# Processing and characterization of polymer-based composites for electronic applications: polymer/ceramic composite grain boundary capacitors*

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A polymer/ceramic composite grain boundary capacitor has been fabricated using a semiconducting ceramic as the conducting phase (reduced barium titanate) and a thermoplastic polyimide as the insulating polymer phase (LaRC-TPI). The ceramic grains and the composite capacitors were characterized using scanning and transmission electron microscopy. The dielectric properties of the capacitors were also measured using an impedance analyser. A composite grain boundary capacitor with a dielectric loss below 0.02 was successfully manufactured. The room temperature dielectric constant of the capacitors ranged from below 30 to approximately 2000, with the value dependent upon the ratio of the diameter of the semiconducting ceramic grains to the thickness of the insulating polymer layer coating the grains.

**(Keywords: processing; characterization; composites)**

## INTRODUCTION

As electronic components become smaller, the continued miniaturization of capacitors has become essential. Several methods have been used to increase the dielectric constant per unit volume for capacitors[1]. One way to increase the dielectric constant of a capacitor is to reduce its thickness. However, there are several limits to using this approach. For example, it is difficult to produce a capacitor with a thickness of less than 200 $\mu$m using conventional processing methods. In addition, very thin capacitors are often difficult to handle[1].

Recently, ceramic grain boundary capacitors, also referred to as barrier capacitors, have been identified as an alternative route to capacitor miniaturization[1,2]. A grain boundary capacitor is a composite material made of conductive grains surrounded by insulating surface layers. When an electric field is applied to a grain boundary capacitor, each pair of adjacent conductive grains separated by an insulating layer forms a miniature capacitor, using the insulating layer as the dielectric. The permittivity of a grain boundary capacitor, $E$, can be calculated by:

$$E = E_{ri}(d_a/d_i) \qquad (1)$$

where $d_a$ is the diameter of the conductive grain, $d_i$ is the thickness of the insulating layer, and $E_{ri}$ is the permittivity of 'free space' ($8.854 \times 10{-}12\,\mathrm{F\,m^{-1}}$). Note that this equation indicates that the performance of a grain boundary capacitor does not depend upon its overall thickness, but only upon the ratio of the diameter of the conducting grain to the thickness of the insulating layer. This makes miniaturizing of a grain boundary capacitor possible.

Two types of grain boundary capacitors have been reported in the literature[1]. One type has been produced by taking ceramic particles, such as $BaTiO_3$, and heat treating under a reducing atmosphere to produce semiconducting particles. The surface of these semiconducting particles is then reoxidized to produce an insulating layer. Another type of grain boundary capacitor currently being studied is a two-phase insulating ceramic/conducting ceramic system, where the insulating layer is chemically different from the semiconducting grain. Previous studies of two-phase ceramic grain boundary capacitors have shown that they are a more efficient type of capacitor as compared with the one-phase ceramic system[1].

In a grain boundary capacitor, homogeneity of the microstructure is an important factor[1,2]. A large grain size distribution with relatively thin insulating coatings may cause a localized short circuit in the capacitor. These localized short circuits will eventually short the entire capacitor if the device is very thin. Therefore, it is best if all of the conducting particles are of uniform size. However, commercially available ceramic particles often have a large size distribution. Therefore, commercially available ceramic grain boundary capacitors must often be designed to be relatively thick to avoid this problem.

In this work, polymers are used in place of the

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insulating ceramic layer to make a polymer/ceramic composite grain boundary capacitor. This concept shows promise for several obvious reasons. First, polymers are typically better insulators than reoxidized ceramics. Second, it is less expensive and more convenient to coat polymers onto semiconducting ceramic particles than to reoxidize the surface of the particles. Third, the polymer coated ceramic grains can be processed into a device at lower temperatures, leading to an easier, less expensive manufacturing process. Finally, the moulded polymer/ceramic composite capacitor will be less brittle and easier to handle than an all-ceramic system. One would expect the same pattern of high efficiency energy storage to be observed in a polymer/ceramic composite grain boundary capacitor as is seen in traditional ceramic grain boundary capacitors. In addition, the performance of the composite grain boundary capacitor may be 'tuned' by varying the thickness of the insulating polymer layer (see equation (1)).

