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# Effect of Fly Ash Cenosphere on Electric Properties of Polypropylene

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***Abstract***
*Present work deals with findings on electrical properties of cenosphere filled polypropylene composites. Frequency dependence of the dielectric constant (ε') of the composite samples was carried out at ambient temperature. A theoretical model is proposed for the electrical conductivity of porous polypropylene/cenosphere composites. Role of addition of these cenosphere particles on electrical properties such as dielectric constant, tanδ, dc conductivity and ac conductivity were investigated. Increase of fly ash cenosphere has decreased the dielectric constant while dissipation factor increased and the dc conductivity decreases with increasing content of fly ash cenosphere. Theoretical results were compared with experimental data.*

***Key Words:*** *Polymer, Electrical properties, Porosity, Particle-reinforced composites*

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## INTRODUCTION

Polypropylene (PP) is a polymer prepared catalytically from propylene having an isotatic replacement of a hydrogen atom by a methyl group on alternate carbon atoms in the main chain. Is PP suitable for items such as trays, funnels, pails, bottles, carbons and instrument jars that have to be sterilized frequently for use in clinical environment? It is a translucent material with excellent mechanical properties. A new class of materials has emerged as conducting polymers due to their excellent electrical, optical and chemical properties. Conductivity of these materials can be varied by properly chosen filler material which offers a new concept of charge transport mechanism[1].

Fly ash (FA) is a coal residual product generated from natural coal fired in thermal power stations. Huge quantity of FA is disposed by large number of coal fired power plants all over the world, causing serious environmental problems[2]. Less than half of the ash is used as a raw material for concrete industrialization and construction; the remaining is openly deserted on land side. Due to environmental convention, new traditions of utilizing FA have to be explored in order to uphold the environment and afford useful habits for its dumping. The main advantages of using cenospheres are: reduced raw materials cost, improved flow ability, reduced resin demand, improved insulation values, reduced end product weight, resistant to resin absorption[3]. Hence, there is considerable interest in utilization of FA cenosphere as filler. Dielectric spectroscopy is a valuable experimental technique for understanding the phenomenon of charge transport in conducting polymers. Low frequency conductivity and dielectric measurements have proven to provide information on the conduction mechanism that d.c. conductivity measurement alone does not provide[1].

It is reported by McLachlan[4] and Vovchenko *et al.*[5] that electrical conductivity is dependent on a number of factors, including filler particle shape, size and distribution, and the ability to form homogeneous mixtures on combination with resin. It is reported in the literature that variations in the porosity, as well as size, orientation and shape of the pores, edge thickness and length, and cell morphology (open-cell or closed-cell structure) cause important variations in their material properties[6,7]. In an effort various models have been proposed to predict the electrical conductivity behavior of composites based on numerous factors as described in detail by Lux[8]. Nikhil Gupta *et.al.* measured dielectric constant, dielectric loss and electrical impedance for syntactic foam composites with respect to temperature and frequency.

Dielectric constant and loss are found to decrease with increase in frequency and with increase in temperature in the range of 40–140°C[9]. Various Fillers are used along with polymers to improve their properties. The performance of filled polymers is generally determined on the basis of the interface attraction of filler and polymers.

Fillers of varying particle size and characteristics are receptive to the interfacial interactions with polymers. Incorporation of cenosphere into the polymeric network introduces uniform porosity throughout the matrix and is advantageous for various applications. Fly ash is used as filler for long. It is a fine ash byproduct commonly produced by the combustion of coal during the generation of electrical power. It is generally spherical in form. Fly ash offers a noteworthy economic advantage over other fillers but does tend to impart a grayish color to the product upon used in large concentrations[10-13]. The present study deals with the effect of its concentration on the properties of flyash filled PP.

## MATERIAL AND METHOD

### Raw Materials

Cenospheres of fly ash used in this investigation were obtained from Sarni Thermal power plant of size less than 355μ, Bulk Density- 10.43–12.70 Kgm$^3$, Color-Grey-Light -Grey - Off White. Isotatic Polypropylene (PP) with density 0.905 gm/cm³ was obtained International Plastic Corporation Limited (IPCL) Vadodara.

### Composite Preparation

Table 1 lists the composite ingredients used for the preparation of composites. Weighed amount of cenosphere were mechanically mixed with PP granules and conglomerated on a two roll mill by keeping the rollers at 200°C. Four compositions 100/00, 90/10, 85/15 and 80/20 of PP/cenosphere were prepared respectively in identical conditions[14]. The films were removed from the rollers and then compression moulded as thick uniform sheets (10cm x 10cm x 0.2cm) in hot press. Approximately 0.2 cm thick circular disc were used for this study.

***Table.1*** *Ingredients used in making PP and cenosphere Composites with density values.*

| S.No. | PP/ Cenosphere Composition | Density of PP/cenosphere composites (g/cc) |
|---|---|---|
| **1** | 100 | 0.915 |
| **2** | 90/10 | 0.837 |
| **3** | 85/15 | 0.763 |
| **4.** | 80/20 | 0.681 |

### Theoretical Aspect

Liu *et.al*.[15,16] developed a theoretical model for DC conductivity in which they considered the pores to be octahedral void units like body centered cubic lattice

$\sigma_{dc}$ = a(1-θ)/ [(1-0.121) (1- θ)1/2] Eq. (1)

Here factor a is considered as the fine structure of the porous body, which is depended on the preparation techniques, θ is the porosity of the porous composites. In our previous published article[17] this model is modified for foamed PP composite which is now applied for cenosphere filled polypropylene composites. In this study PP (Polypropylene) cenosphere composites are considered as porous composites since cenosphere are hollow sphere filled with inert air or gas. Due to the hollow structure cenosphere have low density so these composites can be assumed as foam. It is assumed that equation 1 could also be applied for porous composites, by some needful changes. Such as, constant 'a' is replaced by a density factor α, which is derived from the slope of density and concentration of cenosphere particles in the composites. θ is again porosity but it is assumed that the cenosphere particles are not of same size (1 to 0.121) so the factor which is structure depended will be negligible here .The exponent term is replaced by a term 's' which will be porosity dependent , 's' is derived by equation ,

$$s = (1\text{-}t) + (1\text{-}\theta) \qquad \text{Eq. (2)}$$

*Where,*
t is the thickness of porous PP composites
θ is the porosity of the porous PP composites
Hence the final equation becomes,

$$\sigma_{dc} = a(1\text{-}\theta)/ [\ (1\text{-}\theta)s] \qquad \text{Eq. (3)}$$

DC Conductivity could be calculated based on porosity with Eq. (3)

**Dielectric measurements**
Capacitance (C) and tanδ values of Cenosphere filled PP composites were measured by using a Hewlett - Packard, LCR Meter, model 4274 A, in the temperature range 34 to 110°C and frequency range from 1 to 10 kHz. Heating rate was kept constant at +2 °C/min. Dielectric constant k was calculated by using the following relation

$$\varepsilon' = \frac{C}{C_0} \qquad \text{Eq. (4)}$$

Where C and Co are the capacitance values with and without sample respectively,

$$C_0 = \left[\frac{(0.08854A)}{d}\right] \text{ pF} \qquad \text{Eq. (5)}$$

Where A ($cm^2$) is the area of the electrodes and d (cm) is the thickness of the sample. tanδ is the dissipation factor and is defined as follows

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad \text{Eq. (6)}$$

*Where* $\varepsilon''$ is the dielectric loss.

