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Effect of cenosphere on dielectric properties of low density polyethylene

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ABSTRACT

Dielectric characterization of cenosphere filled low density polyethylene composites is reported in this paper. Cenosphere filled low density polyethylene (LDPE) composites with inhomogeneous dispersions of cenosphere were prepared and dielectric measurements have been performed on these composites in the temperature range 34–110 °C in the frequency range 1–10 kHz. The dielectric constants of the composites with filler concentrations 0%, 10%, 15% and 20 vol.% were measured. Effect of temperature and frequency variations on dielectric constant (ε'), dissipation factor ($\tan\delta$) and a.c. conductivity ($\sigma_{a.c.}$) was also determined. The frequency dependent dielectric and conductivity behaviour of flyash cenosphere filled low density polyethylene (LDPE) polymer composites have been studied. Appearance of peak in the dielectric loss curves for all the concentrations confirms the presence of relaxing dipoles in the cenosphere/LDPE composites. The effect of filler distribution on the dielectric constant is examined and the observed differences are attributed to the differences in two kinds of interfaces present: one formed between the touching cenosphere particles and the other formed between LDPE and cenosphere. With the increase of cenosphere content dielectric constant decreased gradually. Maxwell–Garnett approximation fairly fits for the dielectric data obtained experimentally for these composites.

Introduction

Due to the abundant commercial availability of industrial waste, the need for composite materials with advanced properties and light in weight is felt [1]. The lightweight properties of polymers make them appropriate for weight sensitive structural applications. High cost of the polymer is sometimes a limiting factor so the uses of fillers are preferred for reducing the cost of the components for various applications. Addition of fillers in polymers reduces the cost, but changes the properties. Amendment in the properties of polymers depends on the nature of fillers as well as of the polymers itself. The interaction between the polymer and filler at the interface sometimes improves the mechanical properties of the composite [2–4]. In this communication dielectric of polymer filled with inorganic filler is studied. Changes in the electrical conductivity are reported in the literature with the addition of such fillers. The tensile strength of the composites was influenced by both the fly ash size and the volume fraction. Compared to the largest particle size or the highest volume fraction, an increase in tensile strength was achieved by reducing particle size and/or volume fraction [5–7]. Study of dielectric behaviour and ac conductivity of cenosphere filled polymer composites is a fundamental step towards the engineering materials in future electrical applications.

In the present work, we attempt to understand the effect of distribution of cenosphere on the dielectric constant of polymer. Low-density polyethylene (LDPE) is taken as the representative polymer matrix because it is widely used for electrical wadding in the cable and wire industries due to its high breakdown strength and resistivity [8]. Another advantage of LDPE is that it is relatively easy to mix with inorganic fillers by simple melt mixing; this ensures good dispersion of the filler particles is readily achieved [9]. LDPE composites were used in various applications as decks and docks, packaging film, pipes, tubes, window frames or even as materials in the automobile industry. Various characterizations of such composites are reported [10–15]. This allows us to assume that the addition of fly ash cenosphere into polymers would lead to outstanding ability to control the electrical properties of filler filled polymers. Fly ash is gaining deliberation of forthcoming filler for civilizing various properties of the matrix system whether mechanical, electrical, thermal and rheological studies [16–18]. The conductivity of the cenosphere/LDPE composite is expected to change with increase of the volume fraction of cenosphere. However, the detailed relationship between the cenosphere concentration and the dielectric constant of the composite are still uncertain. The percolation during making of composite needs to understand carefully with consideration of the physical conditions and properties of both filler and matrix that constitutes the composite. Dependence of electrical properties on the shape and distribution of the filler particles was reported by Flandin et al. [19]. The present paper investigates

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Table 1
Chemical composition of fly ash cenospheres.

S. No.	Cenospheres constituents	% Composition (<355 μm)
1	SiO_2	51–58.7
2	Al_2O_3	22.55–25.44
3	Fe_2O_3	3.66–6.6%
4	CaO	0.91–3.89%
5	MgO	0.53.94%
6	Na_2O	0.5–0.6%
7	K_2O	0.5–3.82%

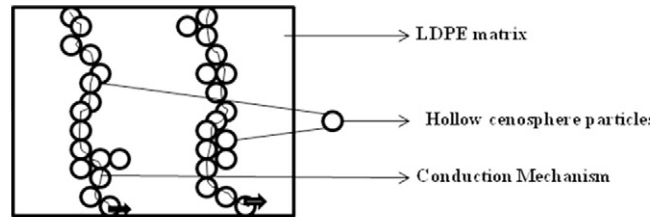

Fig. 1. Schematic illustration of conduction mechanism of inhomogeneous distribution of cenosphere particles in the LDPE matrix.

Table 2
Sample designations with weight % of ingredients in the composite.

S. No.	LDPE/Ceno (wt.%)	Sample designation
1	100/0	Sample 1
2	90/10	Sample 2
3	85/15	Sample 3
4	80/20	Sample 4

Table 3
Density values of the compositions used in the study.

