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Dielectric behaviour of milled carbon fibre reinforced polysulphide modified epoxy gradient composites

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Abstract

Milled carbon fibre reinforced polysulphide modified epoxy gradient composites were developed and characterized for their dielectric and DSC behaviour. It was found that dielectric constant of the composites increased with increase of milled carbon fibre content from 0.45 to 1.66 vol.% which confirmed the formation of a gradient structure in the composite. Both dielectric constant as well as loss tangent (tan δ) increased with an increase of temperature. Dielectric constant data obtained for composites matched with the Maxwell Garnett model. Change in ε' values on adding milled carbon fibre is due to the modification of PSEP structure by milled carbon fibre. Dissipation factor (tanδ) peaks shifted towards lower temperature with increase of carbon content, which was due to the shift in Tg of PSEP. Relaxation time (τ) determined at 80°C decreased from 3.35 x 10^{-5} to 2.25 x 10^{-5} (s) on increase of milled carbon fibre content from 0.45 to 1.66 volume percent. DSC scans also revealed the same Tg behaviour of graded composites. Storage modulus, E', suddenly decreased after 62°C and 60.4 °C for PSEP and composite sample C having 1.66% carbon fibres respectively.

Keywords

Milled Carbon, Polysulphide Modified Epoxy, Gradient, Dielectric Constant

1. Introduction

Most polymers are insulating materials. An improvement in electrical conductivity of polymers, however, allows them to be used in specific industrial applications such as in fuel cells in which electrically conductive polymers are used as bipolar plates that require electrical conductivity, good dimensional stability and low gas permeability.

Electrical conductivity of polymers are generally in the range of 10^{-14} to 10^{-17} $\Omega^{-1}cm^{-1}$ whereas carbon black, synthetic graphite, and metals such as aluminum and copper have conductivity 10^2, 10^5 and 10^6 $\Omega^{-1}cm^{-1}$ respectively [1]. Thus, the latter can be used as fillers in the former to increase its electrical conductivity, and is one of the various methods that have been adopted in the past [2-8]. For instance, Carbon has been added in vinylester resin to produce an electrically conductive bipolar plate material [9-12].

Carbon fibres though offer exceptional mechanical properties along with low weight, which make them ideal reinforcements for polymer composites, the performance of these composites depends greatly on the quality of the matrix, reinforcement and interface [13,14]. It is well known that carbon fibres have poor bonding with the polymer matrix due to their nature of smoothness and chemical inertness. Notwithstanding this fact, development of electrically conductive carbon filled polymer composites continues to be a topic of active research.

The electric conduction process in conductive filler-polymer matrix composites depends upon a number of parameters such as fillers concentration, particle size, shape, structure, aspect ratio, filler orientation, filler-matrix interactions and processing techniques, which control the electrical properties. [15, 16].

In a recent paper it has been reported that graphite filled polysulphide epoxy resin composites prepared by solution casting method and containing 0.99, 1.96 and 2.91 weight percent graphite particles showed an increase in dielectric constant, tan δ and a.c. conductivity with increase of temperature. tan δ and a.c. conductivity peaks shifted towards lower temperature with increasing frequency[17] .

Milled carbon fibre reinforced epoxy gradient composites are promising materials since they carry immense potential for being used as fuel cell, bipolar plates, electrostatic dissipation, chemical sensors, vapor detector arrays or electronic noses applications and as variable sensor.

However, there is no report available in the literature on the dielectric, thermal and dynamic mechanical behaviour of gradient milled carbon fibre reinforced polysulphide modified epoxy gradient composites. In this paper dielectric, thermal and dynamic mechanical behaviour of milled carbon fibre reinforced gradient polysulphide modified epoxy composites have been studied and analyzed.

2. Materials and Methods

Polysulphide modified epoxy (PSEP) resin was used in this study. The density of epoxy resin cured at room temperature (resin to hardener ratio; 2:1) was 1.15 g/cm^3. Milled carbon fibre (Panex 33 MX) used in this study contained 95% Carbon content having an average fibre diameter 7.2 µm and fibre length 150 µm. The density of milled carbon was 1.81 g/cm^3.