## EXPERIMENTAL

### *Materials*

Barium titanate ($BaTiO_3$), supplied by Alfa Chemicals, was chosen as the semiconducting ceramic phase. It is a popular ceramic for use in electronic applications, is readily available, and has been well characterized in the literature[3,4]. Also, $BaTiO_3$ becomes a very good semiconductor upon reducing in a hydrogen atmosphere. This is a characteristic that is essential to the production of a high quality grain boundary capacitor.

A thermoplastic polyimide (LaRC-TPI), supplied by Mitsui Toatsu, was chosen as the insulating polymer layer[5,6]. Other novel polymers which were evaluated for this application include poly(siloxane-*b*-ethyloxazoline) and several phosphonium-containing polyimides. These candidate polymers were manufactured by the Chemistry Department at Virginia Tech. All polymer systems were spin-coated from solution onto $BaTiO_3$ discs to test adhesion to the ceramic substrate. Only the LaRC-TPI system adhered well to the ceramic substrate, and was therefore the only polymer system used for further characterization of composite grain boundary capacitors.

LaRC-TPI polymer was coated onto the $BaTiO_3$ particles from an aqueous polyamic acid solution, and then imidized in order to achieve good wetting and adhesion to the ceramic substrate. The polyamic acid solution coating process was found to be the simplest, most reproducible coating process, and gave the best adhesion performance[6,7].

### *Preparation of a one-layer capacitor*

$BaTiO_3$ ceramic particles were milled to an average size of less than 2 μm and cold-pressed into a pellet (approximately 1 cm in diameter and 3 mm in thickness). The pellet was sintered at 1350°C for 1 h. The sintered pellet was then reduced in a hydrogen atmosphere at 1144°C for 2 h. The dielectric loss of the resulting ceramic disc was measured to be more than 0.7.

An 8% LaRC-TPI polyamic acid solution was prepared by dissolving LaRC-TPI polyamic acid in a water/ammonia solution at a temperature of 50–60°C. The solution was then spin-coated onto both surfaces of the reduced ceramic disc at 3000 rev min$^{-1}$ for 60 s. Residual solvents were evaporated by heating at 100°C for 2 h. The polyamic acid film was then imidized at 300°C for 2 h to produce a polyimide coated ceramic disc capacitor. Finally, silver epoxy paste, supplied by Epoxy Tech Incorporated, was applied to both surfaces of the disc to serve as electrodes for the electrical characterization.

### *Preparation of a multi-layer capacitor*

The polyamic acid solution was coated onto one side of two ceramic discs, the solvents were evaporated, and the polyamic acid films were imidized according to the procedures listed above. The uncoated surfaces were then spin-coated with the polyamic acid solution and dried. The polyamic acid sides of the two discs were then pressed together and clamped using a 7.6 cm C-clamp, and the new polyamic acid surfaces were imidized using the same conditions described earlier. This procedure securely bonded the discs together, producing a multi-layer capacitor structure. Finally, silver epoxy paste was applied to the two exposed polyimide surfaces to serve as electrodes.

### *Preparation of a grain boundary capacitor*

Milled $BaTiO_3$ particles (2 μm in diameter) were reduced in a hydrogen atmosphere at 1144°C for 8 h until the powder turned a deep blue-gray colour, indicating the transformation of the ceramic powder to the semiconducting state. The semiconducting particles were then suspended in the 8% LaRC-TPI polyamic acid solution and shaken for 24 h using a wrist action shaker. This allowed a thin polyamic acid coating to adsorb to the surface of the suspended particles. The resulting suspension was centrifuged and vacuum filtered to collect the coated particles. The particles were dried and cold pressed together into a pellet (approximately 1 cm in diameter and 3 mm in thickness). The disc was heated to 100°C for 2 h to evaporate excess solvent, and the polyamic acid was imidized at 300°C for 2 h to produce a composite grain boundary capacitor. Again, silver epoxy paste was applied to both surfaces of the capacitor to serve as electrodes.

A second grain boundary capacitor with approximately one-quarter the thickness of the adsorbed polymer layer was prepared by diluting the polyamic acid solution to one-quarter of its original concentration (2% LaRC-TPI) and preparing a disc using the same procedure described above.

### *Microscopic characterization*

Coated and uncoated $BaTIO_3$ particles were examined using both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The cross-section of a composite grain boundary capacitor was also observed by SEM.

