Relationship Between Electrical and Mechanical Loss Tangents of Hollow Glass Powder Reinforced Epoxy Composites: A Pilot Study

H. Ku, A. Maxwell, P. Wong, J. Huang, H. Fung

Faculty of Engineering and Surveying, Center of Excellence in Engineered Fibre Composites, University of Southern Queensland, Australia

Received 25 March 2010; accepted 19 June 2010
DOI 10.1002/app.33009
Published online 21 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The mechanical and thermal properties of hollow glass powder reinforced epoxy resin composites have previously been measured and evaluated in earlier studies (Ku et al., J Compos Mater, submitted). These basic, but critical data sets have yielded interest in relevant industries in Australia. This study therefore focused on measuring and evaluating the dielectric properties of these composites with a view to benefit these relevant industries. The relationship between the dielectric and thermal properties was also studied and correlated. The original contributions of this article states that samples postcured in an oven were found to have lower electrical as well as mechanical loss tangent values than their counterparts cured in ambient conditions alone. The storage modulus of all samples conventionally postcured was also higher than their counterparts. The conventionally postcured samples were also found to have lower glass transition temperature than their rivals and softer material. For all percentages by weight of glass powder, the glass transition temperature for the oven cured samples was higher and it can be argued that the composite was stiffer; the opposite was true for the ambient cured sample. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2945–2952, 2011

Key words: polymer-matrix composites (PMCs); particle-reinforced composites; electrical properties; thermal properties; dynamic mechanical thermal analysis (DMTA); casting

INTRODUCTION

The most widely used and least expensive polymer resins are polyesters and vinyl esters, whose matrix materials are primarily used for glass fiber-reinforced composites. These epoxies are generally more expensive and utilized extensively in polymer matrix composites for aerospace applications. They also have more suitable mechanical properties and resistance to moisture than the polyesters and vinyl resins.[2] In this study, composite materials were manufactured from epoxy resin and hollow glass powder to improve the dielectric and thermal properties of the resin. The percentage by weight of the filler was varied from 5–15% in step of 5%. The epoxy resin used for this study was Kinetix R246TX Thixotropic Laminating Resin and the hardener used is Kinetic H160 medium hardener. The glass powder used is SPHERICEL® 60P18 (spherical) hollow glass spheres. An Agilent-4263B type LCR (inductance, capacitance, resistance) meter was used to measure the dielectric properties of the prepared composites; they were then investigated and correlated with the thermal properties obtained in the other study. The aim was to find out what was the optimal percentage, by weight, of the filler as far as the dielectric and thermal properties were concerned. The knowledge of the dielectric properties of the composites will enable one to know the suitability of microwave processing or postcuring of the materials as postcuring composites in microwaves will usually result in higher degree of curing and better mechanical properties.

The materials

The epoxy resin used for this study was Kinetix R246TX thixotropic laminating resin (an opaque liquid) with Kinetic H160 medium hardener (with a pot life of ∼ 120 min). Other hardeners such as Kinetic H126, H128, H161, and H162 could also have been used.[2] The glass powder was first mixed with epoxy resin, after this the hardener, Kinetic H160 medium, was added. The by weight ratio of resin-to-hardener used was 4 : 1.[3] The composite was then cast into profile molds of standard tensile test pieces and left to cure under ambient conditions for 24 h. The tensile test specimens were then removed from the molds and postcured in oven first at 40°C for 16 h, then at 50°C for 16 h and finally at 60°C for 8 h.

Correspondence to: H. Ku (ku@usq.edu.au).

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TABLE I
Typical Properties of Hollow Glass Spheres

Shape	Spherical
Color	White
Composition	Proprietary glass
Density	1.1 and 0.6 g/cc
Particle size	Mean diameter 11 and 18 microns
Hardness	6 (Moh's scale)
Chemical resistance	Low alkali leach/insoluble in water
Crush strength	>10,000 psi

This procedure ensured that the heat distortion temperature (HDT) was maintained above 63°C. To bring the final HDT to 68°C, another 15 h of postcuring was required.[3] The dielectric loss of specimens was then measured.

