Effects of CNT/$BaTiO_3$ Composite Particles Prepared by Mechanical Process on Dielectric Properties of Epoxy Hybrid Films

Hui Joon Park, Seung Min Hong, Sang-Soo Lee, Junkyung Kim, and Min Park

***Abstract*—A new type of composite filler mechanically treated with multi-walled carbon nanotubes (MWNTs) and $BaTiO_3$ (BT) particles was prepared to produce higher dielectric properties in the composite. The hybrid film fabricated by incorporating these composite fillers in an epoxy matrix had a high dielectric constant and similar dielectric loss as compared to the composite which contained neat BT particles. The dielectric properties of these hybrid films were found to be dependent on both the content of MWNTs and mechanical processing time. Results suggest that this novel hybrid film composed of the composite filler and the epoxy matrix can be used for embedded capacitor material.**

***Index Terms*—Barium titanate, composite filler, dielectric property, embedded capacitor, epoxy, hybrid film, mechanical processing, multiwalled carbon nanotubes (MWNTs).**

I. Introduction

RECENTLY, the focus of almost all research related to electronic packages has been on the control of passive components since over 70% of a printed circuit board (PCB) surface area is occupied by passive components. In the case of mobile phones, the number of passive components on the board is 20 times more than active components [1], [2]. Since passive components are individually mounted on the surface of electronic packages as discrete passives, and attached to the board through long interconnections, passive components have consistently been obstacles in efforts to miniaturize the board [3]. To solve these problems, there has been intensive study in recent years concerned with embedding passive components in the substrate. By embedding passive components in the substrate, the size of the board and the number of solder joints can be reduced, thereby decreasing the parasitic loss which is induced by long interconnection lengths. As a result, the reliability and electrical performance of electronic packages can be improved. Among various kinds of passive components, capacitors have been the focus of researchers not only because they underlie various important functions such as bypassing, filtering, and timing, but also because capacitors with higher capacitance and shorter distance from their serving components are required for the development of microelectronics.

The relationship between capacitance C and the dielectric constant is given by

$$C = \frac{\varepsilon_o \cdot \varepsilon_r \cdot A}{t}$$

where ε_0 is the dielectric constant of the free space (8.854×10^{-12} F/m), A is the area of the electrical conductor, t is the thickness of the insulator layer, and ε_r is the dielectric constant of the insulator layer. According to this relationship, the development of a substrate compatible with high dielectric constant material is the major challenge of fabricating capacitors with high capacitance. Ceramics, such as $BaTiO_3$ (BT), have been researched as suitable materials for capacitors because of an inherently high dielectric value of 3000 and a low dielectric loss of 0.01. However, high processing temperatures (above 800 °C) and the low mechanical strength of ceramic materials undermine the capacity to embed high dielectric materials in PCB which begins to thermally degrade at temperatures above approximately 250 °C. Meanwhile, the polymeric matrix is viable at low processing temperatures applicable to PCB applications but has an inherently low dielectric constant value of around 3–5 [4]. Thus, to make up for the weak points in each material, polymer-ceramic composites are often used in embedding capacitors in organic substrates [5]–[7]. The dielectric properties of typical polymer-ceramic composites commercially developed were shown in Table I [8]. Moreover, Wong *et al.* recently obtained a polymer-ceramic composite, which consisted of an 85% by volume ceramic and epoxy matrix and had a dielectric constant value of 150 [9].

Despite these advances, there are still some barriers to using a polymer-ceramic composite in embedded capacitors. To obtain a composite with a high dielectric constant, the loading density of the ceramic filler needed to be increased. Using this approach, Wong *et al.* fabricated a composite with a high dielectric constant value of 150, but as expected, this composite material had a very poor adhesive property. As a result, the application of that composite was limited. In our work, the problem of adhesion was addressed by adding conductive filler instead of increasing the loading density of the ceramic filler. From the percolation theory, it is well known that a composite composed of conductive filler and polymer has a very high dielectric constant when the concentration of conductive filler is close to the percolation threshold [10]–[14]. Based on this theory, multiwalled carbon nanotubes (MWNTs) were chosen as a conductive filler to develop material with a high dielectric constant. MWNTs are a

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TABLE I
COMMERCIAL POLYMER/CERAMIC HYBRID FILMS WITH HIGH DIELECTRIC CONSTANT

