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BaTiO₃–Epoxy Composites for Electronic Applications

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A brief review related with dielectric properties of BaTiO₃/epoxy composites is presented. The composites were obtained using the dipping technique. To facilitate the mixing and modify the filler surface, a solvent and a surface coupling agent were used. Intermediate and low concentrations of solvent and silane improved microstructure and dielectric properties of the composite material, whereas higher concentrations led to composites of poor quality. Finally, a model using finite elements was used, in order to predict the composite permittivity in relation to the percentage of filler. Model results were compared with the effective medium theory and experimental results.

Introduction

The use of passive elements embedded into printed wiring board (PWBs) reduced parasite impedance, assembly cost, and device size. In this sense, embedded capacitors are generally printed portions within the PWB, which provide the charge-storing function, reducing the surface space of the boards.[1–5]

Materials used for integral capacitors (IC) include ceramics like BaTiO₃, Ta₂O₅, and Al₂O₃ and composite materials like BaTiO₃–epoxy composite and epoxy–glass composite. These IC are used in applications like

switching transient capacitance, line-charging capacitance, and bulk capacitance.[6] For successful implementation of these applications, capacitances values from 77 to 16,000 pF/cm² are needed.[7]

By their characteristics, polymer–ceramics composites can be applied as dielectric materials in thick-film IC. These materials offer interesting dielectric constant and low-leakage currents, making then suitable for some applications on multichip module-laminated technologies.[8] Their requirements of low-temperature processing favor the use of polymer composites.[9–12] Moreover, dielectric properties are strongly influenced by the ceramic phase, processing techniques, and additive effects. Also, dielectric performance of the composite is affected by porosity, filler amount, and distribution.

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The filler amount has to be enough ($>30\%$ vol), to change the permittivity but high levels render the material processing difficult.[13] This problem could be reduced using polymers with low viscosities or adding solvents or additives. However, relaxation phenomena and dielectric losses could be increased. Furthermore, the matrix must have very low dielectric losses in order to optimize the device working.

Many additives have been developed to modify the properties of a filled polymer. Among these additives, coupling agents have gained more attention because of their special structures, which have two different functional groups, one that is attracted to the resin and the other that is attracted to the surface of the filler.[14] Coupling agents are usually used for inorganic fillers contained in a polymer matrix to improve the adhesion between both phases and polymer, preferably via chemical bonds; their use improves the performance.[14–16]

The prediction of the dielectric permittivity of ceramic polymer composite is very important. Thus, numerical methods, such as the finite element method (FEM) or boundary element method, seem to be very suitable approaches to describe the behavior of these materials because these methods do not impose restrictions to the geometry, to the nonlinear properties of components, or to the number of phases of the composite material.[17–20]

In this paper, we review our previous works related with dielectric properties of epoxy/BaTiO$_3$ composites. Parts of this information have been reported before but here it is presented in a general and brief way, and related with the dielectric performance of these composites. We report the microstructure characterization and dielectric properties of epoxy/BaTiO$_3$ composite obtained by the dipping process and using different tetrahydrofuran (THF) concentrations and three different silane coupling

agent content. Also, the dielectric response is fitted using a theoretical model, which is solved using the FEM. The model was represented by periodic structures based on face-centered cubic cell (FCC) configurations, introducing novel packaging protocols (defining the packaging directions in which composites are filled).

Experimental Procedure

A commercial epoxy resin DER 325 and a curing agent, triethylenetetramine DEH 324 (both of Dow Chemical), at 12.5 phr were used. Also, THF (Dorwil Chemical) up to 80 wt% was added to reduce the resin viscosity.

Commercial barium titanate, BaTiO$_3$ (TAM, Ceramics Inc.) was doped with 0.6 wt% of Nb$_2$O$_5$ to modify its dielectrical properties. Powders were mixed in isopropilic alcohol by agitation at 6000 rpm during 5 min. The alcohol was then eliminated by heating until a constant weight is reached. The powder was thermally treated at 1350°C for 180 min using a heating rate of 3°C/min. The powder was milled using a planetary mill with ZrO$_2$ balls for 90 min, in isopropilic medium until an average particle size of 1.4 μm was obtained.