### *Dielectric measurements*

Capacitance and dielectric loss of the capacitors were measured using an HP 4192A LF impedance analyser over a frequency range of 0.1 kHz to 1 MHz and temperatures ranging from 25 to 160°C. Leads were attached to the surface of the capacitors using the silver epoxy paste described earlier. The dielectric constant ($K$) was calculated using the formula:

$$K = (Cd)/(E_{\mathrm{ri}}A) \qquad (2)$$

where $C$ is the measured capacitance, $A$ is the surface area of the capacitor and $d$ is the thickness of the coated ceramic pellet.

## RESULTS

### *Microscopic characterization of $BaTiO_3$ particles and polymer coatings*

A scanning electron micrograph of the reduced, uncoated particles is shown in *Figure 1*. It can be seen that the average size of the reduced particles is about 1 $\mu$m and that the particles typically exist in the form of irregular agglomerates which span approximately 30 to 50 $\mu$m. Care must be taken to ensure some degree of dispersion of these agglomerations during the particle-coating process. This was accomplished by vigorously shaking the samples during polymer adsorption as described in the Experimental section.

A closer examination of the polyimide-coated $BaTiO_3$ particles reveals a large variation in the coated particle cluster size. For example, in *Figure 2* the most common size of the coated particle clusters is about 5 $\mu$m. This implies that a typical coated cluster contains 5 to 10 individual $BaTiO_3$ particles. However, if coating conditions are not carefully controlled and monitored, large scale agglomeration can occur. In *Figure 3*, some coated particle clusters as large as 50 $\mu$m are shown which were coated under unfavourable conditions (i.e. conditions deviating from those described in the Experimental section).

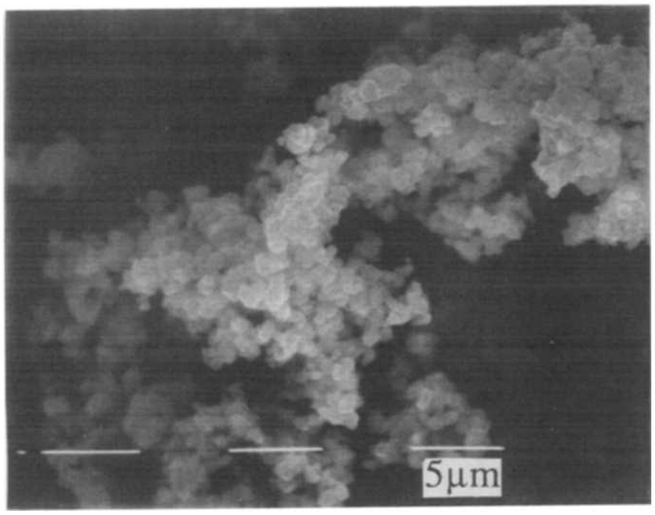

**Figure 1** Scanning electron micrograph of reduced, uncoated $BaTiO_3$ particles

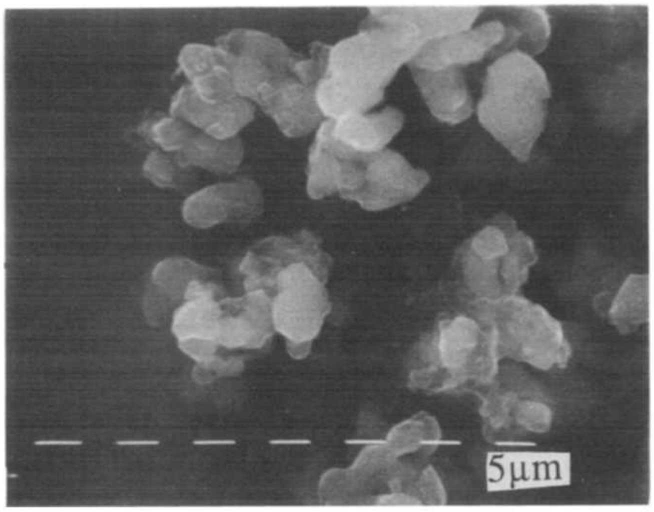

**Figure 2** Scanning electron micrograph of reduced, coated $BaTiO_3$ particle clusters. (Sizes are typical of those most commonly observed in the microscope)

