Effect of Temperature on Electrical Behavior of Flyash-Filled Epoxy Gradient Composites

Navin Chand, Deepak Jain

Regional Research Laboratory (CSIR), Hoshangabad Road, Habibganj Naka, Bhopal, 462026 India

Received 14 September 2004; accepted 21 January 2005
DOI 10.1002/app.22169
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Functionally gradient composites of epoxy resin having different weight percentages of flyash were prepared under centrifugal force to obtain gradient in density, hardness, and electrical properties. Effect of temperature and frequency variation on dielectric constant (ε'), tan δ, and ac conductivity was determined by using a 4274 A Multi-Frequency LCR meter. Electrical measurements were carried out in a temperature range from 40 to 180°C and in a frequency range from 1 to 100 kHz. It was observed that the dielectric constant and tan δ increased with increase in temperature and decreased with increase in frequency. The ac conductivity increases with increase in temperature and frequency. The increased weight percentage of flyash increased the compaction of flyash particle in the flyash-rich phase of graded composites, which would have increased the dielectric constant (ε'), tan δ, and ac conductivity. Shore D hardness and density of the functionally gradient composites has also been determined and reported. A continuous increase in the hardness from 69 to 76 and density from 1.287 to 1.41 g/cc has been observed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1269–1276, 2006

Key words: dielectric constant; composite polymer; flyash; epoxy

INTRODUCTION

In recent years functional gradient composites have been developed as advanced composites. Several methods have been used to obtain the gradient structure in the materials. Molding under centrifugal force is one of the effective methods for fabrication of gradient materials.[1] Functional gradient composites have been prepared with a thermosetting matrix by centrifugation; some work has been done on the creation of a gradient in electrical conductivity. For this purpose long carbon fibers in epoxy resin[2–5] have been used, but there are also some studies concerned with small metal particles[6,7] and short carbon fibers[8–10] for optimized electrical conductivity.

Epoxies are widely used in insulation, such as electrical machinery, switchgears, and bushings in transformers.[11] Polymers have a very low concentration of free-charge carriers and thus are nonconductive and transparent to electromagnetic radiation. Because of this, they are not suitable for use as enclosures for electronic equipment because they cannot shield it from outside radiation. Beyond a critical concentration of filler, the polymer becomes conductive. This formation of a network permits the movement of charge carriers of the fillers through the matrix and therefore the composites achieve a certain degree of electrical conductivity.[12] Several fillers can be added to the insulating polymeric matrix to achieve different conductivities. Filled polymers are required for a variety of industrial applications.[13,14]

Funabashi,[3] Choe et al.,[8,9] and Lee et al.[10] have measured the electrical conductivity of functionally graded materials to verify the concentration and the orientation of fibers inside an epoxy. According to them, the electrical conductivity depends on the volume fraction of the fibers.

Flyash epoxy composites have potential use in the area of thermoelectric power generation. Wu and Tung[11] have reported dielectric properties of pure epoxy resin in the temperature range –50 to 70°C and found a β-relaxation peak in the low temperature range of –30 to –20°C due to the motion of diester segments introduced in the pure epoxy crosslinking network by the reaction of acid anhydride. They studied the relaxation response in a very limited temperature range.

Determination of the dielectric constant, tan δ, and ac conductivity behavior of flyash-filled epoxy gradient composites are very necessary for finding its suitable application. In this article, flyash particles have been incorporated in epoxy resin. Dielectric constant and ac conductivity values have been determined at different temperatures and frequencies and analyzed. Shore D hardness and density of the functionally gradient composites were investigated.

Correspondence to: N. Chand (navinchand15@indianinfo.com).

Journal of Applied Polymer Science, Vol. 100, 1269–1276 (2006)

TABLE I
Composition of Ingredients

Sample no.	Epoxy (wt %)	Flyash (wt %)
1	90.1	9.9
2	80.4	19.6
3	70.9	29.1

EXPERIMENTAL

Materials

A commercial-type room temperature–cured epoxy resin two-part system having a density of 1.201g/cm^3 was supplied by M/s Chouksay Chemicals Pvt. Ltd. India. Flyash having a size less than 45 μm used in this study was obtained from a thermal power plant, Sarni India. The composition of ingredients used in making these composites is listed in Table I. The chemical composition of flyash is listed in Table II.

