

## Properties of treated calcium copper titanate filled epoxy thin film composites for electronic applications

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**ABSTRACT:** In this study, calcium copper titanate (CCTO) fillers were treated with 1%, 5%, and 10% of silane-based coupling agent 3-glycidoxypropyltrimethoxysilane (GPTMS). The CCTO treated with 10% GPTMS filled epoxy thin film composite exhibits a remarkable improvement (60%) of dielectric constant than untreated CCTO/epoxy thin film composite. Besides that, results treated CCTO/epoxy thin film composite produced using various epoxy resins showed that OP 392 epoxy thin film composite exhibited the highest glass transition temperature and degradation temperature, moderate dielectric constant, slightly lower coefficient of thermal expansion and lowest dielectric loss compared with D.E.R. 332 and Epolam 2015 epoxy thin film composites. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43313.

**KEYWORDS:** composites; morphology; properties and characterization; thermal properties

Received 13 August 2015; accepted 29 November 2015

DOI: 10.1002/app.43313

### INTRODUCTION

Ceramic-filled polymer composites with high dielectric constant have been considered as one of the most promising materials for embedded capacitors because of their mechanical flexibility, good processability, and low cost.<sup>1–5</sup> Ceramic fillers such as Bismuth Zinc Niobate ( $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ , BZN), Yttrium Iron Garnet ( $\text{Y}_3\text{Fe}_5\text{O}_{12}$ , YIG), Barium Titanate ( $\text{BaTiO}_3$ ), and Calcium Copper Titanate ( $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , CCTO) have been studied in previous works.<sup>6–11</sup> Among these fillers, CCTO received greatly consideration due to the fact that it is lead-free, environmentally friendly and possesses giant dielectric constant of up to  $10^5$  at 100 Hz.<sup>8,9</sup> Polymers such as epoxy resin, polyarylene ether nitriles (PEN) and polyvinylidene fluoride (PVDF) have broadly utilized as the matrix.<sup>12–16</sup> The thermosetting epoxy resin stands out among these polymers due to its flexibility, compatibility, low processing temperature and ease of fabrication into various shapes. Types of epoxy resins used in the preparation of epoxy thin film composites may influence the properties of the materials to be used in certain applications.

The differences in the surface characteristics of the inorganic filler and organic matrix make it difficult to disperse the filler homogeneously, which might influence the final properties of the composites. Therefore, it is crucial to improve the interface between the inorganic filler and organic matrix. Silane-based coupling agents have gained more attention because of their special structures, which have two different functional groups: one attached to the matrix and the other attached to the surface

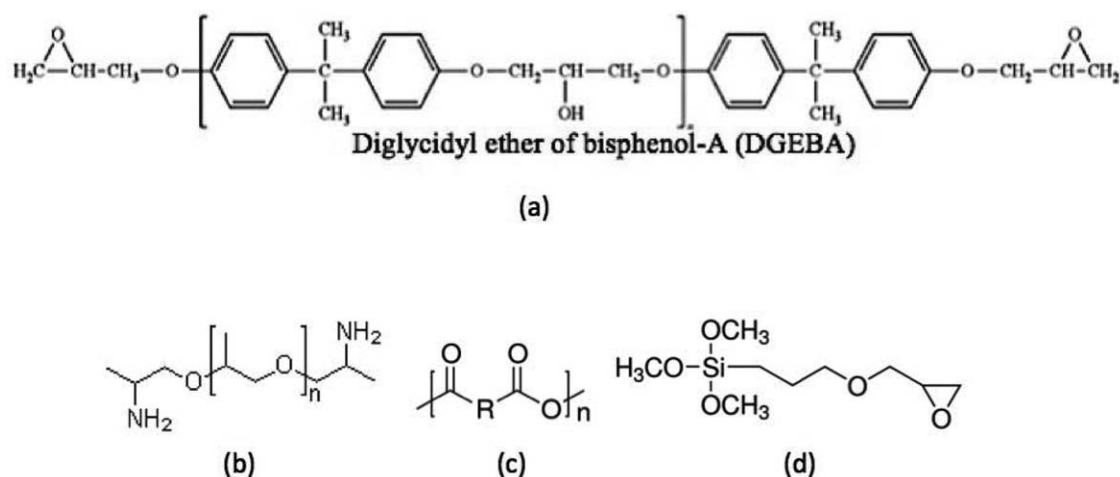
of the inorganic filler.<sup>17,18</sup> Based on literature studies, the silane-based coupling agent showed an improvement in the dielectric and thermal properties of the polymer composites compared with untreated polymer composites due to better dispersion of filler in epoxy matrix and good filler-matrix adhesion.<sup>5,19,20</sup> Huang *et al.* reported that the dielectric constant of surface-modified  $\text{BaTiO}_3$ /PVDF composites increased to 36 (1 kHz), which is six times higher than that of untreated  $\text{BaTiO}_3$ /PVDF composites when the volume fraction of  $\text{BaTiO}_3$  is 60%.<sup>21</sup> Meanwhile, according to Yang *et al.*, the surface-modified CCTO/PVDF composites reached a maximum value of 84 (1 kHz), which is 5.25 times higher than that of untreated CCTO/PVDF composites.<sup>5</sup> Feng *et al.* also reported that the surface-modified CCTO/PEN composites increased to 6 (1 kHz) when the mass fraction of CCTO reached 20%.<sup>15</sup>

In this work, silane-based coupling agent 3-glycidoxypropyltrimethoxysilane (GPTMS) at different concentrations was selected to treat CCTO fillers. The epoxy thin film composites were fabricated using epoxy resin as the matrix and treated CCTO as the filler. Besides that, the effect of various epoxy resins on the dielectric and thermal properties of treated CCTO filler filled epoxy thin film composites was also investigated.

### EXPERIMENTAL

#### Materials

In this study, three types of bisphenol A diglycidylether (DGEBA) epoxy resins (D.E.R.<sup>TM</sup> 332, Epolam 2015 and OP



**Figure 1.** The chemical structure of (a) epoxy resin, (b) polyetheramine curing agents for epoxy type DER 332 and EPOLAM 2015, (c) poly-anhydride curing agent for epoxy type OP 392 and GPTMS silane-based coupling agent.

392) were used. These epoxy resins were used in this study because their properties are suitable for electronic applications. The epoxy resin type D.E.R.<sup>TM</sup> 332 and polyetheramine D230 curing agent used in this study were supplied by Penchem Technologies Sdn. Bhd. and BASF Corporation. For the purpose of comparison, epoxy resin type Epolam 2015 and polyetheramine curing agent supplied by Advance Moulding Chemicals Sdn. Bhd. were used. Epoxy resin type OP 392 (Part A) and poly-anhydride hardener (Part B) supplied by Penchem Technologies Sdn. Bhd were also used. The silane-based coupling agent known as 3-glycidyoxypropyltrimethoxysilane (GPTMS) was used to treat CCTO fillers. It was supplied by Aldrich Inc. in liquid form. The chemical structure of epoxy resin, curing agents and silane coupling agent used in the present study are presented in Figure 1. Ethanol was used for dilution of GPTMS coupling agent due to incomplete wetting of filler by relatively small amount of coupling agent.