**dc Conductivity Calculation**
Sliced samples were coated by air-drying type conducting silver paint on both the sides. Resistance values of these sliced PP cenosphere samples were measured by using a Keithley Electrometer model 61°C. The dc conductivity was calculated from resistance by using following equation

$$\sigma_{dc} = 1/\rho = \frac{L}{RA} \qquad \text{Eq. (7)}$$

*Where,*
$\sigma_{dc}$ is the dc conductivity of PP Cenosphere,
R is the resistance,
A is the area
L is the thickness of the sample.

**ac Conductivity Calculation**
ac conductivity ($\sigma_{ac}$) was calculated using the following relation,

$$\sigma_{ac} = \varepsilon_0 \varepsilon' \omega \tan\delta$$

*Where,* $\varepsilon_0$ is the permittivity of the free space (8 x 85 x 10–12 $Fm^{-1}$), tan d the dissipation factor and ω is the angular frequency, which is equal to $2\pi f$.

**Density Measurement**
Density was tested as per ASTM D 792, of all the samples of PP/cenosphere composites by using a Mettler Toledo

balance listed in table 1.

**RESULTS AND DISCUSSION**

The electrical properties of polymer foams can be affected by the level of porosity present in it. Table 1 lists the ingredients used to prepare the composites with their composition and the density values of the composites. Density values of sample 1 to 4 were 0.905, 0.837, 0.763, 0.681 g/cc respectively. This shows that sample 4 has maximum Cenosphere and sample 1 has no Cenosphere content. It is clear from the values that cenosphere are porous and decreases the density sequentially.

Dielectric constant and dissipation factor are the main indexes of the dielectric to define dielectric properties; frequency and temperature dependence are its characteristics the regions where the mobility of functional group or molecular segment occur some variation or maxima is observed. Maximum Dielectric constant is observed in case of pure PP composite with no cenosphere content. This high Dielectric constant value is contributed by PP (Polypropylene) matrix. Figure 1 shows the schematic of the composites studied. The fluctuations seen are most likely due to non uniformity in temperature and non uniform distribution in the sample disc. Dielectric constant and dielectric loss with respect to frequency and various temperatures for Pure PP are shown in Figure 2 (a and b) respectively. It is seen that at 34°C its value is 3.5 and it is increasing with increasing temperature. Same trend is seen for dissipation factor. A hump is seen around 368 K. Dielectric constant and dissipation factor both decreases with increase in frequency. This may be due to realignment coupled with decrease in moisture content. The other three types of composites show slow increasing trend as the frequency increases. In this study, the dielectric constant was measured in the low frequency region since material used for the sensor (capacitive sensors) work in the low frequency region. With increasing frequency a drop in the dissipation factor was observed at higher temperatures but this effect may be due to the poor contact of the electrode and material.

Figure 3 clearly shows the effect of adding 10% cenosphere in 90% polypropylene matrix. Values of dielectric constant suddenly decreases which shows that the cenosphere are porous and the matrix gets inside it due to bonding between PP and cenosphere which causes decrease in dielectric constant. Similarly increasing the concentration of cenosphere to 15%, 20% it is seen that the dielectric constant continuously decreases which is due to porous nature of these composites show in figures 4 and 5.

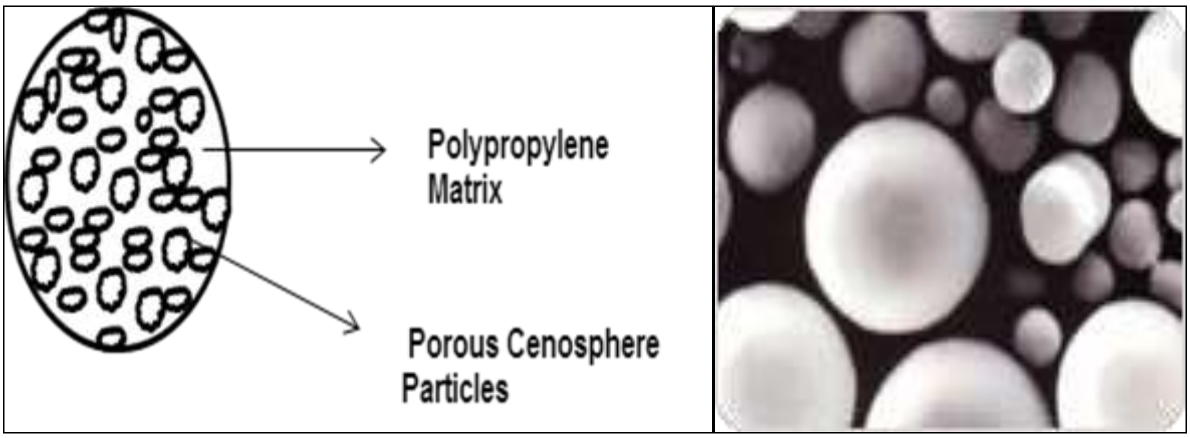
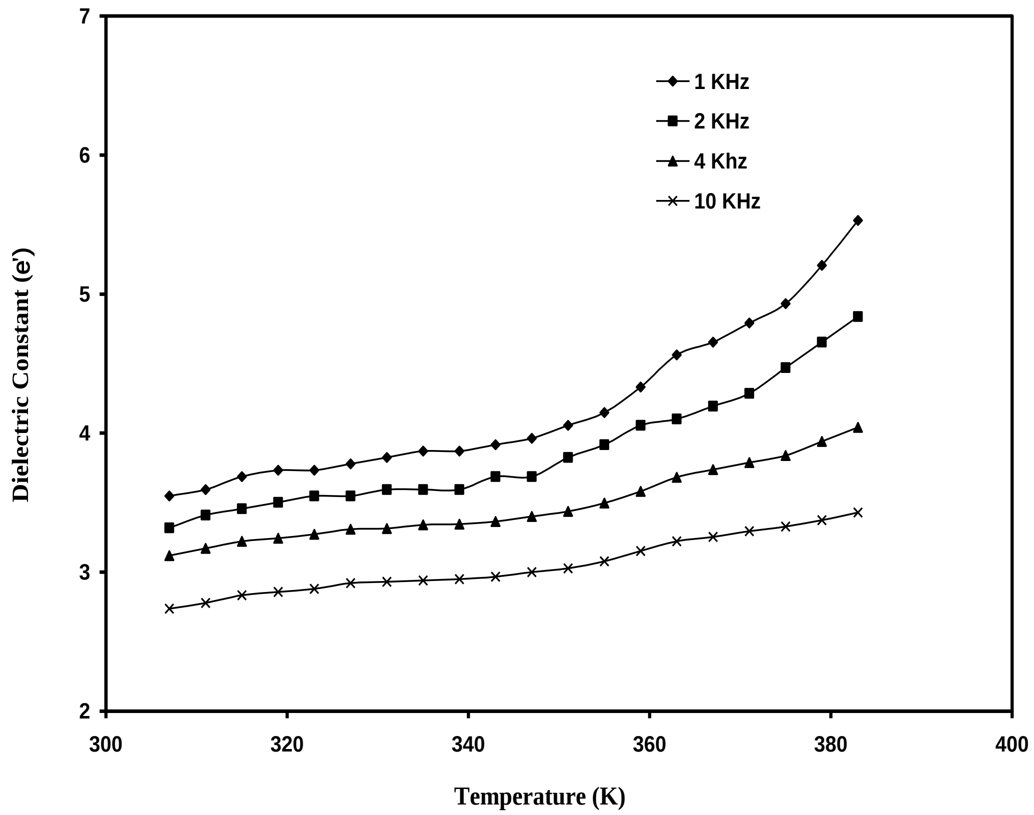



