Dielectric Properties of Filled Composites of Epoxy Resin

Fareeda Farrukh* and Shahid H. Zaidi

Department of Applied Physics, University of Karachi, Karachi-75270, Pakistan

Abstract: The addition of fillers in composite of epoxies, improves the dielectric response of the epoxies. The dielectric properties of unfilled and filled composites of epoxy resins have been studied as a function of thickness in the frequency range 10^{-1} Hz to 10^{5} Hz at room temperature. The response of the unfilled samples shows that the composites behave as an insulator for all thickness. In filled composites at small thickness (0.32 mm) the response shows a loss peak in low frequency regime. The peak is broader than the Debye loss peak which is obscured by the dc conductance. At frequencies greater than ω_p the response shows a well defined power law behaviour after the subtraction of C_∞. Similar behaviour has been observed at different thickness.

Keywords: Dielectric Properties, fillers, loss peak, Debye loss Peak, Power law, localization.

INTRODUCTION

Epoxy resin has high strength, good stiffness, good thermal stability, excellent heat, moisture, and chemical resistance; therefore they are applied in the field of coating, adhesive, casting, potting composite, laminates and encapsulation of semiconductor devices [1, 2]. Epoxy resin is used for moulding integrated circuits, transistors hybrid circuits, and making printed circuit boards [3]. However the increase in electrical conductivity in filled epoxy has opened up the possibility of new application for polymers such as solder replacement, interconnection, sealing, electrical shielding, various electronic components bonding, fastening and brazing [4, 5]. Nowadays a great economic interest in materials has developed because of their technological applications as temperature or current sensors [6], flooring materials to dissipate static electric charge [7], pressure sensitive sensors which can be used for shockproof switches [8], sensors for the measurement of vehicle weight to collect toll tax on roads [9], heater [10], antistatic coating and electromagnetic radiation shielding.

In the present work the dielectric properties of composite of epoxy resin with and without fillers are investigated in a wide range of frequencies at different thickness. To investigate the effect of fillers in composites of epoxy resin, dielectric measurements are performed in the frequency range from 10^{-1} Hz to 10^{5} Hz at room temperature as a function of frequency and thickness [11-13].

*Address correspondence to this author at the Department of Applied Physics, University of Karachi, Karachi-75270, Pakistan; Tel: 92-21-99261300-7, ext 2258, 2564; E-mail: farida_q2000@yahoo.com

EXPERIMENTAL DETAILS

The materials used in this study are epoxy resin as polymer matrix supplied by Buxly Paints Karachi and a filler Kevlar 49 Aramid staple.9 supplied by Du Pont De Nemours & Co. The polymer matrix was Bisphenol-A based epoxy resin of type SF-10, Viscosity of the epoxy is 104 KU at room temperature [14] and the fillers kevlar fiber have following characteristics: the mean length of the fibers is 1mm, and diameter 12-15 µm [15]. The unfilled and filled composites have been made with equal proportion of resin and hardener. In the filled composites the fillers were added by 5% of its weight. Thickness of the samples ranges from 0.32mm to 0.62mm. The method of preparation of the samples is described in detail in [16]

The dielectric measurements were performed on an automated system for recording inphase and quadrature component of current as a function of frequency. The details of equipment are given in [17]. The data has been recorded in the frequency range from 10^{-1} Hz to 10^{5} Hz, with a voltage of $0.7V_{rms}$ and zero dc bias at room temperature. Each sample was placed in a sample holder and the sample holder was placed in the dessicator so that the humidity level remains constant.

RESULTS

The dielectric response of filled epoxy resin as a function of thickness is shown in Figure **1**, the thickness ranges from 0.32mm to 0.62mm. The loss response shows that for all thickness the value of exponent n increases with the increase in thickness (Figure **1**). This behavior is different from the behavior of the unfilled samples as shown in the dielectric

