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Impact of metal filler on the dielectric properties of Nylon 11

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Abstract Dielectric measurements of pure Nylon 11 in comparison with metal (Zn) filled Nylon 11 have been carried out using an impendence analyzer in the frequency range of 10^2–10^7 Hz and temperature range 20–120 °C. Two different concentrations (1% and 5% (w/w)) of metal (Zn) fillers were used. It was observed that at low frequencies and particularly at high temperature dielectric permittivity (ε') for 1% Zn filled sample is more than that of pure Nylon 11 whereas ε' for 5% Zn filler is less as compared to that for pure Nylon 11. But at very high frequencies dielectric permittivity (ε') for pure Nylon 11 is less than Zn filled samples. Also it is found that for all frequencies and particularly at high temperature ε'' as well as tan δ are maximum for pure Nylon 11 and decrease for filled Nylon 11 samples. The Cole–Cole arcs have also been plotted for these samples. Using these plots the static and instantaneous values of dielectric permittivity and orientation polarization parameter 'S' have been calculated.

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Introduction

In search of new potential polymeric materials for future application in electronic devices, pure Nylon 11 filled with metal Zn powder have been prepared and the dielectric properties of Zn filled Nylon 11 along with pure Nylon 11 have been studied.

The dielectric properties of a filled polymer are likely to depend upon the structure of the polymer, the values of the conductivity of the filler and polymer; their relative volume fraction and the morphology of the system. Such systems, being heterogeneous, are subjected to interfacial polarization, which occurs at the interface of dissimilar materials [1]. It was therefore thought interesting to undertake the measurements of dielectric properties of Nylon 11 filled with Zn powder. The change in the dielectric behaviour due to addition of Zn filler has been investigated for two different concentrations i.e. 1% and 5% Zn (w/w).

Literature survey for filled polymers has been carried out and almost all the work is concentrated upon the studies of electrical conductivity of filled polymers [2–4]. Further it is observed that conductivity of filled polymers increases abruptly above a certain concentration of fillers. This is the critical volume fraction (ϕ_c) of high conductivity component at which the insulator to conductor transition occurs. This critical volume fraction (ϕ_c) also depends upon the type of fillers, the polymer matrix etc. The value of this critical concentration ϕ_c for polyethylene, PVC lies between 0.1 and 0.4 etc. Since the filled polymers having good electrical conductivity cannot have dielectric property, the care was taken that volume fraction of added powder do not exceed the ϕ_c. Hence the concentration of the added metal powder was kept low i.e. 1% and 5% (w/w).

In present case the aim was to increase the dielectric properties of filled Nylon 11 and hence low concentrations of metal fillers have been selected.

Dielectric properties of odd Nylons in the temperature range of –160 °C to +100 °C was reported by Wu et al. [5]. Takase et al. [6] reported that dielectric permittivity of Nylon 11 rapidly increases with increasing temperature above T_g due to ionic conduction.

So far, comparatively less attention has been paid to the dielectric properties of Nylon 11. Therefore, much work has not been published on the impact of metal fillers on dielectric properties of Nylon 11.

The present work therefore discusses the dielectric behaviour of Zn filled Nylon 11. For this purpose the measurements of dielectric permittivity (ε'), dielectric loss factor (ε'') as well as tan δ have been carried as a function of frequency and also by varying the temperature. In addition, the Cole–Cole arcs have been plotted and used to calculate the static and instantaneous values of dielectric permittivity and orientation polarization parameter 'S'.

Experimental techniques

The Nylon 11 (Sigma Aldrich CHEMIE GmbH, Germany) in the form of beads was used in the preparation of samples. The average molecular weight of Nylon 11 was 10,11,130. Zinc powder (Ranabaxy) having atomic weight 65.38 was used. The particles of Zinc were spherical in shape with 2–3 μm size. Samples of pure and Zn filled (1% and 5%, w/w) Nylon 11 was prepared in the form of circular discs using hot press molding. The thickness of the circular discs was 1.5 mm. The Zn powder was uniformly distributed in the sample. For the dielectric measurements, the samples were coated with gold on both sides (circular, ½ inch diameter) by vacuum deposition (10^{-7} Torr).

Two terminal electrode system with an Impedance Analyzer (HP 4192A) was used. The dielectric permittivity was measured as a function of frequency (range of 10^2–10^7 Hz) and temperature (range 20–120 °C). The temperature being controlled by means of a Honeywell BC 1010 programmable temperature controller with precision of ±1 °C over the entire measurement range. The experimental error in the dielectric parameters was ±0.5% and ±1.5% for ε' and ε'', respectively.

