



Available online at: www.basra-science journal.org

ISSN - 1817 - Ü2695



Dielectric properties of Carbon Black /PVC (cement) Composites

Shemaa H. Jasem and Waleed A. Hussain

Physics Department in College of Education-Basra University, Basra, Iraq

e- mail: walee_dah@yahoo.com

Received 15-12-2011, Accepted 15-2-2012

Abstract

The dielectric and a.c. conductivity behavior of CB / PVC (cement) composites was studied. The measurements were taken in the frequency range from 1kHz to 1MHz and the temperature range from 30 °C to 90 °C. The composites permittivity ϵ' shows a strong dependence on CB loading and increases as CB loading increases until percolation at (~ 13% vol) loading is reached after which decreases sharply to zero . Frequency dependency of ϵ' show dependence on filler loading, at low CB loading percentages , ϵ' is nearly stable versus frequency . ϵ' increases with the temperature rise of the composites. The a.c conductivity increases with the increase of loading and temperature, and shows frequency independency at higher loading.

Keywords: thermoplastic composites, PVC, a.c conductivity, carbon-black, dielectric properties.

1.Introduction:

Polymer composites are considered as heterogeneous systems which are usually consist of a polymer matrix (first phase), mixed with inorganic conductive or non conductive particles (second phase).

Polymeric composites filled with conductive fillers are of intrest for many fields of electronic industry such as encapsulating , thin film coating , packing of electronic circuits , protective coatings electromagnetic frequency interference shield , antistatic devices , thermistors,[1-3]. This interest arises from the fact that their electrical properties (electrical conductivity) are close to the properties of metals, whereas the mechanical properties are typical for plastics [4].

The electrical properties of these kinds of composites depend on the filler content , size and shape of the particles , and other factors : such as adhesion between the

filler and the matrix , and the method of processing [5-7], and the effective use of these composites depends strongly on the ability to disperse the fillers homogeneously throughout the polymeric matrix [8] .

Most of the polymers used in the field of composites are insulator such as : epoxy , PVC , PE , PMMA,..... etc. When such polymers are chosen for conductive composites fabrication , conductive fillers like (metal- particles , carbon black (CB) , graphite,.....) are used . These fillers are inert and increase the electrical conductivity and interfacial polarization or (Maxwell-Wanger- sillars polarization). This increase depends on the filler concentration and is characterized by a drastic change at critical concentration of the conductive filler , which is attributed to the formation of continuous network of the conductive phase that spans throughout the insulating polymer matrix ,

called percolation threshold [2,9] . Percolation occurs when there are enough particles for a consistent electrical network to be formed by physical contact or tunneling of electrons through thin layers of matrix separating the inclusions [10].

The value of the percolation concentration depends on the materials used, type of polymer, conductive filler surface area, electric charge, particle size and their distribution [2, 10- 11]. Different electrical percolation thresholds of carbon black (CB) / composites were found for different species of carbon- black [12]. CB as a fillers are characterized by , the uniqueness of being small and inert spherical conductors (150-750 Å⁰) of almost electrical conductivity in the

range (0.1 to 1000 S/cm) and aggregate/ aglomated into chain like structure with different over all aspect ratios [12,13] . The dielectric properties of CB composites are strongly dependent on the particle size, the aggregate structure of the CB, and a higher conductivity of CB usually results in higher dielectric constant in its composites [14].

In the present work , a carbon black-thermoplastic composite system, (carbon black-polyvinyl chloride) CB / PVC (cement) composites are prepared , and the dielectric properties as well as a.c conductivity of the composites are investigated as a function of filler content , frequency in the range (1kHz- 1MHz) and temperature in the range (30-90 °C) .

2.Experimental:

2.1 materials

The polymeric matrix used in this work was a commercial Polyvinylchloride cement PVC (cement) (N LICHIDE PVC cement 717-21 heavy duty-clear) from SWAN TRADING (L.L.C), it is solvent borne PVC resin based , single component cement most suitable for PVC pipe joining required for portable water irrigation, natural gas pipe, conduit , drain ... etc

Carbon Black (Mert-Germany) with particle size (130 Å⁰) is used as a filler component in the composites.

To insure a good dispersion of the filler and to provide a homogeneous composite ,

CB in different volume fractions (0.7, 1.4, 2.1, 2.8, 3.5, 7.1, 8.9, 9.3, 10.8, 12.7, 14.6 vol%) are put in a Petri dish and then PVC cement were added .

The mixture was suitably mixed for (15 minutes) and left in the lab for (48 hours), followed by post curing at (80 °C) for (2 hours). A thick circular sheet of (4.5 cm) diameter and (1mm) thickness was produced. The loading fraction percentage was measured relative to neat weight of PVC (cement) after curing processes.

2.2 measurements

The samples capacitance (C) and the loss tangent (tanδ) of the composites were measured by digital RCL bridge type (MEGGER B131), at 1kHz. At continuous frequencies in the range (50Hz -1MHz) RCL type (Programmable automatic RLC meter, FLUKE PM6306) was used to measure the capacitance of the samples.