The glass powder used was SPHERICEL® 60P18 (spherical) hollow glass spheres. These are typically used to enhance performance and reduce viscosity in paints and coatings and as lightweight additives in plastic parts, and are chemically inert, nonporous, and have very low oil absorption. Typical properties of these glass spheres are shown in Table I.[4] SPHERICEL® 60P18 hollow sphere products offer formulators flexibility in polymer composites. The addition of hollow spheres into fiberglass reinforced plastics, epoxy, compounds, and urethane castings can typically provide weight reduction cost, savings and improved impact resistance. Insulating properties of hollow spheres are also advantageous in thermal shock and heat transfer applications. Two densities of sphere were available, 0.6 and 1.1 g/cc, which provided the option to best fit the applications mixing and target weight requirements.[5] The density of the hollow glass powder selected for this study was 0.6 g/cc. This was selected to allow future comparison with ceramic hollow spheres (envirospheres) used in prior similar study having a density of 0.7 g/cc.[6] When used in polymer concrete, hollow spheres provided a cost effective alternative without degrading the physical properties.[6] Safety considerations when using SPHERICEL® 60P18 was taken through careful examination of the material safety data sheet.[7]

The particle size of the white glass powder ranged from 6 to 32 microns with an average size of 20 microns, hence being defined as "micron" fillers. In addition, the fused inorganic oxides were spherical in shape and nonporous.

The composite samples

The reinforcer was glass powder particulates (glass hollow spheres) and they were made 5, 10, and 15% by weight in the cured epoxy composite, EP/GP (X%), where X was the percentage by weight of the filler. As the raw materials of the composites were only comprised of liquid and glass hollow spheres, specimens of 120 mm (L) × 120 mm (W) × 6 mm (T) were cast to shape.

The procedure used is detailed below:

1. The opaque liquid resin was first mixed with the catalyst.
2. The glass powder was then added to the mixture, and mixed to yield an uncured composite. Table II shows the mass, in grams, of resin, catalyst and glass powder required, respectively, to produce 1000 g of uncured composite of 10% by weight of glass powder.
3. The mixture of glass powder, resin and hardener was then blended with a mechanical blender to ensure a final homogenous mixture.
4. Before pouring the uncured composite into the prepared mold, all faces which would come into contact with the composite were sprayed with a wax releasing agent to facilitate easy release of the samples after curing from the mold.
5. The uncured composite was then cast into the molds and cured in ambient conditions.
6. After an initial ambient-cure of 24 h, half of the test pieces were removed from the mold and their dielectric loss tangent were measured. The other half was inserted into an oven for further curing. Oven temperatures and times were:
   - 16 h at 40°C,
   - 16 h at 50°C, and
   - 8 h at 60°C.
7. The dielectric loss tangent of these additionally cured specimens was then also measured.

Dielectric loss tangent

Electrical dielectric properties can be used to classify materials as conductors, quasi conductors or insulators. The alternating polarization of the molecules can consume energy. This is polarization loss and

TABLE II
Weight of Materials Required to Make 1000 g of EP/GP (10%)

Materials	Resin (R)	Hardener (H)	R + H	Glass powder	Composite
Parameters					
Ratio by weight	4	1	–	–	–
Percentage by weight	–	–	90	10	–
Weight of materials in 1000 g of EP/GP (20%)	720(g)	180 (g)	900 (g)	100 (g)	1000 (g)