The real part of the dielectric permittivity (ε') and the loss (tan δ) were obtained experimentally, while dielectric loss factor (ε'') was evaluated using the relation

$$\varepsilon''/\varepsilon' = \tan\delta \qquad (1)$$

Results and discussion

Temperature dependence of ε' and ε''

Graph is plotted between ε', ε'' with respect to temperature in the range 20 °C–120 °C for 100 KHz (Fig. 1a). It has been observed that ε' increases with increase in temperature. It is about 4.5–5 at room temperature.

For low temperature (20–50 °C) referred figure shows that there is negligible effect on the dielectric permittivity (ε') due to addition of Zn fillers. However the effect of addition of Zn fillers in pure Nylon 11 can be visualized above 55 °C. It can be revealed from Fig. 1a that though

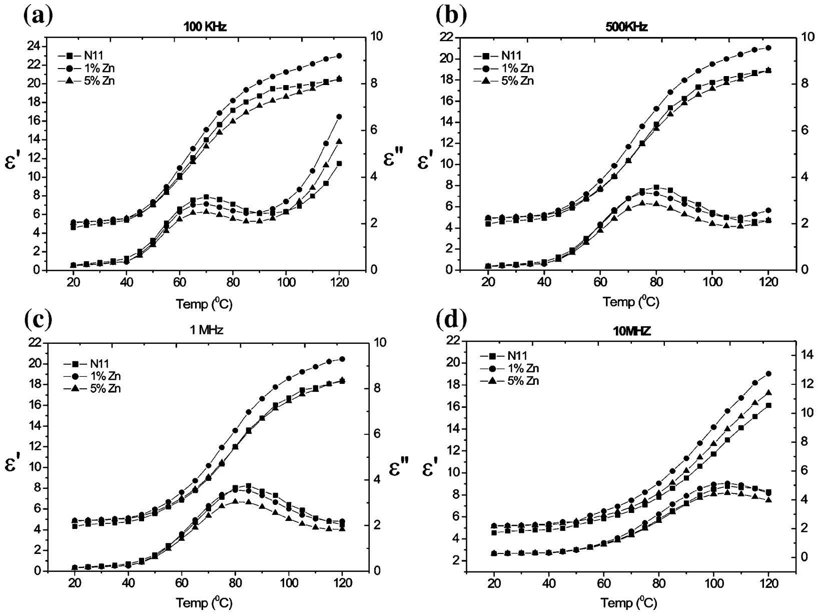

Fig. 1 Temperature dependence of ε' and ε'' for pure and Zn filled Nylon 11 at various frequencies: (**a**) 100 KHz, (**b**) 500 KHz, (**c**) 1 MHz, (**d**) 10 MHz

there is increasing tendency of dielectric permittivity (ε') for all the curves, still due to addition of 1% Zn, the value of ε' is higher, whereas for 5% Zn filled the value of (ε') is less than the pure Nylon 11.

As the temperature rises above 100 °C the curve for ε' of pure and that of 5% Zn filled Nylon 11 overlaps.

Figure 1b, c (for 500 KHz and 1 MHz), almost similar features are observed for all the three samples. Variation of ε' for pure and 5% Zn filler with temperature is almost identical. Also variation of ε'' for all the samples is almost similar. It has been observed from the graph that a peak appears at 80 °C for 500 KHz and around 85 °C for 1 MHz.

From Fig. 1d, it has been observed that for 10 MHz frequency and at low temperatures (20–50 °C) dielectric permittivity has been increased with addition of Zn powder in pure Nylon 11. The value of ε' almost coincides for 1% and 5% Zn filled Nylon 11 upto 50 °C. As the temperature rises above 50 °C, the two curves (i.e. for 1% & 5% Zn) split from each other, wherein value of ε' is more for 1% Zn filled sample than 5% Zn filled sample. The value of ε' for pure Nylon 11 is even less than that for 5% Zn filled Nylon 11.

Thus it has been observed that the dielectric permittivity (ε') at very high frequencies (10 MHz) follows the following relationship: dielectric permittivity (ε') for pure Nylon 11 < 5% Zn filler < 1% Zn filler

Thus the impact of the addition of metal filler (Zn) in the pure Nylon 11 resulted into an increase in the value of ε'.