Sample preparation

The method of preparation of the test sample is shown schematically in Figure 1.[15] Weighed amounts of dried flyash particles for 9.9, 19.6, and 29.1 wt % were mechanically mixed with epoxy resin at room temperature until a homogeneous mixture was obtained. The homogeneous mixture was then poured into a circular mold cavity with a diamter of 60 mm and a thickness of 12 mm. The samples were centrifuged for a constant time of 60 min and speed of 700 rpm. The centrifugation speed was measured by phototachometer and controlled by variator.

From the circular block, a cylindrical rod of 10 mm diameter and 30 mm length was obtained and cured further for 7 days at room temperature and was then sliced using a diamond cutter (Leco VC-50) into six pieces of 5 mm length. The pellet formed in the perpendicular direction to the centrifugal force direction. From these sections, 2-mm-thick specimens were prepared. Uniformity of surfaces was obtained by polishing the sample using a polishing cloth. Both sides of the samples were coated with an air-drying graphite-conducting paint before electrical measurements. Samples are numbered from 1 to 6 starting from the periphery toward the center.

Testing

Electrical

Capacitance and tan δ values were measured by using a Hewlett–Packard LCR Meter model 4274 A in the temperature range 40 to 180°C. Heating rate was kept constant at 1°C/min.

$$\varepsilon' = C/C_o,$$

where C and C_o are the capacitance of the electrodes with and without dielectric, respectively; C_o is given by

$$C_o = [(0.08854A)/d]\text{pF},$$

where A (cm^2) is the area of the electrodes and d (cm) is the thickness of the sample. The ac conductivity (σ) was calculated using the relation

$$\sigma_{ac} = \varepsilon_o \omega \varepsilon' \tan\delta,$$

where ε_o is the permittivity of the free space (8.85 $\times 10^{-12}$ fm^{-1}), tan δ is the dielectric dissipation factor, and ω is the angular frequency, which is equal to $2\pi f$.

The dissipation factor, tan δ. is defined as follows:

$$\tan\delta = \varepsilon''/\varepsilon'$$

where ε'' is the dielectric loss.

Hardness

Hiroshima hardness tester (Durometer) model RHT-1 was used to determine the hardness of the specimen. The hardness is defined as the resistance of a specimen to the penetration of a hardened steel truncated cone (Shore A), a radius cone (Shore D), or a spherical flat indenter. For this test the cylindrical samples were cut parallel to their axes (centrifugal force direction) and polished. The hardness was measured at room temperature along the axis over the length of the sample.

Density

For this test the cylindrical samples were cut into the pellet form of 2 mm thickness perpendicular to the centrifugal force direction. The density was measured by a Mattler Toledo machine using the Archimedes principle at room temperature.

TABLE II
Chemical Composition of Flyash[15]

Sample no.	Composition	Value
1	SiO_2	65.1
2	Al_2O_3	25.1
3	Fe_2O_3	4.2
4	CaO	1.4
5	Other-metal oxide	4.2

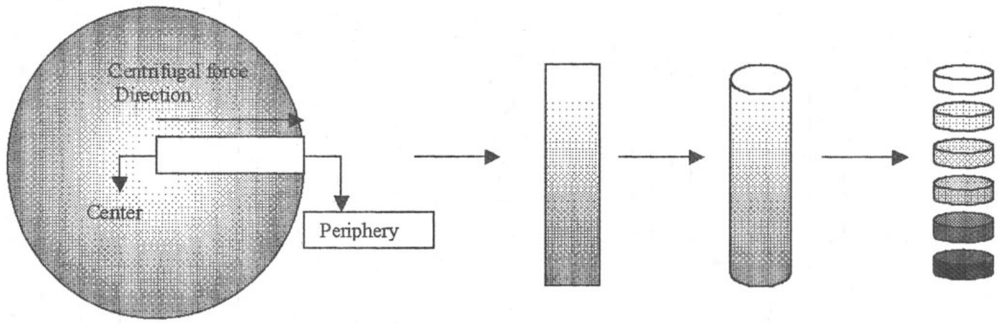

Figure 1 Schematic diagram of epoxy gradient composite.

RESULTS AND DISCUSSION

Figure 2 shows the effect of temperature on the dielectric constant (ε') for 29.1 wt % flyash-filled epoxy gradient composites (samples 1 and 6) in the temperature range 40–180°C and at 1 kHz frequency. It was observed that the dielectric constant increased with increasing temperature. The dielectric constant value increased sharply and thereafter suddenly increased with respect to temperature variation for all the samples. Another interesting observation in the dielectric constant (ε') with temperature behavior is that, at higher temperatures, the difference in dielectric constant between samples increased compared to lower temperatures. This increase of the dielectric constant value at higher temperatures between samples is due to the availability of more space for the easy rotation of dipoles with increasing temperature.