Milled carbon fibre reinforced polysulphide modified epoxy gradient composites were developed by using a centrifugation technique described elsewhere [18]. Gradient samples were prepared from 3 vol. % of milled carbon fibre reinforced epoxy material. The milled carbon fibre was added to a mix of epoxy resin and hardener. Total mix was thoroughly stirred with the help of a glass rod. Details of set up and process of making gradient composites are as reported in an earlier patent [18]. The total mix was filled in the mould to make sample. The sample was rotated at 800 $\pm$ 50 RPM at a radius of 130 mm. The mould having mix was rotated for 2 hours till it was set and fibres distributed radially forming a gradient from inner side to outer side. The sample was left in the mould for 24 hours for curing. The mould was designed to make rectangular samples of desired dimensions. Samples were removed from the mould after curing at room temperature.

Samples were sliced from the carbon fibre reinforced polysulphide modified epoxy block prepared by the centrifugal casting method. These samples were sliced from the outer side to inner side. Maximum centrifugal force was exerted on the outermost sample, sample C and minimum at sample A. Sample designation, volume fraction of sample is listed in table1.

2.1. Dielectric Measurements

Capacitance (C) and tan δ values of milled carbon fibre reinforced epoxy samples were measured by using a Hewlett - Packard, LCR Meter, model 4274 A, in the temperature range 30 to 150 °C and frequency range from 1 to 10 kHz. Heating rate was kept constant at $\pm$1 °C/min. Dielectric constant (ε') was calculated by using the following relation

$$\varepsilon' = C/C_o \tag{1}$$

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

C_o is [(0.08854 A)/d] pF (pico farad),
where A (cm^2) is the area of the electrodes and d (cm) is the thickness of the sample. Tan δ is the dissipation factor and is defined as follows

$$\tan\delta = \varepsilon''/\varepsilon' \tag{2}$$

where ε'' is the dielectric loss.
Relaxation time of milled carbon fibre reinforced polysulphide modified epoxy sample A, sample B and sample C are determined at 80°C by using the following relation (17)

$$\tau(s)= (1/ \omega) *([\sqrt{((\varepsilon_0 -\varepsilon_\infty)/(\varepsilon'-\varepsilon_\infty))}-1]) \tag{3}$$

where τ(s) is the relaxation time in seconds. ω is the angular frequency, ε_0 is the dielectric constant of the sample at minimum frequency and ε_∞ is the dielectric constant of the sample at maximum frequency.

2.2. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) scans of PSEP and composite samples were carried out at a constant heating rate of 10 °C/min to measure peak temperature, onset and end set temperature by using a DSC (Mettler Toledo model DSC 822e). DSC scans of the composites were run in the temperature range 40–300 °C at a heating rate of 10 °C/min.

2.3. X-Ray Analysis

X ray diffraction patterns of pure PSEP composites were recorded by using a Philips X-ray diffractometer, Model 1700.CuK$_\alpha$ source was used.

2.4. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was carried out in air with a Dynamic mechanical spectrometer model (DMS 6100 SSI Nanotechnology Inc). Measurement of the storage modulus (E'), loss modulus (E'') and tanδ of the samples was carried out under compression mode at 1,2,5 and 10 Hz frequencies in the temperature range from 30°C to 190°C.

3. Results and Discussion

Fig.1-a shows the variation of dielectric constant (ε') with temperature for polysulphide modified epoxy resin at 1, 2, 4 and 10 kHz frequencies [17]. It was observed in this

Fig. that ε' increased with increase in temperature and decreased with increase in frequency. Initially at low temperatures, ε' at different frequencies merged. At low temperatures, thermal energy was not sufficient to activate the charge carriers and gave stable polarizability which lead to constant ε' values.