Company	Hadoco®	3M®	DuPont®	VANTICO®
Trade Name	EmCap	C-Ply	Hi-K	CFP
Hybrid Film	Epoxy /Ceramic	Epoxy /BT	Polyimide /BT	Epoxy /Ceramic
Dielectric constant (at 1GHz)	36	22	11.6	20.5
Dielectric loss (at 1GHz)	0.06	0.10	0.01	-
Thickness (μm)	100	4 ~ 25	25	12

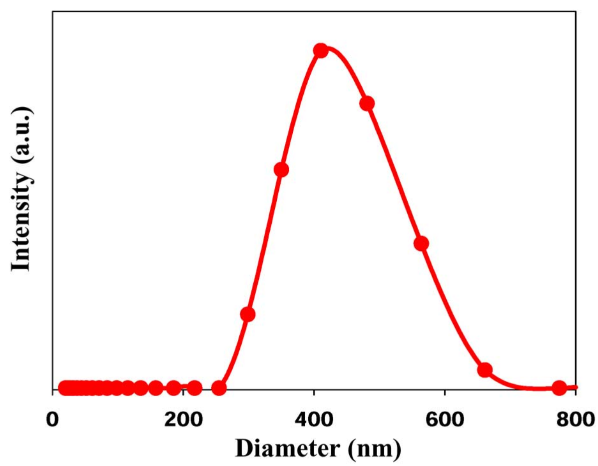


Fig. 1. Particle size analyzer results of $BaTiO_3$ particles.

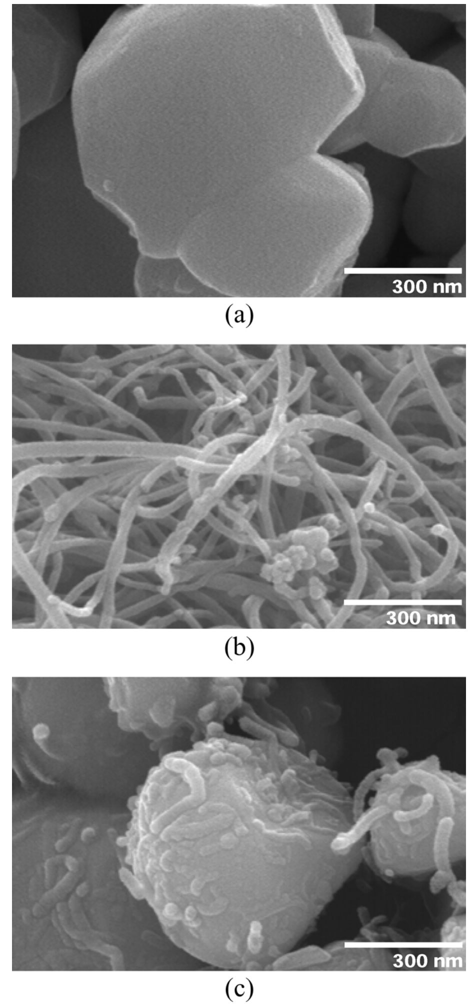


Fig. 2. FE-SEM images of (a) $BaTiO_3$, (b) MWNTs, and (c) MWNTs-$BaTiO_3$ composite filler treated by mechanical processing.

highly conductive material with a large aspect ratio and good electrical property [15], but it is difficult to control the percolation threshold of MWNTs because of the weak affinity of MWNTs with the matrix and its very low percolation threshold. Therefore, we prepared complexes of MWNTs and ceramic BT, which served as the composite filler, via a simple mechanical treatment for controlling the percolation threshold. The composite material loaded by the composite filler gave a higher dielectric constant than that of the composite fabricated only by ceramic particles.

II. EXPERIMENT

A. Materials

A commercial epoxy resin modified by urethane, UME 305 (EEW: 250, Kukdo Chemicals), was used as polymer matrix. Methyl tetrahydrophthalic anhydride (MTHPA, Hitachi Chemicals) was chosen as an epoxy hardener. $BaTiO_3$ (BT 045, Samsung Fine Chemicals) and MWNTs (Dobong, Hanyang University) were used as fillers. The size distribution of the BT particles was analyzed by the particle size analyzer (ELS-8000, Otsuka). The BT particles were dispersed in ethanol by the sonicator, and the particle size analyzer results are shown in Fig. 1.