Dielectric behavior of flyash-filled epoxy composite is very similar to the finding obtained for a silica-filled resin system. Tim et al.[16] reported that the dielectric constant of polymeric systems results from permanent dipole motions within the system. The cynate ester resin has a characteristically low dielectric constant due to low polarity of the central trazine ring. The addition of untreated silica filler, with its surface hydroxide groups being polar, was thought to act to increase composite dielectric constant.

Figure 3 shows the variation of tan δ with temperature for 29.1 wt % flyash-filled epoxy gradient composites (samples 1 and 6) in the temperature range 40–180°C and at 1 kHz frequency. It was observed that tan δ increased with increasing temperature. The sample shows that, after 110°C, there is a sudden increase in tan δ, while the other sample shows that this type of sudden increase in tan δ behavior is delayed to 128°C.

Figure 4 shows the variation of ac conductivity with temperature for 29.1 wt % flyash-filled epoxy gradient composites (samples 1 and 6) in the temperature range

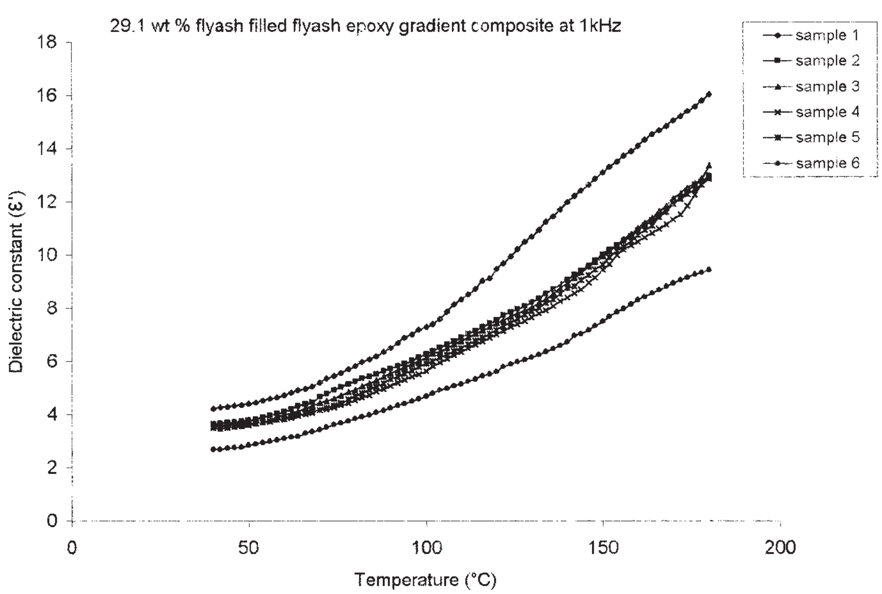

Figure 2 Variation of ε' versus temperature for 29.1 wt % flyash-filled flyash epoxy gradient composite (samples 1 and 6) at 1 kHz frequency.