Sample No.	LDPE compound weight (%)	Cenosphere weight (%)	Density g/cc (LDPE cenosphere composites)
1	100	0	0.91951
2	90	10	0.90203
3	85	15	0.89070
4	80	20	0.85550

Table 4
Calculated and experimental values of the dielectric constant for all compositions.

Volume % of cenosphere	Experimental dielectric constant	Theoretical dielectric constant
0	2.323	2.323
10	2.317	2.313
15	2.314	2.313
20	2.312	2.311

a.c. conductivity, dielectric constant and dielectric loss of four types of cenosphere/LDPE composites. The temperature dependence of dielectric constant is investigated in the temperature range of 32–110 °C. Fly ash is used in this used due to its low weight and cost effective nature. The filler is purposefully used to fulfil the environmental needs.

Experimental procedure

Materials

Cenospheres of fly ash used in this investigation were obtained from Sarni Thermal power plant India, of size less than 355μ. Chemical composition of Sarni cenosphere is listed in Table 1. Low density polyethylene (LDPE), trade name Indothene, grade 16 MA 400 was obtained from IPCL Vadodra India.

Composite preparation

Table 2 lists the composite ingredients used for the preparation of composites. Composites were prepared by these ingredients.

Experiment

Dielectric measurement

Capacitance (C) and $\tan\delta$ values of Cenosphere filled LDPE composites were measured by using a Hewlett–Packard, LCR Meter, model 4274 A, in the temperature range 34–110 °C and frequency range from 1 to 10 kHz. Heating rate was kept constant at 2 °C/min. Dielectric constant (ε') was calculated by using the following relation:

$$\varepsilon' = \frac{C}{C_0}$$

where C and C_o are the capacitance values with and without sample, respectively;

$$C_0 = \left[\frac{(0.08854A)}{d}\right]$$

where A (cm^2) is the area of the electrodes and d (cm) is the thickness of the sample. $\tan\delta$ is the dissipation factor and is defined as follows:

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

where ε'' is the dielectric loss.a.c. conductivity ($\sigma_{a.c.}$) was calculated using the following relation,

$$\sigma_{a.c.} = \varepsilon_0 \varepsilon' \omega \tan\delta$$

where, ε_0 is the permittivity of the free space ($8 \times 85 \times 10^{-12}$ Fm^{-1}), $\tan\delta$ the dissipation factor and ω is the angular frequency, which is equal to $2\pi f$.

Density measurements

Density of the cenosphere/LDPE samples was determined by using a high precision Citizen machine, Model CX 265 as per ASTM D 792.

Thermal properties

The measurements were performed using a Mettler Toledo DSC (model 822e). Thermal scan of LDPE/cenosphere samples was run at a heating rate of 10 °C/min in the temperature range from 30 to 130 °C.

Theoretical aspect

Dielectric behaviour of porous particle filled materials has a potential use for the PbZr/Ti filled polymer composites developed by Yamada et al. [20] and proposed the following equation for determining dielectric constant for fillers of ellipsoidal shaped particles [20].

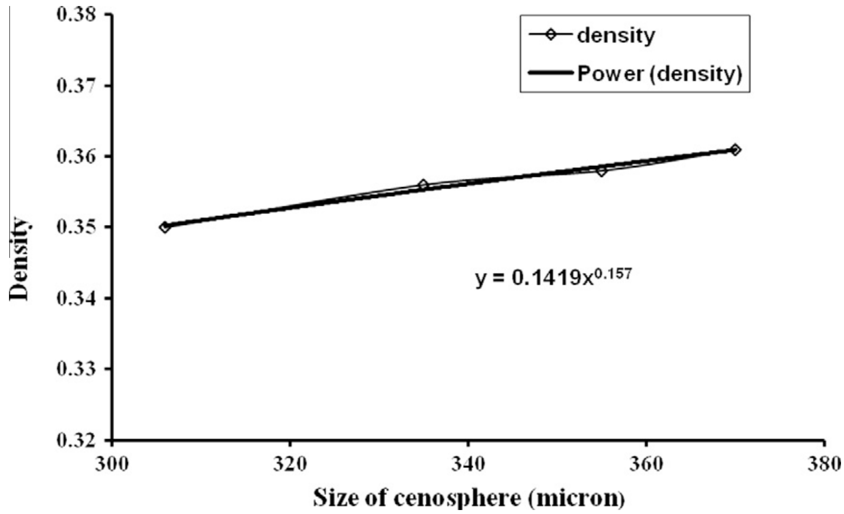

Fig. 2. Exponential relation between densities of cenosphere with size.