Fig.1-b shows the dependence of ε' on temperature for sample A. In this case, at higher temperatures gap in ε' values increased. Figs. 1-c and 1-d show the variation of ε' with temperature for sample B and C respectively. After 65°C there is a sudden increase in ε' values due to the glass transition temperature of PSEP. After Tg there is an increase in segmental mobility of polymer molecules due to the availability of more space for the easy rotation of dipoles. An increase of milled carbon fibre content increased the ε' value at all the temperatures, which confirms the gradient structure formation . Maximum increase in ε' is found in case of sample C,having 1.66 vol.% milled carbon fibres. Increase in ε' on addition of milled carbon fibres is due to the conducting nature of milled carbon fibres and interfacial polarization taking place in the composites.

Increased polarization in dielectric process in case of milled carbon fibre reinforced polysulphide modified epoxy composites is similar to graphite filled polystyrene observed by Xiao et al [19].

The dielectric constant data obtained experimentally for different composites was compared with the calculated values obtained from different theoretically models such as Linchtenecker model ,eqn. 4 , Maxwell -Garnett model ,eqn.5 and in Rao's equation, eqn. 6 ,listed below [20-22].

Linchtenecker model

$$\varepsilon = v_1 * \ln \varepsilon_1 + v_2 * \ln \varepsilon_2 \quad (4)$$

Maxwell-Garnett Model

$$\varepsilon = \varepsilon_1 (\varepsilon_2 + 2* \varepsilon_1 + (2* v_2 *(\varepsilon_2 - \varepsilon_1))) / (\varepsilon_2 + 2 * \varepsilon_1 - (v_2 *(\varepsilon_2 - \varepsilon_1))) \quad (5)$$

Rao equation

$$\varepsilon = \varepsilon_1 * ((1+ v_2*(\varepsilon_2 - \varepsilon_1)) / (\varepsilon_1 + n*(1- v_2)*(\varepsilon_2 - \varepsilon_1))) \quad (6)$$

Where ε is the dielectric constant of composite.ε_1 is the dielectric constant of matrix .ε_2 is the dielectric constant of filler and is taken as 2300 [23].v_1 is the volume fraction of matrix.v_2 is the volume fraction of fillers .n is the morphology of filler and is taken as 0.5 for this case.

Fig. 2 shows the variation of ε' with volume percent of milled carbon present in the composite. It is found that experimentally data matches with the Maxwell Garnett model.

Fig. 3(a-c) show the variation of dielectric constant (ε') with frequency (log f) at different temperatures for sample A ,B and C respectively. Fig. 3-a showed an initial decrease in ε' then a plateau appeared and finally it decreased. This plateau shifted towards left side with the increase of temperature. Slope of the initial curve decreased with the decrease of temperature. These composites show a frequency independent and temperature dependent zone. Frequency independent plateau corresponds to the d.c. conductivity. Dielectric constant dependence on frequency gives rise to Maxwell-wagner Sillars interfacial polarization. In case of sample B (Fig. 3-b), a plateau appeared at 105°C. No plateau was observed In sample C, having 1.66 vol.% milled carbon fibres (Fig.3-c).

Fig. 4(a-c) show the variation of tan δ with temperature for 0.45, 0.60 and 1.66 vol. % milled carbon fibre reinforced polysulphide epoxy composites respectively. These plots show that tan δ increased with increase in temperature but decreased with increasing frequency for all the samples. In case of 0.45 vol % milled carbon fibre reinforced polysulphide epoxy composite (sample A) tan δ peak appeared at 135 °C corresponding to 1 and 2 kHz frequencies. While in case of 0.60 vol.% milled carbon fibre reinforced polysulphide epoxy composite (sample B), tan δ peak appeared at 125°C corresponding to 1,2 and 4kHz frequencies. Carbon fibre reinforced polysulphide epoxy composite having 1.66 vol % milled carbon fibres (sample C) exhibited a tan δ peak at 115 °C corresponding to 1, 2 and 4 kHz frequencies. On increase in the milled carbon fibres content tan δ peak shifted towards lower temperature side due to the conducting nature of milled carbon fibres and defects present in the composite. The increase in tan δ value with temperature can be attributed to the space charge polarization effect produced from the sample electrode interface. This observation is similar to the work of Lingwal et al [24].They observed that tan δ peak shifted to lower temperature side with decreasing height and increasing frequency, showing the relaxation behaviour.