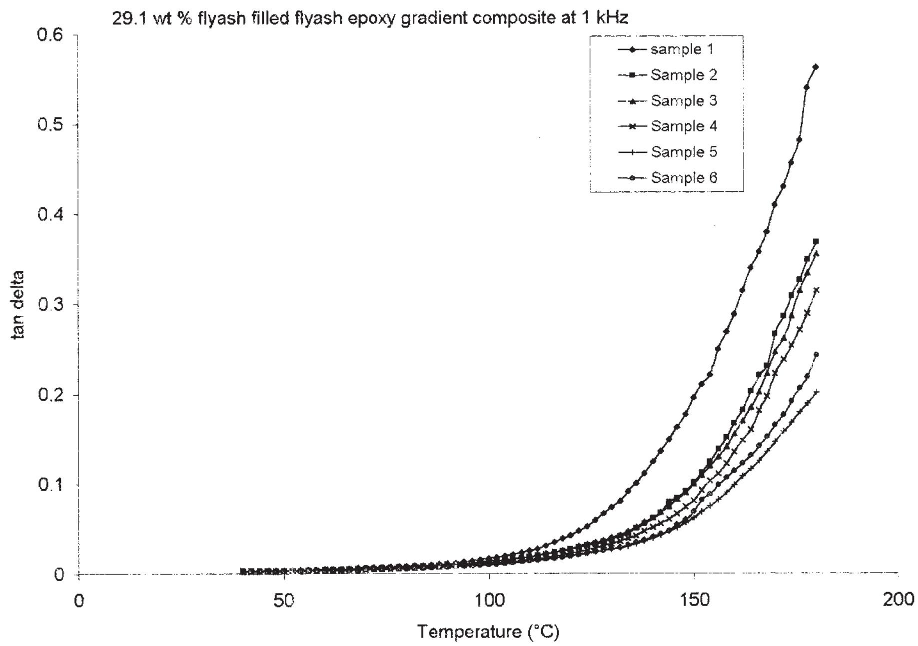

Figure 3 Variation of tan δ versus temperature for 29.1 wt % flyash-filled flyash epoxy gradient composite (samples 1 and 6) at 1 kHz frequency.

40–180°C and at 1 kHz frequency. These plots show that ac conductivity increased with increasing temperature. The ac conductivity behavior of flyash-filled gradient epoxy composite is very similar to its tan δ behavior. The sudden increase in ac conductivity matches the temperatures observed in tan δ behavior.

Similar to our observation, the temperature dependence of ac conductivity has been explained by considering the mobility of charge carriers responsible for hopping. As temperature increases, the mobility of hopping ions also increases, thereby increasing conductivity. The electrons that are involved in hopping are responsible for the electronic polarization of these composites.[17]

Tim et al.[16] reported that the two main factors influencing conductivity in filled AroCy B composites

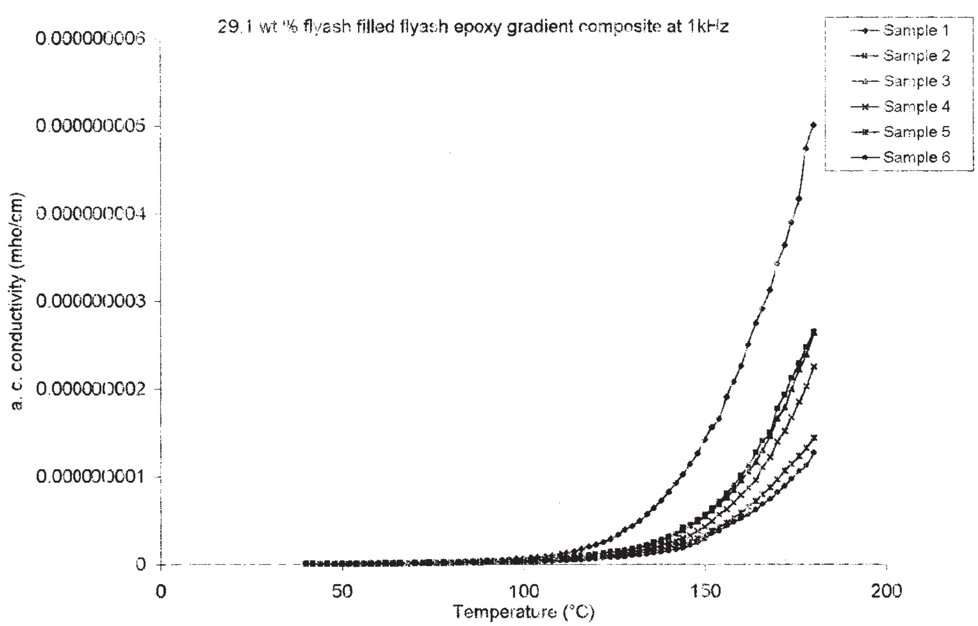

Figure 4 Variation of ac conductivity versus temperature for 29.1 wt % flyash-filled flyash epoxy gradient composite (samples 1 and 6) at 1 kHz frequency.