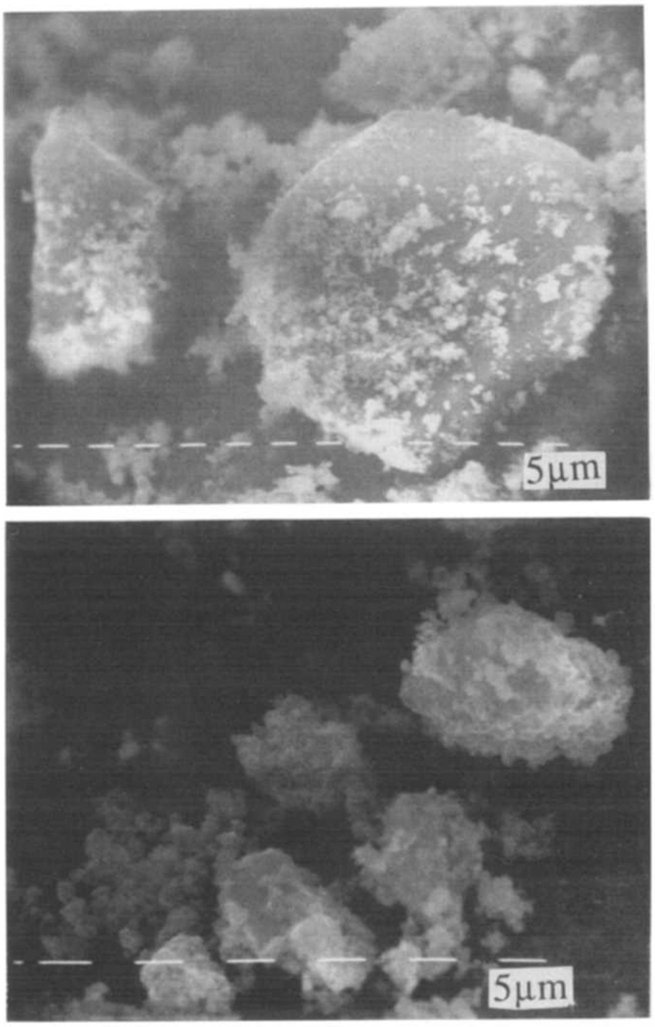

**Figure 3** Scanning electron micrographs of coated $BaTiO_3$ particle agglomerates which can occur if samples are prepared under non-ideal coating conditions

Although some degree of particle agglomeration does occur, TEM images confirm that LaRC-TPI polyamic acid does adsorb to the individual ceramic particles before cluster formation. At higher adsorbed polymer layer thicknesses (i.e. adsorption from an 8% LaRC-TPI solution), a relatively uniform coating of polymer is observed on the individual ceramic grains. However, if the adsorbed polymer layer thickness is reduced below a critical limit (i.e. adsorption from a 2% LaRC-TPI solution), non-uniform coating will occur and capacitor performance will be degraded. An example of the TEM images obtained from a non-uniform coating experiment performed using a 2% LaRC-TPI solution is shown in *Figure 4*. These TEM images clearly indicate that the adsorbed polymer layer on individual $BaTiO_3$ particles is not uniform under these coating conditions. Some regions of the particles have a relatively thick coating, while other regions are essentially uncoated. Although these coatings tend to flow and become more uniform during the moulding process, this initial non-uniformity will lead to particle–particle 'shorts' which will drain charge from the grain boundary capacitor and adversely affect ultimate electrical performance. This demonstrates

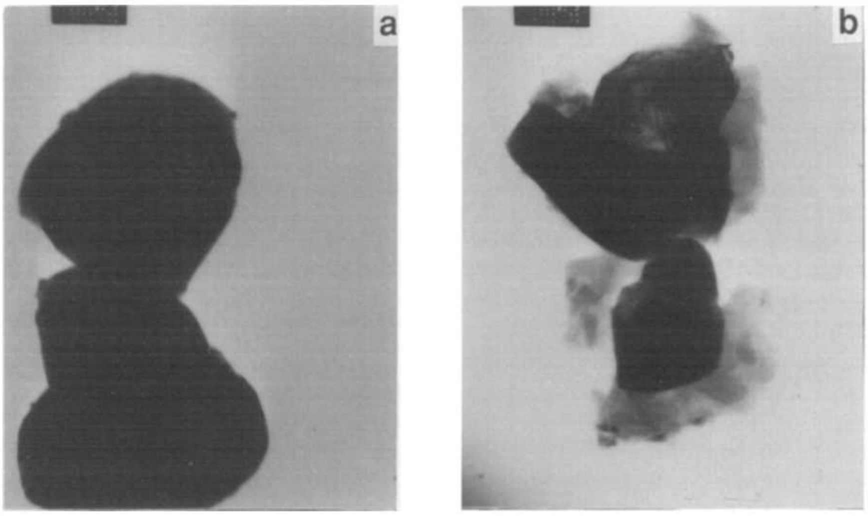

**Figure 4** Transmission electron micrographs of (a) uncoated and (b) coated individual $BaTiO_3$ particles showing the possibility of non-uniform polymer coating at low coating thicknesses

the importance of maintaining a uniformly thin particle coating on capacitor performance. If the coating is too thick, the dielectric constant will decrease (see equation (1)). However, if the coating is too thin, the dielectric loss will increase (i.e. the capacitor efficiency will decrease) due to charge leakage[1,2].