***Fig 1:*** *Schematic of Composites.*



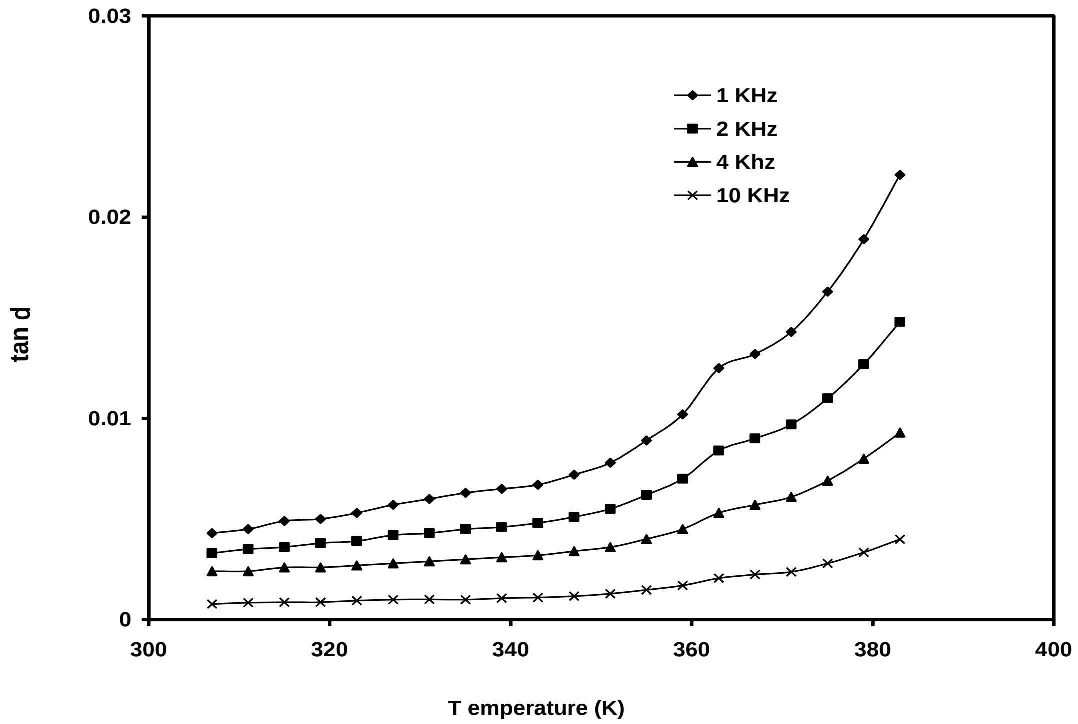
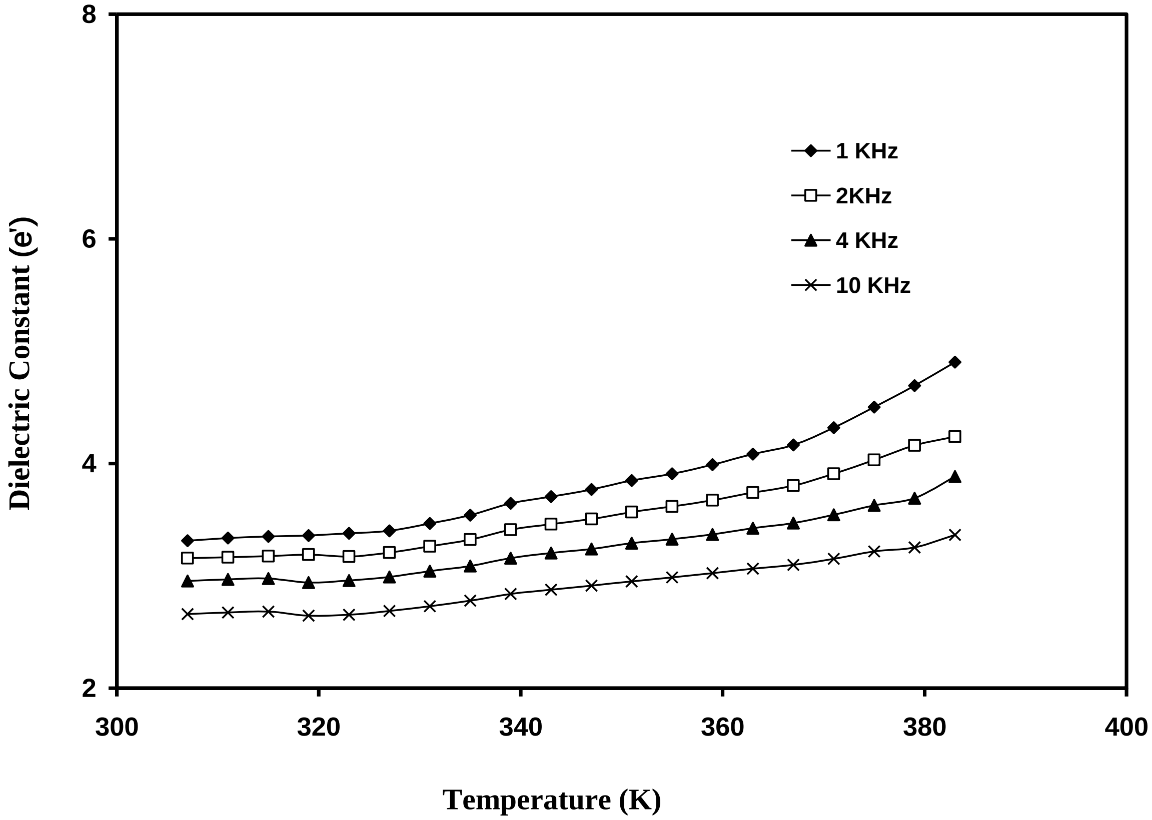




