With less than 22 vol % silver, tan δ of those composites is below 0.05, which is significantly lower than those values reported.[9–11,13–15]

According to the mixing rule[7]

$$K^{\alpha} = \sum_{i=1}^{n} (v_i \cdot K_i^{\alpha}) \qquad (7)$$

where K, K_i, v_i, α are the properties of composite, property of the ith component, volume fraction of the ith component and influencing factor, respectively.

The incorporation of BaTiO$_3$ particles into a polymer host will result in a composite with enhanced ε_r because BaTiO$_3$ is a high-dielectric-constant material. In this work, silver–BaTiO$_3$–epoxy samples were prepared with four different silver concentrations (5, 10, 15, and 22 vol %). Various amounts of BaTiO$_3$ were added to determine the optimum conditions to achieve a high dielectric constant. The highest ε_r value ($\approx$450) was obtained with 22 vol % silver and 30 vol % BaTiO$_3$, as shown in Figure 4(a). This high ε_r value, which is 110 times higher than that of the epoxy resin, benefits from the high ε_r value ($\approx$300) of the prepared silver–epoxy host.[12] BaTiO$_3$ addition increases not only the dielectric constant but also tan δ, especially at a BaTiO$_3$ concentration above 20 vol %. However, there are a number of applications, such as flash lamps and heart actuators, working at a low frequency, for which a large capacitance is more important than tan δ. Our silver–BaTiO$_3$–epoxy composites are flexible materials and can be easily manufactured into large-area rolls at a low temperature. Figure 4(b) shows tan δ of the as-prepared silver–BaTiO$_3$–epoxy composites

as a function of both the BaTiO$_3$ and silver compositions. A microstructural investigation revealed that with a silver loading of 22 vol % and BaTiO$_3$ loadings of more than 25 vol %, the sample porosity noticeably increased; this must have caused the decrease in ε_r and increase in tan δ.

The dielectric strength of the composites decreases as the silver loading increases, as shown in Figure 5(a), with the calculated maximum surface charge. The dielectric strength decreases from 28 to 5.1 kV/mm as the silver content increases to 22 vol %. This must be caused by the space charges generated at the interface of silver and epoxy under the applied electric field. The space-charge-induced decrease in the dielectric strength has been observed in both polymer–metal[10] and ceramic–metal[8] systems. The temperature dependence of ε_r of the as-prepared silver–BaTiO$_3$–epoxy composites is shown in Figure 5(b). In the temperature interval from 20 to 140°C, the dielectric constant of the prepared composites increases modestly, and the greater the silver content is, the greater the ε_r sensitivity is to temperature. This may be due to the increasing amount of the capping agent (MSA), which has a different temperature response in dielectric relaxation behavior than the epoxy matrix.
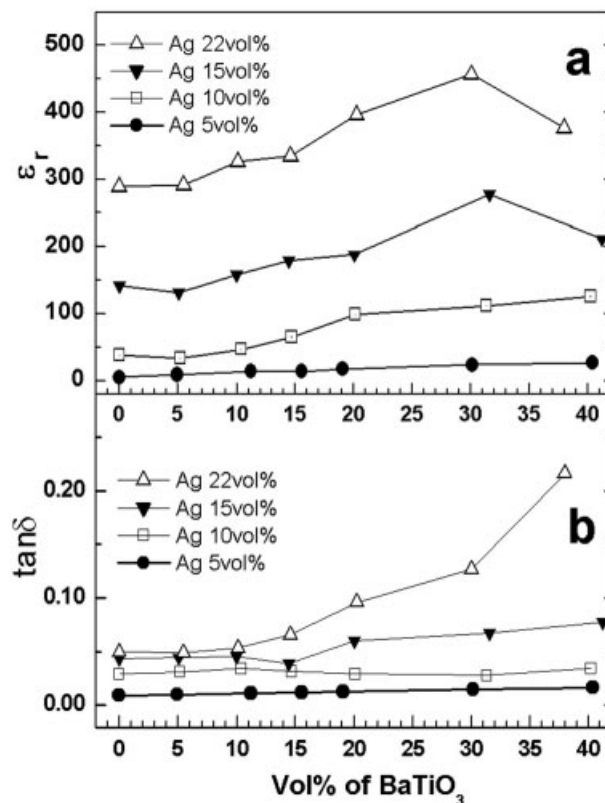