#### Preparation of CCTO and Treated CCTO Fillers

Figure 2 shows the flowchart of the CCTO filler fabrication process. CCTO powder was prepared using a solid-state reaction as reported by Huang *et al.*<sup>21</sup> All the starting materials used were of analytical grade: CaO (Aldrich, 99%), TiO<sub>2</sub> (Merck, 99%), and CuO (Aldrich, 99%). These materials were ball milled for 24 h in a polyethylene bottle using zirconium balls. The ball-to-powder weight ratio used was in the range of 10:1. The powder was then calcined at 900 °C for 12 h using a heating and cooling rate of 5 °C/min. It was used as the ceramic filler in the production of the composites.

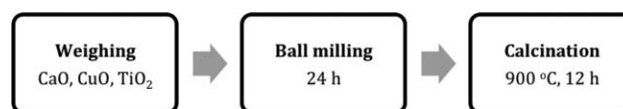
As Figure 3 illustrates, CCTO filler was treated with 1%, 5%, and 10% GPTMS. The concentrations of GPTMS were varied between 1%, 5%, and 10%. It was poured into a 50 mL beaker containing corresponding amounts of ethanol. The solution was stirred for 15 min. After the preparation of GPTMS solution in ethanol solvent, the CCTO filler was added to the solution and stirring was carried out at 30 °C for a further 15 min. Next, an ultrasonic bath was used to treat the CCTO/GPTMS/ethanol suspension for 30 min at an ultrasonic power of 100%. Lastly, the treated suspension was dried in an oven at 100 °C for 90

min before being ground to powder form for the following process.

#### Preparation of Treated CCTO Filler Based Epoxy Thin Film Composites

Figure 4 presents the flowchart of fabrication of untreated and treated CCTO filled epoxy thin film composites. The loading of untreated and treated CCTO filler in the epoxy resin type D.E.R. 332 was fixed at 20 vol %. The mixture of epoxy and particulate filler was sonicated at room temperature for 10 min with 50% amplitude and 0.5 sonication cycle. Once the sonication was completed, the hardener (polyetheramine D230) was added at a ratio of 100:32 by weight (epoxy: curing agent), and the mixture was sonicated for another 10 min in an ice water bath. It should be noted that the stoichiometric ratios of epoxy resins and curing agents were provided by the supplier. The mixture was placed in a vacuum oven (Nuve EV 018) for 1 h of degassing to remove the air entrapped in the mixture during mixing and then spin-coated by a model G3P-12 Desk-Top Precision Spin Coater at 250 rpm to 750 rpm for 180 s. Then, the film was cured at 80 °C for 2 h. Untreated and treated CCTO/epoxy thin film composites with thicknesses ranging from 30 μm to 70 μm were produced. The samples were labeled as UCEC and TCEC for untreated and treated CCTO/epoxy composites, respectively. The numbers in front of the TCEC samples refer to the silane concentrations used to treat the fillers; that is, 1% TCEC refers to treated CCTO@1% GPTMS/epoxy composite, 5% TCEC refers to treated CCTO@5% GPTMS/epoxy composite and 10% TCEC refers to treated CCTO@10% GPTMS/epoxy composite. Various composites are listed in Table I.

In order to study the effects of different epoxy resins, treated CCTO at 20 vol % and the silane coupling agent with a concentration of 10% were used in different types of epoxy resins:



**Figure 2.** Preparation of CCTO filler.

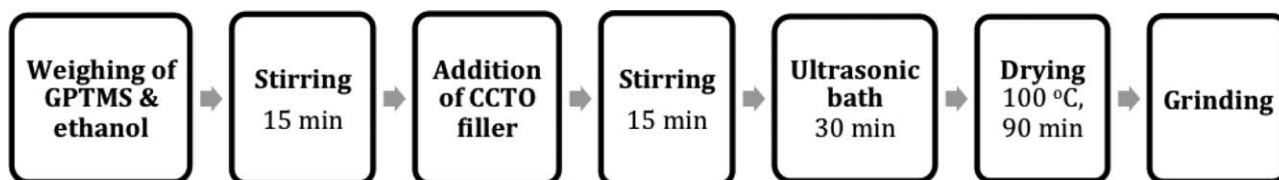


Figure 3. Preparation of treated CCTO filler.

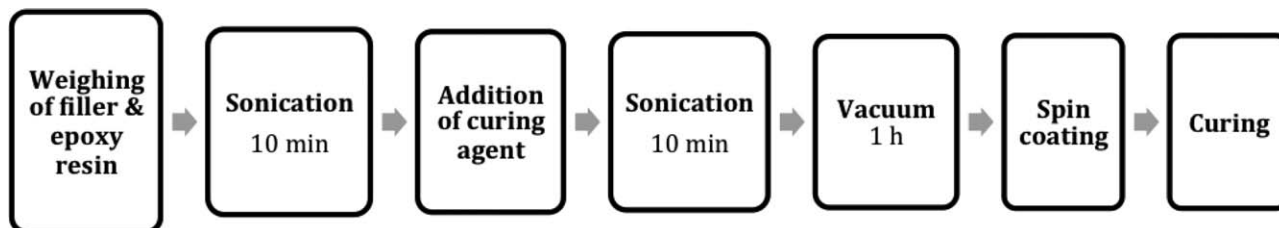


Figure 4. Fabrication of untreated and treated CCTO filler filled epoxy thin film composites.

D.E.R. 332, Epolam 2015, and OP 392. For epoxy type Epolam 2015, the same procedures and parameters of the spin coating method and curing agent method were used to produce treated CCTO/epoxy thin film composite. However, for epoxy type OP 392, the curing agent was added at a ratio of 1:1 by weight (epoxy: curing agent). The epoxy thin film composites were then produced by spin coating, precured at 125°C for 1 h and finally post-cured at 135°C for 2 h. It should be noted that different curing procedures were used based on the information given by the supplier to reach a complete degree of conversion of the obtained composites. The treated CCTO/epoxy composite samples were labeled as TCEC. The words following the TCEC sample names refer to the types of epoxy resins used in the fabrication of the treated CCTO/epoxy composites; e.g. TCEC (D.E.R. 332) refers to treated CCTO/epoxy composite produced using epoxy resin type D.E.R. 332, TCEC (Epolam 2015) refers to treated CCTO/epoxy composite produced using epoxy resin type Epolam 2015 and TCEC (OP 392) refers to treated CCTO/epoxy composite produced using epoxy resin type OP 392. Various composites are listed in Table II.

#### Characterization

Energy dispersive spectroscopy (EDS) analysis was carried out using a Zeiss Supra 35VP to identify the presence of silicon (Si) element on the surface of CCTO filler after chemical treatment by GPTMS silane coupling agent. A Perkin Elmer Fourier Transform-Infrared (FT-IR) spectrometer with a typical wave number range of 4000 to 400  $\text{cm}^{-1}$  was used in an open air

environment in reflectance mode. The purpose of performing FT-IR spectrometry analysis is to obtain information regarding the type of possible chemical bonding formed between CCTO filler and epoxy matrix before and after the surface treatment of CCTO filler. Dielectric properties, such as the dielectric constant and dielectric loss, were measured using an Agilent LCR meter. A frequency range of 100 Hz to 1 MHz was used for the testing. In the testing, the samples were evenly painted with silver conductive paint on both sides. The morphology of the fractured samples of untreated and treated composites was characterized by field emission scanning electron microscopy (FESEM) (Zeiss Supra 35VP). Thermogravimetric Analysis (TGA) was carried out using a Perkin Elmer Pyris 6 to determine the change in mass or weight loss with respect to temperature. The temperature was set from 30 to 600°C with a heating rate of 10°C/min and the test was conducted under an  $\text{N}_2$  atmosphere. Dynamic Mechanical Analysis (DMA) was carried out using a Mettler Toledo DMA 861<sup>e</sup> analyzer to determine the storage modulus and  $\tan \delta$  under oscillating load. The temperature was increased from room temperature to 130°C at a heating rate of 5°C/min and a frequency of 1 Hz. The coefficient of thermal expansion (CTE) before  $T_g$  was measured using a thermomechanical analyzer (TMA) (Perkin Elmer TMA-7). The temperature range used was 30 to 130°C and the heating rate was 10°C/min for both first and second heatings.