B. Composite Fillers Composed of BT and MWNTs

Vibration-milling equipment (Pulveriser, Retsch) was used to fabricate mechanically treated composite fillers which were composed of BT and MWNTs. The processing condition of the vibration-milling equipment was 1800 vibrations/min under atmospheric pressure and the processing time of that equipment was 3, 5, and 10 min. The MWNTs content of the composite fillers was varied from 1 PHR (parts per hundred resin, grams of MWNTs/100 g of BT) to 5 PHR with BT content held constant. The structure of MWNTs was characterized by a Raman spectroscope (Jasco, NIS 3100, Argon source laser with an excitation wavelength of 514.5 nm), and the morphology of composite fillers was examined by a scanning electron microscope (Hitachi, S-4200, 10 kV). The scanning electron microscope (SEM) images of BT, MWNTs, and composite filler are shown in Fig. 2(a)–(c), respectively.

C. Fabrication of Hybrid Films and Capacitors

First, the epoxy resin was mixed with the hardener, and then the composite filler was added into the epoxy matrix. The compound was mixed by a paste mixer (Thinky, AR-250) for 7 min (2 min at 500 r/min → 2 min at 2000 r/min → 3 min

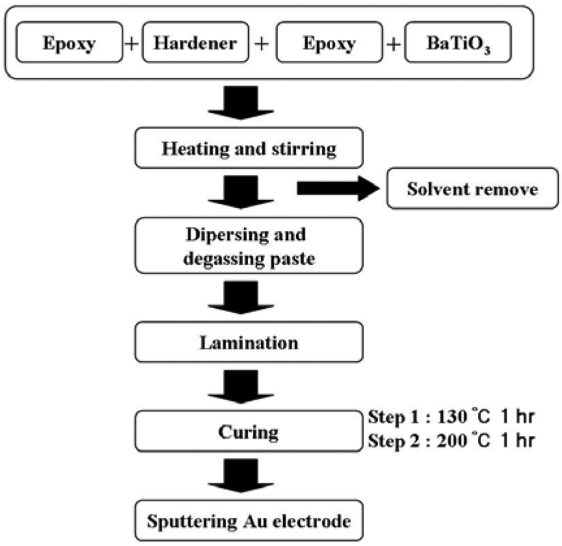


Fig. 3. Flow chart of experimental procedure to fabricate hybrid films and capacitors.

at 800 r/min). Hybrid films were fabricated by injecting this suspension into a hot press mold (Tetrahedron, MTP-8). The suspension made by a paste mixer was poured on release film and covered with another release film, then this suspension was treated under high heat and pressure in a hot press mold for curing. Finally, the top and bottom electrodes of the capacitor were fabricated by sputtering 10-mm diameter Ag circles onto the composite through a shadow mask. These processing conditions are shown in Fig. 3. The capacitance was directly measured at 10 kHz with a Hewlett Packard 4273A LCR meter. Each sample was measured seven times, and capacitance data for each sample was averaged.

III. Results and Discussions

Fig. 4(a) shows the change of dielectric constant and dielectric loss induced by the treatment of MWNTs. The dielectric constant of the composite in which the MWNTs, nontreated with BT, were simply loaded as conductive filler increased compared to that of the composite which contained only BT particles in the epoxy matrix; however, the dielectric loss increased as well. This indicates that the content of MWNTs had already exceeded the percolation threshold, according to the percolation theory of conductive filler addition. In other words, the conductive filler, MWNTs, clustered together and created a dielectric substance which caused dielectric loss. This was also confirmed by observing that a uniform film was not easily produced as phase separation occurred between the MWNTs, BT and epoxy matrix. Meanwhile, the hybrid film fabricated by loading a composite filler mechanically treated with BT and MWNTs for 3 min in the same content as the composite merely mixed with BT and MWNTs also had a higher dielectric constant than the composite which contained neat BT, but it showed similar dielectric loss to them. This result indicates that MWNTs of which structures were damaged through mechanical treatment process and combined with the insulator BT could not make the network of conductive paths. Consequently, dielectric loss of the hybrid film did not increase and the percolation threshold of the composite could be changed. In case of the dielectric constant, as the free electron of which the free movement was restricted was kept in the boundary of the composite filler and high surface polarization was generated, the higher dielectric constant was made than the neat BT system.