Dielectric properties of polymers are closely related to the chemical and dipole density in the crystalline unit cell. All transconformation of the odd nylon chains such as Nylon 9 and Nylon 11 give large dipoles perpendicular to the chain axis and all the dipoles are aligned in the same direction. So the odd nylons can have a spontaneous polarization in the unit cell of the crystalline phase. It has been reported that Nylon-11 exists in two crystalline forms: a triclinic α and a pseudo hexagonal γ form [7]. Dielectric behaviour of Nylon 11 films in α and γ forms at 10 Hz was studied by Wu et al. [5]. They reported that dielectric permittivity of Nylon 11 (γ - form) specimen was higher than that of Nylon 11 (α-form).

Several researchers [8–11] have proposed that the field induced dipole alignment might more effectively occur in the γ structure than in the ordinary α structure.

In the present work, in case of 1% Zn filled Nylon 11 the dielectric permittivity ε' is more as compared to Nylon 11 and 5% Zn filled sample.

It has already been reported [12] that in 1% Zn filled samples, the metal enters into the crystalline region of pure Nylon 11. The WAXD analysis of pure and Zn filled samples of Nylon 11 have been carried out and reported elsewhere [12]. The result of this analysis shows that the crystallinity of Nylon 11 increases due to addition of Zn powder (1% and 5% Zn (w/w)). The crystallinity of pure Nylon 11 is 37% whereas for 1% and 5% Zn samples the crystallinity is 52% and 53% respectively [12].

Further it has been revealed through WAXD analysis that pure Nylon 11 exhibits presence of both α and γ crystalline form whereas 1% Zn filled samples shows the existence of γ form. Thus it may be concluded that due to addition of 1% Zn powder the chains of Nylon 11 have been arranged in more ordered form and the phase transition from $\alpha \rightarrow \gamma$ takes place. This must be the reason for obtaining high dielectric permittivity for 1 % Zn filled sample.

The WAXD analysis for 5% Zn filled Nylon 11 indicates the presence of both α and γ crystalline form as is also observed in pure Nylon 11. But the crystallinity of 5% Zn filled sample is more than that of pure Nylon 11 and therefore the content of γ crystalline structure in 5% Zn filled samples can be more than the contents of γ crystalline structure in pure Nylon 11. Therefore the dielectric permittivity of 5% Zn filled sample is more than that of pure Nylon 11.

However it is interesting to mention here that even though % crystallinity for 1% and 5% are almost equal, the value of ε' between them differ significantly. The reason for this behaviour may be assigned to the difference in the crystalline form of the sample. The WAXD studies reveal the crystalline form for 1% Zn sample as purely γ whereas for 5% Zn filled, it shows presence of both α and γ forms. This might result into reducing the value of ε' for 5% Zn filled sample than 1% Zn filled sample. Thus dipole alignment occurs in the γ structure, increasing the value of dielectric permittivity (ε') for 1% Zn filled sample as compared with pure and 5% Zn filled Nylon 11

From Fig. 1a–d, for dielectric loss factor (ε'') versus temperature, it can be observed that ε'' at very high frequency shows:

5% Zn Filler < Nylon 11 < 1% Zn Filler

Figure 2 below shows the temperature dependence for dielectric loss (tan δ) for pure and Zn filled Nylon 11. Figure 2 shows that the glass transition temperature (T_g) for all the samples is same at 100 KHz (T_g = 60 °C) and 500 KHz (T_g = 70 °C), but at high frequency i.e. 1 MHz and 10 MHz it is observed that T_g decreases for 1% Zn as compared to other samples i.e. pure and 5% Zn filled Nylon 11.

The plot of dielectric loss (tan δ) with respect to temperature is used to measure the glass transition temperature (T_g). From Table 1, it is further revealed that decrease in T_g of a polymer indicates the plasticizing effect of additive. In the present case 1% Zn filled Nylon 11 sample shows