## RESULTS AND DISCUSSION

### Characterization of Raw Materials

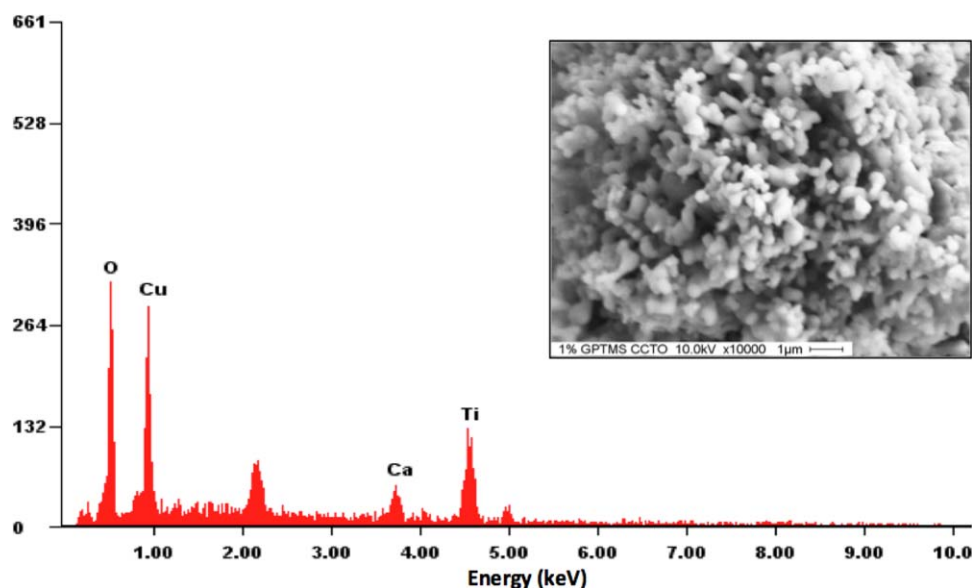
**Elemental Analysis.** EDS analysis was carried out to investigate the presence of silicon (Si) element on the surface of CCTO

Table I. Description of the Sample Codes for Untreated and Treated CCTO/Epoxy Thin Film Composites at Different Silane Concentrations of GPTMS

| Composite                    | Sample code |
|------------------------------|-------------|
| Untreated CCTO/epoxy         | UCEC        |
| Treated CCTO@1% GPTMS/epoxy  | 1% TCEC     |
| Treated CCTO@5% GPTMS/epoxy  | 5% TCEC     |
| Treated CCTO@10% GPTMS/epoxy | 10% TCEC    |

Table II. Description of the Sample Codes Treated CCTO/Epoxy Thin Film Composites Produced Using Various Types of Epoxy Resins

| Composite                      | Sample code        |
|--------------------------------|--------------------|
| Treated CCTO/epoxy-DER 332     | TCEC (DER 332)     |
| Treated CCTO/epoxy-EPOLAM 2015 | TCEC (EPOLAM 2015) |
| Treated CCTO/epoxy-OP 392      | TCEC (OP 392)      |

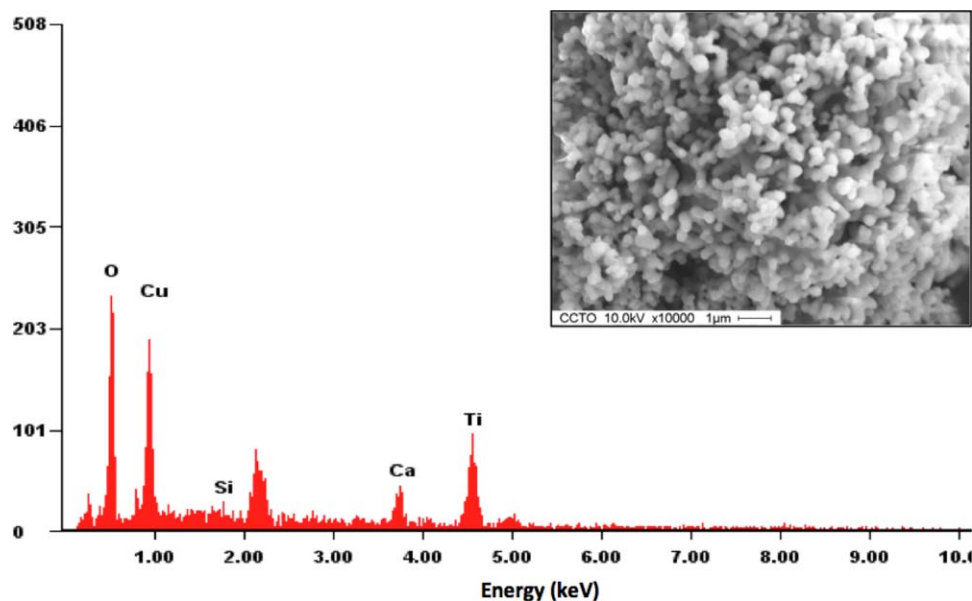


**Figure 5.** EDS analysis on untreated CCTO filler which shows the absence of Si element on the surface of CCTO particles, the inset is the spot taken for EDS analysis. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

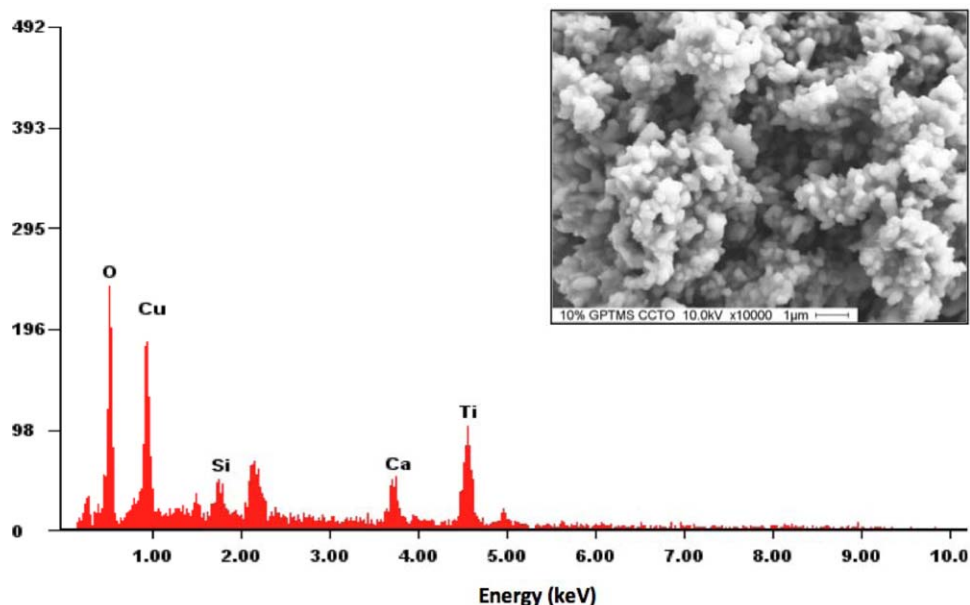
particles after chemical treatment with GPTMS silane coupling agent. The CCTO particles are believed to be coated with a thin layer of Si-based compound after the treatment with silane-based coupling agent. Figures 5 to 8 display the EDS spectra obtained for untreated and treated CCTO with different silane concentrations, respectively. It is confirmed that the treated system using 5% and 10% silane coupling agent shows the presence of Si element on the CCTO particles as indicated by the presence of a small peak at around 1.8 keV, as shown in Figures 7 and 8. The peak is detected at much lower concentrations compared with the peaks of Ca, Cu, Ti, and O elements obtained from CCTO particles. This is reasonable due to the lower concentration of GPTMS silane coupling agent being