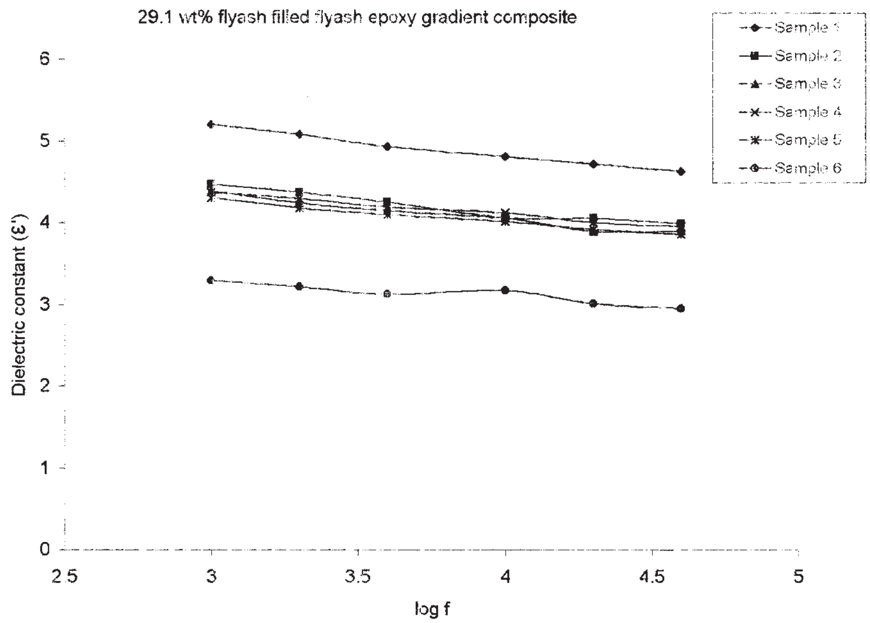

Figure 5 Variation of ε' versus log f for 29.1 wt % flyash-filled flyash epoxy gradient composite (samples 1–6) at 40°C.

are ion concentration and ion motion. Furthermore, ion motion in this system is likely to be governed by polymer backbone motion. The motion of the thermoset backbone becomes significant in the region 40–50°C below their glass transition temperatures.

Figure 5 shows the effect of logarithm of frequency with dielectric constant for 29.1 wt % flyash-filled epoxy gradient composites (samples 1–6) in the frequency range 1–100 kHz. Measurements were done at 40°C. This shows that the dielectric constant decreases with increasing frequencies. Figure 6 shows the effect of logarithm of frequency with tan δ for 29.1 wt % flyash-filled epoxy gradient composites (samples 1–6). This shows that tan δ decreases with increasing frequencies. At a critical frequency all of the gradient composites have shown that there is peak in the tan δ plots. Figure 7 shows the effect of logarithm of frequency with ac conductivity for 29.1 wt % flyash-filled epoxy gradient composites (samples 1–6). It was observed that ac conductivity increases with increasing frequency. The increase of frequency increased ac conductivity by increasing the hopping of conducting

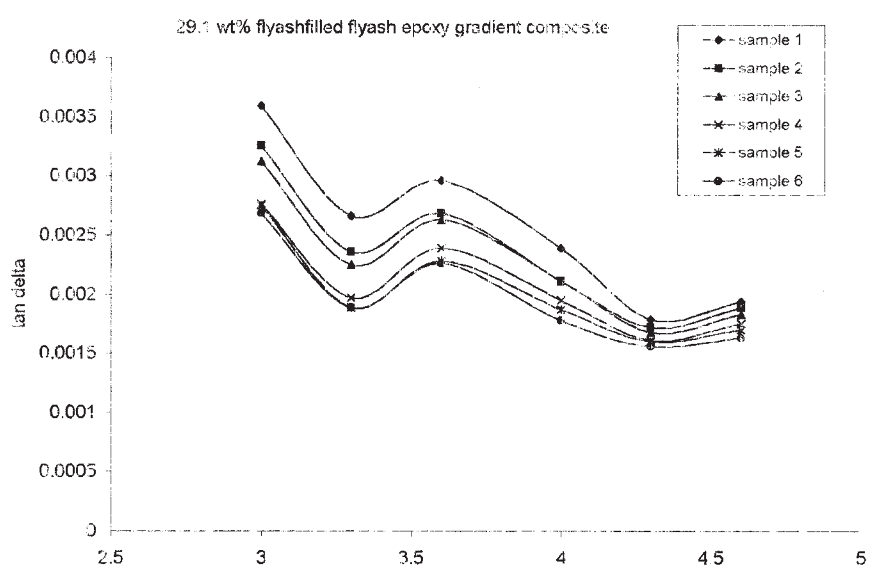

Figure 6 Variation of tan δ versus log f for 29.1 wt % flyash-filled flyash epoxy gradient composite (samples 1 and 6) at 40°C.