Figure 4 (a) Room-temperature ε_r values of the silver–BaTiO$_3$–epoxy composites at 1 kHz as a function of both the BaTiO$_3$ and silver concentrations and (b) corresponding tan δ values of the silver–BaTiO$_3$–epoxy composites at 1 kHz.
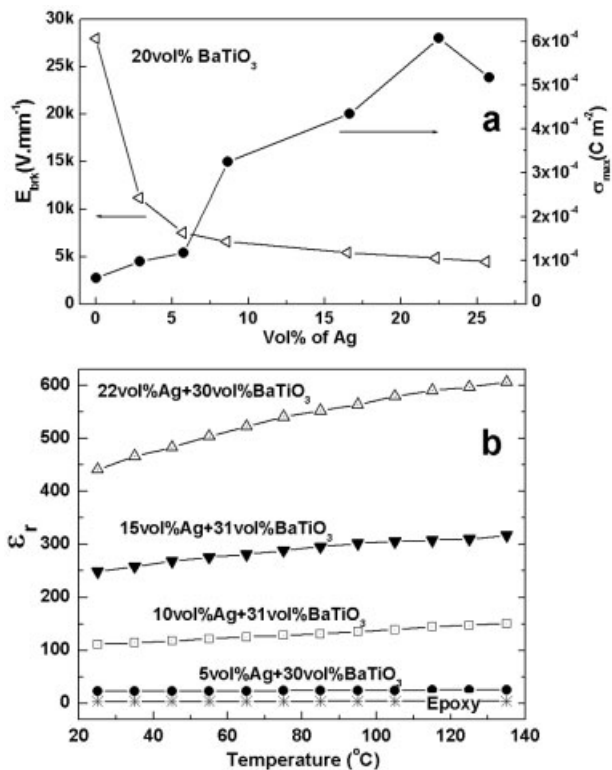
Figure 5 (a) Breakdown field (E_{brk}) at 200 V/s and maximum surface charge (σ_{max}) of the silver–BaTiO₃–epoxy composites as a function of the silver volume fraction at room temperature and (b) temperature dependence of ε_r of the silver–BaTiO₃–epoxy composites at 1 kHz.

CONCLUSIONS

On the basis of these results, we conclude that percolative epoxy-based composites with randomly dispersed nanometer-size metallic and ceramic inclusions have promising potential for use as embedded dielectrics because of their high dielectric constants and compatibility with the current PWB manufacturing methodologies. Further investigation of the influence of the filler size on the dielectric properties and the dielectric behavior at gigahertz frequencies, as well as improvements in capacitor fabrication techniques, will make these composites more advantageous for device applications.

References

1. Funer, R. Printed Circuit Des 2002, 19, 8.
2. Ulrich, R. Circuit World 2004, 30, 20.
3. Kim, H.; Sun, B. K.; Kim, J. IEEE Microwave Compon Lett 2004, 14, 71.
4. Rao, Y.; Wong, C. P. J Appl Polym Sci 2004, 92, 2228.
5. Bai, Y.; Cheng, Z. Y.; Bharti, V.; Xu, H. S.; Zhang, Q. M. Appl Phys Lett 2000, 76, 3804.
6. Bhattacharya, S.; Tummala, R. R. J Electron Packag 2002, 124, 1.
7. Coelho, R. Physics of Dielectrics for the Engineer; Elsevier: Amsterdam, 1979; p 71.
8. Pecharromán, C.; Esteban-Betegón, F.; Bartolomé, J. F.; López-Esteban, S.; Moya, J. S. Adv Mater 2001, 13, 1541.
9. Huang, C.; Zhang, Q. M.; Su, J. Appl Phys Lett 2003, 82, 3502.
10. Dang, Z. M.; Lin, Y.-H.; Nan, C.-W. Adv Mater 2003, 15, 1625.
11. Rao, Y.; Wong, C. P. IEEE Proc Electron Compon Technol Conf 2002, 256, 920.
12. Qi, L.; Lee, B. I.; Chen, S. H.; Samuels, W. D.; Exarhos, G. J. Adv Mater 2005, 17, 1777.
13. Dang, Z.-M.; Shen, Y.; Nan, C.-W. Appl Phys Lett 2002, 81, 4814.
14. Huang, C.; Zhang, Q. M.; deBotton, G.; Bhattacharya, K. Appl Phys Lett 2004, 84, 4391.
15. Dang, Z.-M.; Fan, L.-Z.; Shen, Y.; Nan, C.-W. Mater Sci Eng B 2003, 103, 140.
16. Kirkpatrick, S. Rev Mod Phys 1973, 45, 574.
17. Stauffer, D. Phys Rep 1979, 54, 1.
18. Nan, C. W. Prog Mater Sci 1993, 37, 1.
19. Jana, N. R.; Peng, X. G. J Am Chem Soc 2003, 125, 14280.
20. Bruggeman, D. A. G. Ann Phys (Leipzig) 1935, 24, 636.
21. Skipetrov, S. E. Phys Rev B 1999, 60, 12705.
22. Chen, S. H.; Kimura, K. Langmuir 1999, 15, 1075.