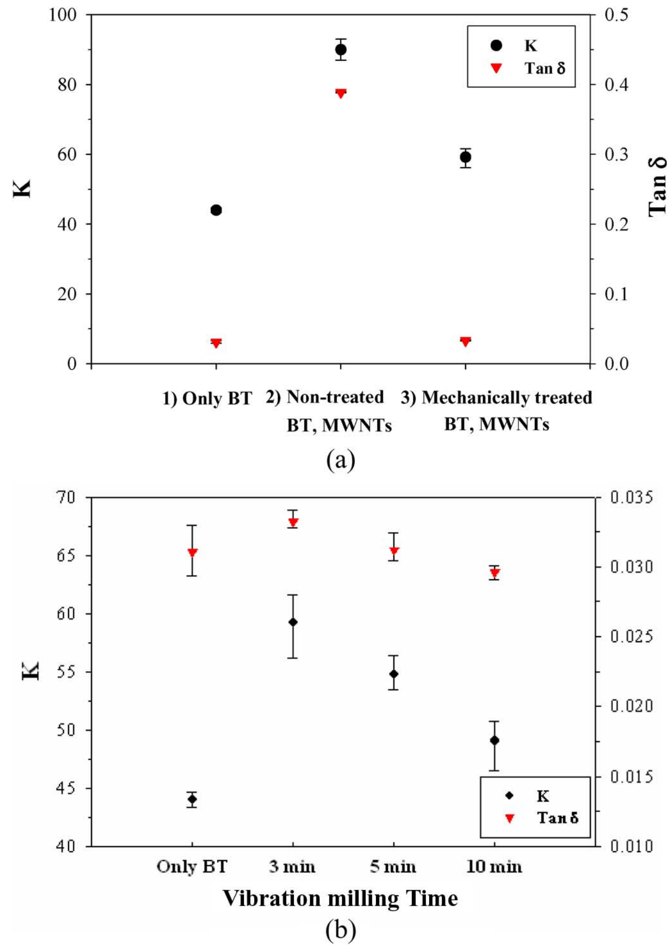
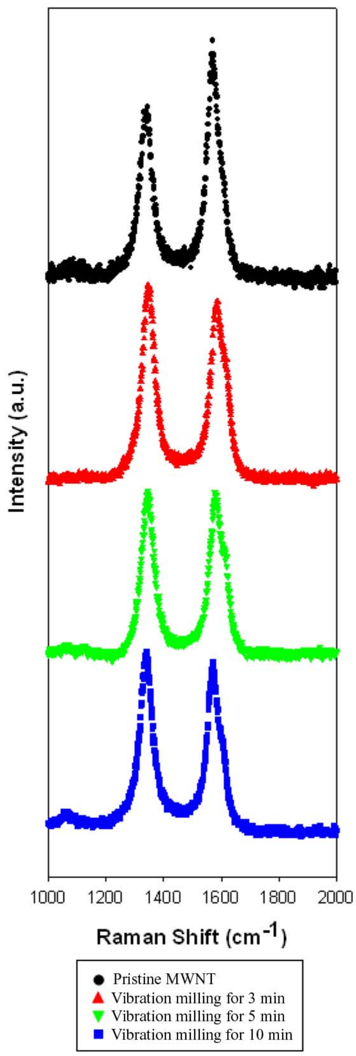
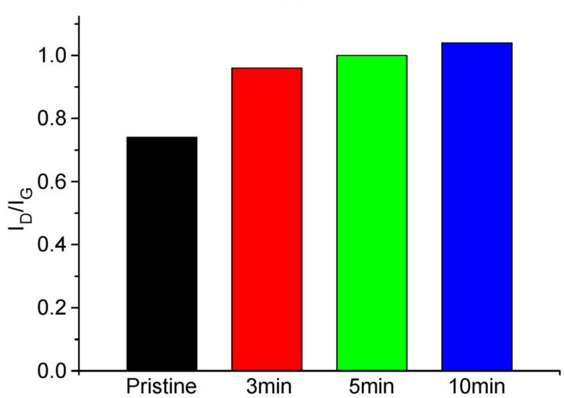


Fig. 4. Variation of dielectric constant and tan δ of composite films induced by (a) MWNT treatment method: 1) 50% by volume $BaTiO_3$, 2) Nontreated 3 PHR (3.4% by volume) MWNT/48.3% by volume $BaTiO_3$, and 3) mechanically treated 3 PHR (3.4% by volume) MWNT/48.3% by volume $BaTiO_3$. (b) Mechanical processing time at 3 PHR (3.4% by volume) MWNT/48.3% by volume $BaTiO_3$.