ISSN: 1814-8085 / E-ISSN: 1927-5129/14

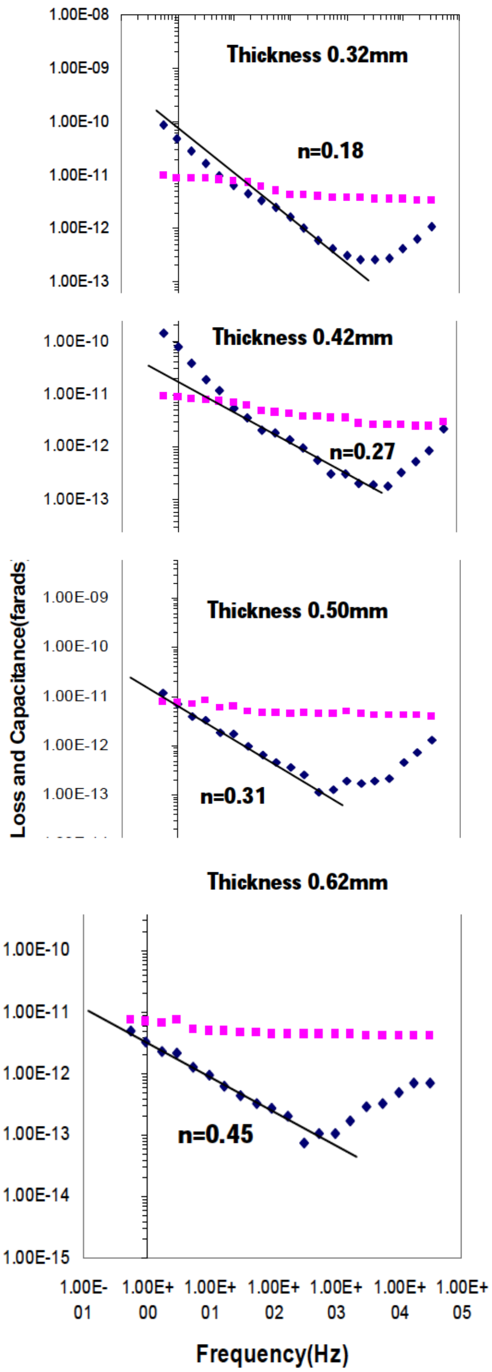


Figure 1: Dielectric response of four different samples of thickness ranges from 0.32mm to 0.62mm of set3 with zero bias at room temperature. The loss points are shown by (♦) and the capacitance by (■). The successive curves are placed vertically by three to five decades. The symbols are the experimental values and the line through the points is theoretical fit.