***Fig 2:*** *(a) Dielectric Constant & (b) Dissipation Factor for Pure PP Composite with 0% Cenosphere.*



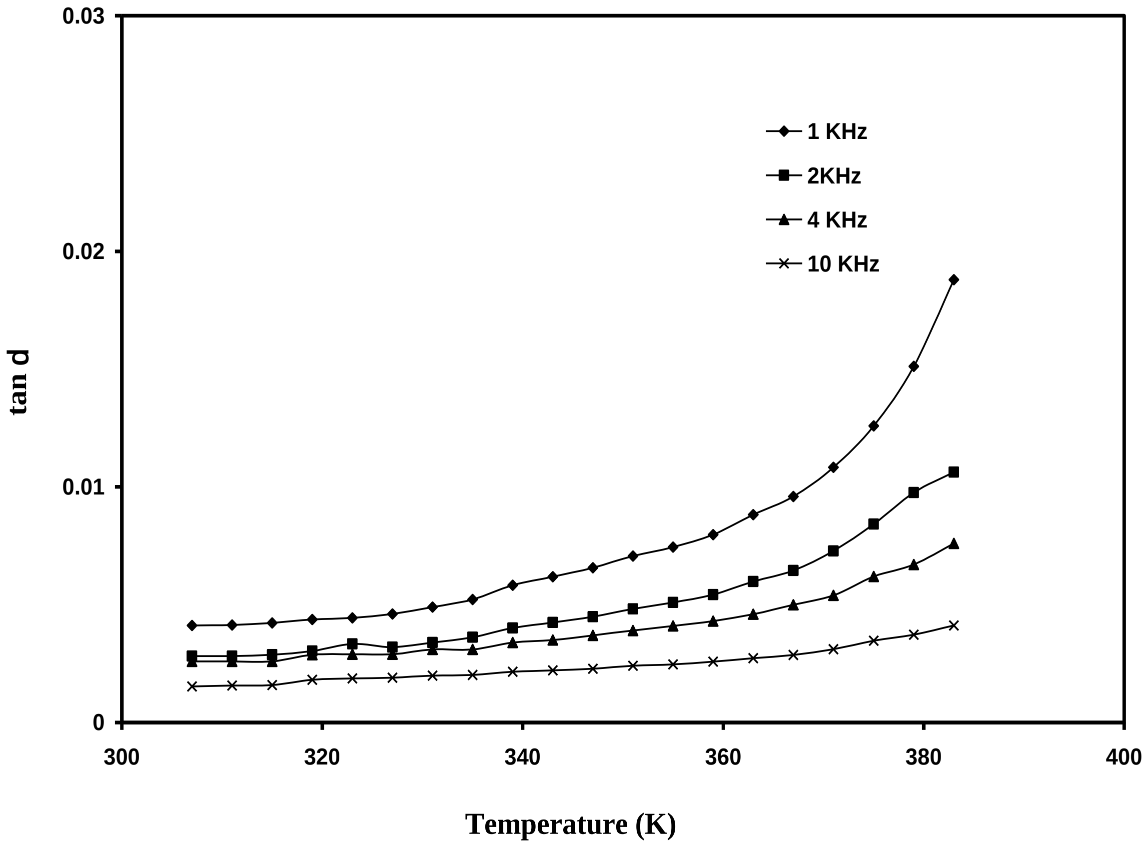
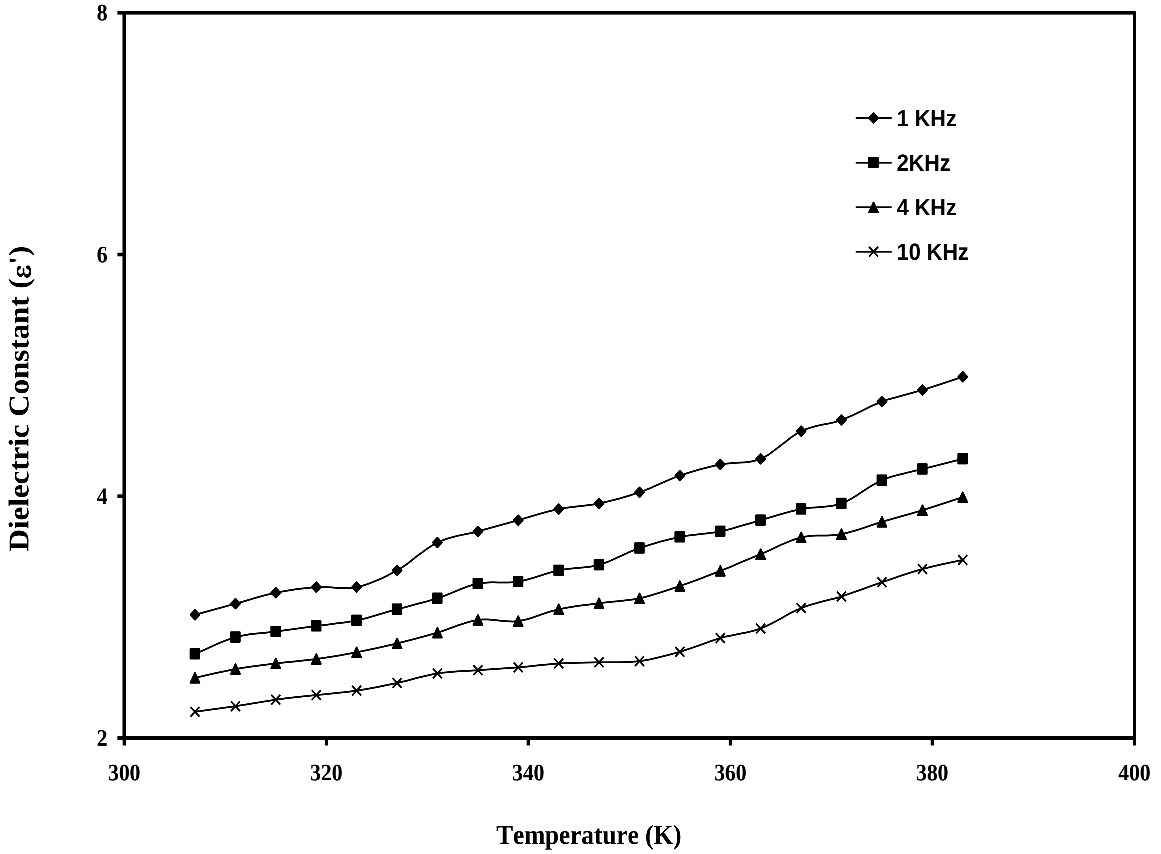