As seen in Fig. 4(b), the dielectric property of the composite filler treated by mechanical processing could be controlled depending on processing time. Fig. 4(b) illustrates the dielectric properties of a hybrid film, which is composed of 3 PHR (3.4% by volume) MWNTs and 48.3% by volume BT, at different mechanical processing times. As processing time increased, the dielectric constant and loss of hybrid film decreased. The dielectric constant of the hybrid film treated for 10 min decreased by a 20% compared to the one treated for 3 min. The reason for the decrease of dielectric properties was investigated by means of Raman spectrum data. The analysis of Raman spectroscopy of MWNTs revealed information on the evolution of MWNTs during mechanical treatment [16]. In the range of 1300–1700 cm^{-1}, the spectra of carbon nanotube (CNT) generally shows two specific peaks. The peak around 1580 cm^{-1} corresponds to the tangential C-C stretching modes (G band) that are characteristic of graphitic structure in CNT and the other one around 1350

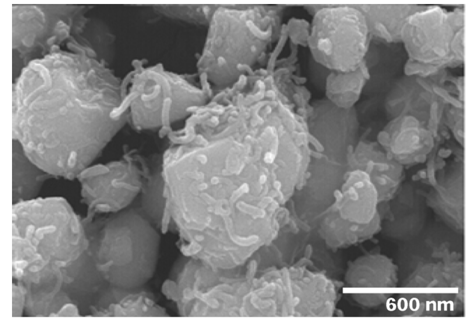


(a)

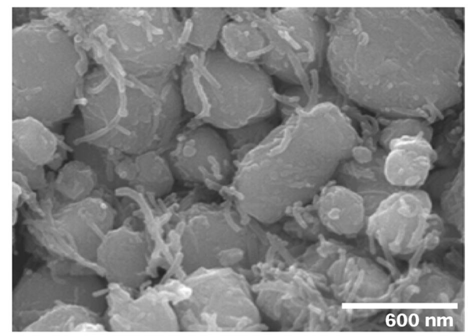


(b)

Fig. 5. (a) Variation of Raman spectra of MWNTs by vibration milling time (b) Variation of quality factor I_D/I_G versus vibration milling time.



(a)



(b)

Fig. 6. FE-SEM images of 3 PHR (3.4% by volume) MWNTs-$BaTiO_3$ composite filler treated by mechanical processing for 3 min: (a) Before sonication and (b) after sonication for 30 min.

cm^{-1} (asymmetric mode: D band) is assigned to the residual ill-organized graphite (impurities and defects on CNT). Thus, the ratio between the intensity of the D and G bands is a factor indicating the quality of CNT and can be used to characterize the CNT content of the samples [17]. The Raman spectrum of the composite filler treated by vibration milling for 3, 5, and 10 min is shown in Fig. 5(a). As the time of mechanical treatment increased, the intensity of the D band increased while that of the G band decreased. Fig. 5(b) shows that the quality factor ID/IG increased progressively with the mechanical treatment time. The quality factors resulting from the three processing times were 0.96, 1, and 1.04 and had higher values of 30%, 35%, and 41%, respectively, as compared to the pristine MWNTs. These results suggest that the structure of MWNTs is destroyed by mechanical energy during vibration milling thereby reducing the power of surface polarization of the MWNTs. As a result, the dielectric property of the hybrid film can be controlled by changing the structure of MWNTs through the mechanical treatment of the composite filler.

Fig. 6(a) shows the SEM image of the surface morphology of the composite filler treated by vibration milling for 3 min. The surface morphology image shows MWNTs cut into 100 $\sim$ 300-nm size fragments (from an original size of 10–30 μm) and coated on the surface of BT. Fig. 6(b) shows an image of the same type of composite filler, but this sample had been sonicated at 25 kHz for 30 min. The SEM image of the sonicated composite filler was very similar to that of the nonsonicated composite filler indicating that the composite filler which is mechanically treated has strong absorption stability between BT and MWNTs.