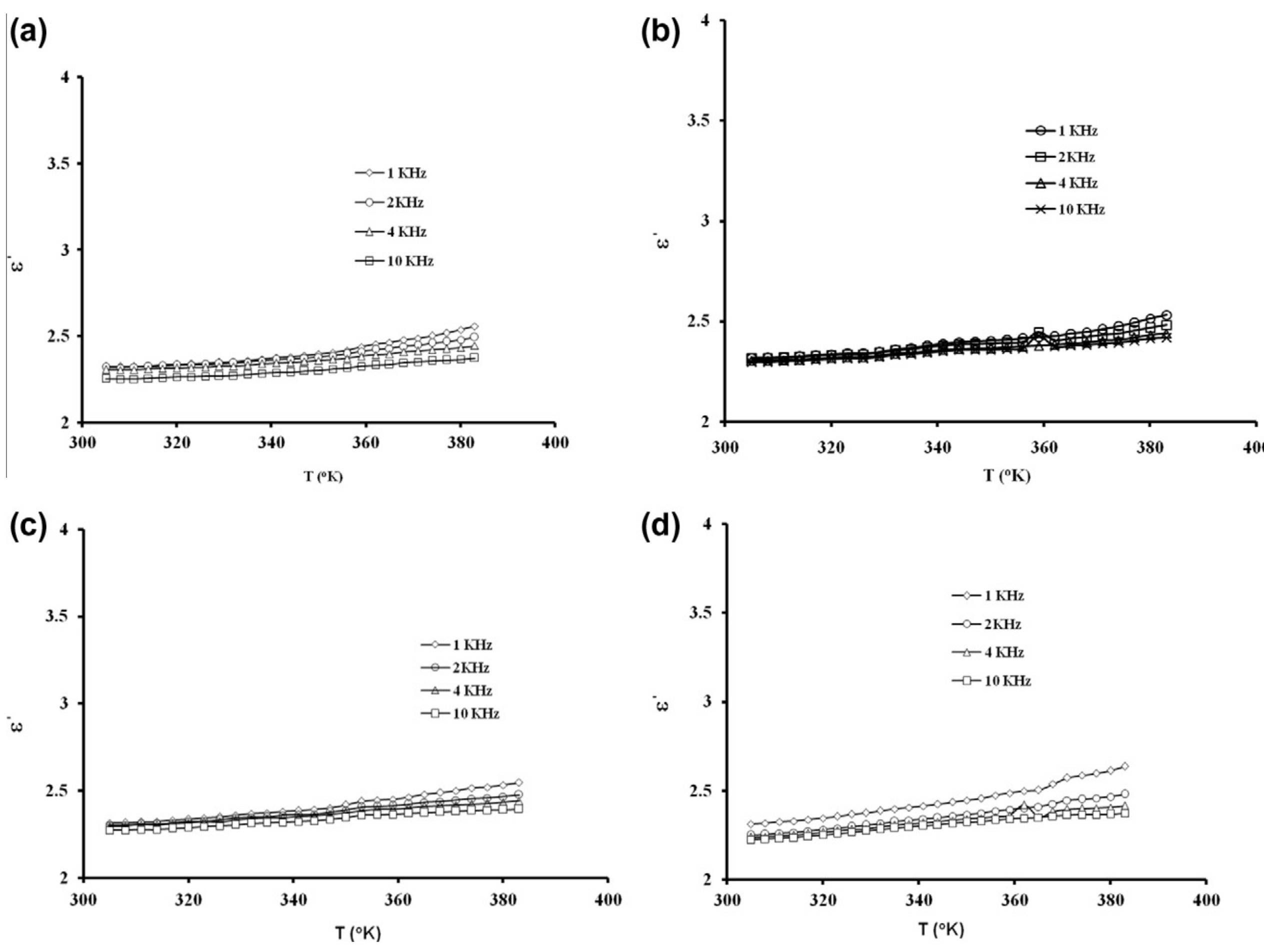

Fig. 3. Dielectric constant for 0% (a), 10% (b), 15% (c) and 20% (d) cenosphere in LDPE matrix.

$$\varepsilon' = \varepsilon_1\left[1 + \frac{mq(\varepsilon_2 - \varepsilon_1)}{m\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)(1 - q)}\right] \tag{1}$$

where, m = parameter attributed to the shape of the filler particles, q = the volume fraction of the particle, ε_1 = permittivity of continuous system, ε_2 = permittivity of ellipsoidal particles.

Here LDPE/Cenosphere composites are taken as the porous particles filled material whose dielectric behaviour is to be determined. LDPE is assumed as the heterogeneous system with spherical cenosphere particles. Eq. (1) could be modified by changing the parameter attributed to the shape of the filler particles (m).