Glycidoxy methoxy silane (Z-6040, Dow Corning) was applied on the ceramic particles as diluted aqueous solutions of 0.25, 0.35, and 0.50 wt% (Z-6040:BaTiO$_3$) of silane in order to improve processability and increase filler wet out and dispersion. An aqueous solution was prepared, adjusting the pH of the water to 3.5 with acetic acid, and then introducing the silane. After the silane was added to the acidified water, the system was stirred for about 15 min before it hydrolyzed and formed a clear and homogeneous solution. The filler was mixed with the silane at low shear for several min-
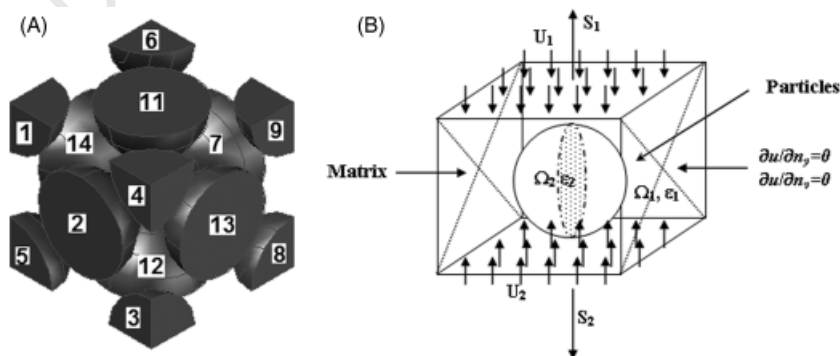

Fig. 1. (A) Packaging configuration (B) boundary conditions applied over the computational domain.

utes without additional solvent. After applying the silane, the $BaTiO_3$ particles were dried briefly at $110°C$ to avoid condensation of silane groups at the surface. Residual silane was eliminated by washing the particles in toluene at $25°C$ and then, the resulting powder was dried and sieved through a 40-μm mesh.

Suspensions containing $BaTiO_3$ powder (fractions around 45–70 vol%), solvent (fractions around 60, 75, and 85 wt% of THF), epoxy, and curing agent were prepared in a glass container. The suspensions were then agitated at 2000 rpm during 3–5 min to avoid ceramic agglomerations.

The composite films were obtained using the dipping technique. The samples were placed on a glass substrate with gold electrodes deposited previously by dc sputtering, using a dipping rate of 3 cm/min. Afterwards, the films were cured at $100°C$ for 2 h. Top electrodes were deposited by dc sputtering through a shadow mask.

Each composite was analyzed by thermal gravimetric technique (Shimadzu TGA-50, Tokyo, Japan) in nitrogen atmosphere using a heating rate of $10°C/min$ from room temperature to $800°C$.

Finally, dielectric measurements were performed using a Hewlett Packard 4284A Impedance Analyzer in the frequency range 20 Hz–1 MHz and $30°C$. Microstructures of the composites were analyzed through scanning electron microscopy (SEM, JEOL 6460LV, Tokyo, Japan).

Theoretical and Semiempirical Models

Finite Element Model

A theoretical model considering a cell volume $\Delta\Omega$ filled with spherical inclusions of $BaTiO_3$ located in a FCC distribution was proposed. Particles were placed following the sequence indicated in Fig. 1A. First, each particle grows until it reaches the maximum particle diameter (ϕ_{max}) before a new particle is located in the next position (ϕ_{max} is limited by geometrical restrictions to $\sqrt{2}L/2$, L being the cell size). This methodology has the effect to fill the main packaging directions at first.[20] In this model, the FEM was used to solve the mathematical problem.[17,20,21]