The relative complex permittivity (ϵ^*) can be expressed as $\epsilon^* = \epsilon' - i\epsilon''$, the real part (ϵ') or relative permittivity where, and the imaginary part (ϵ'') or

dielectric loss is calculated by using the measured capacitance and loss tangent, according to the relations, $\epsilon' = Cd / \epsilon_0 A$, and, $\epsilon'' = \epsilon' \tan\delta$, respectively. Where, d is the separation between the two electrodes, A is the area of the electrodes, ϵ_0 is permittivity of the free space, ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m). A.C. conductivity ($\sigma_{a.c}$) is calculated according to the relation. $\sigma_{a.c} = \epsilon_0 \omega \epsilon''$ where, ω is the angular frequency[15] .

3. Results and Discussion

3.1 permittivity:

3.1.1 Loading dependency of permittivity:

The variation of permittivity ϵ' (dielectric constant) as a function of CB content at frequency (1kHz) and room temperature (27 C°) is depicted in Fig.(1) . It is obvious that ϵ' increases with increase of C.B loading . This is a common behavior for heterogeneous systems consisting of two different phases, and has been observed by many workers [1, 9,16-20]. The increase in permittivity is attributed to interfacial polarization (Maxwell- Wagner- Sillers polarization phenomenon).

At low CB loading the mean separation between CB particles is large and the permittivity is limited by PVC (cement) matrix. The increase of CB loading enhances the permittivity, this is attributed to CB aggregation or clustering to form larger particles compared to individual particles

with greater interfacial area and, hence, the polarization associated with it becomes larger leading to an increase in permittivity.

According to percolation theory, conductor – insulator system shows a divergent in dielectric permittivity versus conductive filler loading near the percolation threshold [21]. As CB loading is raised, clusters of conductive particles are formed by physical contact, the dimensions of these clusters increase with the increase of filler loading and a conductive network structure will start to form. This process explains the sharp decrease in ϵ' at (~ 13% vol) loading , which attributed to already well connected electrically conductive network formation (percolation) , resulting in a conductor- like conduction with the applied measuring field leading ϵ' to be zero [12].

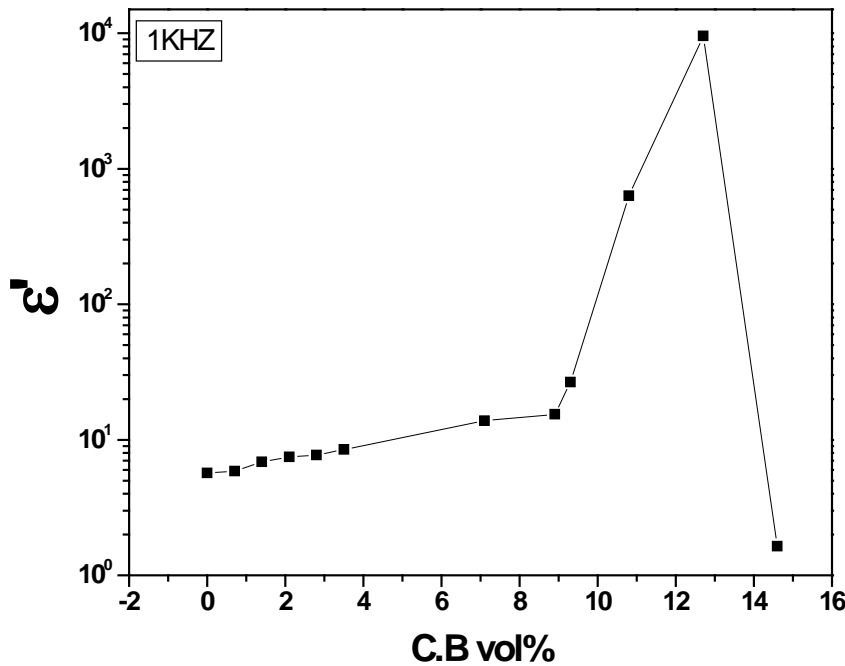


Figure (1): Variation of ϵ' with CB loading vol% at room temperature and 1kHz frequency.

3.1.2 Frequency dependency of permittivity:

The variations of ϵ' as a function of frequency in the range (1kHz-1MHz) for CB / PVC (cement) composites at different loading and pure PVC (cement) at room temperature are shown in Fig.(2). At low

loading there is a slight increase in ϵ' with the decrease of frequency, the increase becomes more obvious at (10.8 vol%) and (12.7 vol%) loadings. The higher values of ϵ' at lower frequencies, are attributed to the

process of interfacial polarization and polarization induced by segmental mobility in the polymer which appears more effective at low frequencies and high temperature respectively [22]. At higher frequencies the dipole responsible for this polarization can not keep up orientation in the direction of the alternating field, which lead to a decrease in ϵ' .

It can be seen that, for loading up to (9.3 vol%) the permittivity of the composite is stable versus frequency (resume the frequency dependency of the PVC matrix permittivity) . Xu and et al [14], S. Nakamura and et al [23] have observed the same behavior and concluded that the frequency dependence is also dependent on the filler loading.