introduced into the surface of CCTO particles. The EDS analysis confirms the presence of Si-based compound on the surface of CCTO particles. Meanwhile, the treated system using 1% silane coupling agent did not really show the presence of Si element on the CCTO particles due to the small amount of silane coupling agent used to treat the CCTO filler. The spectra also show an Au peak at around 2 keV due to sputter coating of gold on the CCTO surface.

**FT-IR Analysis.** Analysis of the FT-IR spectra of the composites enabled the identification of interactions before and after surface treatment of CCTO fillers. Figure 9 presents the FT-IR spectra of untreated CCTO and treated CCTO fillers. The



**Figure 6.** EDS analysis on treated 1% GPTMS@CCTO filler which shows the presence of Si trace on the surface of CCTO particles, the inset is the spot taken for EDS analysis. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



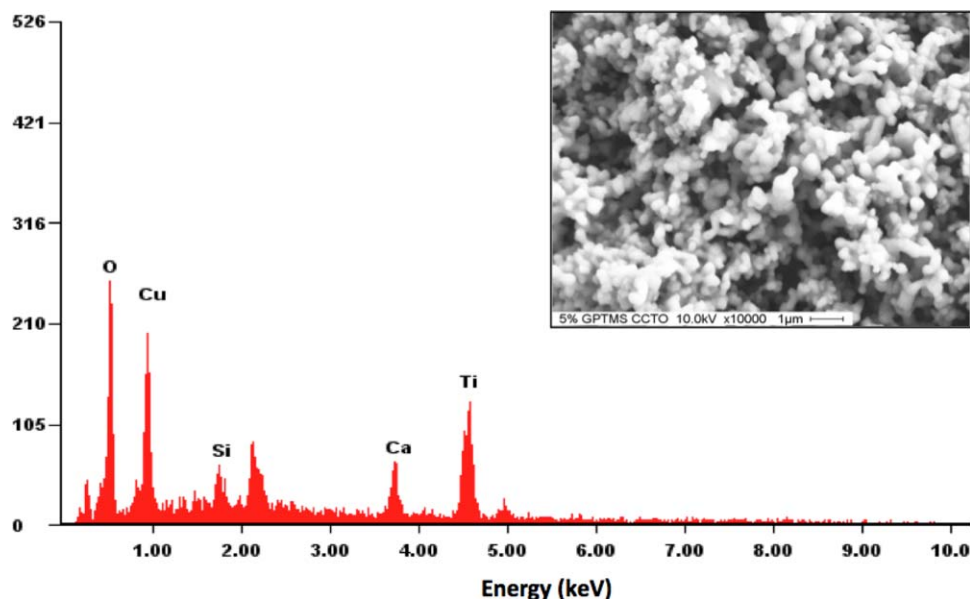
**Figure 7.** EDS analysis on treated 5% GPTMS@CCTO filler which shows the presence of Si trace on the surface of CCTO particles, the inset is the spot taken for EDS analysis. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

spectra (a) and (b) are almost the same due to the small amount of GPTMS (1%) used to treat the CCTO filler in both cases. Meanwhile, the peaks appearing at  $1115$  and  $957\text{ cm}^{-1}$  in the spectra (c) and (d) are attributed to the stretching vibrations of Si-O and S-O, respectively. The stretching vibrations of Si-O and S-O are an indication that internal interfaces formed between the silane coupling agent GPTMS and the CCTO filler.<sup>5</sup>

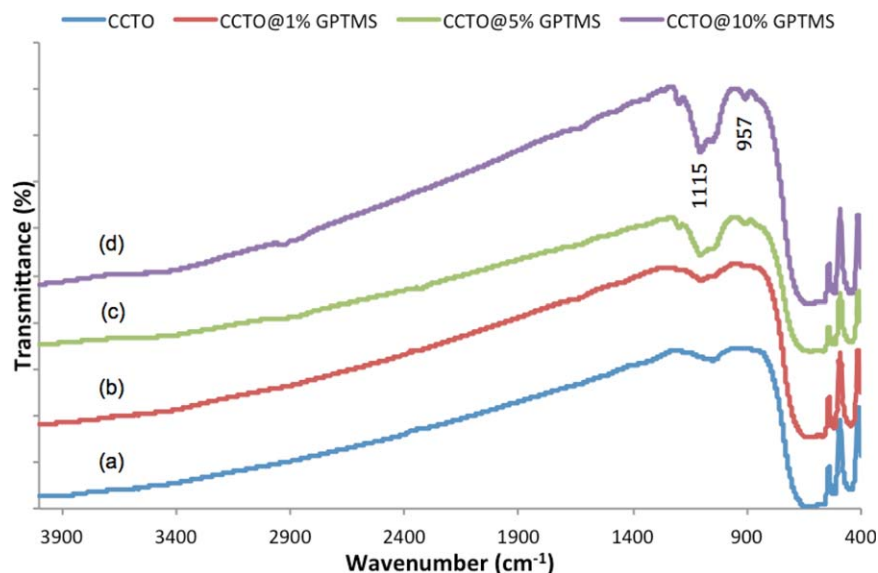
#### Effect of Concentration of Silane-Based Coupling Agent

**FT-IR Analysis.** FT-IR spectroscopy is useful for studying the type of possible chemical bonding formed between the ceramic

filler and the epoxy matrix. Figure 10 presents the FT-IR spectra of untreated and treated CCTO/epoxy thin film composites at different concentrations of silane coupling agent. With regard to the UCEC spectrum, the characteristic absorption bands detected at around  $920$ ,  $1241$ , and  $1299\text{ cm}^{-1}$  may be attributed to the epoxy group. The broad and medium peaks at  $2881$  to  $2997\text{ cm}^{-1}$  are related to CH stretching in C-CH<sub>3</sub> compounds, which could possibly be due to several band defects. Absorption bands indicating the presence of hydroxyl hydrogen (O-H), CH<sub>3</sub> deformation, and C-O were observed at around  $3442$ ,  $1508$ , and  $1036\text{ cm}^{-1}$ , respectively. The appearance of a sharp and strong peak at  $1182\text{ cm}^{-1}$  reveals the formation of a C-N



**Figure 8.** EDS analysis on treated 10% GPTMS@CCTO filler which shows the presence of Si trace on the surface of CCTO particles, the inset is the spot taken for EDS analysis. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