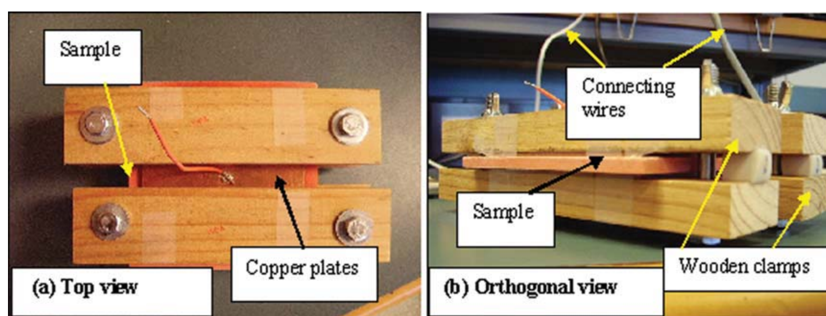

Figure 1 Two views of the parallel plate capacitor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a complex numerical permittivity is required to characterize these materials. Materials can for instance be good conductors at particular frequencies while becoming electrical insulators at others. A dielectric material is a substance that is a poor conductor of electricity, but an efficient sustainer of electro static fields. An important property of a dielectric is its ability to support an electrostatic field while dissipating minimal energy in the form of heat. The lower the dielectric loss, i.e., the proportion of energy lost as heat, the more effective is a dielectric material.

The dielectric loss tangent of the samples of glass powder-filled epoxy composites were measured for two curing conditions:

- cured under ambient conditions and
- cured under ambient conditions plus postcuring in an oven.

The complex relative permittivity of a dielectric is defined as $\varepsilon = \varepsilon' - j\varepsilon''$; where the real part is the dielectric constant; and the imaginary part is referred to as the loss factor. The ratio of these two values is defined as the loss tangent, $\tan \delta = \frac{\varepsilon'}{\varepsilon''}$.[8]

Figure 2 The Agilent 4263B LCR meter with the parallel plate capacitor and sample ready for testing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

An Agilent-4263B type LCR (inductance, capacitance, resistance) meter was used to measure the dielectric tangent loss of the samples mounted into a custom measurement assembly. Two copper plates formed a parallel plate capacitor with the flat-cured sample sandwiched in between so as to form the dielectric, as shown in Figure 1. The sample size was selected to be at least 120 mm × 120 mm to ensure sufficient generation of electro static fields. This experimental configuration was then connected to the inputs of the LRC meter to complete the circuit for measurement as shown in Figure 2. Recordings of the loss factor for selected frequencies were made for each of the sample pairs, and then post analyzed.

Figure 3 shows the schematic for the parallel connection of *C* and *G*. The distributed shunt capacitor, *C*, and the conductance, *G*, are both dependent on the properties of the dielectric material which separates the two line conductors. The current flowing through the parallel combination of *C* and *G* is shown in Figure 3(a) and their phasor relationship in Figure 3(b).

From the measurements, the real and imaginary parts of the dielectric loss can be calculated from the following relationships[9]:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{S} \tag{1}$$

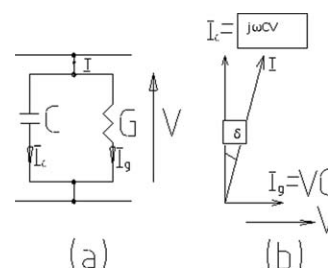

Figure 3 (a) Parallel connection of Capacitance and Conductance, G (b) Phasor diagram showing the relationship for loss tangent.

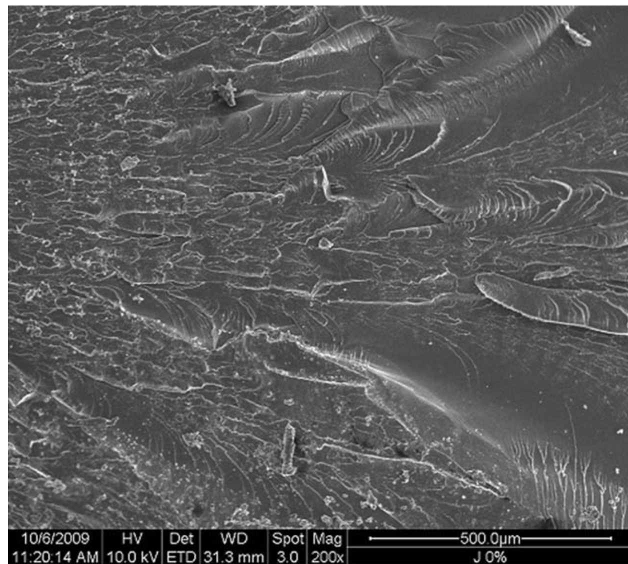

Figure 4 SEM micrographs of neat epoxy resin.