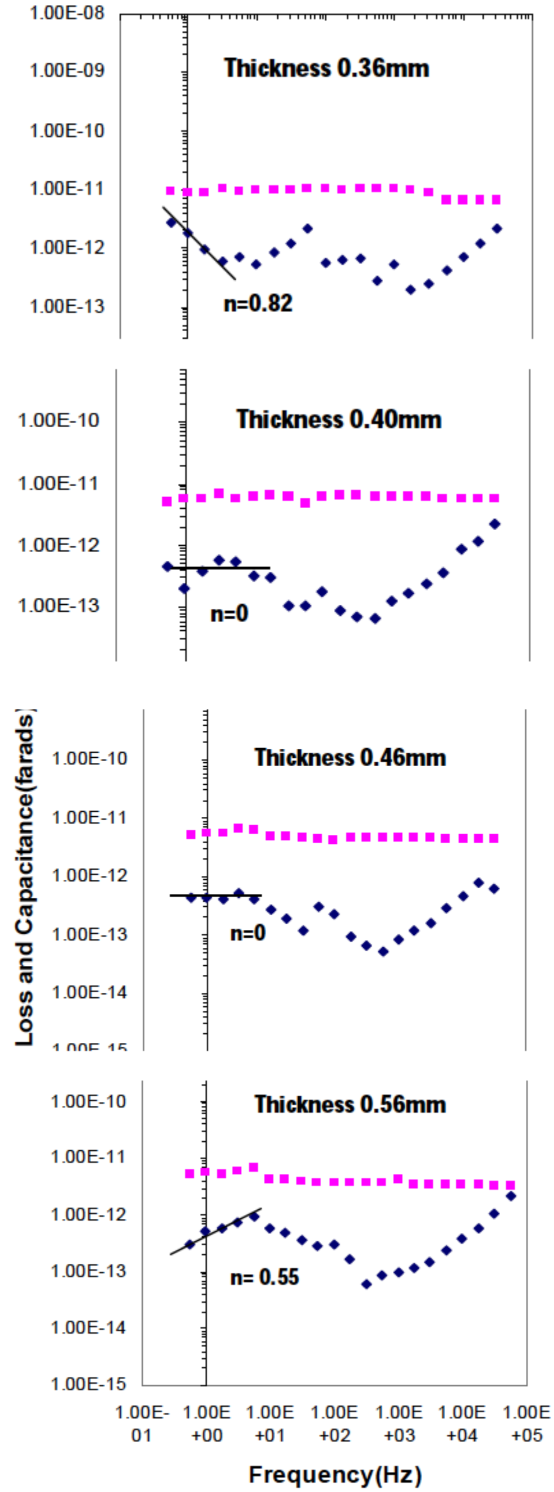


Figure 2: Dielectric responses of the matrix have equal proportion of resin and hardener set1of four different thicknesses. The range of thickness is 0.36mm to 0.56mm. The loss points are shown by (♦) and the capacitance by (■). The successive curves are placed vertically by four to five decades. The symbols are the experimental values and the line through the points is theoretical fit.

response in Figure **2** in this case the thickness ranges from 0.36mm to 0.56mm. For filled composites the response shows that as the thickness increases the density of low mobility charge carriers increases. In polymers the presence of weak Van der Waals bonds gives rise narrow allowed bands with corresponding high effective masses of charge carriers. These charge carrier together with the presence of disorder, contribute to the processes of localization. In filled samples at thickness 0.32mm and 0.42mm there is an appearance of loss peak in the low frequency region near 30 Hz, which is obscured by the dc conductance. For all thickness the capacitance C'(ω) changes very slowly in the whole frequency range, whereas for the thickness 0.32mm and 0.42mm there is a kink in the C'(ω) 10 Hz, which is a dipolar response. For the whole range of thickness the series resistance effect is prominent in the high frequency region above 10^3 Hz.

Figure **3** shows the dielectric response of the filled sample have a thickness 0.32mm the value of exponent n for the loss data is 0.18 in the frequency range of 30 Hz to near 10^3 Hz below 50 Hz there is an appearance of loss peak which is obscured by the dc conductance G_o/ω because below 50 Hz the loss factor rises steeply with slope -1 leaving the real part independent of frequency. The subtraction of the dc conductance from the loss data gives the loss peak near 10 Hz (Figure **4**). The response shows extended dipolar effect with m slope at less than ω_p equals 0.82 and n slope at greater than ω_p equals 0.18 or symmetric response with m=1-n [18-21]**.** The sample follows power law behavior in the range of 50 Hz to 10^3 Hz showing less dispersive behavior in this range, the subtraction of C_∞ from the data of real values gives K-K compatibility between dielectric loss and capacitance in the frequency range of 50 Hz to about 10^3 Hz shown in Figure **5**. For this process we choose value of C_∞ 3.6378 e^{-12} farads such that the subtraction of this value brings the points to their proper position up to the low frequency range at the room temperature the value of C_∞ agrees with the geometrical value C 3.98 e^{-12} farads having relative permittivity of 3.6.

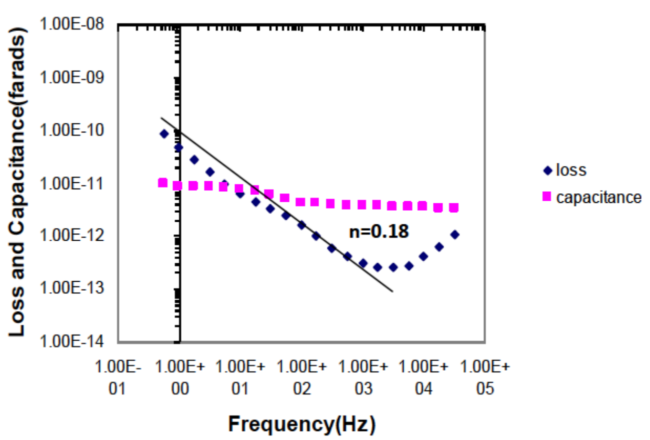


Figure 3: Dielectric response of sample of thickness 0.32mm of set3 with zero dc bias, the line through the points is theoretical fit shows that the value of n is different in low frequency region and high frequency region.