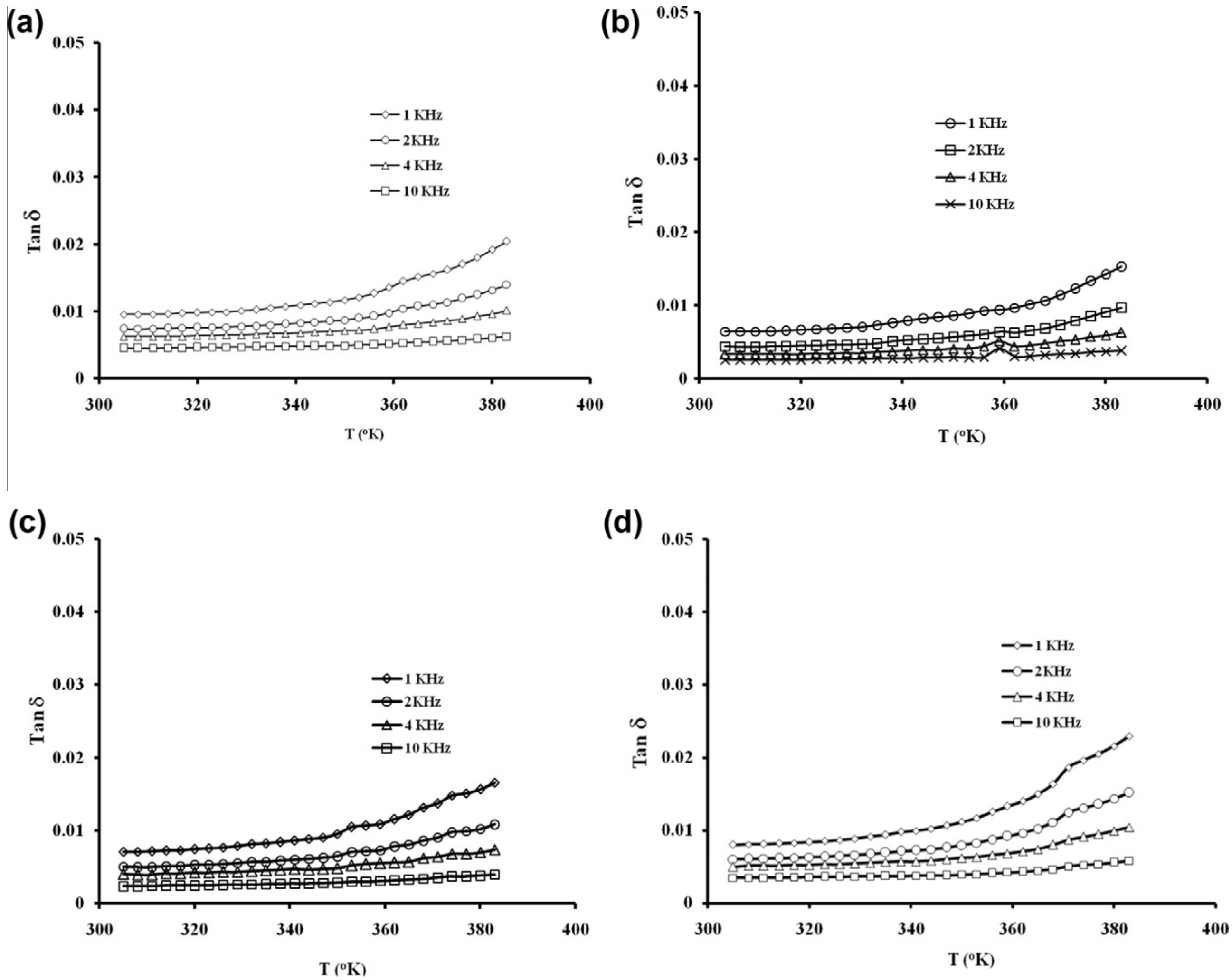

Fig. 4. Dissipation factor for 0% (a), 10% (b), 15% (c) and 20% (d) cenosphere in LDPE matrix.

$$\varepsilon' = \varepsilon_1\left[1 + \frac{(s+d)q(\varepsilon_2 - \varepsilon_1)}{(s+d)\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)(1-q)}\right] \tag{2}$$

where, s is the slope of density and size of cenosphere, d is the difference between the density of composite and matrix, q = the volume fraction of the particle, ε_1 = permittivity of continuous system, ε_2 = permittivity of ellipsoidal particles.

Dielectric permittivity of LDPE at room temperature for 1 kHz is 2.32 where as for cenosphere dielectric permittivity is 2.3. Volume fractions of filler particles are different for all composites.

Calculation of shape parameter

Cenosphere particles are considered as spherical and porous in nature. Therefore, shape parameter depends on porosity dependence also. Constant 's' is involved which is the slope of density vs size of cenosphere particles. For porosity, dependence a constant 'd' is involved which is the difference in the density of composite and density of matrix. Considering the above two factors Eq. (1) can be,

$$\varepsilon' = \varepsilon_1\left[1 + \frac{(0.1419x^{0.157} + d)q(\varepsilon_2 - \varepsilon_1)}{(0.1419x^{0.157} + d)\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)(1-q)}\right] \tag{3}$$

where, s is the slope of density vs size of cenosphere, x is the size of cenosphere in the composite, d is the difference between the density of composite and matrix.