***Fig 3:*** *(a) Dielectric Constant & (b) Dissipation Factor for 90% PP with 10% Cenosphere.*



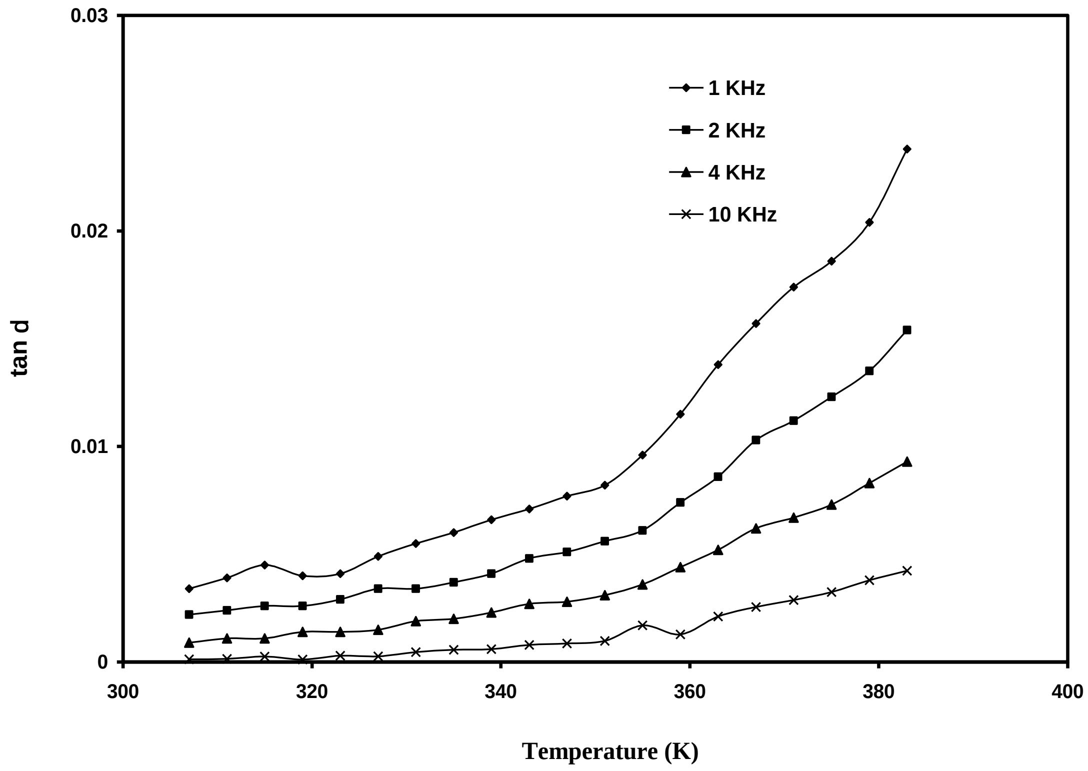
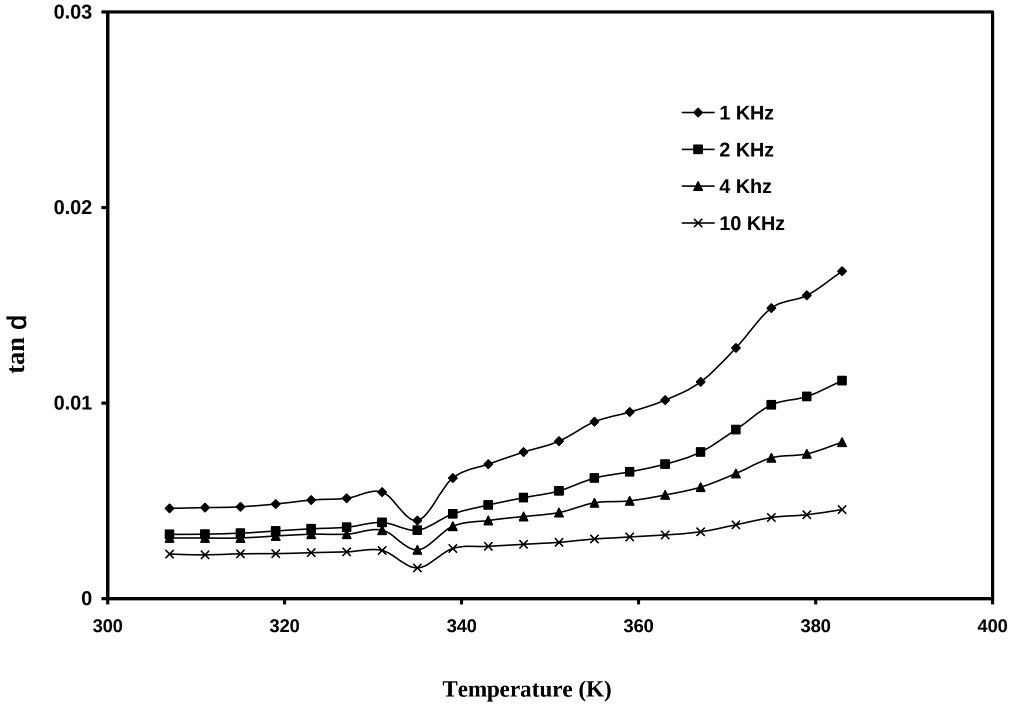