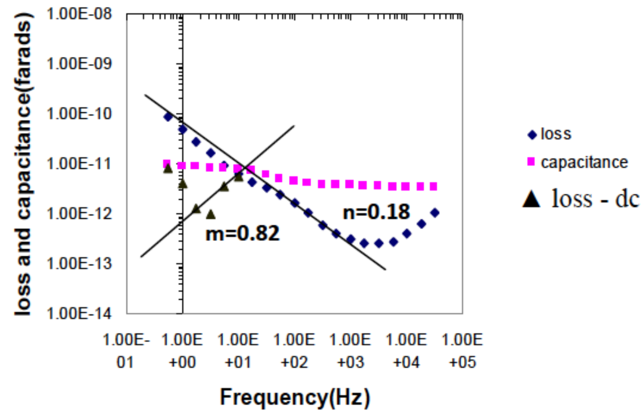


Figure 4: Dielectric response of sample of thickness 0.32 of set3, subtraction of dc conductance from the loss gives a symmetrical loss peak shown by the symbol ▲.

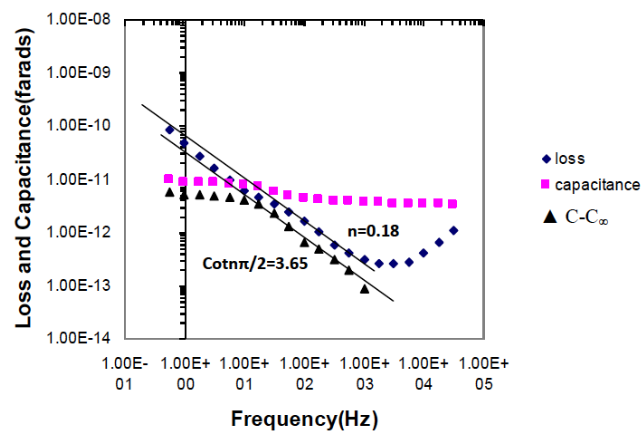


Figure 5: Dielectric response of sample of thickness 0.32mm of set3, Subtraction of C_∞ from high frequency capacitance brings capacitance parallel to loss in high frequency region shown by symbol ▲. The line through the points is theoretical fit.

C_∞ is the frequency independent capacitance arising from the hopping of ions. The subtraction of suitable value of C_∞ from the data gave a well defined power law over in the frequency range from 50 Hz to about 10^3 Hz that is two responses are separated by Cot $(n\pi/2)$=3.65 distance with a slope of n-1.

Figure **6** shows the dielectric response of filled samples of thickness 0.42mm. The response shows that below 10 Hz the slope of the dielectric loss is -1 and the real data is frequency independent similar trend as of thickness 0.32 of filled samples. In the frequency region below 50 Hz there is an appearance of loss peak which is obscured by the dc conductance G_o/ω below the frequency 10 Hz. The subtraction of the dc conductance from the loss data gives the loss peak near 30 Hz (Figure **7**). The response shows extended dipolar effect with a slope m<1-n or m equals 0.68 and n equals 0.27**.** The response follows power law

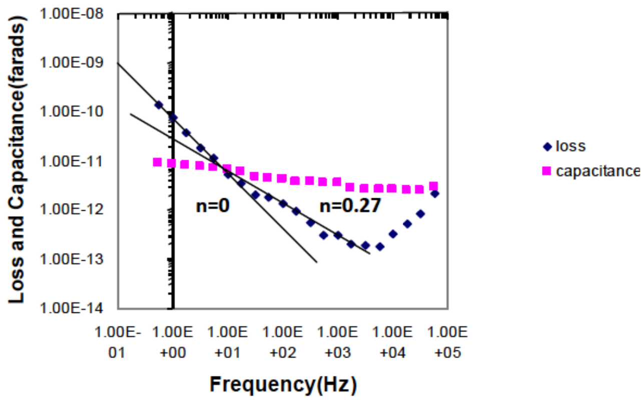


Figure 6: Dielectric response of sample of thickness 0.42mm of set3 with zero dc bias, the line through the points is theoretical fit shows that the value of n is different in low frequency region and high frequency region.