Results and discussion

Dielectric properties

Table 1 gives the chemical composition of cenosphere particles. Table 2 shows the ingredients of the composites prepared with filler concentration. Table 3 lists the density values of the composite samples. Density values of samples 1–4 were 0.9195, 0.9013, 0.8971 and 0.8555 respectively. This shows that sample 1 has no cenosphere content and sample 4 has maximum cenosphere. Table 4 gives the experimental and theoretical values of dielectric constant with volume fraction of the filler. Values of ε' calculated for samples 1–4 at 32 °C were 2.323, 2.317, 2.314 and 2.312 respectively. Minimum ε' value is observed in the case of sample 4. This decrease in value with filler concentration is due to the porous quality of cenosphere particles. Fig. 1 describes the conduction path of the inhomogeneous filler in the matrix. Fig. 2 shows the relation between the sizes of the cenosphere particles with the density; density increases with the size of the particles.

Fig. 3(a–d) shows the dielectric constant for 0%, 10%, 15%, and 20% cenosphere composite samples respectively. Dielectric constant for 0% cenopshere is largest was as for 20% cenosphere is lowest this is due to high porosity in the composite with cenosphere. As the temperature increases dielectric constant also increases up to certain limit (85 °C) but after that not much variation is observed. Between 32 °C and 60 °C these plots show that there is high

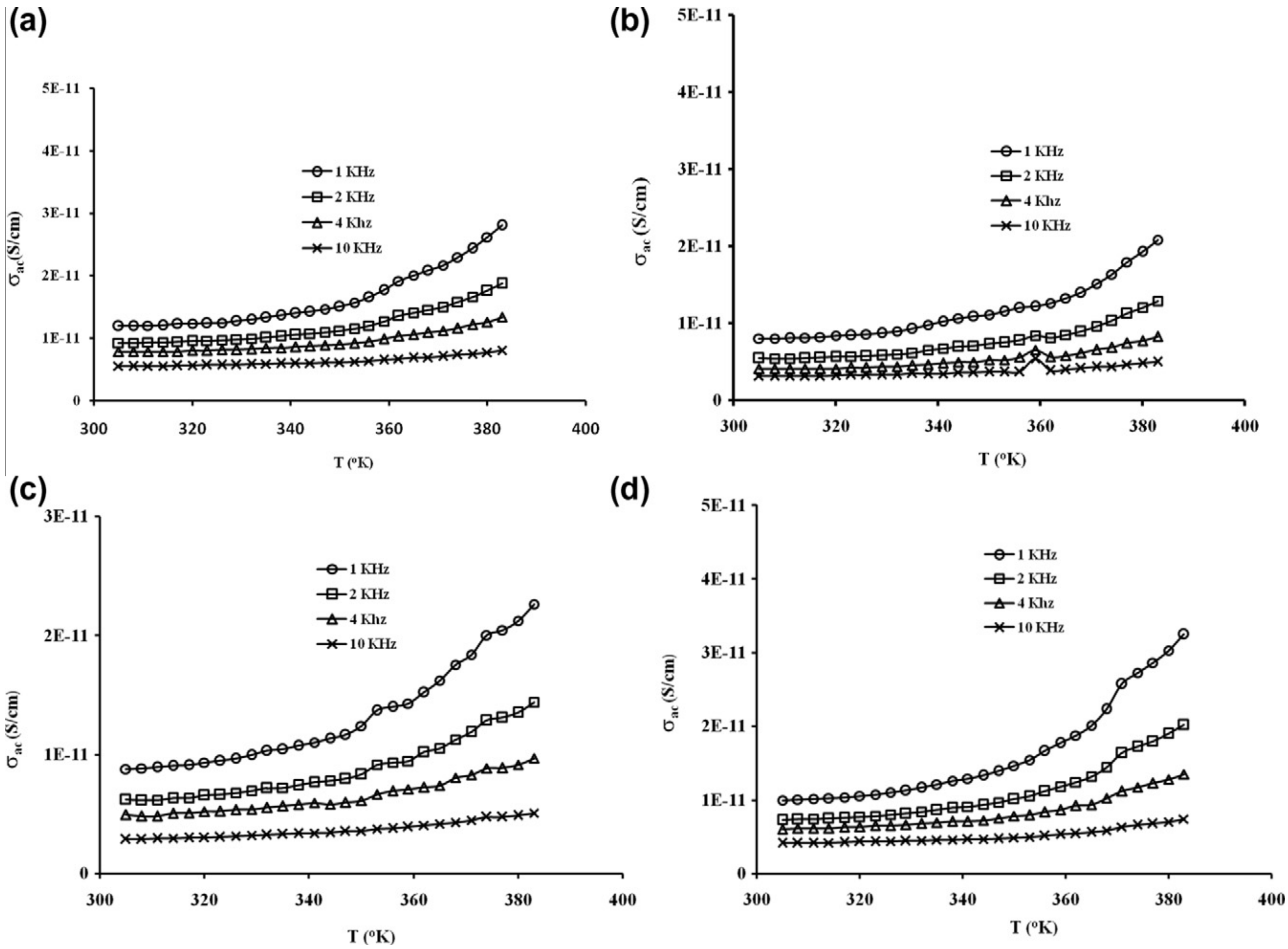

Fig. 5. A.c. conductivity for 0% (a), 10% (b), 15% (c) and 20% (d) cenosphere in LDPE matrix.