where C is the capacitance in Fm^{-1};

ε_0 is the dielectric permittivity of free space = $\frac{1}{36\pi} \times 10^{-9}$;

ε_r is the dielectric constant of the composite;

A is the surface area of the samples in mm^2; and

s is the thickness of the composite sample in mm^2.

and

$$G = \frac{\sigma A}{S} \tag{2}$$

where G is the conductance of the composite in Sm^{-1} and

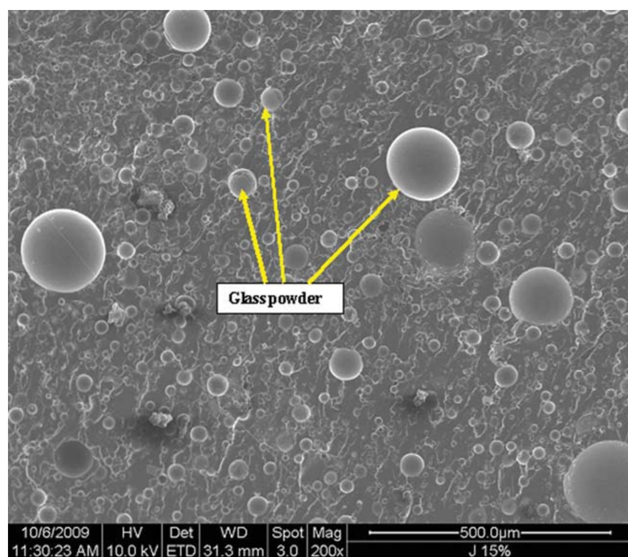

Figure 5 SEM micrographs of epoxy composites filled with 15 w/t % of glass powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

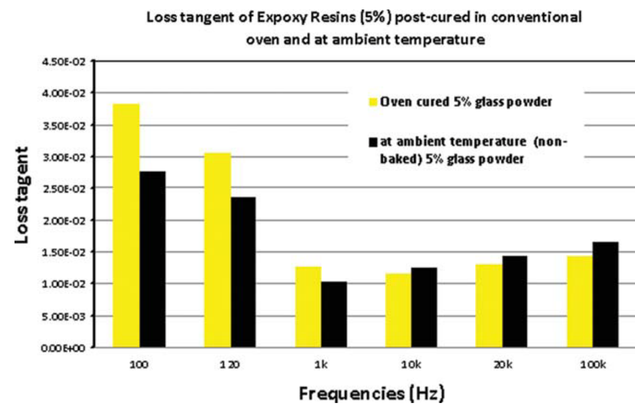

Figure 6 Loss tangent of epoxy-glass powder (5%) post-cured in oven and microwaves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A and s are the same as above.

and

$$\sigma = \omega \varepsilon_0 \varepsilon'' \tag{3}$$

where ω is the frequency in the range of 10–100 kHz,[10] and the loss tangent[7] is defined as

$$\tan\ \delta = \frac{\varepsilon''}{\varepsilon'} \tag{4}$$

It is also seen that from the above relationships that the loss tangent is frequency dependant. Experimental data was collected at the following frequencies: 100 Hz, 120 Hz, 1 kHz, 10 kHz, 20 kHz, and 100 kHz.

If the properties of the dielectric are assumed to be constant across the frequency range of interest, then C becomes constant with G proportional to the frequency, hence the loss tangent can be easily calculated by the formula[11]:

$$G = \omega C\ \tan\ \delta \tag{5}$$

RESULTS AND DISCUSSION

Figure 4 shows the SEM micrograph of neat epoxy resin. No hollow glass balls can be found in the matrix of the polymer. Figure 5 shows the SEM micrograph of epoxy composite filled with 15 wt % glass powder and it can be found that the hollow glass balls were evenly distributed in the matrix of the composites.