The final density of the grain boundary capacitor is another important factor in determining processability and electrical performance[1,2]. SEM cross-sections of a typical grain boundary capacitor produced in this study are shown in *Figure 5*. The individual ceramic grains and the polymer layers around the grains can be seen. Some level of open porosity can also be seen in these micrographs. Some open porosity is necessary to ensure removal of the condensation by-products of the imidization reaction which occurs after the grain boundary capacitor has been pressed into a pellet. However, dielectric properties can be maximized by minimizing porosity, thus increasing the final density of the composite capacitor. Therefore, an optimum porosity level must be determined in order to balance processability with good electrical properties. The processing conditions described in this paper were found to produce good capacitor properties, but were not optimized to determine the minimum amount of porosity that would still allow for the removal of condensation products from the imidization reaction.

### *Dielectric loss measurements*

Dielectric loss *versus* temperature curves were measured for frequencies ranging from 0.1 kHz to 1 MHz. The observed trends were the same for each test frequency, therefore typical results are presented here for one intermediate frequency. The measured dielectric loss response at 100 kHz is shown in *Figure 6* for a one-layer disc-type capacitor, a multi-layer disc-type capacitor, a composite grain boundary capacitor with a thicker insulating polymer layer, and a composite grain boundary capacitor with a thinner insulating polymer layer.

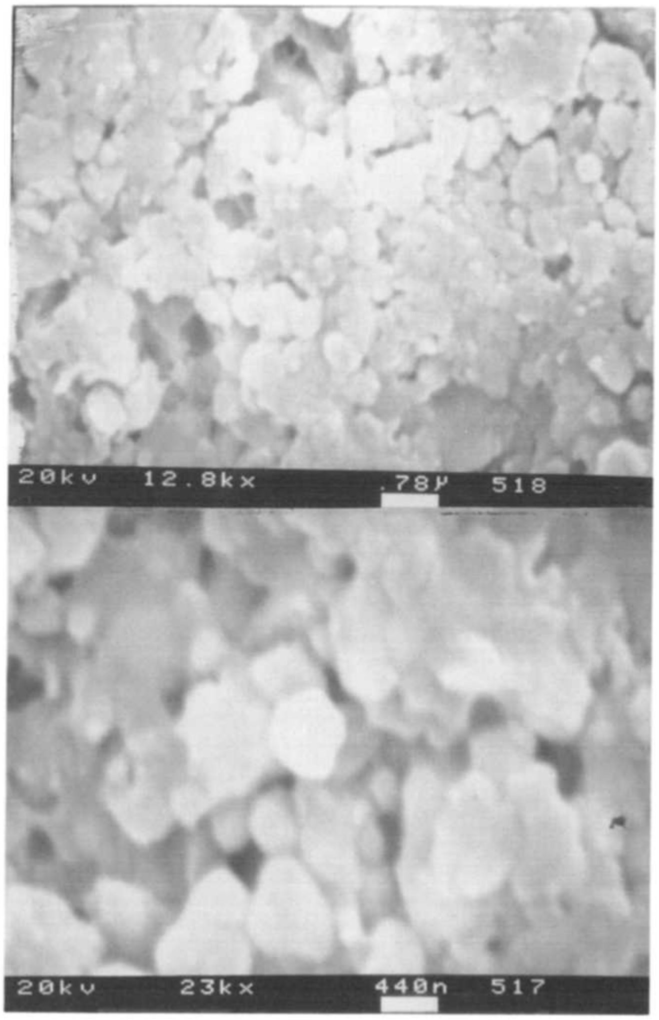

**Figure 5** Scanning electron micrographs showing the typical porosity level present in cold-pressed composite grain boundary capacitors prepared in this study