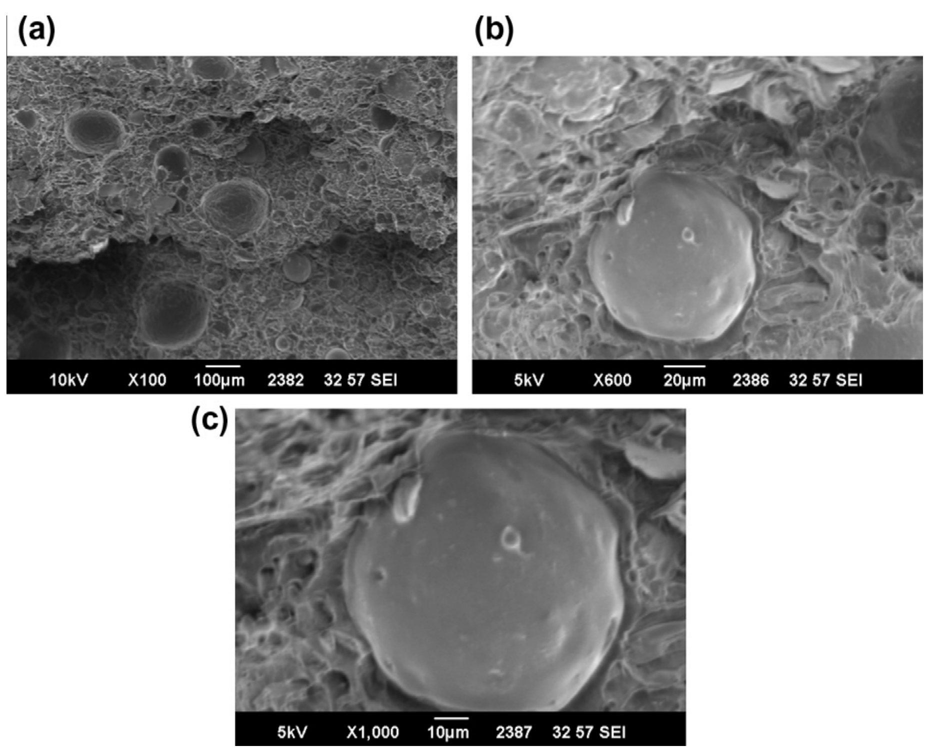

Fig. 6. SEM micrographs of fracture surfaces from LDPE/cenosphere (20 vol.%) cenosphere particles appear as spherical in the micrographs.

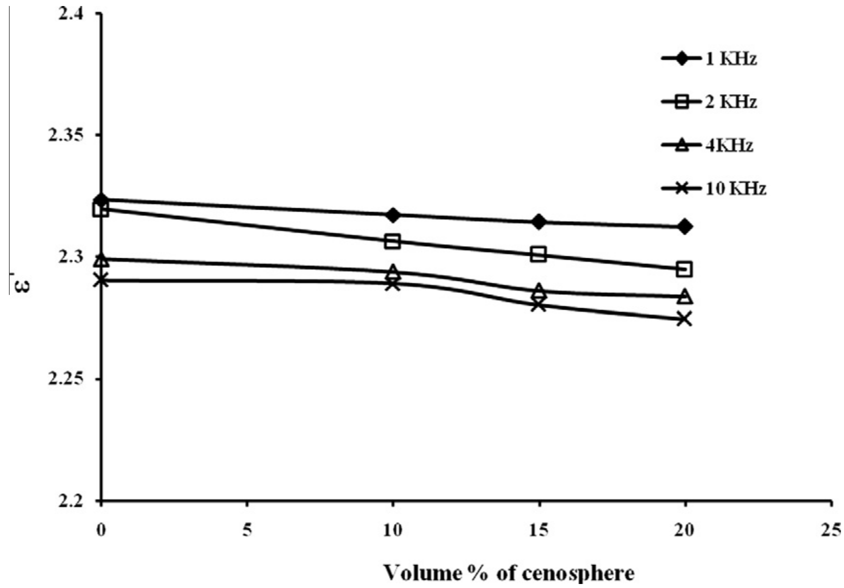

Fig. 7. Variation of dielectric constant filler concentration for different frequencies at room temperature.