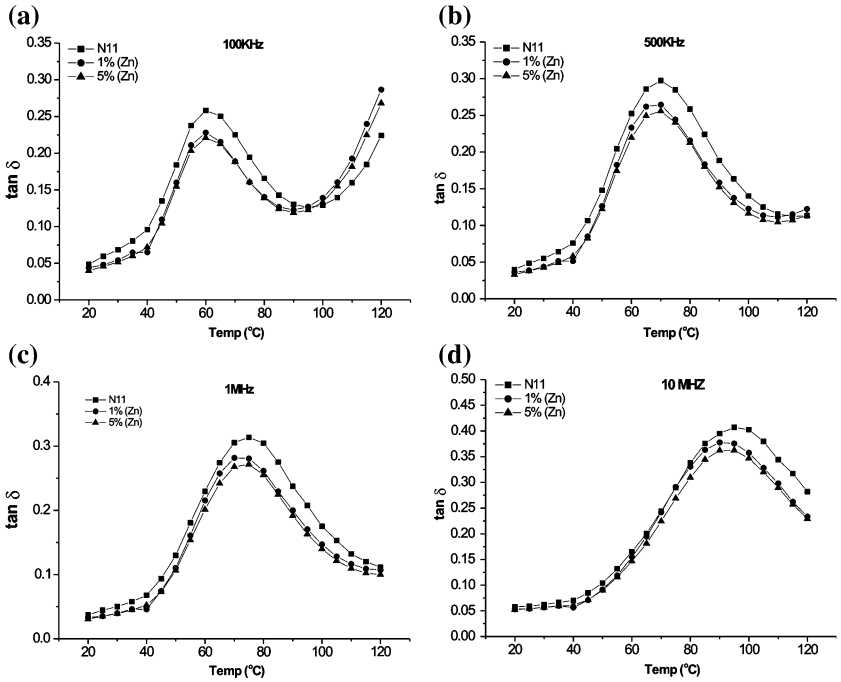

Fig. 2 Temperature dependence of tan δ for pure Zn filled Nylon 11 at various frequencies: (**a**) 100 KHz, (**b**) 500 KHz, (**c**) 1 MHz, (**d**) 10 MHz

Table 1 Glass transition temperature for pure and Zn filled Nylon 11 at various frequencies

Sample	Glass transition temperature (T_g °C)			
	100 KHz	500 KHz	1 MHz	10 MHz
Pure Nylon 11	60	70	75	95
1% Zn	60	70	70	90
5% Zn	60	70	75	95

reduction in T_g values at high frequencies. The added Zn does not form any complex with Nylon 11 and exists as a separate phase in the polymer matrix. However, effect of addition of Zn powder on T_g is similar to that of a plasticizer.

Similar results have been observed when the T_g of these samples were measured using DMTA. These results have been reported elsewhere [12]. The samples were scanned with an imposed frequency of 1 Hz. It was also observed from these results that for 1% Zn sample, T_g reduces. In the present work, the frequencies employed are quite large, reduction in T_g is observed only for 1% Zn samples. In case of 1% Zn filled Nylon 11; the added Zn particles entered into the crystalline phase of Nylon 11 and thus phase transformation from $\alpha \rightarrow \gamma$ has taken place. The interposition of Zn particles in between the Nylon 11 chains therefore can have the effect of weakening of second order (Van der Waal's) attractive forces between the polymer chains and hence glass transition temperature (T_g) reduces.

For 5% Zn filled samples, it is observed from Table 1 that values of T_g are equal to those for pure Nylon 11. However, the DMTA results for 5% Zn filled sample show decrease in T_g as compared to pure Nylon 11. The DMTA measurements were carried out at very low frequency i.e. 1 Hz and in present work frequencies employed are very high. It is therefore possible that decrease in T_g values of 5% Zn filled Nylon 11 are not revealed by the measurement carried out at high frequency. Also the results have further been verified using DSC technique, which shows similar trend.

The activation energy corresponding to α_a relaxation process is a measure of the energy required to take polymer from glassy to a rubbery state, which can be achieved by creation of a free volume for segmental motion. Hence activation energy is expected to depend on the structural and morphological factors.

For decade change in frequency the activation energies are calculated for all the three samples by using the following equation [13]:

$$\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{2.303\,R}{H} \tag{2}$$

where R is the gas constant, H is the activation energy, T_1 °K is the glass transition temperature at lower frequency and T_2°K is the glass transition temperature at higher frequency.

The frequencies selected for calculation are 100 KHz–1 MHz and 1 MHz–10 MHz and the values for different samples are tabulated in the Table 2. From Table 2, it is evident that activation energy for all sample is almost equal for 1 MHz–10 MHz whereas for frequency 100 KHz–

Table 2 Activation energy for pure and Zn filled Nylon 11

Sample	Activation energy in eV	
	100 KHz–1 MHz	1 MHz–10 MHz
Pure Nylon 11	1.53	1.27
1% Zn	2.20	1.24
5% Zn	1.53	1.27

1 MHz, activation energy for 1% Zn filled sample is more than that for pure and 5% Zn filled samples because activation energy is expected to depend on the structural and morphological factors.