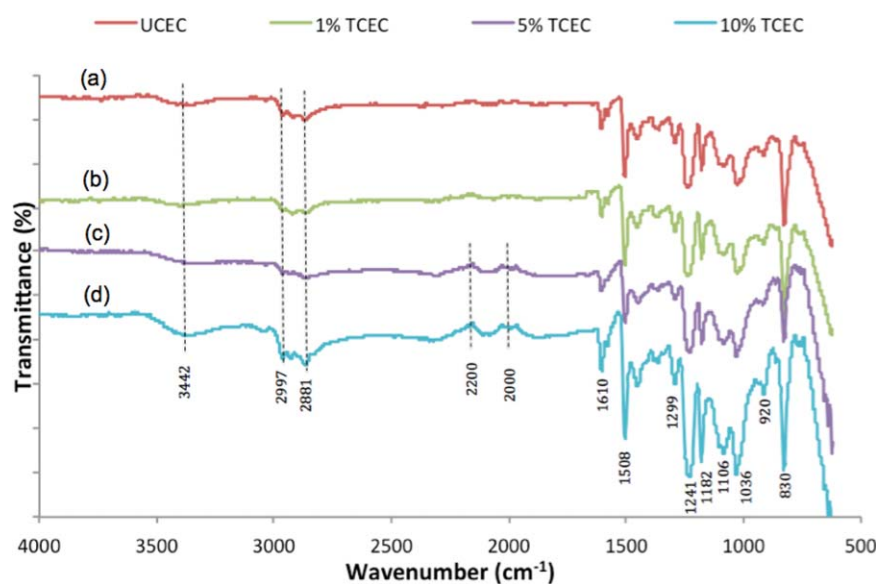
**Figure 9.** FT-IR spectra of (a) CCTO, (b) CCTO@1% GPTMS, (c) CCTO@5% GPTMS, and (d) CCTO@10% GPTMS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

stretching bond, which is most probably contributed by the reaction between amine groups (N-H) from the curing agent and C from the epoxy matrix. It is shown that the spectra (a) and (b) are almost the same due to the small amount of silane coupling agent used to treat CCTO filler and therefore do not have any significant effect on the treated CCTO/epoxy thin film composite.

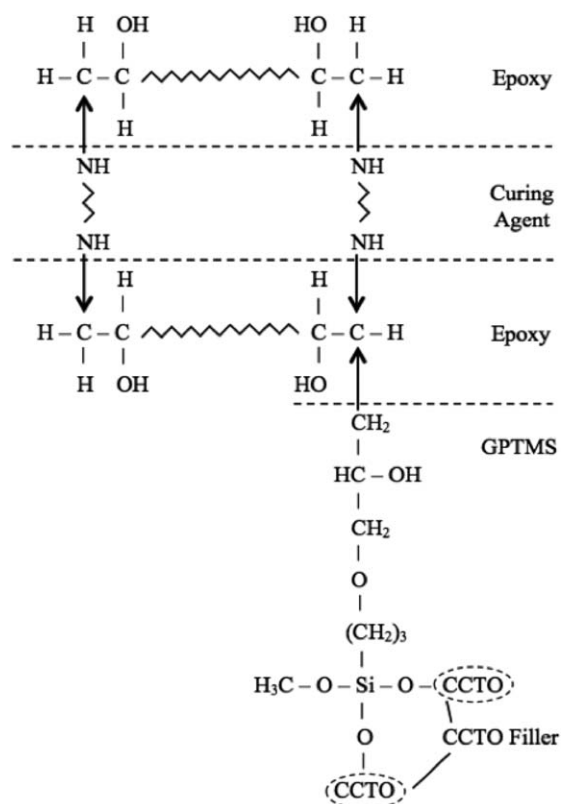
On the other hand, in the case of 5% and 10% treated CCTO/epoxy thin film composite, the silane bonding which was indicated by absorption bands at around 2200 and 2000  $\text{cm}^{-1}$  could be due to the interaction of siloxane with the amine type hardener. It is noteworthy that the appearance of peak 1106  $\text{cm}^{-1}$  can be referred to the formation of a Si-O-C stretching bond in

the treated system. The role of surface treatment of CCTO filler using silane-based coupling agent GPTMS is inferred to be a success due to the formation of chemically bonded silane coating on the surface of CCTO filler.

Based on the analysis (according to Figures 5–8), the mechanism of silane-based coupling agent GPTMS during the formation of the interface between the CCTO filler and the epoxy matrix is illustrated in Figure 11. The chemical bonding of  $-\text{C}-\text{O}-\text{Si}-\text{O}-\text{CCTO}$  and  $-\text{Si} \dots \text{O}-\text{C}-\text{C}-\text{C}-\text{C}-$  might have formed between filler, silane compound, and epoxy. It is noteworthy that these bonds can offer better adhesion between filler and matrix, which then promotes better filler-to-matrix interaction at a higher volume fraction of resin.

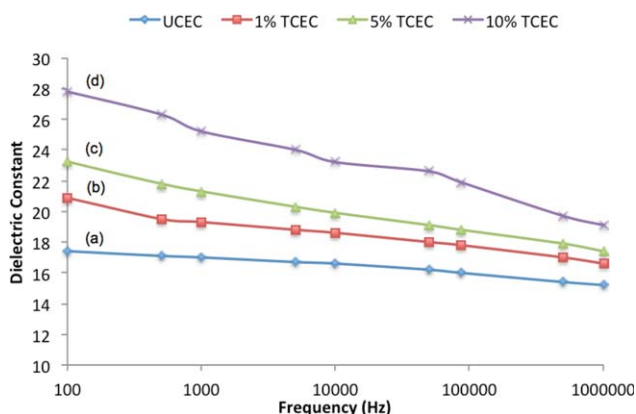


**Figure 10.** FT-IR spectra of (a) UCEC, (b) 1% TCEC, (c) 5% TCEC, and (d) 10% TCEC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

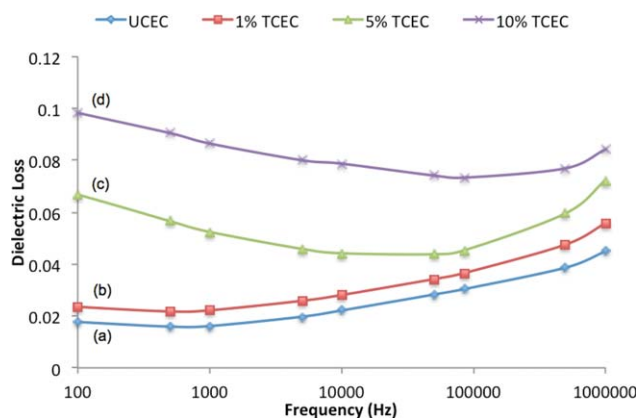


**Figure 11.** Schematic illustration of the action mechanism of silane coupling agent during the formation of interface between CCTO fillers and epoxy matrix.