Relaxation time values of milled carbon reinforced polysulphide modified epoxy composites at 80°C are listed in table 2, which shows a decrease in relaxation time with increase of milled carbon content. Interface of carbon fibres and epoxy resin would have influenced the relaxation time of epoxy. At low frequencies the complete orientation of the molecules is possible and at medium frequencies there is a little time for the orientation and at high frequencies the orientation of the molecules is not possible [25].

Table 3. Lists the DSC peak positions for different samples. This shows a peak around 64.9, 60.1 and 60.1°C corresponding to PSEP, 0.45vol. % milled carbon fibre PSEP composite (sample A) and 1.66 vol. % milled carbon fibre PSEP composite (sample C). Similar observation was found in dielectric behaviour of these composites.

Table 4. Lists the d and 2θ values for pure PSEP and milled carbon fibre reinforced PSEP composites. This table shows an additional peak at d (= 3.35A°) corresponding to milled carbon fibres. Figs. 5-a and b show the X-ray diffraction pattern for typical sample A and sample C respectively. Fig. shows a broad peak corresponding to PSEP resin and peak at 3.35,d due to milled carbon fibre [26]. This shows that addition of milled carbon fibre

modified the structure of PSEP, which influenced the dielectric and thermal behaviour of composite.

A graph was plotted between E’, E”, tan δ vs. temperature for. Pure PSEP which shows that after 62°C storage modulus E’ decreased suddenly at 1Hz frequency. While tan δ plot showed a peak at 73.6 ,75.5,77.7 and 80.7°C for 1, 2 , 5 and 10Hz frequency respectively. This is due to the glass transition relaxation of PSEP. Similar trend is observed for loss modulus (E”).

A graph was plotted between E’, E” and tan δ vs. temperature for sample A .This plot shows that E’ exhibited a peak at 66.3°C at 1Hz frequency. Dissipation factor (tan δ) peak appeared at 74.9, 79.5,81.5 and 83.7°C corresponding to 1,2,5 and 10 Hz frequencies. This peak shifted to higher temperature side with increase in frequency. Similar trend is observed for E”.

In case of 1.66 vol% in the composite (sample C), E’ shifted towards lower temperature side to 58.9°C at 1 Hz frequency .

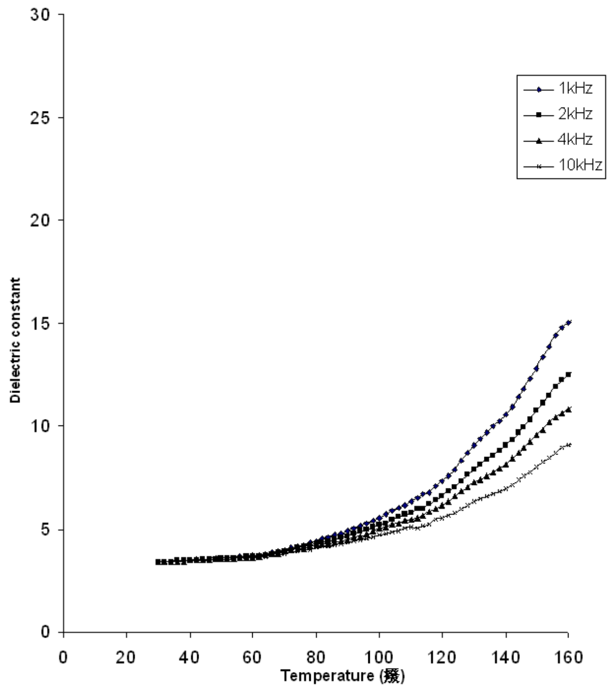

Fig 1-a. *variation of ε’ vs. temperature for polysulphide modified epoxy at 1,2,4 and 10 kHz frequencies.*