The boundary conditions applied were a potential difference ($\Delta V = U_2 - U_1$) of 1 V along the z direction (Dirichlet boundary condition) and gradients of potential equal to zero (Neumman boundary condition) for the other two Cartesian directions ($\partial u/\partial n_x = 0$ and $\partial u/\partial n_y = 0$), as shown in Fig. 1B. Simulations were
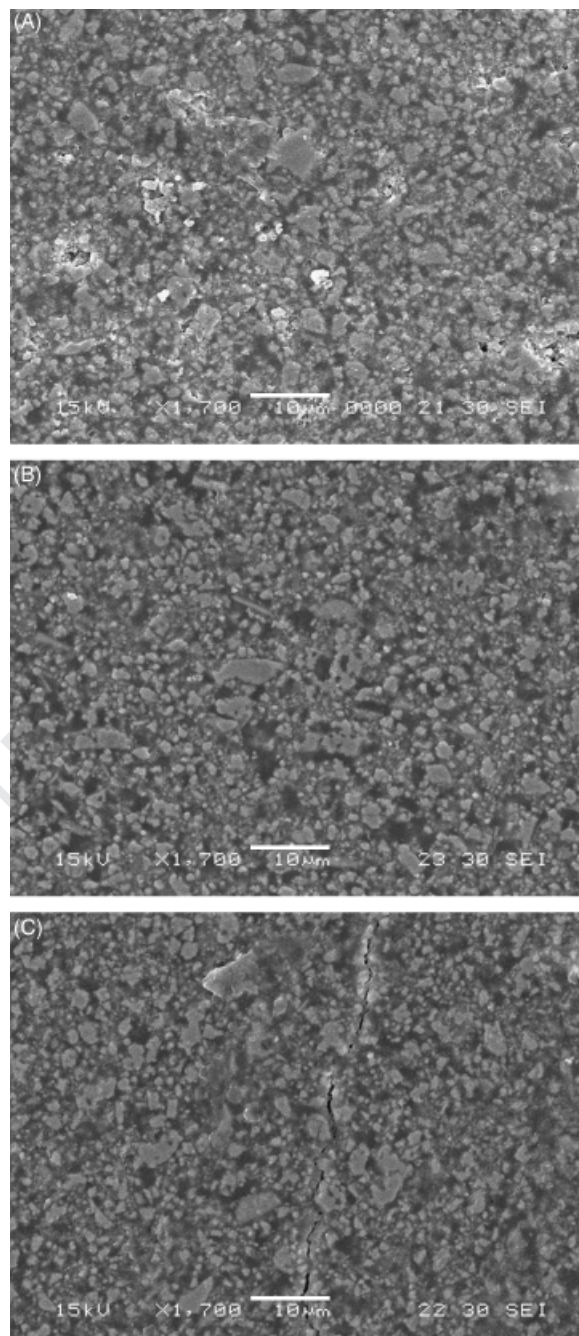

Fig. 2. Scanning electron microscopy of composites with 60 vol% of $BaTiO_3$ particles and (A) 60 wt%, (B) 75 wt%, and (C) 85 wt% of tetrahydrofuran (THF). Scale bar: 10 μm.

performed using a software developed by the authors, while postprocessing of results was carried out with MATLAB.

Effective Medium Theory (EMT)

The EMT considers the composite as an effective medium whose effective dielectric permittivity (ε_c) can be obtained by a suitable averaging over the dielectric permittivity of the two constituents. The model uses a morphology factor "n" that can be determined empirically. The mathematical equation to EMT is described as follows:[22,23]

$$\varepsilon_c = \varepsilon_m \left[1 + \frac{f_p(\varepsilon_p - \varepsilon_m)}{\varepsilon_m + n(1 - f_p)(\varepsilon_p - \varepsilon_m)} \right] \quad (1)$$

where f_p is the filler volume fraction and ε_c, ε_m, and ε_p are the composite, matrix, and filler permittivities, respectively, and n is an empirical constant (0.13).[23] The only restriction of this model is that the particle size should be very small because the model does not consider particle interaction or particle contact.

Results and Discussion

Solvent Effect

Micrographs obtained by SEM of samples prepared with 60 vol% of BaTiO₃ and different THF amounts are showed in Fig. 2. All systems showed small areas without filler, although samples made with 60 and 85 wt% of THF revealed on the entire surfaces, important trails of microporosity and macroscopic defects, respectively (Fig. 2A and C). On the other hand, the system prepared with the addition of 75 wt% of THF showed a better particle distribution (Fig. 2B). The microstructure differences among the composites suggested that high solvent

concentration generated macrodefects during the curing step (due to THF evaporation), and lower THF amounts produced microdefects due to the air introduction during the mixing step (due to higher viscosity of the system) that would not leave after the curing step.