**Dielectric Properties.** Figure 12 illustrates the dielectric constant of the untreated and treated CCTO/epoxy thin film composites. Measurements were carried out at a frequency of 100 Hz to 1 MHz. It can be seen that the dielectric constant of the composite evidently increased with increasing concentration of the silane-based coupling agent GPTMS. The largest dielectric constant was 27.8 at 100 Hz when 10% silane-based coupling agent GPTMS was used in treated CCTO/epoxy thin film composite. Compared with the dielectric constant of the untreated



**Figure 12.** Dielectric constant of (a) UCEC, (b) 1% TCEC, (c) 5% TCEC, and (d) 10% TCEC as a function of frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

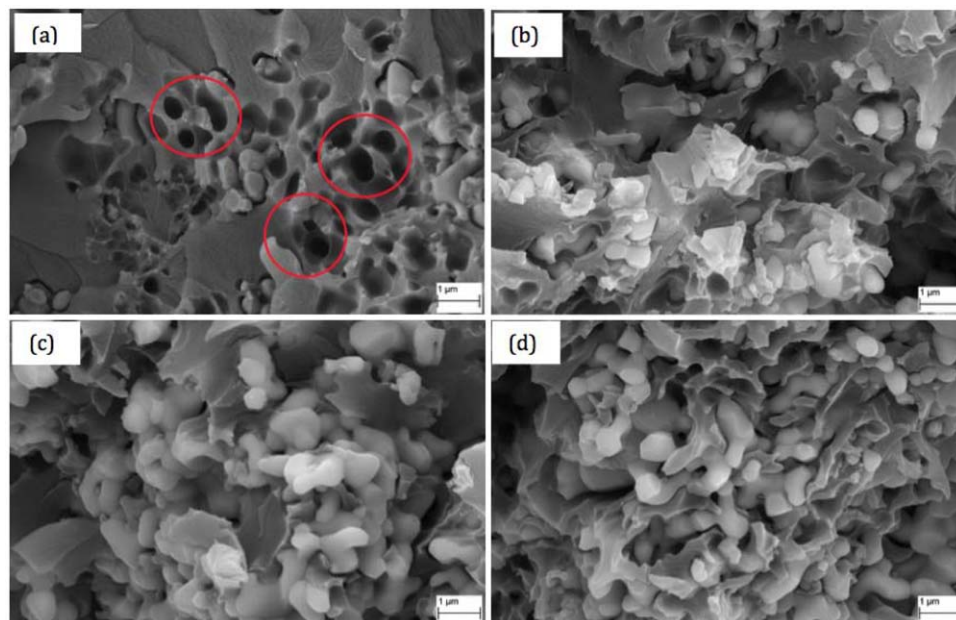


**Figure 13.** Dielectric loss of (a) UCEC, (b) 1% TCEC, (c) 5% TCEC, and (d) 10% TCEC as a function of frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CCTO/epoxy thin film composite, the dielectric constant of the CCTO/epoxy thin film composite treated with 10% silane-based coupling agent increased by 60%. According to Ramajo *et al.*,<sup>13</sup> the silane coupling agent acts as a molecular bridge between the ceramic filler and the polymer matrix, resulting in the formation of covalent bonds across the interface, which significantly improve the dielectric properties. The increase in the dielectric constant of the treated composite is attributed to the interfacial polarization of the chemical bonds formed between GPTMS and CCTO.

The dielectric loss of the untreated and treated CCTO/epoxy thin film composites is shown in Figure 13. It was observed that the dielectric loss of the composite increased gradually with increasing concentration of silane-based coupling agent GPTMS. Compared with the dielectric loss of the untreated CCTO/epoxy thin film composite ( $1.8 \times 10^{-2}$ ) measured at 100 Hz, the dielectric loss of the CCTO/epoxy thin film composite treated with 10% silane-based coupling agent is about four times higher, with a value of  $9.8 \times 10^{-2}$ . This might be due to the small amount of silane coupling agent, which might possibly have caused an interfacial polarization loss to occur at the bridging of GPTMS between the CCTO filler and epoxy matrix. In their previous work, Huang *et al.*<sup>21</sup> reported that treated CCTO filled PVDF composite showed an increment in the dielectric loss due to the polarization effect.

Figure 14 shows SEM micrographs of the untreated and treated 20 vol % CCTO/epoxy thin film composites with different concentrations of silane coupling agent varying between 1%, 5%, and 10%, respectively. The fractured surfaces of treated composites differ compared with those of untreated composites [Figure 14(a)]. It was observed that treated composites showed coarser fractured surfaces as compared with the untreated composites. This indicates that stronger adhesion and compatibility between CCTO fillers and epoxy matrix could be found in the treated composite, which contributed to the vast improvement in the dielectric properties. It was also observed that the treated surfaces of CCTO fillers were embedded well in the epoxy matrix, and it could be seen that the presence of large voids was reduced upon surface modification of the CCTO particles.



**Figure 14.** SEM micrograph of fracture surface of (a) UCEC, (b) 1% TCEC (c) 5% TCEC, and (d) 10% TCEC [magnifications of 10,000 $\times$ ]. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

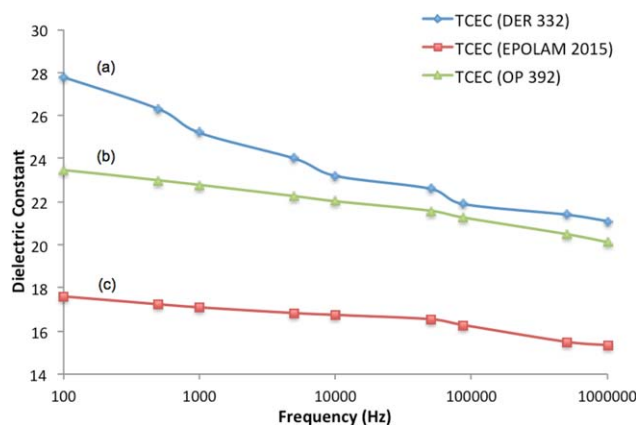
Compared with the treated CCTO/epoxy thin film composite, the interfacial adhesion and filler distribution of the untreated CCTO/epoxy thin film composite were obviously poor and weak, as shown in Figure 14(a).

#### Effect of Various Epoxy Resins

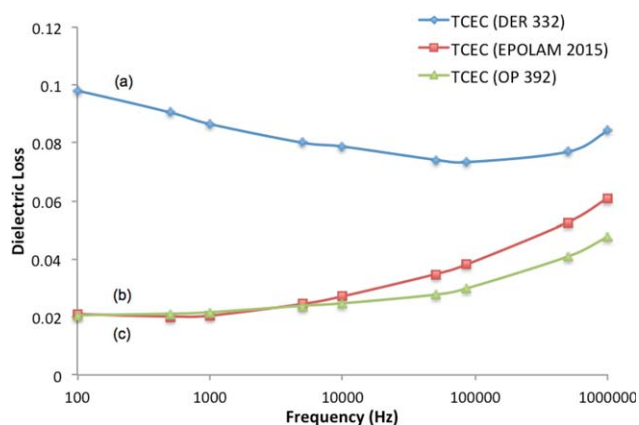
**Dielectric Properties.** Figure 15 shows a comparison of 10% treated CCTO filled D.E.R. 332, Epolam 1015, and OP 392 epoxy thin film composites in the frequency range of 100 Hz to 1 MHz. The dielectric constants of treated CCTO filled D.E.R. 332, Epolam 1015, and OP 392 epoxy thin film composites were 27.8, 23.5 and 17.6, respectively. It was observed that the dielectric constant values for Epolam 1015 and D.E.R. 332 epoxy thin composites were slightly higher than that of OP 392 epoxy thin film composite but the differences were not too sig-

nificant. Therefore, the use of a similar amount of CCTO filler with various types of epoxy resins did not have a significant effect on the dielectric constants of the composites.