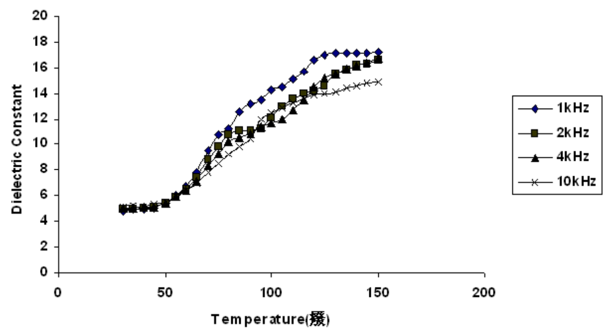

Fig 1-b. *variation of ε’ vs. temperature for milled carbon fibre reinforced polysulphide modified epoxy sample A at 1,2,4and 10 kHz frequencies.*

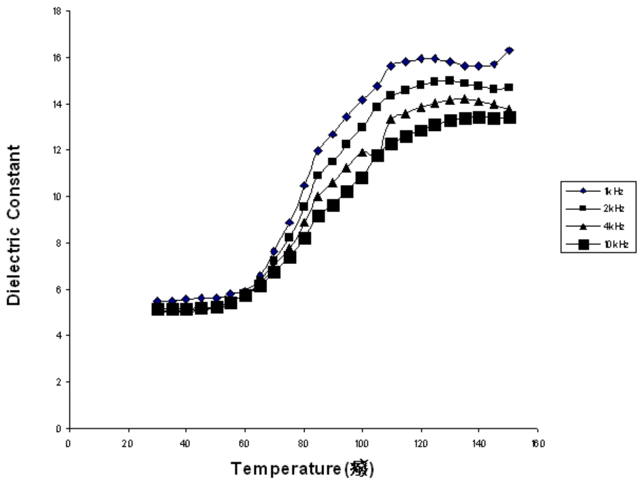

Fig 1-c. *variation of ε’ vs. temperature for milled carbon fibre reinforced polysulphide modified epoxy sample B at 1,2,4 and 10 kHz frequencies.*

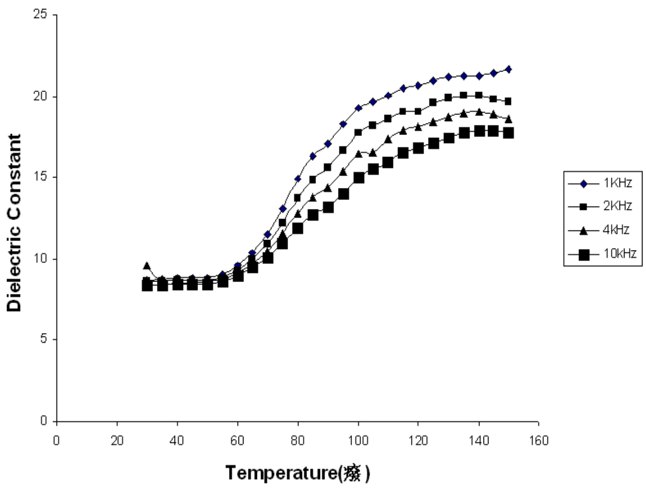

Fig 1-d. *variation of ε’ vs. temperature for milled carbon fibre reinforced polysulphide modified epoxy sample C at 1,2,4 and10 kHz frequencies.*

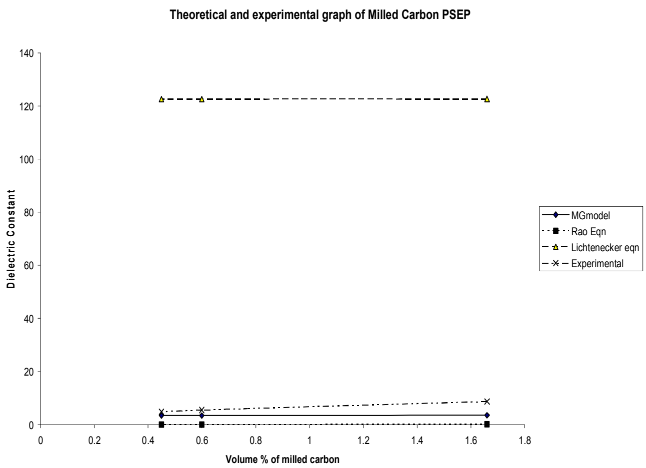

Fig 2. *variation of ε’ with Volume % of milled carbon fibre reinforced polysulphide modified epoxy composites.*