The solvent effect (THF) on dielectric properties (at 2500 Hz) of composites prepared with different concentration of ceramic particles are shown in Table I. It can be seen that samples prepared with higher THF amount (85 wt%) presented poor dielectric constant and high loss; while systems prepared with 75 wt% showed better properties. In all cases, dielectric loss increased when the ceramic amount was higher than 60 vol%.

Dielectric constant (ε') and loss tangent (tanδ) values of composites with $\sim$60 vol% of BaTiO₃ as a function of frequency and the THF amount are plotted in Fig. 3.

Table I. THF Effect on the Dielectric Properties of BaTiO₃/Epoxy Composites (at 30°C and 2500 Hz—Determined Through[§] TGA)

THF (wt%)	BaTiO₃[§] (vol%)	ε'	tanδ
60	38	30	0.025
	52	37	0.022
	58	40	0.023
75	49	37	0.020
	59	46	0.021
	68	39	0.035
85	58	32	0.026
	59	26	0.033

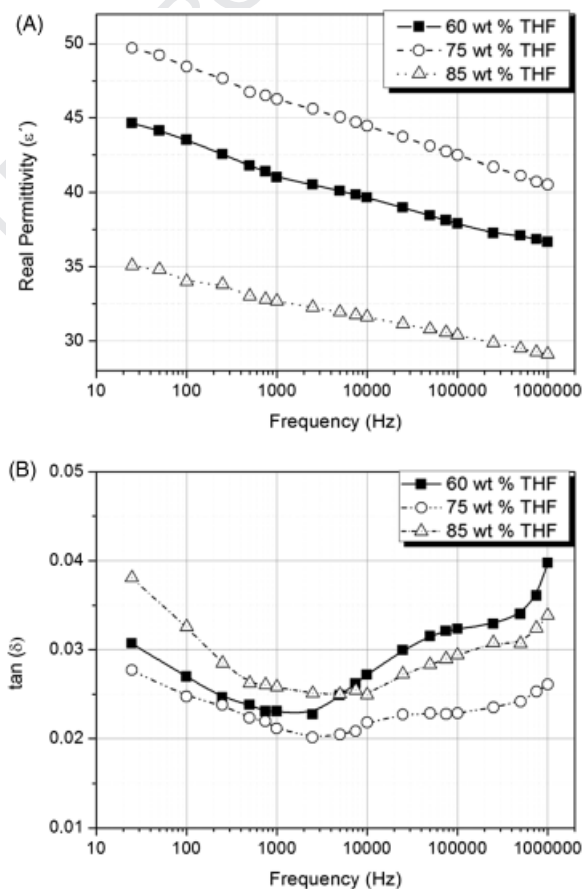TGA, thermal gravimetric technique; THF, tetrahydrofuran.

Fig. 3. *Real (A) and imaginary (B) permittivities of composites with 60% vol of particles vs. frequency and different tetrahydrofuran (THF) amount.*
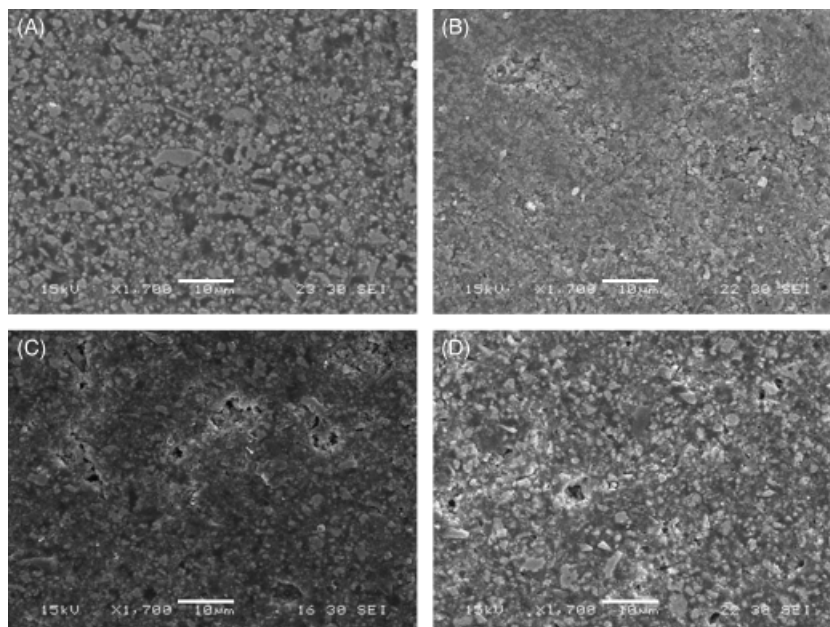
Fig. 4.   Scanning electron microscopy of composites with (A) 0 wt%, (B) 0.25 wt%, (C) 0.35 wt%, and (D) 0.50 wt% of Z-6040 (50 vol% of BaTiO$_3$). Scale bar: 10 μm.