***Fig 4:*** *(a) Dielectric Constant & (b) Dissipation Factor for 85% PP with 15% Cenosphere.*



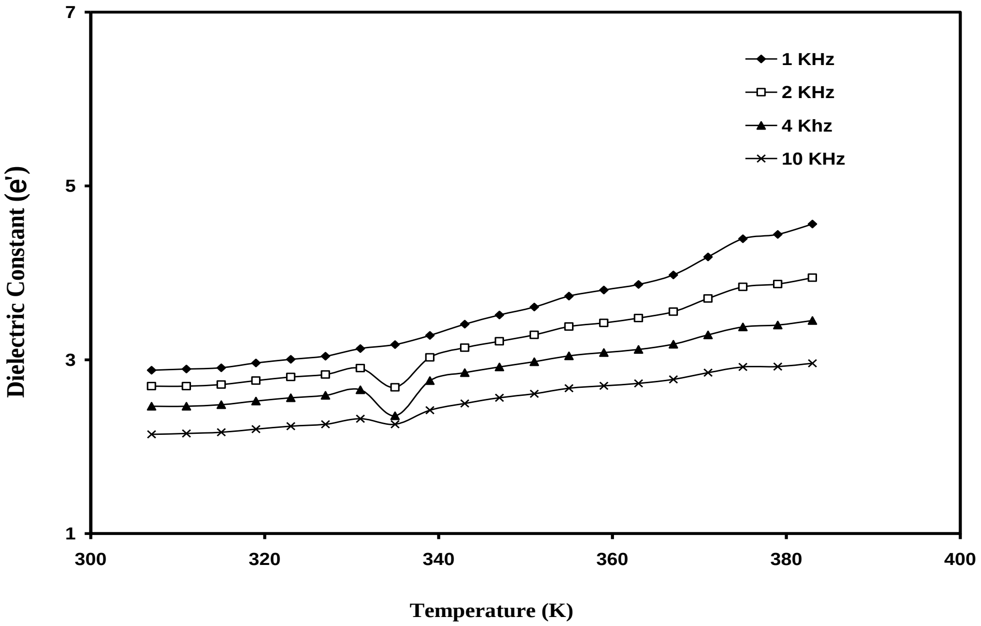




***Fig 5:*** *(a) Dielectric Constant & (b) Dissipation Factor for 80% PP with 20% Cenosphere.*

At low temperature (approximately 333 K) it is noticed that tan δ variation is small which may be due to insignificant vibrations of polymer chain which in agreement with the observations of Wintersgill and Fontanella[19]. It is clear from figure 5, when 20% cenosphere is added to PP dielectric constant is decreased up to 2 for 10 kHz and decreasing trend is also observed in dissipation factor. It is observed that an endothermic valley (small value of tan δ) is seen at 335K for every frequency. It is also eminent that by increasing the percentage of cenosphere there is no effect of temperatures is observed which might be a result of systematic segregation of composite particles. These variations in dielectric constant are due to voids, moisture and the size and shape of the filler particle.

Figure 6 presents the dependence of the dielectric constant, on the weight percent of fly ash in polypropylene, obtained at the frequency of 1, 2, 4, 10 kHz and at room temperature (32°C). A sharp decrease of the dielectric constant values is clearly observed for all the composites studied.

dc Conductivity of the composites with different weight % of cenosphere is seen in figure 7 it is clear that dc conductivity decreases with increasing the % of cenosphere in the composite. Using the proposed equation 3[17], dc conductivity of PP/cenosphere composites is calculated. Validation of theoretical σdc with experimental results is shown in figure 8. Decrease in ac and dc conductivity is also studied by Murugendrappa *et.al* in their communication for polypyrrole–fly ash composites[18]. From the study of dc conductivity as a function of temperature, it is uncertain that both the pure PP as well as the PP/FA composites was semiconducting in nature. Moreover, the conductivity was found to decrease with the addition of FA in PP, the decrease of conductivity with the addition of FA may be attributed to the localization of charge carriers. In PP/Cenosphere composites, polarization due to hopping of charge carriers dominates. This decrease in conductivity values is attributed due to presence of fly ash particles of larger dimensions, which constrains the hopping of charge carriers between the available sites. Same trend in dc conductivity is observed by Murugendrappa *et al*[18] Figure 9 shows the ac conductivity of the pure PP composite. ac conductivity as obtained from experiment shown in figure.9 that except for the amplitude all ranges of frequencies show first slow rise in ac conductivity with increase in temperature. But beyond 360 K ac conductivity increases sharply. Figure 10 shows an endothermic valley at 335 K for ac conductivity plot with 20% cenosphere in the composite and an exothermic peak at 374 K same peak is seen at 333 K by Singh[19] for ac electrical properties of PP films measured at temperature range between 303 and 413 K. This shift in peak shows gradual decrease in ac conductivity by increasing weight percent of cenosphere in PP up to 20%. Very slight variations were observed for 10% and 15% cenosphere. Table 2 lists the ac conductivity values of different composites of cenosphere in PP.

***Table 2** ac conductivity values of the composites.*

| S.No. | PP/ Cenosphere Composition | ***ac* conductivity values (Mho)** | | | |
|---|---|---|---|---|---|
| | | 1 kHz | 2 kHz | 4 kHz | 10 kHz |
| 1 | 100 | $8.48 \times 10^{-12}$ | $1.21 \times 10^{-12}$ | $1.86 \times 10^{-11}$ | $2.27 \times 10^{-11}$ |
| 2 | 90/10 | $7.59 \times 10^{-12}$ | $9.89 \times 10^{-11}$ | $1.70 \times 10^{-11}$ | $2.26 \times 10^{-11}$ |
| 3 | 85/15 | $7.38 \times 10^{-12}$ | $9.86 \times 10^{-11}$ | $1.69 \times 10^{-11}$ | $2.15 \times 10^{-11}$ |
| 4. | 80/20 | $6.87 \times 10^{-12}$ | $9.78 \times 10^{-11}$ | $1.54 \times 10^{-11}$ | $1.94 \times 10^{-11}$ |