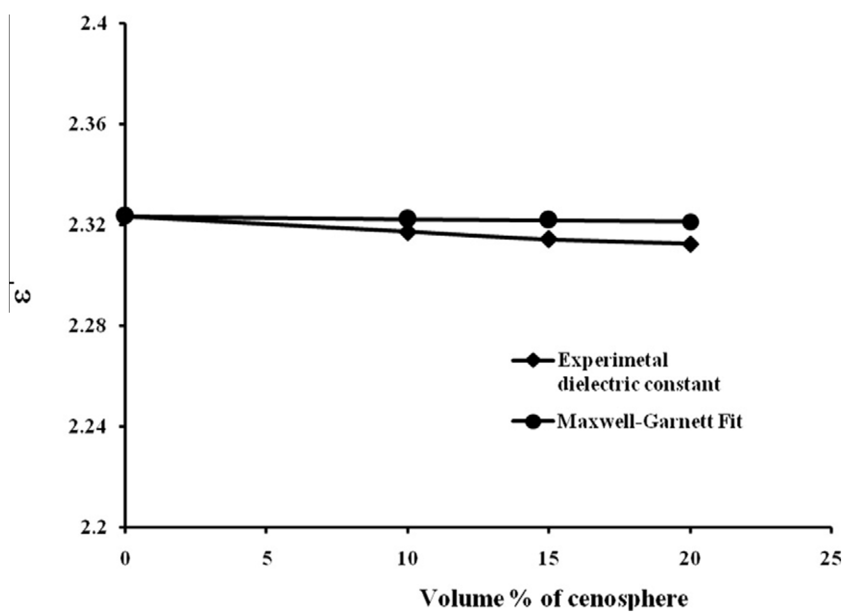

Fig. 8. Maxwell–Garnett approximation fit for the dielectric constant data for various compositions 32 °C.

rise in value. Segmental mobility of the polymer increased with temperature, due to which dielectric constant improved and near the glass transition temperature, the segmental mobility of the polymer chains gave high rise in dielectric permittivity. No major difference between the variation of in case of sample 1 which shows the contribution of the matrix only, because filler is absent in sample 1. The increase in value at higher temperatures between 1 kHz and 10 kHz is due to the availability of more space for the easy rotation of dipoles. Figs. 4(a–d) and 5(a–d), shows the dissipation factor and a.c. conductivity for 0%, 10%, 15%, and 20% cenosphere composite samples respectively. Variations in dielectric properties as seen above are almost similar for 0%, 10% and 15% but some difference is seen in case of 20% cenosphere particles this is made clear by SEM images in Fig. 6(a–c). LDPE is instinctively stronger than the cenosphere aggregates and so the composite ruptures through the interface. Therefore, cenosphere particles were exposed on the fracture surface of the composites. Fig. 6(a) shows that the particles are well dispersed and homogeneously distributed in the matrix. Picture shows that the cenosphere particles are embedded on the LDPE surfaces. At high temperatures the LDPE particles flow to fill any empty spaces between the cenosphere particles, but do not considerably move these filler particles. Dielectric constant of the composites with heterogeneous filler distribution was found to be roughly proportional to the volume fraction of the cenosphere. Fig. 7 shows the variation of dielectric constant filler concentration for different frequencies at room temperature (32 °C) this is clear from the graph that the dielectric constant decreases with frequency also with filler concentration i.e. lowest values of dielectric constant are for 20% cenosphere same trend is seen for dissipation factor from the above graphs. Experimental dielectric constant values were validated with the existing model (Maxwell–Ganett [21]). Fig. 8 shows Maxwell–Garnett

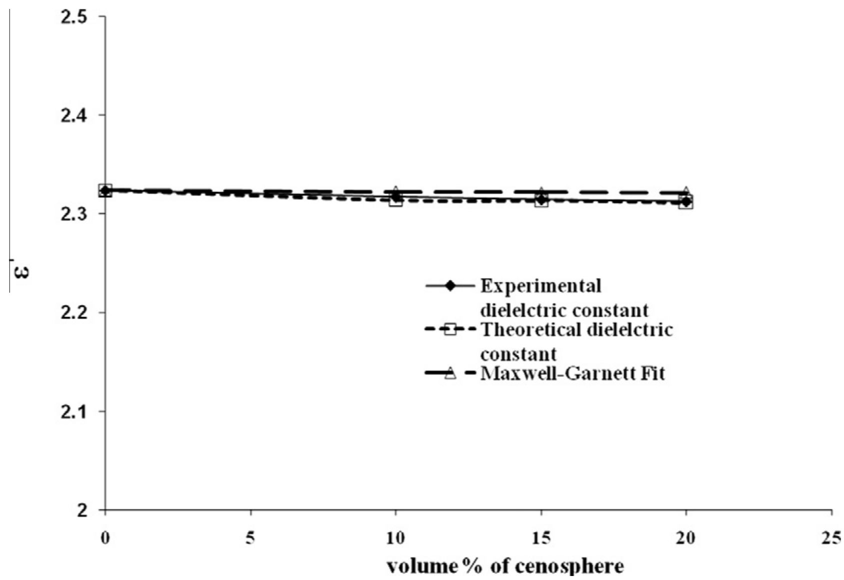

Fig. 9. Theoretical fit for the experimental and Maxwell–Garnett (MG) approximation dielectric constant data of all compositions at 32 °C and 1 kHz.