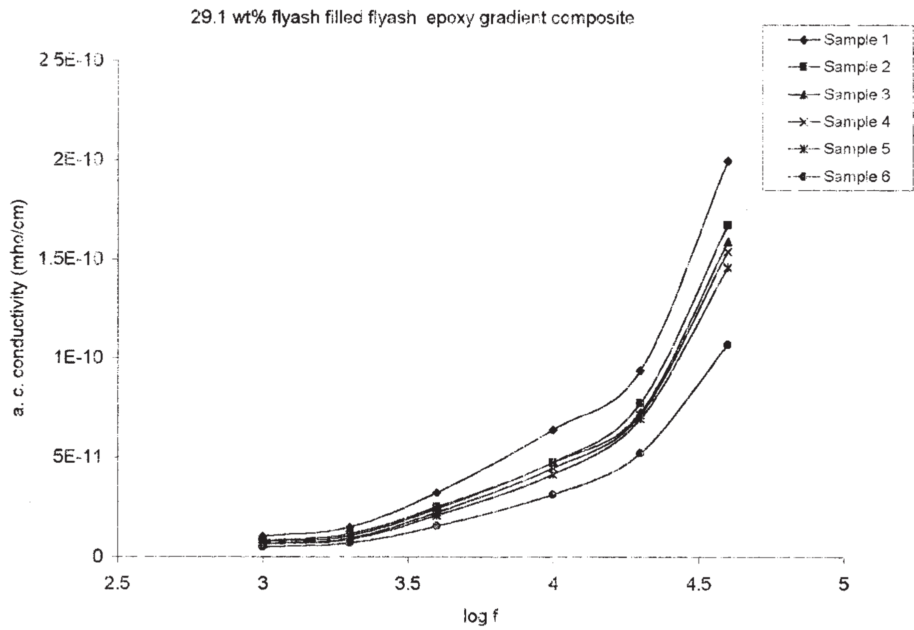

Figure 7 Variation of ac conductivity versus log *f* for 29.1 wt % flyash-filled flyash epoxy gradient composite (samples 1 and 6) at 40°C.

electrons present in flyash. At higher frequencies, this hopping frequency could not match the applied field frequency.

Maximum dielectric constant, tan δ, and ac conductivity values were observed at the bottom of the sample for 29.1 wt % flyash-filled epoxy gradient composites. These maximum dielectric constant, tan δ, and ac conductivity values decreased from periphery to center at all frequencies, because sample 1 has maximum flyash content compared with sample 6, which has minimum flyash content. Between samples 1 and 6 there exists a gradient decrease of flyash and hence there is a gradual decrease in dielectric constant, tan δ, and ac conductivity.

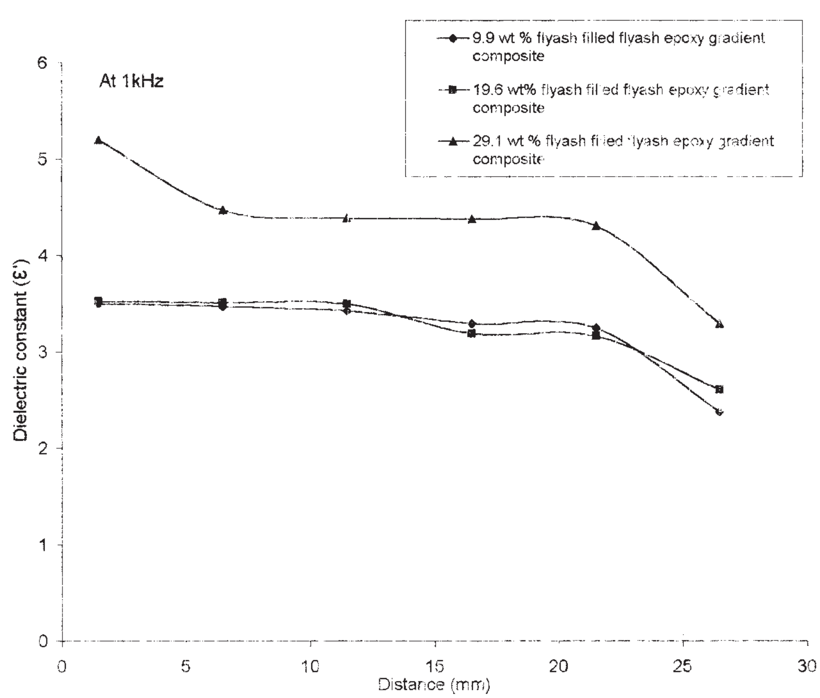

Figure 8 Variation of ε′ versus distance for 9.9, 19.6, and 29.1 wt % flyash-filled flyash epoxy gradient composite at 1 kHz frequency.