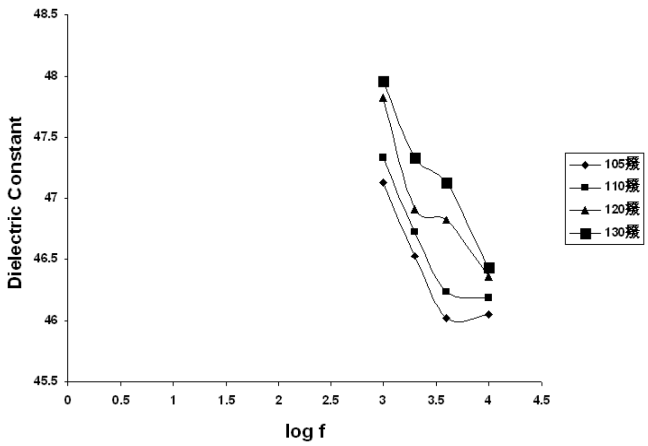

Fig 3-a. *variation of ε' vs. log f for milled carbon fibre reinforced polysulphide modified epoxy sample A at different temperatures.*

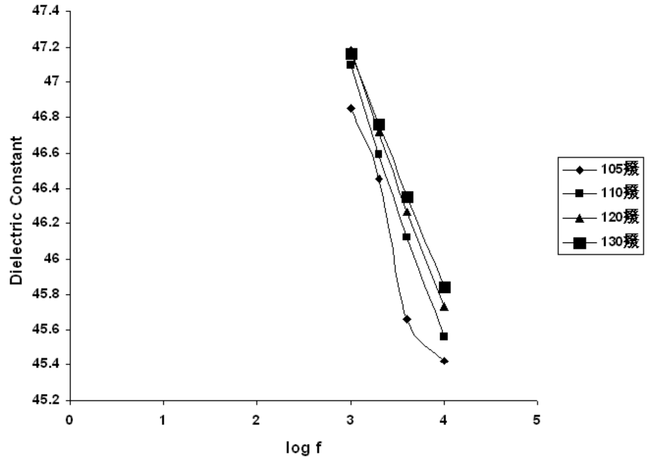

Fig 3-b. *variation of ε' vs. log f for milled carbon fibre reinforced polysulphide modified epoxy sample B at different temperatures.*

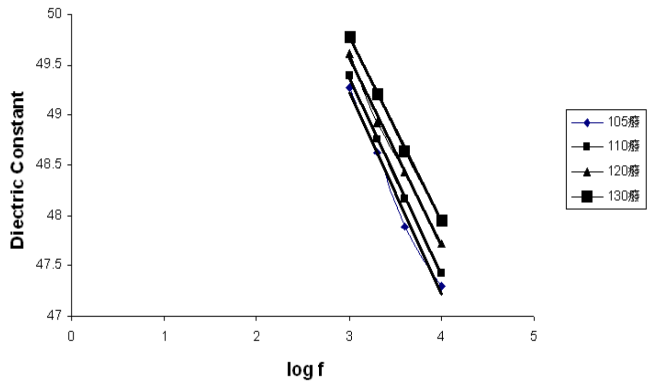

Fig 3-c. *variation of ε' vs. log f for milled carbon fibre reinforced polysulphide modified epoxy sample C at different temperatures.*

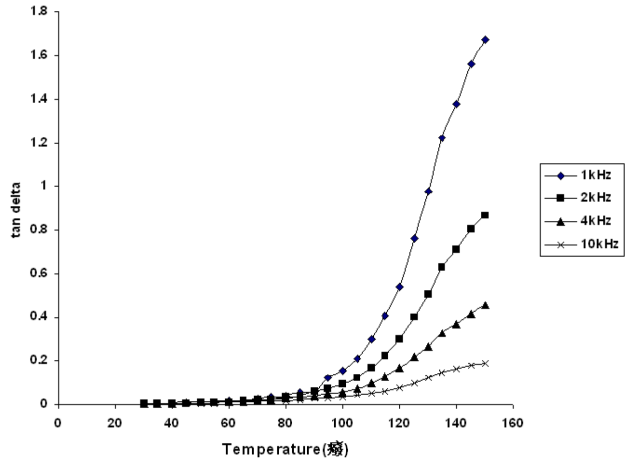

Fig 4-a. *variation of tan δ vs. temperature for milled carbon fibre reinforced polysulphide modified epoxy sample A at 1, 2, 4 and 10 kHz frequencies.*