Although not reported in this work, as expected, the dielectric constant of BaTiO$_3$–epoxy composites increases with the increase in BaTiO$_3$ content.[15,17–20] Both measures, ε' and tanδ, were influenced by the THF addition and frequency. Dielectric loss decreases when frequency rises, until 1 kHz due to dc conductivity effect, and after that a broad peak is observed in all the samples. On the other hand, real permittivity decreases in all the analyzed frequency range due to relaxation process type Debye.[24,25] As it was observed previously, composites prepared with the highest THF amount presented the worst dielectric permittivity due to macrodefects generated by THF elimination. Composites prepared with 60 wt% had better performances, even though they were worse than systems prepared with 75% due to the presence of micropores (Table I and Fig. 3). Permittivity as high as 46ε at 2500 Hz was obtained in samples with 75 wt% of THF.

Coupling Agent Effects

Micrographs obtained by SEM of composites with 60 vol% of BaTiO$_3$, and treated with different silane (Z-6040) amounts are observed in Fig. 4 (composites prepared with 75 wt% of THF content). It shows that samples with high quantities of coupling agent (0.35 and 0.50 wt%) presented small trails of microporosity (Fig. 4C and D). In these specimens, particle distribution was not homogeneous and some particle agglomeration appeared. The addition of 0.25 wt% (Fig. 4B) of silane provided a more homogeneous distribution and a better microstructure. It is suggested that high silane concentration resulted in poor filler dispersion when a high solid loading ($>$50 vol%) is used. These agglomerates increase the effective particle size, restricting the filling of voids between particles. Nevertheless, when particles were treated with 0.25 wt% of Z-6040, a better dispersion was attained, providing easy deagglomeration and efficient packing.

Real permittivity as a function of silane (at 2500 Hz) is shown in Table II. It is clearly seen that real permittivity was influenced by the coupling agent. The system with lower silane concentration (0.25 wt%) has a better permittivity than the system without silane addition. Nevertheless, higher Z-6040 amounts (0.35 and 0.50 wt%) presented important reductions in the dielectric permittivity.

Table II. Silane Effect on the Dielectric Properties of BaTiO₃/Epoxy Composites (at 30°C and 2500 Hz— Determined Through§ TGA)

Silane (wt%)	BaTiO₃§ (vol%)	ε'	tanδ
0.00	49	37	0.023
	59	46	0.020
0.25	49	39	0.024
	61	49	0.019
0.35	48	29	0.022
	60	20	0.020
0.50	51	21	0.022
	60	25	0.017

TGA, thermal gravimetric technique.

Dielectric constant (ε') and loss tangent (tanδ) values of composites with 60 vol% of BaTiO₃ as a function of frequency and silane are shown in Fig. 5. In all cases, at low frequency, dielectric loss decreases when frequency increases due to electrode and/or interfacial polarization.[26] Nevertheless, after 5000 Hz it increases and a soft loss peak at around 100 kHz is formed. Real permittivity decreases monotonically as a function of frequency due to relaxation process type Debye.[22–25] However, composites made of BaTiO₃ treated with 0.25 wt% silane had highest dielectric constant than untreated filler all over the frequency range. It appears that silane acts as a molecular bridge between the polymer and the ceramic filler, which improves the dielectric properties, at least at low concentrations.[17] Besides the good microstructure obtained in these composites, the presence of the coupling agent assures higher permittivity values.[27] Nevertheless, higher silane amounts tend to lower dielectric properties because of higher porosity, particle agglomeration, and defect content.