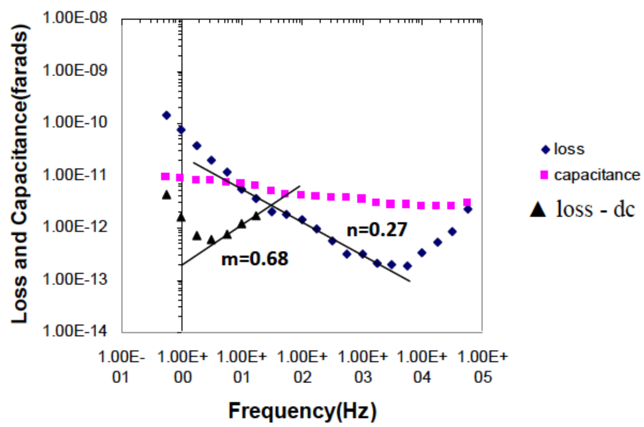


Figure 7: Dielectric response of sample of thickness 0.42, subtraction of dc conductance from the loss gives a loss peak shown by the symbol ▲.

behavior in the frequency range 10 Hz to 500 Hz the subtraction of C_∞ from the data of real values of capacitance gives K-K compatibility between dielectric loss and capacitance in the frequency range of 10 Hz to about 500 Hz that is the real data parallel to the loss data in the defined frequency range with a separation cot $(n\pi/2)=2.21$ as shown in Figure **8** we choose C_∞ 3.331 e^{-12} farad the value of C_∞ agrees with the geometrical value C = 3.0356 e^{-12} farads having relative permittivity of 3.6.

Figure **9a** and **9b** shows the dielectric response of filled samples having thickness 0.50 mm and 0.62 mm respectively. For the filled sample having thickness 0.50mm the response shows that in the frequency region below 300 HZ the loss data has a slope of 0.31 and above 300 Hz series resistance shows a prominent effect. For this sample transition frequency is 9.8 10^{-1} Hz. For the whole range of frequency the real data

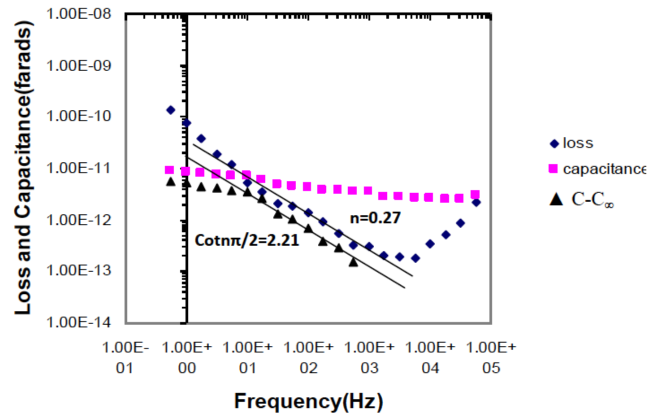
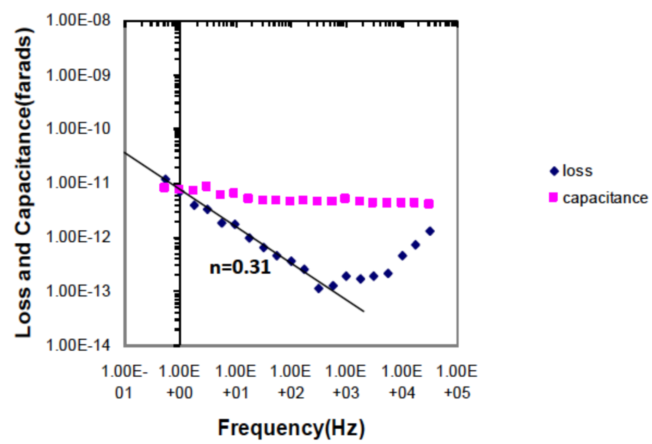
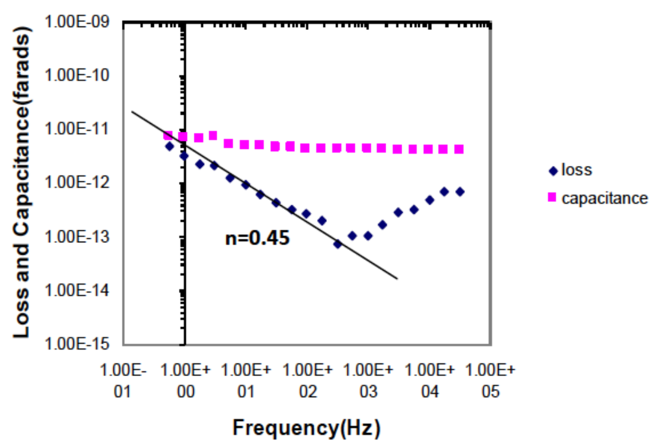