Figures 6–8 show the electrical loss tangents of glass powder filled epoxy composites with varying percentages of glass powder by weight postcured in ambient conditions and cured in ambient conditions plus postcured in an oven for 40 h. It was thought appropriate to divide the results into two groups: a low frequency group (<1 kHz) and a high frequency

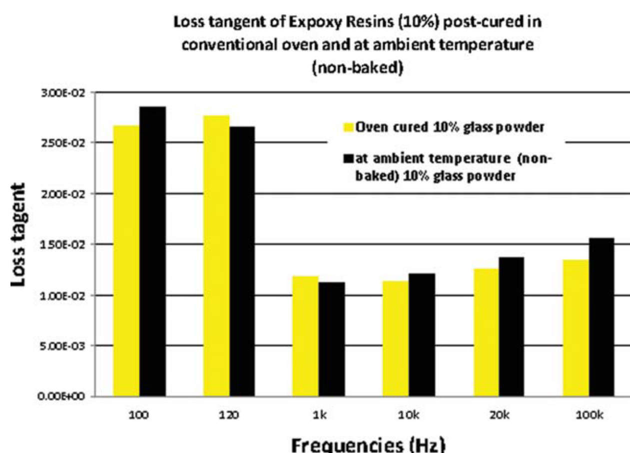

Figure 7 Loss tangent of epoxy-glass powder (10%) post-cured in oven and microwaves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

group (>10 kHz). In the low frequency group, for all glass powder by weight, the ambient cured specimens had lower electrical loss tangent values than their counterparts. The opposite was true however for the higher frequency group. It can be argued that the dielectric behavior of the low frequency group was due to the fact that the frequency change in polarity of the excitation used in the study was too low to initiate the change of polarity for water molecules resulting in low loss tangent values for materials supposed to have high water content. On the other hand, the dielectric behavior of the higher frequency group was normal because samples post-cured in an oven were expected to have less water content and hence lower electrical loss tangent values. This may be due to higher degree of curing and less water content.

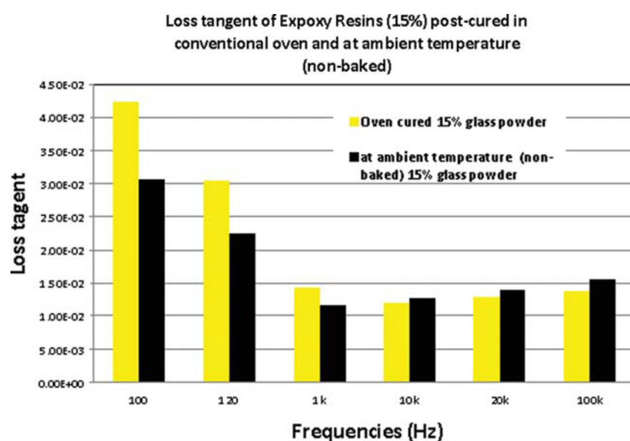

Figure 8 Loss tangent of epoxy-glass powder (15%) post-cured in oven and microwaves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

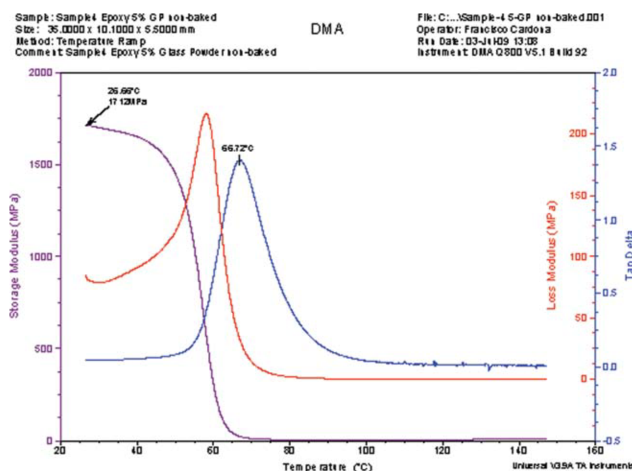

Figure 9 DMA results of 5% glass powder filled epoxy resin cured at ambient conditions for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Since the loss tangents of the ambient cured samples were relatively high, they could be further processed by using microwaves to 100% to make them stiffer in a much shorter time duration.[12] It can be argued that the postcuring could be completely performed through microwave irradiation to reduce processing time and increase degree of cure.[12]