A comparison of the dielectric losses of treated CCTO filled D.E.R. 332, Epolam 1015, and OP 392 epoxy thin film composites is shown in Figure 16. It can be observed that the dielectric losses of treated CCTO filled D.E.R. 332, Epolam 1015, and OP 392 epoxy thin film composites were  $9.8 \times 10^{-2}$ ,  $2.1 \times 10^{-2}$ , and  $2.1 \times 10^{-2}$ , respectively. The dielectric losses of Epolam 1015 and OP 392 epoxy thin film composites were slightly lower than that of D.E.R. 332 epoxy thin film composite. A low dielectric loss value is required for electronic packaging applications. Nevertheless, due to the similar amount of CCTO filler used to fabricate D.E.R. 332, Epolam 1015, and OP 392 epoxy

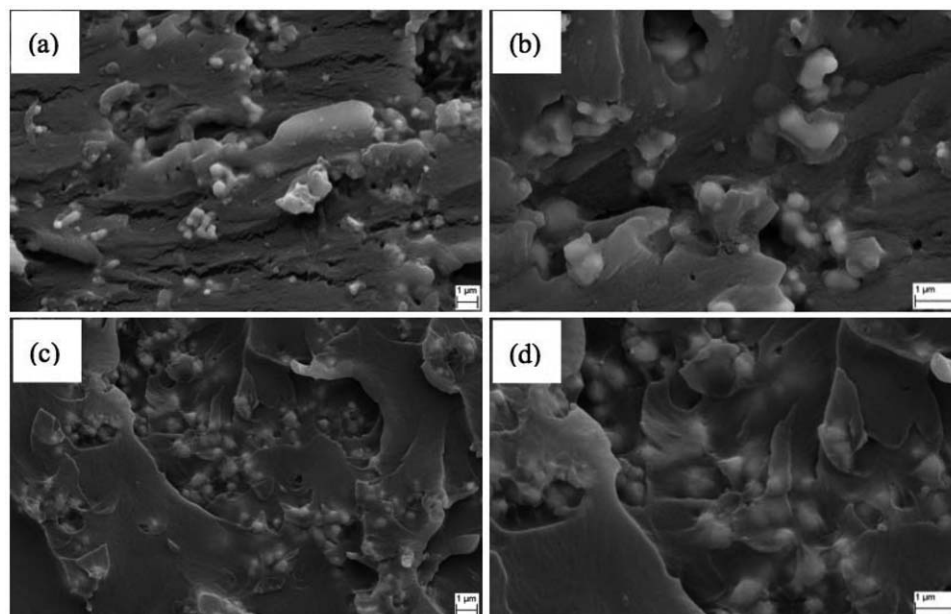


**Figure 15.** Dielectric constant of (a) TCEC (DER 332), (b) TCEC (EPOLAM 2015), and (c) TCEC (OP 392) as a function of frequency. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 16.** Dielectric loss of (a) TCEC (DER 332), (b) TCEC (EPOLAM 2015), and (c) TCEC (OP 392) as a function of frequency. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 17.** SEM micrograph of fracture surface of (a,b) TCEC (EPOLAM 2015) and (c,d) TCEC (OP 392) [magnifications of 5000 $\times$  was used for (a,c) and 10,000 $\times$  for (b,d)].

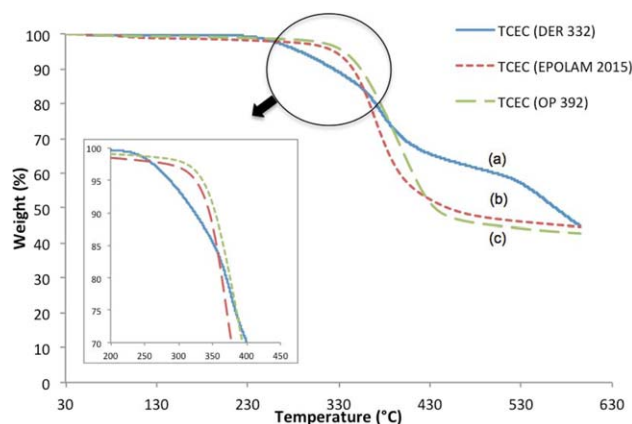
thin film composites, a slight difference in dielectric loss values was observed.

SEM images of the fractured surface of treated CCTO/epoxy thin film composites using epoxy resins Epolam 2015 and OP 392 are shown in Figure 17. It was observed that the incorporation of treated CCTO in epoxy Epolam 2015 and OP 392 was similar to that of treated CCTO in epoxy D.E.R. 332, as shown in Figure 14. Both types of epoxy resins show good interaction with treated CCTO and fewer voids can be seen in Figure 17(a,c) due to the better surface adhesion and compatibility between the treated CCTO filler and epoxy matrix. According to Salmah *et al.*,<sup>22</sup> the improvement of the surface adhesion between filler and matrix indicates a decrease in the hydrophi-

licity of the fillers through surface treatment, which then increases the compatibility of the fillers with the hydrophobic polylactic matrix.

**Thermal Stability.** Figure 18 and Table III present the TGA curve and thermal analysis data of treated CCTO-filled D.E.R. 332, Epolam 2015, and OP 392 epoxy thin film composites. It was found that the degradation temperature of OP 392 epoxy thin composite was higher than those of D.E.R. 332 and Epolam 2015 epoxy thin film composites. From Table III, the value of  $T_{5\%}$  of OP 392 epoxy thin film composite was 12% and 2% higher than those of treated D.E.R. 332 and Epolam 2015 epoxy thin film composites, respectively. Meanwhile the value of  $T_{onset}$  of OP 392 epoxy thin film composite was 17% and 5% higher than those of D.E.R. 332 and Epolam 2015 epoxy thin film composites.

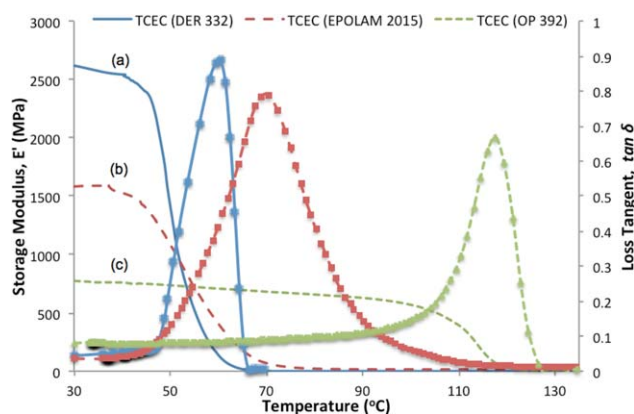
Besides that, the TGA curve of OP 392 epoxy composites tends to be shifted to the right compared with those of D.E.R. 332 and Epolam 2015 epoxy thin film composites. This could be because OP 392 epoxy has a higher  $T_g$  than D.E.R. 332 and Epolam 2015. Epoxy with a high  $T_g$  offers superior performance at high temperature.