It can be seen in *Figure 6* that, at higher temperatures, the dielectric loss of the best composite grain boundary capacitor is approximately an order of magnitude less than that of the one-layer capacitor. Recall that the dielectric loss of the uncoated $BaTiO_3$ disc is 0.7. When the disc is coated with polymer, forming a one-layer capacitor, the dielectric loss reaches a value of 0.26 at higher temperatures (see *Figure 6*). This indicates that LaRC-TPI is a good insulator and that it adheres well to the ceramic disc. The dielectric loss is further reduced

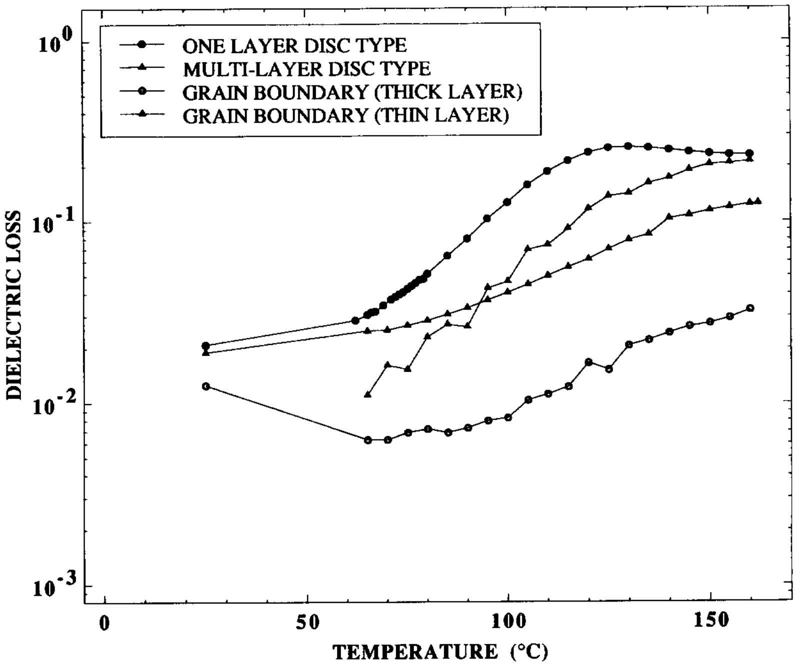

**Figure 6** Dielectric loss *versus* temperature performance for various LaRC-TPI/BaTiO$_3$ composite capacitors measured at 100 kHz

by approximately a factor of two in going to the multi-layer capacitor structure. Finally, note that the grain boundary capacitor with a thick polymer insulating layer exhibits a dielectric loss of less than 0.02 at the same temperature and frequency. This decrease in dielectric loss indicates a large improvement in the efficiency of charge storage (i.e. low charge leakage rates) in the grain boundary capacitor as compared with the one-layer capacitor made from the same materials.

The grain boundary capacitor with a thinner polymer insulating layer (coated with a 2% polymer solution) exhibits a substantially higher dielectric loss as compared with the grain boundary capacitor which has a thicker insulating polymer layer (coated with an 8% polymer solution), as shown in *Figure 6*. This is because the polymer layer was too thin in the former case to ensure uniform coverage of the semiconducting grains during the solution coating process (see micrographs in *Figure 4*). This led to electrical 'shorts' between grains, which promoted charge leakage in the moulded capacitor. This reconfirms the importance of maintaining a uniform polymer coating in optimizing capacitor performance. As stated earlier, the dielectric constant will decrease if the coating is too thick (see equation (1)). However, *Figure 6* demonstrates that the dielectric loss will increase due to charge leakage if the coating is too thin to maintain a uniform insulating layer.

### *Dielectric constant measurements*

Dielectric constant *versus* temperature curves were also measured for frequencies ranging from 0.1 kHz to 1 MHz. Again, the observed trends were the same for each frequency measured, and typical results at 100 kHz are presented. The measured dielectric constant at 100 kHz is shown in *Figure 7* for a one-layer disc capacitor, a multi-layer disc capacitor, and for the two composite grain boundary capacitors with thicker and thinner insulating polymer layers. Note that the dielectric constant of the one-layer capacitor ranges from 1000 to 4000 over this temperature range, while the dielectric constant of the grain boundary capacitors ranges from approximately 25 to 35. The multi-layer disc capacitor has intermediate dielectric constant values.