Dielectric Behavior Fitting

Figure 6 show the plots of FEM and EMT models as a function of the filler volume fraction. The BaTiO₃ permittivity of $\varepsilon_f = 2300$ and the pure resin permittivity of $\varepsilon_m = 4.55$ were used. The experimental values were measured at 2500 Hz. Both models show an excellent prediction at low volume fractions, even though EMT cannot represent very well the composite behavior beyond 60 vol% of particle concentration recording to the
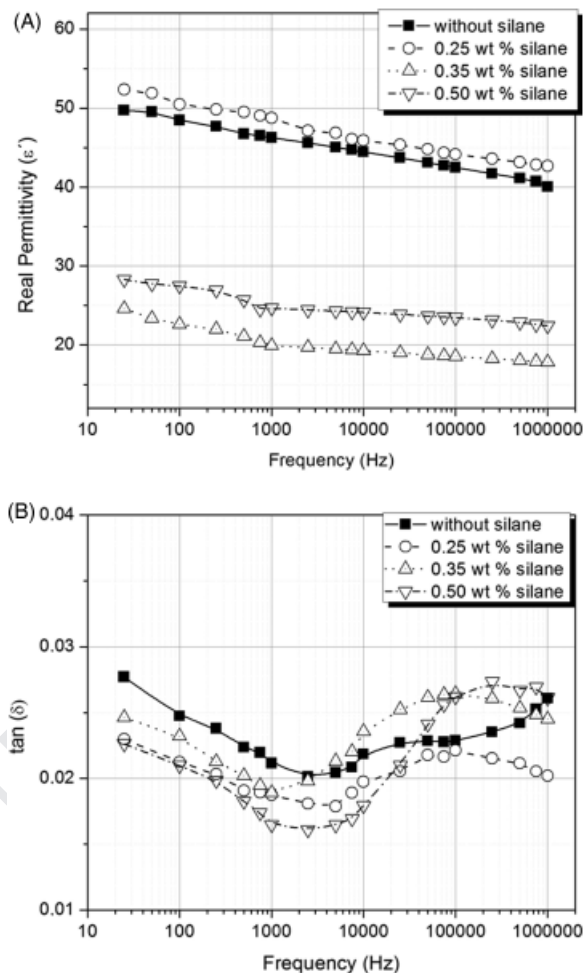

Fig. 5. Real (A) and imaginary (B) permittivities vs. frequency curves of the composites with different silane amounts (50 vol% of BaTiO₃).

assumption of this model. FEM model shows a tendency to fit experimental data for all particle concentrations although it fails to predict correctly the range of particle concentration from 10 to 30 vol%, overestimating the dielectric permittivity. This concentration range counts as a transition state where the composite is neither a diluted system nor a concentrated one. Results improve from 25 vol% when particle interaction gets more relevant. In this model, the electric field flow turns to the particles following the easier path provided by them. Thus, if the particle–particle interaction increases, the electric field will grow and subsequently higher dielectric constants will be produced.[20,28]
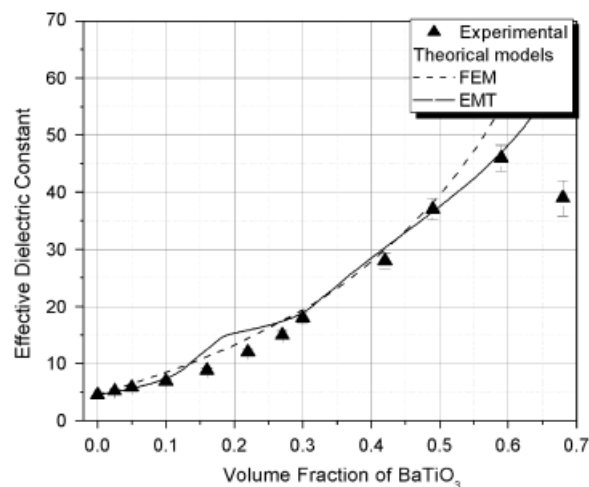
Fig. 6.   *Experimental results at 2500 Hz, fitting with effective medium theory (EMT) model and the proposed model solved using finite element method (FEM) predictions.*