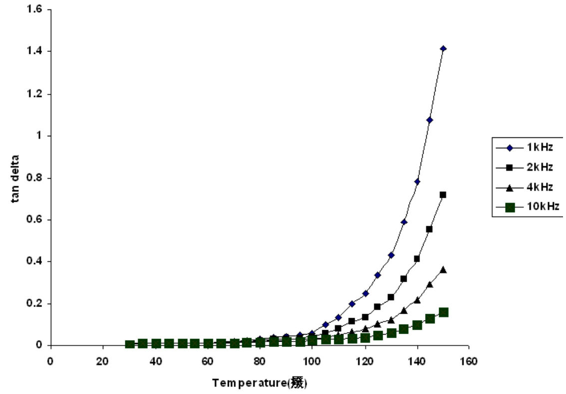

Fig 4-b. *variation of tan δ vs. temperature for milled carbon fibre reinforced polysulphide modified epoxy sample B at 1, 2, 4 and 10 kHz frequencies.*

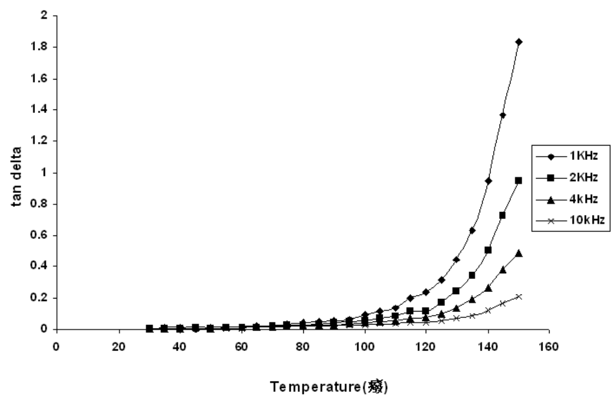

Fig 4-c. *variation of tan δ vs. temperature for milled carbon fibre reinforced polysulphide modified epoxy sample C at 1,2, 4 and 10 kHz frequencies.*

Table 1. *Sample Designation of milled carbon polysulphide modified epoxy gradient composites*

Vol.% of milled Carbon	Sample Designation
0.00	PSEP
0.45	Sample A
0.60	Sample B
1.66	Sample C

Table 2. *Relaxation time τ(s) of milled carbon fiber reinforced polysulphide epoxy gradient composites at 4 kHz at 80 °C*

Milled Carbon Fibre reinforced PSEP Sample A	Milled Carbon Fibre reinforced PSEP Sample B	Milled Carbon Fibre reinforced PSEP Sample C
$3.35x10^{-5}$	$2.28x10^{-5}$	$2.25x10^{-5}$

Table 3. *DSC data of pure and milled carbon PSEP composites*

Sample Designation	Heating Rate (°C /min)	Onset Temperature (°C)	Peak Temperature (°C)	Endset Temperature (°C)
Pure PSEP	10	60.5	64.9 240.7	68.3
Sample A	10	60.5	60.1 233.4	63.4
Sample C	10	55.8	60.1 226.7	63.3

Table 4. *Comparison of d values of pure and milled carbon reinforced PSEP composites*

PSEP		0.45vol. % milled carbon PSEP Sample A		0.60 vol. % milled carbon PSEP Sample B		1.66 vol. % milled carbon PSEP Sample C	
d(A°)	2θ	d	2θ	d	2θ	d	2θ
3.03	29.37	3.03	29.36	3.03	29.40	3.03	29.36
3.86	22.98	3.86	23.01	3.85	23.02	3.86	23.01
2.02	44.63	2.02	44.60	3.24	27.44	2.02	44.62
2.28	39.42	2.28	39.40	2.09	43.20	3.35	26.55