Many amorphous polymers are hard, rigid glasses below the glass transition temperature, T_g. This glassy region, where the modulus is greater than 10^{10} dynes/cm^2. In this glassy region, energy is insufficient to surmount the potential barriers for translational and rotational motions/ segments of the polymer molecules. The chain segments are frozen in fixed position. Above the glass transition temperature the amorphous polymers are soft and flexible, wherein the modulus in this rubbery region is about the 10^7–10^6 dynes/cm^2. This reduction of modulus is due to the initiation of micro-Brownian motion of the molecular chains from the frozen state with increasing temperature. In the present case the amorphous contents measured at low frequencies appear to be less as compared to those measured at high frequencies which were also observed from Fig. 4. As a result the segmental motions at high frequencies is more easy requiring less activation energy for the motion as compared to the motion at low frequencies and therefore from Table 2 it was observed that in low frequency (100 KHz–1 MHz), the activation energy calculated are more than that calculated at higher frequency (1 MHz–10 MHz).

Frequency dependence of ε' and tan δ

Figure 3 of dielectric permittivity ε'as a function of frequency over a wide range (0.005 Hz–13 MHz) for pure and Zn filled Nylon 11 at room temperature have been studied. It has been observed that ε' remains almost constant in the frequency range of 5 Hz–10 MHz for all the three samples. It has been summarized from the Table 3 that the dielectric permittivity (ε') of: Nylon 11 < 5% Zn filler < 1% Zn filler.

Figure 4 shows a plot of tan $\delta_{\max}$ versus log f for all the three samples at room temperature. The graph is a straight line having nearly equal slope for all the three lines corresponding to the three samples.

From the same Fig. 4 it may be observed that value of tan $\delta_{\max}$ reduces by addition of Zn powder. The decrease in height of tan $\delta_{\max}$ indicates the decrease in amorphous content in the sample. In other words, more the crystalline content in a sample, the less is the height of tan $\delta_{\max}$. Similar results for Zn filled samples have been obtained in respect of the crystalline content of Zn filled Nylon 11 and have been investigated using WAXD analysis and reported [12].

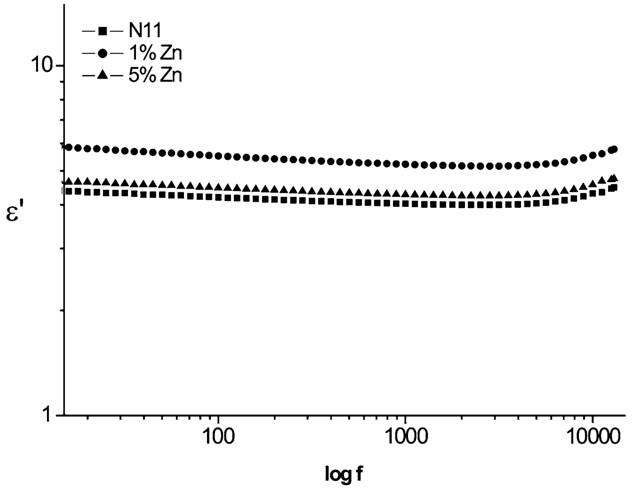

Fig. 3 Frequency dependence of ε' for pure and Zn filled Nylon 11 at room temperature

Bishay [14] cited that the Cole–Cole model function [15] has been used successfully to describe the experimental data for the dielectric permittivity of many materials as a function of frequency [16–20]. In this model the ε' depends mainly on four parameters, the static dielectric permittivity ε'_s, the dielectric permittivity at infinite frequency ε'_∞, the relaxation time τ, an exponent factor α and orientation polarization parameter S. In principle, ε'_s and ε'_∞ can be experimentally measured and the other parameters have to be treated as fitting parameters whose values can be retrieved from the best fit to the experimental data.

The measurement of ε' and ε'' as function of frequency and temperature are used to obtain Cole–Cole plots for pure Nylon 11, 1% Zn filled and 5% Zn filled Nylon 11 respectively. All the measurements were made at three different temperatures (T = 60, 70 and 80 °C). Measured data for the samples follow the expected Cole–Cole arc only at studied frequencies which is depicted in the Fig. 5a–c.