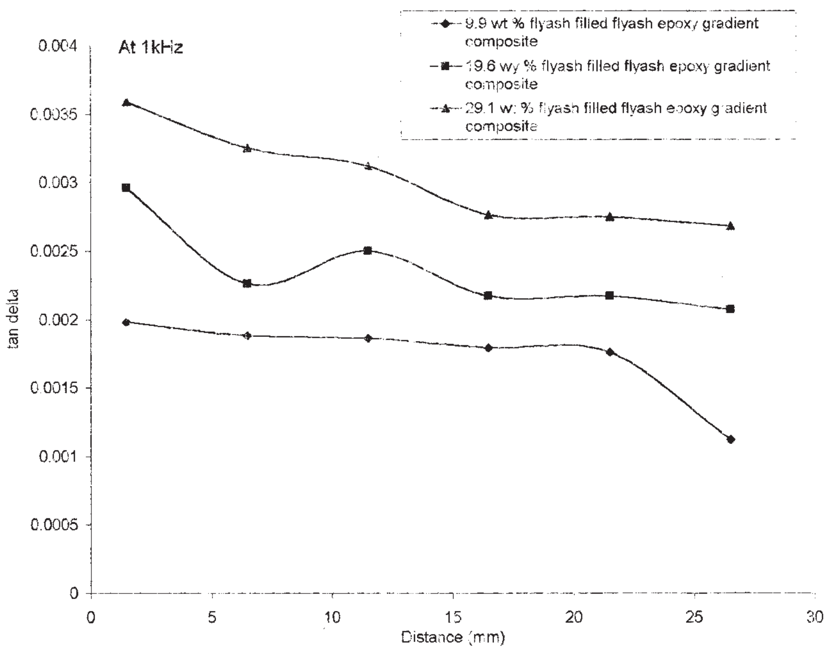

Figure 9 Variation of tan δ versus distance for 9.9, 19.6, and 29.1 wt % flyash-filled epoxy gradient composite at 1 kHz frequency.

Figures 8, 9, and 10 show the variation of dielectric constant, tan δ, and ac conductivity with distance for 9.9, 19.6, and 29.1 wt % flyash-filled epoxy gradient composites (samples 1–6) at 1 kHz frequency. It was observed that for the increase in distance from periphery to center, which is 30 mm, dielectric constant, tan δ, and ac conductivity decrease with increasing different wt % of flyash, because sample 1 has maximum flyash content compared with sample 6, which has minimum flyash content. Between samples 1 and 6 there exists a gradient decrease of flyash and hence there is a gradual decrease in dielectric constant, tan δ, and ac conductivity.

Figure 11 shows the variation of hardness and density with distance. Maximum and minimum shore D hardness values observed were 78 and 69 (Table III. It

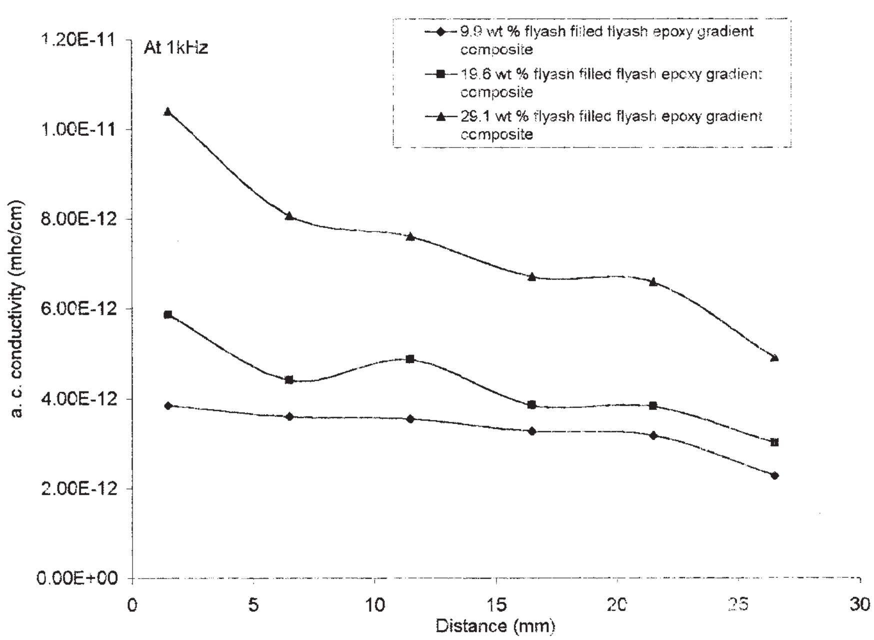

Figure 10 Variation of ac conductivity versus distance for 9.9, 19.6, and 29.1 wt % flyash-filled flyash epoxy gradient composite at 1 kHz frequency.