Fig. 7 indicates the dielectric properties of hybrid films with varying MWNTs content, mechanically treated for 3 min, the time at which the highest dielectric constant had been generated in our previous experiments. As MWNTs' content increased, the dielectric constant and loss also increased. It appears that the dielectric property of the hybrid film was increased by the higher

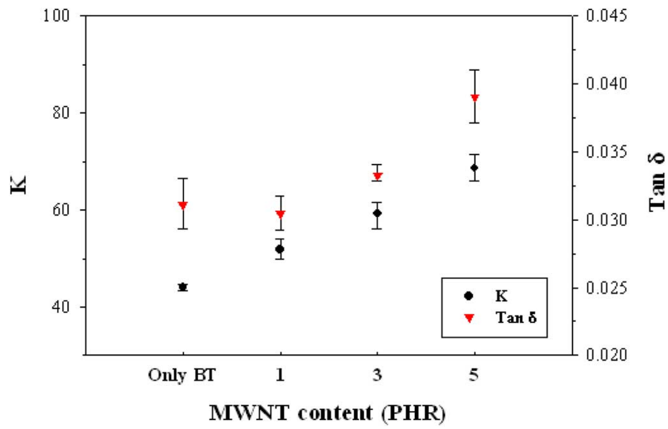


Fig. 7. Variation of dielectric constant and tan δ of hybrid films composed of mechanically treated composite filler and epoxy matrix: effect of MWNT content.

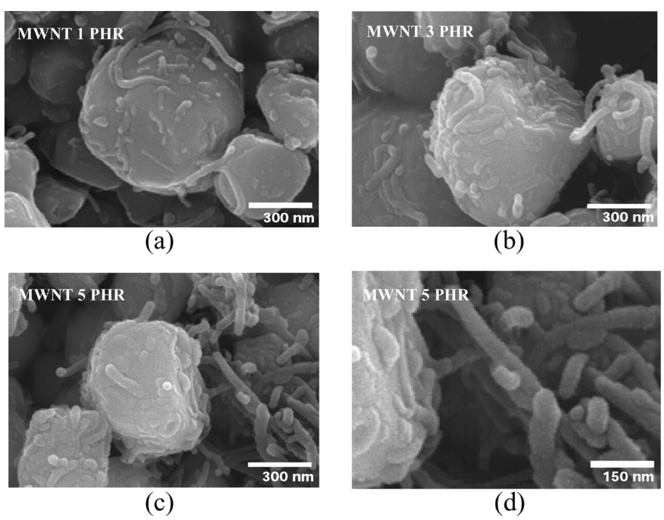


Fig. 8. FE-SEM images of MWNTs-$BaTiO_3$ composite filler treated by mechanical processing for 3 min: (a) 1 PHR (1.2% by volume) MWNTs/49.4% by volume $BaTiO_3$, (b) 3 PHR (3.4% by volume) MWNTs/48.3% by volume $BaTiO_3$, (c) 5 PHR (5.5% by volume) MWNTs/47.25% by volume $BaTiO_3$, and (d) 5 PHR (5.5% by volume) MWNTs/47.25% by volume $BaTiO_3$: high magnification.

surface polarization occurring with increases in MWNTs content in the hybrid film. Fig. 8 is the SEM image of composite fillers mechanically treated with different contents of MWNTs. In the case of the composite filler produced from MWNTs of 3 PHR (3.4% by volume), most of the MWNTs were attached to the surface of BT; however, for the composite filler with MWNTs of 5 PHR (5.5% by volume), many MWNTs had combined with themselves rather than attaching to the surface of BT. As a result, it can be concluded that MWNTs combined with themselves to make networks within the composite and bring about the increase in dielectric loss of the composite.

IV. Conclusion

In order to increase the electrical property of the composite, composite fillers consisting of $BaTiO_3$ with a high dielectric property and MWNTs with strong surface polarization were prepared through a vibration milling treatment. As the treatment processing time and content of the composite filler were varied, the electrical properties of the composite shifted. An optimal dielectric property was obtained by using a composite filler with MWNTs of 3 PHR (3.4% by volume), loaded with 48.3% by volume $BaTiO_3$, and treated for 3 min by vibration milling. This hybrid film produced a dielectric constant about 30% higher than the composite loaded by only $BaTiO_3$. Due to these demonstrated properties, hybrid film composed of composite filler and epoxy was shown to be a very good material for embedded capacitors.

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