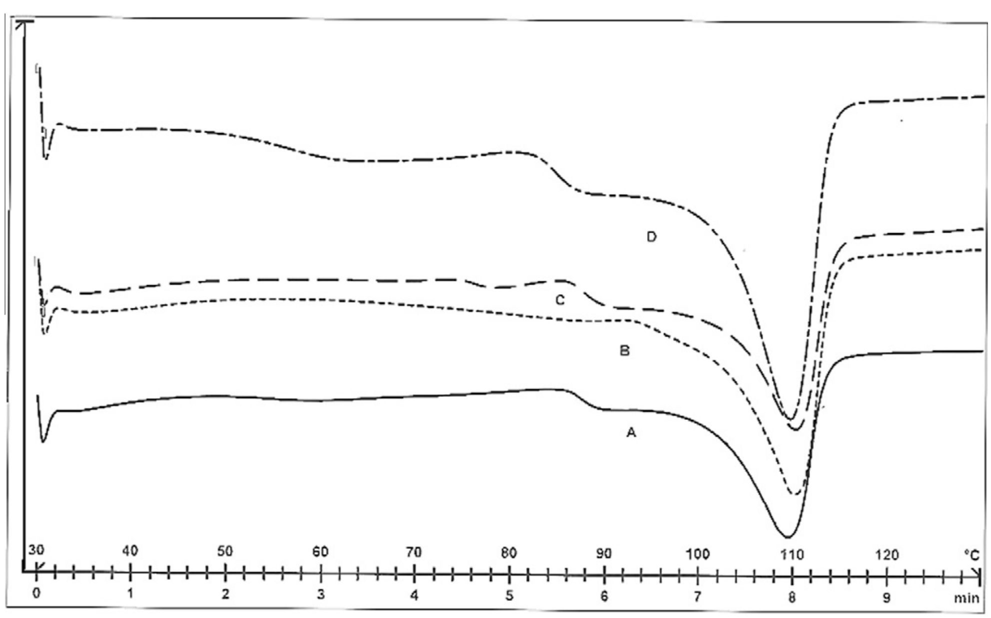

Fig. 10. DSC curves at 10 °C/min heating rate for cenosphere LDPE composites.

Table 5
DSC data of LDPE pure and silane treated cenosphere composite.

S. No.	Sample No.	Heating rate (°C)	Integral (mJ)	Normalized enthalpy (J/g)	Onset (°C)	Peak (°C)	Endset (°C)
1	100/0	10	−138.79	−24.05	118.86	124.24	127.43
2	90/10	10	−189.41	−33.08	116.8	123.07	126.99
3	85/15	10	−92.55	−21.62	115.69	120.97	124.80
4	80/20	10	−136.33	−23.57	112.06	119.97	125.55

approximation fits quite well for this dielectric data. Maxwell–Garnett approximation for dielectric constant of composite is given as follows:

$$\varepsilon' = \frac{v_m \varepsilon_m \left(\frac{2}{3} + \frac{\varepsilon_d}{3\varepsilon_m}\right) + v_d \varepsilon_d}{v_m \left(\frac{2}{3} + \frac{\varepsilon_d}{3\varepsilon_m}\right) + v_d}$$

where ε' is the dielectric constant of composite. ε_m is the dielectric constant of matrix. ε_d is the dielectric constant of cenosphere, v_m is the volume fraction of matrix, v_d is the volume fraction of fillers [21]. Theoretically calculated dielectric constant values are compared with the experimentally determined values and fitted with Maxwell–Garnett model.

From Fig. 9 compares the experimental and Maxwell–Garnett (MG) model with the predicted theoretical results. MG model results comply with experimental data much better than the proposed theoretical model results that use of shape and porosity parameter for the filler. It is obvious that shape and porosity parameter are sensitive to both the density and the size of the cenosphere in the composite. However, volume fraction and dielectric constant are the only subjects of filler constant in MG model, which makes it easier to use. It is reported that almost all simulation models lose their validity, when filler loading of the composite is high which is due to imperfect dispersing of filler particles at high loading. Another possible reason is that air bubbles may be included in the composite.

Fig. 10 shows the DSC curves at 10 °C/min heating rate for cenosphere LDPE composites. The endothermic peak temperature and melting heat were acquired from the figure. Table 5 gives the DSC data for LDPE/cenosphere composites. It is seen that melting peaks of all the composites are between 119.97 °C and 124.24 °C. It means that when cenosphere content is increased the melting temperature shifts to higher but after 15% it again decreases with 20%.

Conclusion

The effect of fly ash cenosphere on dielectric properties of low-density polyethylene (LDPE) has been studied.

1. At low frequency, the variation of relative dielectric constant with frequency shows the presence of material interface polarization processes.
2. The loss tangent peaks appearing at a characteristic frequency suggest the presence of relaxing dipoles in all the samples.
3. The a.c. conductivity shows not much variation with increasing concentration of cenosphere.
4. Proposed theoretical model well fits the experimental data and the existing Maxwell–Garnett approximation.

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