Referring to Figures 9–14, for all samples, irrespective of the percentage by weight of glass powder, postcured samples had higher modulus values, which implied that the ambient-cured samples were softer materials than their counterparts and this is on par with the glass transition temperatures found. In general, ambient-cured samples have higher electrical loss tangent as well as higher loss modulus and higher mechanical loss tangent (tan δ). Higher loss

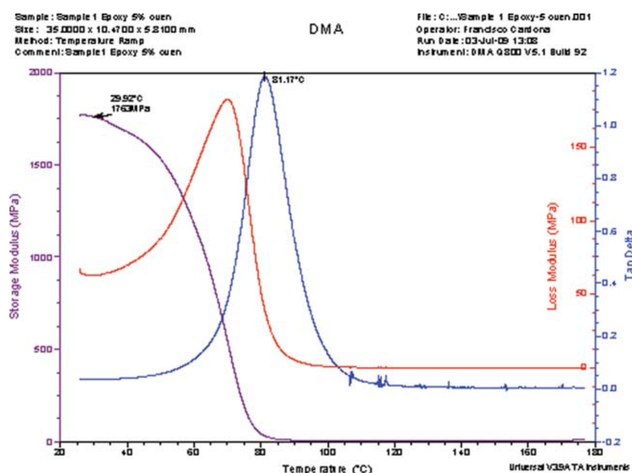

Figure 10 DMA results of 5% glass powder filled epoxy resin cured at ambient conditions for 24 h and then post-cured in an oven for 40 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

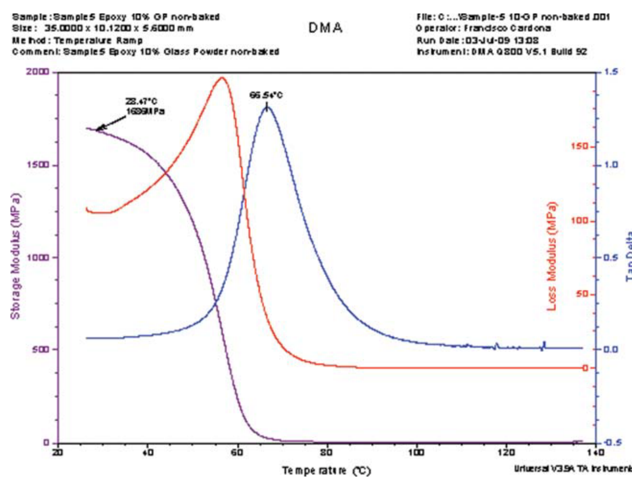

Figure 11 DMA results of 10% glass powder filled epoxy resin cured at ambient conditions for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

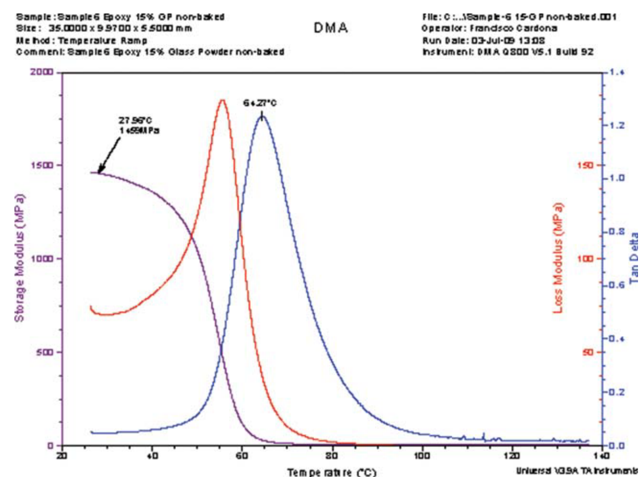

Figure 13 DMA results of 15% glass powder filled epoxy resin cured at ambient conditions for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modulus and mechanical loss tangent mean softer material, which in itself may have higher water content and less degree of cure. This was supported by the lower glass transition temperatures encountered.