4. Conclusions

a) Gradient in dielectric constant (ε') exists in milled carbon fibre reinforced epoxy gradient composites.
b) Dielectric tan δ peak of milled carbon fibre reinforced composite shifted towards lower temperature side with increase of milled carbon content.
c) Relaxation time decreased with the increase of milled carbon fibre content.
d) DSC curves exhibited a decrease in Tg on adding Milled carbon fibres.
e) Additional peak at 3.35 d value was observed for sample C.
f) ε' data of composites with volume percent of milled carbon fits well with the Maxwell Garnett model.
g) Storage modulus, E', suddenly decreased after 62 °C and 60.4°C for PSEP and composite sample C having 1.66% carbon fibres respectively.

References

[1] Chand N. and Naik A., Polym.Compos. 2008, 29,736-744.

[2] Agari Y. and Uno T.J. ,J.Appl.Polym.Sci. 1985, 30, 2225.

[3] Bigg D.M., Polym.Eng.Sci. 1977, 17,pp.842-847.

[4] Bigg D.M., Adv.Polym.Technol. 1984, 4, 255.

[5] Narkis M., Lidor G., Vaxman A. , and zuri L. , J.Electrost. 1999, 47, 201-214.

[6] Nagata K., Iwabuki H. , and Nigo H., compos. Inerfac. 1999, 6,483.

[7] Demain A., "Thermal conductivity of polymer-chopped carbon fibre composites" PhD Dissertation, Universite Catholique de Louvain, Louvain-la-Neuve,Belgium, 1994.

[8] King J.A., Tucker K.W., Meyers J.D., Weber E.H., Clingerman M.L. and Ambrosius K.R., polym.Compos. 2001, 22, 142.

[9] Wilson M.S. and Busick D.N., "Composite Bipolar Plate for Electrochemical Cells". US patent No. 6, 248, 2001, 467.

[10] Loutfy R.O. and Hecht M., "Low cost Molded Plastic Fuel Cell Separator plate with Conductive Elements", US patent No.6, 511, 2003, 766.

[11] Chand N. and Nigrawal A., Bull.Mater.Sci., Indian Academy of sciences. 2008, 31(4) ,1-4.

[12] Mehta V. and Cooper J.S.,J.Power Source. 2003, 114, 32-53.

[13] Jia –Xiang Zhao, Carbon fibres and composites materials in HEXEL corporsation, U.S.A., Thermo setting Resin. 2001,16,44-48.

[14] H.Hug , JDH. The Carbon fibre/Epoxy interface–A review. Compos.Sci.Technol. 1991, 41, 13-45.

[15] Mair H.J. and Roth S. Elektrischleitende Kunststoffe, Cral Hanser Verlag, Vienna 1989.

[16] T.A. Skotheim Handbook of conductive polymers, MarcelDekker, Basel (1986).

[17] Chand N. and Jain D. Bull.Mater.Sci. Indian academy of sciences. 2004,27, 227-233.

[18] Chand N. and Hashmi SAR, Indian Patent 438, 2003.

[19] Xiao M., Sun L., J Li Y and Gong K. Polymer 2002, 43, 2245.

[20] Linchtenecker K., Die Dielektrizitatskonstante natuarlicher and Kunstlicher Misckorper.Physikalische zeitschrift, 1926, 27, 115-158.

[21] Maxwell-Garnett JC. Trans.Roy.Soc 1904, 203,385-420.

[22] Rao Y., Qu Jm, Marinis T., Wong C.P. IEEE Trans.compon.Pack.Technol. 2000, 23, 680-683.

[23] Jianwen Xu, Wong M. and Wong C.P., Electronic components and technology conference,Proceedings 2004, 54(1), 536-541.

[24] Lingwal V., Semwal B.S. and Panwar N.S. Bull. Mater. Sci. 2003, 26, 619-625.

[25] Paul A. and Thomas S. J.Appl.phys. 1997, 63, 247-266.

[26] Fitzer E, HeineM.In:Bunsell A.R.,Editor.Fiber reinforcements for composite materials,composite materials series 2.Amsterdam: Elsevier,1988:73-147.