Figure 8: Dielectric response of sample of thickness of set3 subtraction of C_∞ from the high frequency capacitance brings capacitance parallel to loss data in high frequency region shown by symbol ▲. The line through the points is theoretical fit.



(**a**)



(**b**)

Figure 9: Dielectric response (**a**) thickness 0.52mm and (**b**) thickness 0.6mm of set3 the line through the points is theoretical fit.

varies between minimum 2.2891 e^{-12} farads to maximum 8.1686 e^{-12} farads. The response of the filled sample having 0.62mm shows that the loss data has exponent n=0.45 in the frequency range below 10^3 Hz. In the whole frequency range the corresponding loss data has a value less than the capacitance data as shown in Figure **9b**. The capacitance varies between maximum 7.4859 e^{-12} farads to minimum 4.0159 e^{-12} farads.

DISCUSSION

The response of unfilled epoxy resin having equal proportion of resin and hardener has exponent m tending to zero at small thickness corresponds to weakly correlated flip-flop transition [22, 23]. The increase in exponent m with the increase in thickness reflects strong correlated flip-flop transition due to the increase in chain length of the composite that changes structural order of the epoxy resin. As the chain length increases the composite becomes heavily cross-linked material having dense three-dimensional network of covalent bonds in them, with little freedom for motion by the individual segments of molecules involved in structure [20].

Addition of the filler content of Kevlar fiber in the composite of epoxy resin, results in a small change in the loss and capacitance values at large thickness (greater than 0.5mm) in the low frequency region. The weak dependence of the loss and capacitance from the organic filler is because of close value of permittivity of epoxy resin and Kevlar fiber [24-28].

There is a clear loss peak at 10Hz in the response of filled sample of thickness 0.32mm (Figure **4**) which appears after the subtraction of dc from loss with a slope m=0.82 at the frequencies smaller than the loss peak and with a slope n=0.18 at the frequencies greater than the loss peak. The loss peak frequency ω_p shift to 30 Hz with a slope m=0.68 at the frequencies smaller than the loss peak and with a slope n=0.27 at the frequencies greater than the loss peak when the thickness is increased (Figure **7**). The response of the filled samples of small thickness follows the power law behaviour with a separation of cot $n\pi/2$ above the loss peak frequency ω_p after the subtraction of high frequency capacitance [28-35].

CONCLUSION

The dielectric response of filled samples depict that at small thickness (thickness ranges 0.46mm to 0.32mm) the system follows the extended hopping which obey the universal law at frequencies above loss peak ω_p up to 1KHz and their response below loss peak and above 1KHz is governed by a second power law relation, this relation is limited by the onset of direct conduction below 10Hz, while at frequencies above 1 KHz by a perturbing processes arising from the presence of some series resistance of the system.

Concerning the frequency dependence of the loss in filled specimens with samples of unfilled epoxy resin in the frequency region above the loss peak frequency ω_p the response follows the power law behaviour with a separation of cot $n\pi/2$ after the subtraction of high frequency capacitance, which confirms that the response follows bound charge dipolar behaviour.

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Received on 16-06-2014 Accepted on 16-09-2014 Published on 03-10-2014

http://dx.doi.org/10.6000/1927-5129.2014.10.60