In the Cole–Cole plot, graph of ε'' versus ε' curve changes to the opposite sign as the ionic contribution dominates. This qualitative value makes it easy to distinguish the intrinsic dielectric permittivity from the ionic contribution. The extrapolation of the data by using an arc determines the static ε'_s, and the instantaneous value ε'_∞, of the dielectric permittivity. The dielectric relaxation time τ [21] was also calculated by the following equation:

Table 3 Dielectric permittivity for pure and Zn filled Nylon 11 at room temperature

Dielectric permittivity (ε') at room temperature	Pure Nylon 11	1% Zn filled Nylon 11	5% Zn filled Nylon 11
	4.0–4.5	5.2–5.8	4.2–4.7

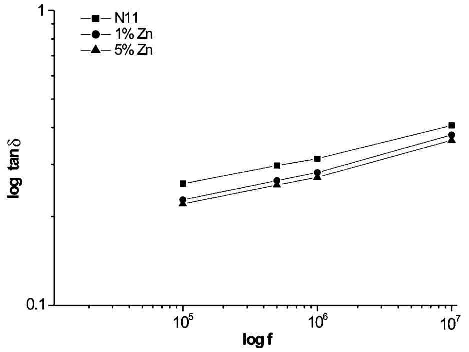

Fig. 4 Logarithmic plot of tan δ as a function of frequency for pure and Zn filled Nylon 11

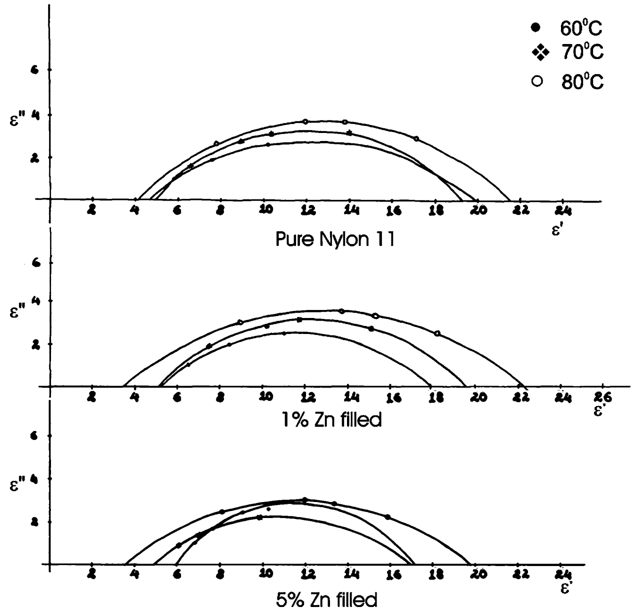

Fig. 5 Cole–Cole plot for pure and Zn filled Nylon 11

$$\tau = \frac{\varepsilon''(\omega)}{(\varepsilon'(\omega) - \varepsilon'_{\infty})} \tag{3}$$

The data observed for Cole–Cole plot is given in the Table 4 below.

By comparison of experimental values of ε' to the graphical values obtained (Cole–Cole plot) it was observed that the value of ε' for pure Nylon 11 at 100 Hz (lowest measured frequency) at 60 °C is 23.76 whereas the value obtained as ε'_s is 19.9. Similarly ε' measured at 10 MHz (maximum frequency) is 5.8 and the graphical value obtained at ε'_{∞} is 4.6.

Thus from the above discussion it can be summarized that the experimental values are quite comparable to the values obtained using Cole–Cole plot with respect to temperature. Similar results are also obtained for the Zn filled samples at various temperatures.

Conclusion

The effect of addition of Zn powder in pure Nylon 11 on the dielectric permittivity has been explored. It was found that at very high frequency, Zn additives in pure Nylon 11 increase the dielectric permittivity. At low frequency it was found that for 1% Zn filled Nylon 11 the dielectric permittivity is higher, while for 5% Zn filled Nylon 11 it is lower as compared to pure Nylon 11. This can be attributed to the phase transformation that has taken place in pure Nylon 11 due to addition of Zn powder.

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Table 4 Dielectric parameters observed for pure and Zn filled Nylon 11

Sample	T (°C)	ε'_s	ε'_{∞}	α	S	τ (μs)
Nylon 11	60	19.9	4.6	0.566	7.65	0.750
1% Zn filled		17.9	5.3	0.523	6.30	0.710
5% Zn filled		16.9	4.9	0.533	6.00	0.700
Nylon 11	70	19.3	5.0	0.455	7.15	0.554
1% Zn filled		19.5	5.2	0.466	7.15	0.454
5% Zn filled		17.1	6.0	0.388	5.55	0.545
Nylon 11	80	21.5	4.5	0.488	8.50	0.353
1% Zn filled		22.3	3.5	0.545	9.40	0.271
5% Zn filled		19.7	3.6	0.544	8.05	0.285

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