Conclusions

Microstructure characterization and dielectric properties of epoxy/BaTiO$_3$ composites obtained by dipping process, using THF and silane coupling agent have been investigated. From this study the following conclusions were reached:

- Solvent and silane coupling agent influence the microstructure and dielectric properties of composites. Specimens prepared with 75 wt% of THF and 0.25 wt% of silane Z-6040 presented higher dielectric permitivities than systems prepared with higher concentrations.
- In general, THF reduced the matrix viscosity and facilitated the mixing step while silane Z-6040 helped to wet particles and improved the interfaced contact. Low solvent amounts were not enough to reduce the viscosity and release the air introduced during the mixing step while higher concentration generated macrodefects due to THF evaporation. In a similar fashion, high silane concentrations increased the porosity and defects, and degraded the dielectric properties.
- The implemented FEM reproduces the experimental behavior better than the EMT model. A periodic structure based on an FCC configuration and a desirable packaging strategy could be used in order to represent composites with different dielectric properties between the matrix and the inclusions.

References

1. H. Windlass, P. Markondeya Raj, D. Balaraman, S. Bhattacharya, and R. Tummala, "Polymer–Ceramic Nanocomposite Capacitors for System-on-Package (SOP) Applications," *Part B: Adv. Packaging, IEEE Trans.*, 26 10–16 (2003).
2. T. R. Shrout, W. Hackenberger, S. J. Jang, Q. M. Zhang, and C. A. Randall "Novel dielectric Materials", IMAPS Third Advanced Technology Workshop on Integral Passives Technology, Pennsylvania, (1998).
3. T. Thongvigitmanee and G. S. May, "Modeling and Optimization of Integral Capacitor Fabrication Using Neural Networks," *Twenty Sixth IEEE/CPMT International Electronics Manufacturing Technology*, 47–54, 2000. Q8
4. T. Hu, J. Juuti, H. Jantunen, and T. Vilkman, "Dielectric Properties of BST/Polymer Composite," *J. Eur.Ceram. Soc.*, 27 3997–4001 (2007).
5. S. Lee, J.-G. Hyun, H. Park, J. Kim, and K.-W. Paik, "Frequency Behavior of Embedded Epoxy/SrTiO₃ Composite Capacitor Materials," *IEEE Electronic Components and Technology Conference*, 1222–1227, 2005. Q9
6. M. Jacksom, M. Pecht, S. Bok Lee, and P. Sandborn, "Integral, Embedded, and Buried Passive Technologies," 2004. Available at http://www.ca-lce.umd.edu.
7. J. Rector, J. Dougherty, V. Brown, J. Galvagni, and J. Prymak, "Integrated and Integral Passive Components: A Technology Roadmap," IEEE Electronic Components and Technology Conference, 713–723, 1997. Q10
8. P. Chahal, R. R. Tummala, and M. G. Allen Packaging Research Center, "Integral Capacitors Using Polymer-Ceramic Components for MCL", *Proceedings of the International Symposium on Microelectronics*, Georgia, 126–131, 1996.
9. L. Ramajo, M. M. Reboredo, and M. S. Castro, "Characterisation of Epoxy/BaTiO₃ Composite Processed by Dipping for Integral Capacitor Films (ICF)," *J. Mater. Sci.*, 42 3685–3691 (2007).
10. Y. Imanaka and J. Acedo, "Embedded Capacitor Technology Using Aerosol Deposition," *Int. J. Appl. Ceram. Tech.*, doi 10.1111/j.1744-7402.2009.02359. Q11
11. Z.-M. Dang, L.-Z. Fan, Y. Shen, and C.-W. Nan, "Dielectric Behavior of Novel Three-Phase MWNTs/BaTiO₃/PVDF Composites," *Mater. Sci. Eng. B*, 103 140–144 (2003).
12. E. Tuncer, I. Sauers, D. R. James, A. R. Ellis, and R. C. Duckworth, "Nano-dielectric System for Cryogenic Applications: Barium Titanate filled Polyvinyl Alcohol," *IEEE Trans. Dielectr. Electr. Insul.*, 15 236–242 (2008).
13. S. Ramesh, B. A. Shutzberg, C. Haung, J. Gao, and E. P. Giannelis, "Dielectric Nanocomposites for Integral Thin Film Capacitors: Materials Design, Fabrication, and Integration Issues," *IEEE Trans. Adv. Packaging*, 26 17–24 (2003).
14. E. P. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York, 1982.
15. L. Ramajo, M . Castro, and M. Reboredo, "Influence of Silane Coupling Agents on BaTiO₃-Filled Epoxy Resin," *Composites Part A*, 28 1852–1859 (2007).
16. Z.-M. Dang, Y.-F. Yu, H.-P. Xu, and J. Bai, "Study on Microstructure and Dielectric Property of the BaTiO₃/Epoxy Resin Composites," *Composites Sci. Tech.*, 68 171–177 (2008).