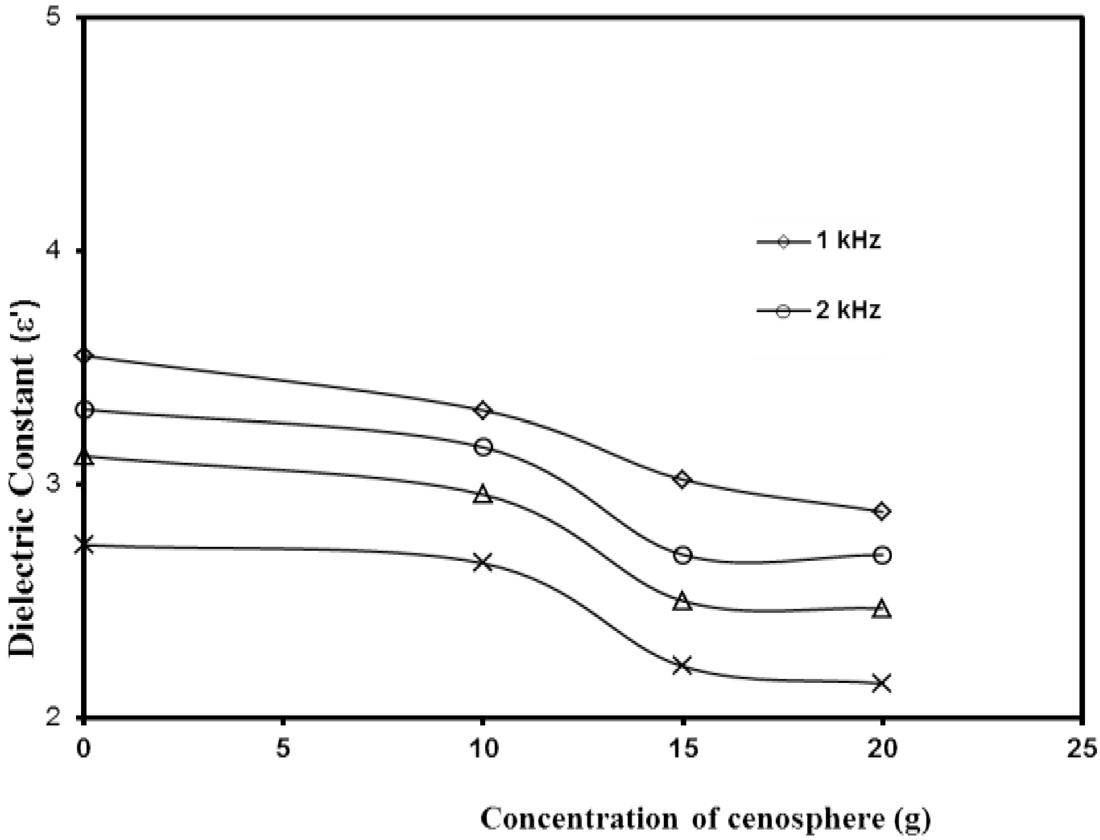



***Fig 6:*** *Variation of Dielectric Constant for Different Volume Fractions of Cenosphere.*

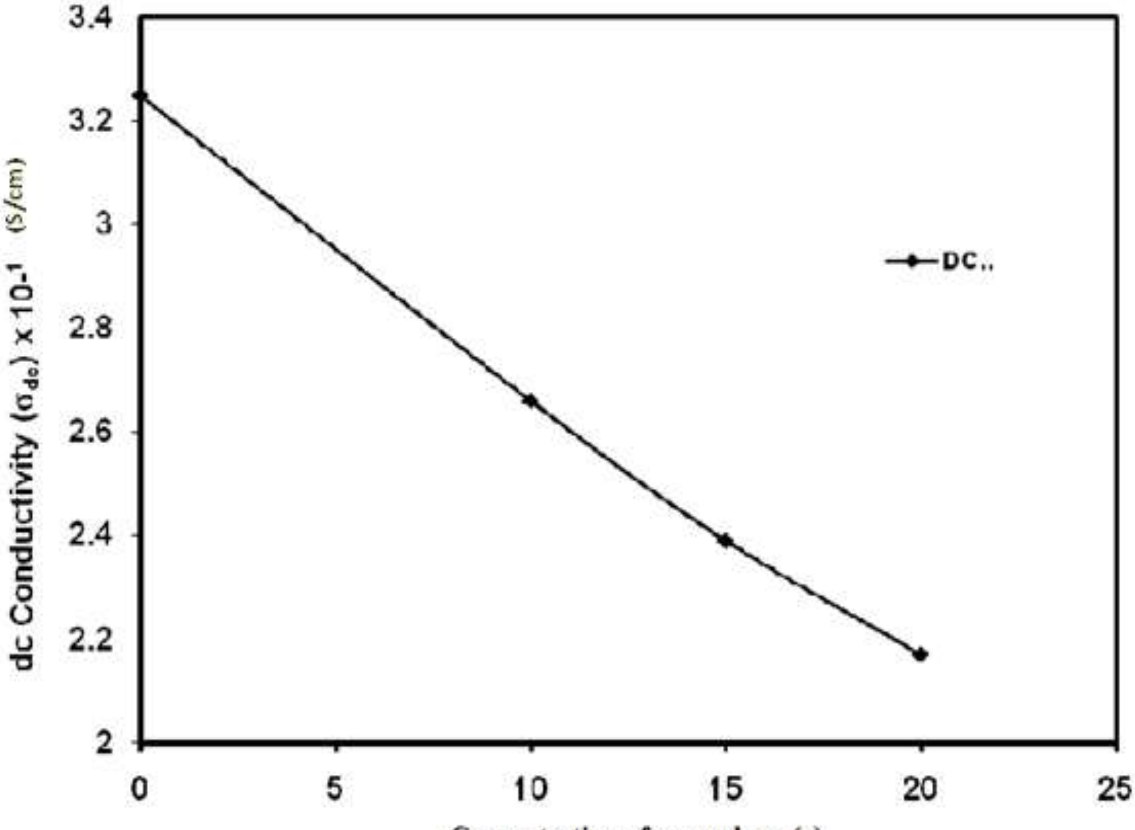



***Fig 7:*** *DC Conductivity for Different Weight Percentage of Cenosphere.*

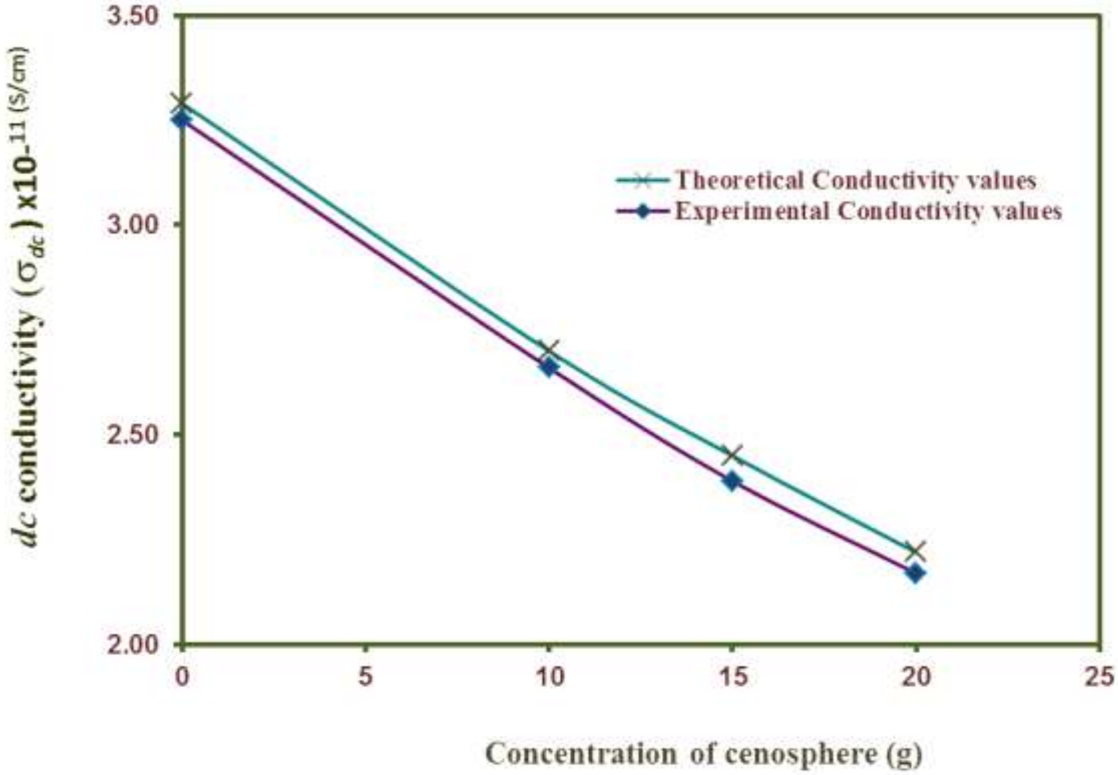



***Fig 8:*** *Experimental & Theoretical DC Conductivity for Different Weight Percentage of Cenosphere.*

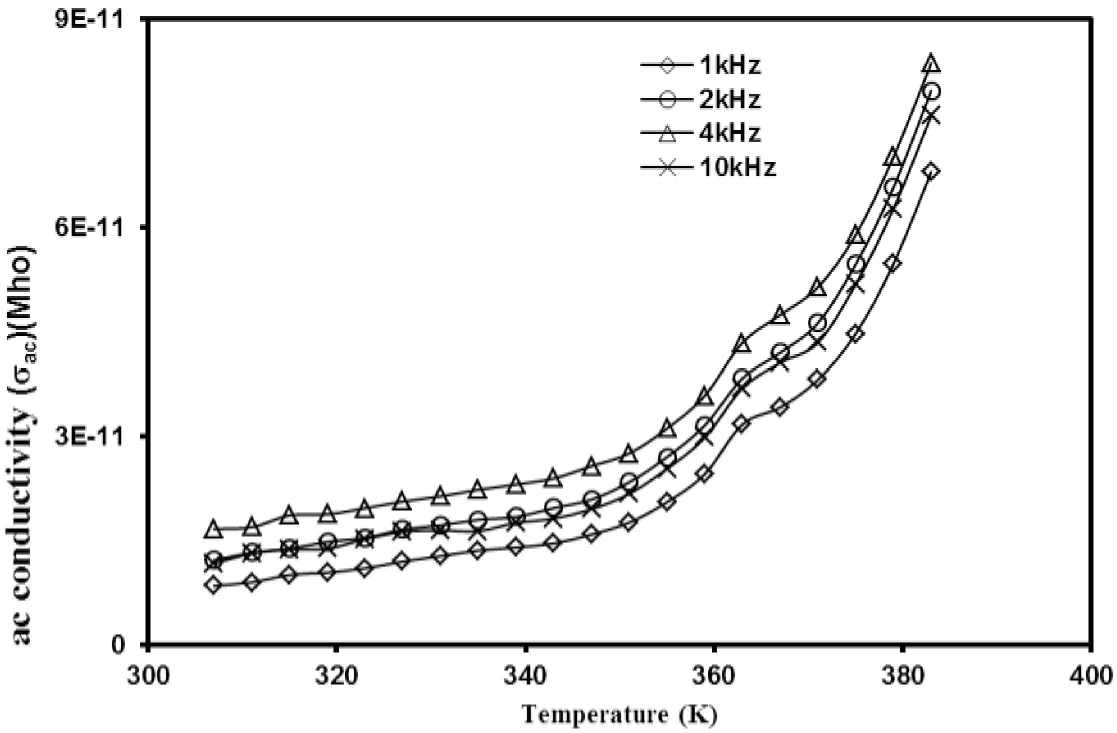



***Fig 9:*** *AC Conductivity ($\sigma_{ac}$) for Pure PP.*

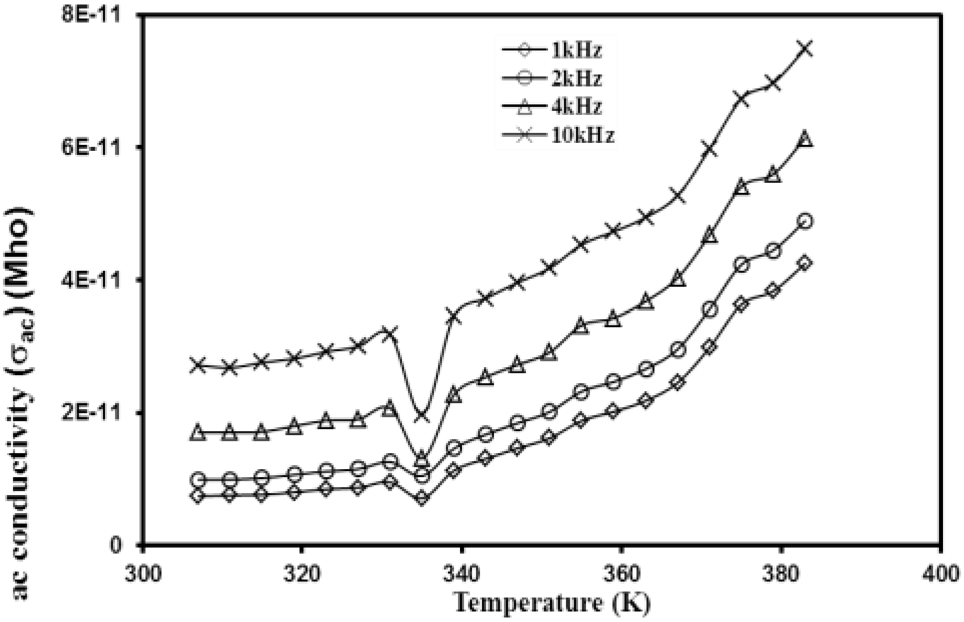



***Fig 10:*** *AC Conductivity ($\sigma_{ac}$) for PP with 20% of Cenosphere.*

## CONCLUSIONS

These results prove the efficiency of cenosphere to increase the dielectric constant. These composites are cost effective and ecofriendly composites as cenosphere could be utilized in such composite. The investigation of electrical properties of cenosphere filled polypropylene composites informs that

1. Dielectric constant decreases with increasing cenosphere volume fraction. It is found to decrease with test frequency and increased with temperature.
2. Dissipation factor follows the trend observed for dielectric constant with respect to the material and electrical test parameters.
3. The results of both a.c. and d.c. conductivity show a strong dependence on the weight percent of fly ash in polypropylene.
4. Validation of theoretical (eqn 3) and experimental dc conductivity values shows satisfactory results at higher concentration of cenosphere.

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