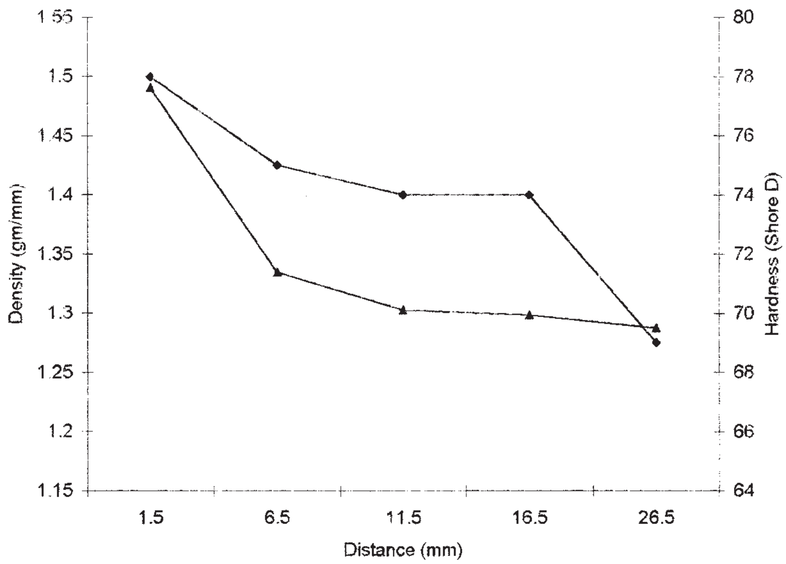

Figure 11 Variation of hardness and density versus distance for 29.1 wt % flyash-filled flyash epoxy gradient composite at 40°C.

was found that the hardness values were very high at maximum flyash contents. Minimum hardness values were observed in the composites, which had the lowest flyash content. This is because increased flyash content increased the silica in the composites.

CONCLUSIONS

1. Gradient composites of epoxy resin filled with different flyash weight percentages were successfully developed.
2. An increase in hardness from 69 to 76 and density from 1.287 to 1.41 g/cc has been observed for the distance from center to periphery.
3. The dielectric constant, tan δ, and ac conductivity increased with the distance from the center to periphery.
4. The dielectric constant and tan δ increased with increased temperature and decreased with increased frequency.
5. The ac conductivity increased with increased temperature and frequency.

TABLE III
Density and Hardness of Graded Flyash Epoxy Composites

Sample no.	Density (g/cc)	Hardness (Shore D)
1	1.4901	78
2	1.3341	75
3	1.3021	74
4	1.2981	74
5	1.2871	69

The authors acknowledge the CTSM, CMM-0022 project for support of this work.

References

1. Funabashi, M. Composite Part A 1997, 28, 731.
2. Funabashi, M.; Kitano, T. In Proceedings of the 67th JSME Spring Ann Meeting, Yokohama, Japan, 1990.
3. Funabashi, M. In Proceedings of the 5th Japan SAMPE Symposium Tokyo, Japan, 1997; p 187.
4. Funabashi, M.; Kitano, T. In Proceedings of the 69th JSME Spring Annual Meeting, Yokohama, Japan, 1992; p 142.
5. Funabashi, M. In Proceedings of the 4th Japan SAMPE Symposium Tokyo, Japan, 1995; p 813.
6. Funabashi, M. J JSME Ser A 1997, 1022.
7. Vinarcik, E. J. SAMPE J 1998, 34, 40.
8. Choe, C. R.; Park, M.; Lee, N. J. In Conference on Composite Materials and Energy, Montreal, Canada, 1995; p 293.
9. Choe, C. R.; Park, M. Proc Macromol Symp 1997, 118, 389.
10. Lee, N. J.; Jang, J.; Park, M.; Choe, C. R. J Mater Sci 1997, 32 2013.
11. Wu, S. L.; Tung, C. J Polym Compos 1995, 16, 233.
12. Tsotra, P.; Freidrich, K. Composite Part A 2003, 34, 175.
13. Delmonte, J. Metal/Polymer Composites. New York: Van Nostrand Reinhold, 1990; 4.
14. Neelakanta, P. S. Handbook of Electromagnetic Materials. CRC Press: Boca Raton, FL, 1995.
15. Chand, N.; Hashmi, S. A. R. Indian Pat. Application 2004.
16. Tim, I.; Simmi, A.; Jeffrey, M.; Douglas, R. Composite Part A 2004, 35, 75.
17. Sindhu, S.; Ananthraman, M. R.; Bindu, P.; Malini, K. A.; Kurian, P. Bull Mater Sci 2002, 25, 599.