17. L. Ramajo, D. Ramajo, D. Santiago, M. Reboredo, and M. Castro, "BaTiO$_3$-Filled Epoxy Resin Composites: Numerical Modelling of Dielectric Constants," *Ferroelectrics*, 338 117–126 (2006).

18. A. Beroual and C. Brosseau, "Comparison of Dielectric Properties Determined from a Computational Approach and Experiment for Anisotropic and Periodic Heterostructures," *IEEE Trans. Dielectr. EI*, 8 921–929 (2001).

19. D.-H. Yoon, J. Zhang, and B. I. Lee, "Dielectric Constant and Mixing Model of BaTiO$_3$ Composite Thick Films," *Mater. Res. Bull.*, 38 765–772 (2003).

20. L. Ramajo, D. Santiago, D. Ramajo, M. Reboredo, and M. Castro, "Computational Approach of Dielectric Permitivities in BaTiO$_3$–Epoxy Composites," *J. Composite Mater.*, 42 2027–2037 (2008).

21. O. C. Zinhiewicz and R. L. Taylor, *The Finite Element Method*, MacGraw Hill Book Company, London, 1989.

22. G. Sumesh and M. T. Sebastian, "Three-Phase Polymer–Ceramic–Metal Composite for Embedded Capacitor Applications," *Composites Sci. Tech.*, 69 1298–1302 (2009).

23. Y. Rao, J. Qu, T. Marinis, and C. P. Wong, "A Precise Numerical Prediction of Effective Dielectric Constant for Polymer–Ceramic Composite Based on Effective-Medium Theory," *IEEE Trans. Comp. Packaging Tech.*, 23 680–683 (2000).

24. G. Tsangaris and G. Psarras, "The Dielectric Response of a Polymeric Three-Component Composite," *J. Mater. Sci.*, 34 2151–2157 (1999).

25. C. V. Chanmal and J. P. Jog, "Dielectric Relaxations in PVDF/BaTiO$_3$ Nanocomposites," *Express Polymer Lett.*, 2 294–301 (2008).

26. A. Patsidis and G. C. Psarras, "Dielectric Behaviour and Functionality of Polymer Matrix—Ceramic BaTiO$_3$ Composites," *Express Polymer Lett.*, 2 718–726 (2008).

27. Z.-M. Dang, Y.-F. Yu, H.-P. Xu, and J. Bai, "Study on Microstructure and Dielectric Property of the BaTiO$_3$/Epoxy Resin Composites," *Composites Sci. Tech.*, 68 171–177 (2008).

28. K. S. Deepa, S. Kumari Nisha, P. Parameswaran, M. T. Sebastian, and J. James, "Effect of Conductivity of Filler on the Percolation Threshold of Composites," *Appl. Phy. Lett.*, 94 142902 (2009).

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