The values of electrical loss tangent to that of the mechanical ones were now compared. Postcured samples, irrespective of glass powder content by weight, had lower electrical loss tangent (Figs. 6–8) and mechanical loss tangent (Figs. 9–14) and it can be argued that by measuring electrical loss tangent of a material, it is possible to deduce its mechanical loss tangent.[13]

Zee et al. manufactured epoxy resin composites filled with alumina powder (XA3500 from ALCOA) and ceramic powder (ADT-50 from Ampex), respectively. The epoxy resin used was EPON 828 from Shell Chemical. Anhydride hardeners were used; they were NMA (NADIC methyl anhydride), MTHPA (methyl tetrahydrophthalic anhydride), and MHHPA (methyl hexahydrophthalic anhydride); the accelerator used was BDMA (benzyldimethylamine). The dielectric constant and dielectric loss of the made composites were measured from 1 to 100 kHz. Table III shows the dielectric constant and dielectric loss of differently mixed and manufactured composites at 10 kHz. Zee et al. found that within the range of the frequency examined, the dielectric constants in the materials were independent of frequency. On the other hand, the dielectric loss was found to increase with increasing frequency. For example, the dielectric loss of EPON 828/NMA/DBMA/ATD50(30%) was 0.65×10^{-2} at 1 kHz and

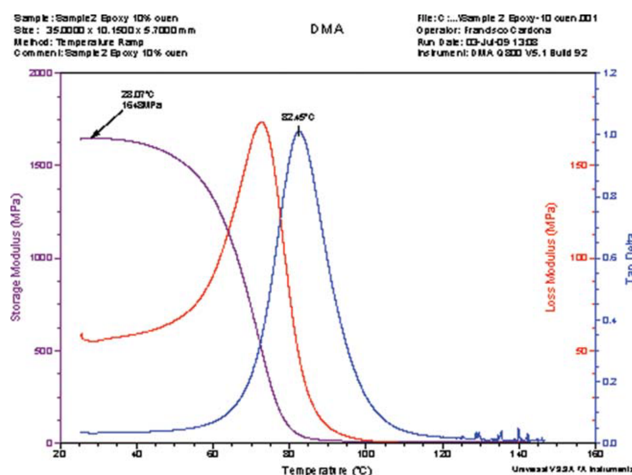

Figure 12 DMA results of 10% glass powder filled epoxy resin cured at ambient conditions for 24 h and then postcured in an oven for 40 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

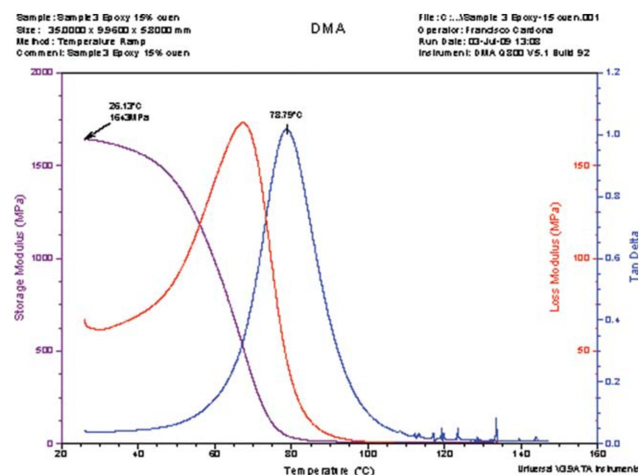

Figure 14 DMA results of 15% glass powder filled epoxy resin cured at ambient conditions for 24 h and then postcured in an oven for 40 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

this value increased to 1.3×10^{-2} at 100 KHz. The presence of filler did enhance the dielectric constant. Zee et al. also claimed that the choice of the filer materials did not significantly affect the mechanical properties of the composites but it did affect the mixing process.[14] The amount of glass powder added could not be more than 15% otherwise the mixture would be too sticky and could not be mixed properly. In this study, it was also found that the dielectric loss increased with increasing frequency. Therefore, at higher frequencies, e.g., 2.45 GHz, frequency used in microwave oven, it can be argued that the dielectric loss would be higher and hence the composite materials of this study and those of Zee et al. are suitable for microwave processing.