**Figure 18.** Comparison weight loss of (a) TCEC (DER 332), (b) TCEC (EPOLAM 2015), and (c) TCEC (OP 392) with respect to temperature, the inset is an enlargement of weight loss-temperature curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table III.** Decomposition Temperature of Treated CCTO/Epoxy Thin Film Composites Produced Using Various Types of Epoxy Resins

| Fillers loading on epoxy thin film | Initial degradation temperature, $T_{5\%}$ (°C) | Onset degradation temperature, $T_{onset}$ (°C) |
|------------------------------------|---|---|
| TCEC (DER 332)                     | 287   | 311   |
| TCEC (EPOLAM 2015)                 | 320   | 340   |
| TCEC (OP 392)                      | 335   | 348   |



**Figure 19.** Storage modulus,  $E'$  and loss tangent,  $\tan \delta$  spectra recorded at 1 Hz of (a) TCEC (DER 332), (b) TCEC (EPOLAM 2015), and (c) TCEC (OP 392) with respect to temperature. Noted that line with symbols refer to  $\tan \delta$  spectra. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** Glass Transition Temperature,  $T_g$  and Storage Modulus,  $E'$  of Treated CCTO/Epoxy Thin Film Composites Fabricated Using Various Types of Epoxy Resins

| Composite          | Glass transition temperature, $T_g$ ( $^{\circ}$ C) | Storage modulus, $E'$ at 30 $^{\circ}$ C (MPa) | Coefficient of thermal expansion, CTE before $T_g$ (ppm/ $^{\circ}$ C) |
|--------------------|---|--|--|
| TCEC (DER 332)     | 57  | 2254   | 15   |
| TCEC (EPOLAM 2015) | 71  | 1588   | 25   |
| TCEC (OP 392)      | 118   | 773  | 20   |

According to Arends and Hudgin,<sup>23</sup> a thermoset resin with very high cross-link density such as OP 392 epoxy requires higher thermal energy to break the cross-link structure of the epoxy composite as the mobility of the polymer chain is reduced. This proves that OP 392 epoxy thin film composite has better thermal stability than D.E.R. 332 and Epolam 2015 epoxy thin film composites.

**Dynamic Mechanical and Thermal Mechanical Properties.** Figure 19 presents the storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of treated CCTO/epoxy thin film composites fabricated

using various epoxy resins, that is, D.E.R. 332, Epolam 2015, and OP 392. As seen in Table IV, the storage moduli of treated CCTO/epoxy thin film composites using epoxy resins D.E.R. 332, Epolam 2015, and OP 392 at 30 $^{\circ}$ C are 2254, 1588, and 773 MPa, respectively. The sample of treated OP 392 epoxy thin film composite shows a slightly lower storage modulus compared with D.E.R. 332 and Epolam 2015 epoxy thin film composites. From this point of view, this could possibly be due to the easy formation of cracks during the fabrication of treated OP 392 epoxy thin film composite, because the sample produced was too thin and brittle. The DMA test might be difficult to carry out and might therefore affect the storage modulus of OP 392 epoxy thin film composite.<sup>24</sup>

Figure 19(b) shows the loss tangent,  $\tan \delta$ , spectra of treated CCTO/epoxy thin film composites produced using different types of epoxy resins. The glass transition temperature,  $T_g$ , of epoxy thin film composites was obtained from the maximum curve of the  $\tan \delta$  spectrum. From the figure, the  $T_g$  values of treated D.E.R. 332, Epolam 2015, and OP 392 epoxy thin film composites are 57.3 $^{\circ}$ C, 70.5 $^{\circ}$ C, and 117.7 $^{\circ}$ C. OP 392 epoxy thin film composite exhibits the highest  $T_g$  compared with D.E.R. 332 and Epolam 2015 epoxy thin film composites. According to Urbaniak,<sup>25</sup> this is because of the highly crosslinked structure of OP 392 epoxy, which hinders the mobility of polymer chains and therefore requires a higher temperature to soften the polymer chain from glassy state to rubbery state.

Table IV presents the CTE values of treated D.E.R. 332, Epolam 2015 and OP 392 epoxy thin film composites. The CTE value is obtained from the temperature below  $T_g$  because the polymers or composites lost most of their thermal properties above  $T_g$ . The result shows that the CTE values before  $T_g$  of treated D.E.R. 332, Epolam 2015 and OP 392 epoxy thin film composites were nearly constant at 15 ppm/ $^{\circ}$  C, 25 ppm/ $^{\circ}$  C, and 20 ppm/ $^{\circ}$  C, respectively. Therefore, the use of a similar amount of treated CCTO filler with various epoxy resins did not have a significant effect on the CTE properties.

**Comparison of Properties of the Commercial Dielectric Material and the Present Study.** A comparison of selected properties of commercial dielectric material with the dielectric materials used in the present study, that is, treated CCTO/epoxy-D.E.R. 332, treated CCTO/epoxy-Epolam 2015 and treated CCTO/epoxy-OP 392, respectively, is shown in Table V. From the table, it can be seen that the dielectric materials used in the present study show higher values of dielectric constant,

**Table V.** Comparison Properties of the Commercial Dielectric Material and the Present Study

|  | Commercial dielectric material | TCEC (DER 332) | TCEC (EPOLAM 2015) | TCEC (OP 392) |
|--|--------------------------------|----------------|--------------------|---------------|
| Dielectric Materials                         | BaTiO <sub>3</sub> /epoxy      | CCTO/epoxy     | CCTO/epoxy         | CCTO/epoxy    |
| Dielectric constant (1 kHz)                  | 16                             | 27.8           | 23.5               | 17.6          |
| Dielectric loss (1 kHz)                      | 0.005                          | 0.098          | 0.021              | 0.021         |
| Glass transition temp, $T_g$ ( $^{\circ}$ C) | 115                            | 57             | 71                 | 118           |
| CTE (ppm/ $^{\circ}$ C) (below $T_g$ )       | 32                             | 15             | 25                 | 20            |
| Degradation temperature ( $^{\circ}$ C)      | 345                            | 311            | 340                | 348           |

$T_g$  and degradation temperature as compared with the commercial dielectric materials. Among the dielectric materials used in the present study, treated CCTO/epoxy-OP 392 exhibits good dielectric properties and an excellent  $T_g$  and degradation temperature compared with those of treated D.E.R. 332 and Epolam 2015 epoxy thin film composites. However the dielectric losses of the present dielectric materials were slightly higher than that of commercial dielectric material but the dielectric loss values still lie within the acceptable limit, which is less than 0.1. Besides that, the CTE values of the treated D.E.R. 332, Epolam 2015, and OP 392 epoxy thin film composites used in the present study were lower than those of the commercial dielectric material. A low CTE value is required to minimize the CTE mismatch between components in the printed circuit board. Therefore, treated CCTO/epoxy thin film composites produced in the present study are suitable and can be considered for use in the fabrication of dielectric materials for embedded capacitor applications.

## CONCLUSIONS

Chemical bonds are formed between the silane-based coupling agent GPTMS and epoxy matrix. The interfacial polarization between the silane-based coupling agent GPTMS and CCTO filler increased the dielectric constant of the CCTO/epoxy thin film composites. Based on the results, the CCTO/D.E.R. 332-epoxy composite treated with 10% silane-based coupling agent GPTMS shows the highest dielectric constant compared with unfilled epoxy and other composites with 1% and 5% silane-based coupling agent. Meanwhile, treated CCTO-filled OP 392 epoxy thin film composite exhibits excellent thermal stability and  $T_g$  compared with D.E.R. 332 and Epolam 2015 epoxy thin film composites.

## ACKNOWLEDGMENTS

The authors acknowledge financial support from the Ministry of Education through Exploring Research Grant Scheme (ERGS) (Grant No.: 6730109). The authors gratefully acknowledge support from Universiti Sains Malaysia and the School of Materials & Mineral Resources Engineering.

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