The grain boundary capacitors have dielectric constants which are about 10 times higher than that of the polymer alone, but about 1000 times smaller than that of the one-layer capacitor. The systematic decrease in dielectric constant in going from the one-layer capacitor, to the multi-layer capacitor, to the grain boundary capacitors confirms that the dielectric constant is dependent upon the ratio of the characteristic 'thickness' of the conducting ceramic phase in the capacitor to that of the insulating polymer phase. This ratio of characteristic dimensions is larger for the one-layer and multi-layer capacitors, therefore the dielectric constants for these samples are relatively high. However, recall that the dielectric losses were also relatively high for these samples. Therefore, these capacitor structures can store a relatively large charge, but cannot store the charge very efficiently. On the other hand, the ratio of characteristic dimensions for the grain boundary capacitors is small, and the measured dielectric constants are also small. However, the grain boundary capacitors can store charge much more efficiently since the dielectric losses are much lower in these systems. Therefore, the grain boundary capacitors can only store small charges, but they can store the charges very efficiently.

## SUMMARY AND CONCLUSIONS

The objective of this work was to process and characterize a polymer/ceramic composite grain boundary capacitor. In achieving this objective, four different novel capacitor structures were manufactured:

1. a one-layer capacitor using reduced BaTiO$_3$ as the conducting ceramic layer and LaRC-TPI as the insulating polymer layer;

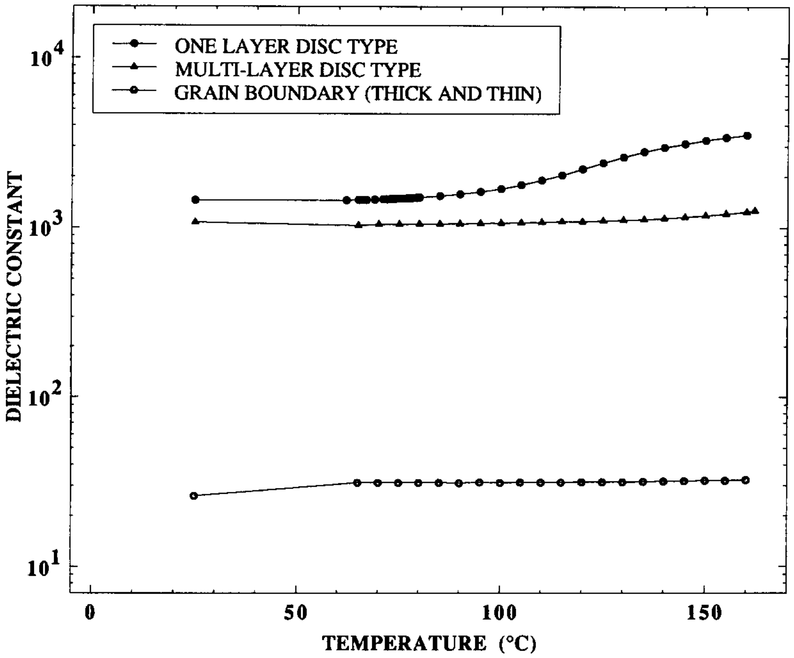

**Figure 7** Dielectric constant *versus* temperature performance for various LaRC-TPI/$BaTiO_3$ composite capacitors measured at 100 kHz

2. a multi-layer capacitor consisting of two one-layer capacitors moulded together in series;
3. a composite grain boundary capacitor consisting of small $BaTiO_3$ semiconducting grains coated with a relatively thick layer of adsorbed LaRC-TPI (i.e. coated from an 8% polymer solution), which were then moulded together to form a disc;
4. a second composite grain boundary capacitor with a somewhat thinner LaRC-TPI layer adsorbed to the $BaTiO_3$ grains (i.e. coated from a 2% polymer solution).

Dielectric loss properties of these capacitor structures are shown to improve in going from the one-layer capacitor, to the multi-layer capacitor, to the grain boundary capacitor. This is indicated by a decrease in the dielectric loss by approximately an order of magnitude, which corresponds to an increase in the efficiency of storing charge in the grain boundary capacitor.

The dielectric constant is shown to decrease in the grain boundary capacitor as compared with the one-layer and multi-layer capacitors. It has also been shown that the dielectric constant can be controlled by manipulating the ratio of the diameter of the conducting grain to the thickness of the adsorbed insulating polymer layer.

Suggested future work includes optimization of the composite grain boundary capacitor processing conditions, along with varying and controlling the type, thickness and uniformity of the polymer coating in order to balance the dielectric loss and dielectric constant of the capacitor. The overall dielectric properties can also be improved by increasing the final density of the capacitor through the reduction of void formation during the disc moulding process.

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