Cheng et al. made epoxy composites from DGEBA type epoxy resin, D.E.R. 331 and barium titanate, Y5V fillers. The dielectric constants and loss tangents of the composites were measured at room temperature by an impedance analyser (HP model 4291B) at the frequency range of 1 MHz to 1 GHz. By adding the ceramic powder, the dielectric constant, ε, can be raised. It was also found that, at a lower frequency, the permittivity decreases with increasing frequency, but after about 100 MHz the changes can be ignored. It is believed that a decrease in the dipolar polarization of the matrix and the accumulation of charges at the interface between ceramic particles and polymers results in a large scale field distortion. Table IV shows the dependences of the dielectric constant at 1 GHz, of the epoxy composite containing Y5V ceramic. By adding 80 wt % (about 45 vol %) of Y5V fillers, the dielectric constant could be increased from 3.2 to 13.1, and the loss tangent was lower than 0.03 but increased with filler content.[10] This is again good for microwave processing of the compoasites. However, Cheng et al. did not mention whether the loss tangent increased with frequency or not and it was not sure whether the composites were suitable or not for microwave processing or application required by Cheng et al.

Wu et al. prepared epoxy composites filled with ceramic powder. The epoxy resin used was O-Cresol Novolac (OCN) epoxy resin, Chang Chun Chemical, CNE-200EL. The hardener was Phenol-Novolac (PN), Chang Chun Chemical, 1120. The ceramic powder was self-synthesized $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})O_3$ (BSTZ) ceramic powder. The dielectric constants of epoxy/BSTZ composites with various content of BSTZ ceramic powder measured at 1 MHz as a function of equivalent weight ratio are shown in Figure 13. No apparent change was found as the equivalent weight ratio was changed, which was the ratio of hardener/epoxy. This result suggested that the amounts of epoxy and hardener had no apparent effects on the dielectric constants of epoxy/BSTZ composites. The loss tangents (tan δ) of epoxy/BSTZ composites were measured at 1 MHz, and that the loss tangent was almost unchanged as the measured frequency increased.[15] This is not in line with that of this study and is not good for microwave processing.

TABLE III
Dielectric Properties of the Epoxy Composites at 10 kHz[11]

Composites tested	Dielectric constant	Dielectric loss (10^{-2})
828/NMA/BDMA	4.08	0.60
828/NMA/BDMA/XA3500(10%)	4.75	0.62
828/NMA/BDMA/XA3500(30%)	6.35	0.70
828/NMA/BDMA/ATD50(30%)	9.58	0.74
828/MTHPA/BDMA	3.88	0.85
828/MTHPA/BDMA XA3500(20%)	5.05	0.90
828/MTHPA/BDMA XA3500(40%)	6.05	0.93

TABLE IV
Properties of the Composites with Various Contents of Y5V Ceramics[12]

Y5V filler	ε_c (1 GHz)	Tan δ (1 GHz)
0%	3.2	0.022
25 wt % (6 vol %)	3.9	0.023
40 wt % (12 vol %)	4.6	0.026
60 wt % (24 vol %)	6.5	0.027
70 wt % (33 vol %)	10.3	0.028
80 wt % (45 vol %)	13.1	0.025

CONCLUSION

From the electrical loss tangent measurements, it was found that the postcured samples had lower electrical loss tangent than their counterparts in the higher frequency range. This equated to the samples having absorbed less heat during the microwave process. The main contributor to this phenomenon was the absence of, or having very few, water molecules present in the specimens due to the higher degree of curing and therefore it can also be argued that the absence or having few water molecules also makes the samples stiffer.

From the mechanical loss tangent measurements, it was found that the postcured samples had a lower mechanical loss tangent because the energy that can be converted into heat was less during deformation and the specimens were stiffer. Again, it can be argued that the absence or very few water molecules in the composites made the samples stiffer.

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