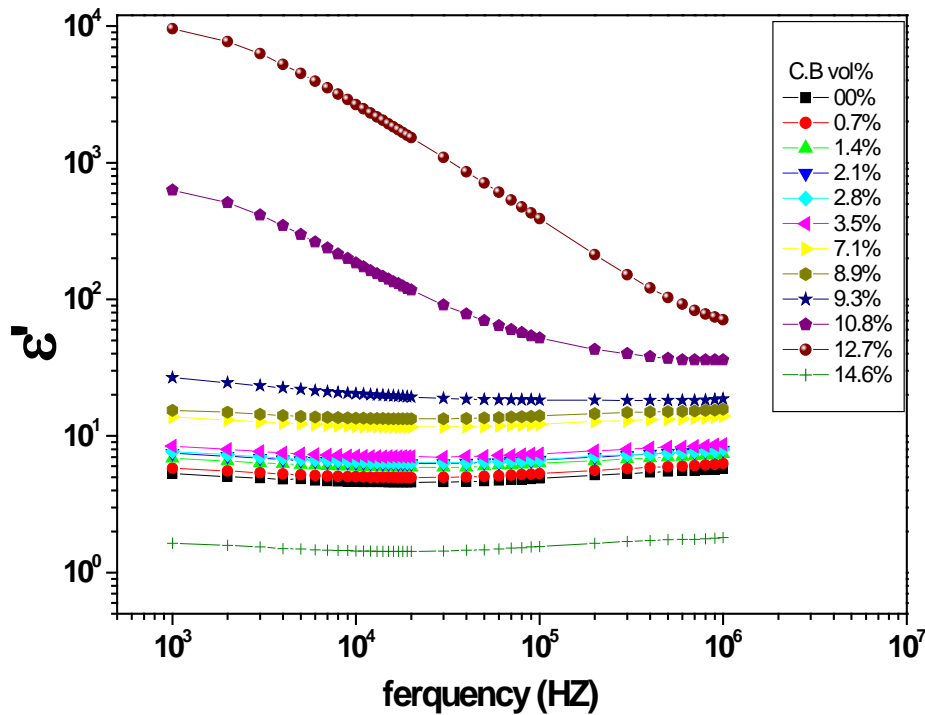


Figure (2): Variation of ϵ' with frequency at room temperature for different CB loadings.

3.1.3 Temperature dependency of permittivity:

The effect of temperature on ϵ' of CB composite in the temperature rang (30-90 °C) is depicted in Fig. (3). It is clear that for all filler loading, ϵ' increases with the temperature raise (in the temperature range studied) . As mentioned formerly , polarization induced by segmental mobility in

the polymer appears more effective at high temperature . At higher temperature below the transition temperature, the consequence drop in viscosity of polymer enhances the segmental mobility of the polymer making the orientation of the dipoles much easier with the alternating field .

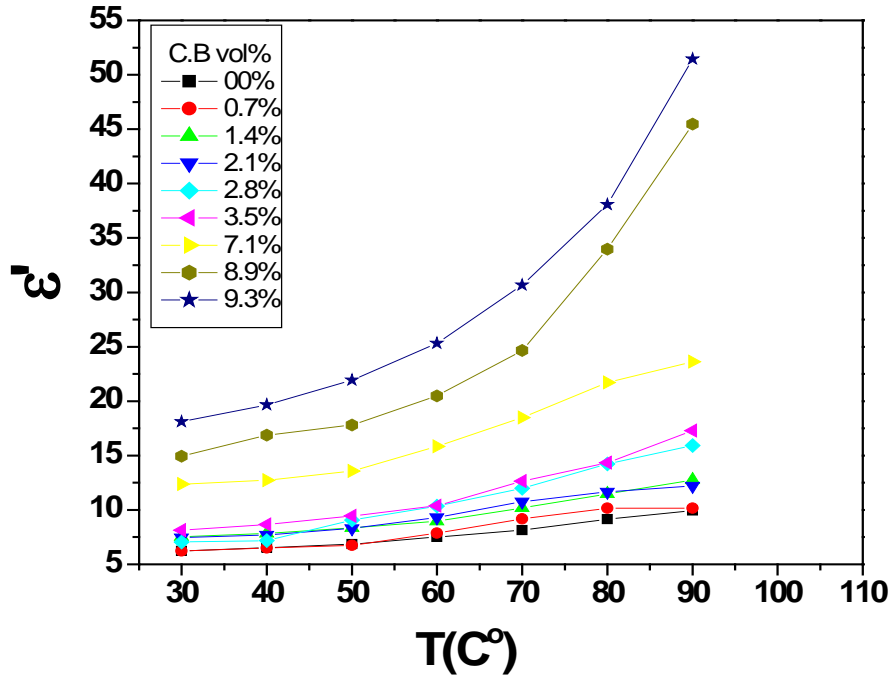


Figure (3): Variation of ϵ' with temperature at 1KHz frequency for different CB loading .

3.2 Dielectric loss ϵ'' :

The variation of dielectric loss ϵ'' as a function of loading is illustrated in Fig. (4) . It is clear that ϵ'' values increase with the increase of CB loading . This is attributed to

interfacial polarization and the increase in D.C conductivity which can lead to higher rates of decay of stored charges [14].

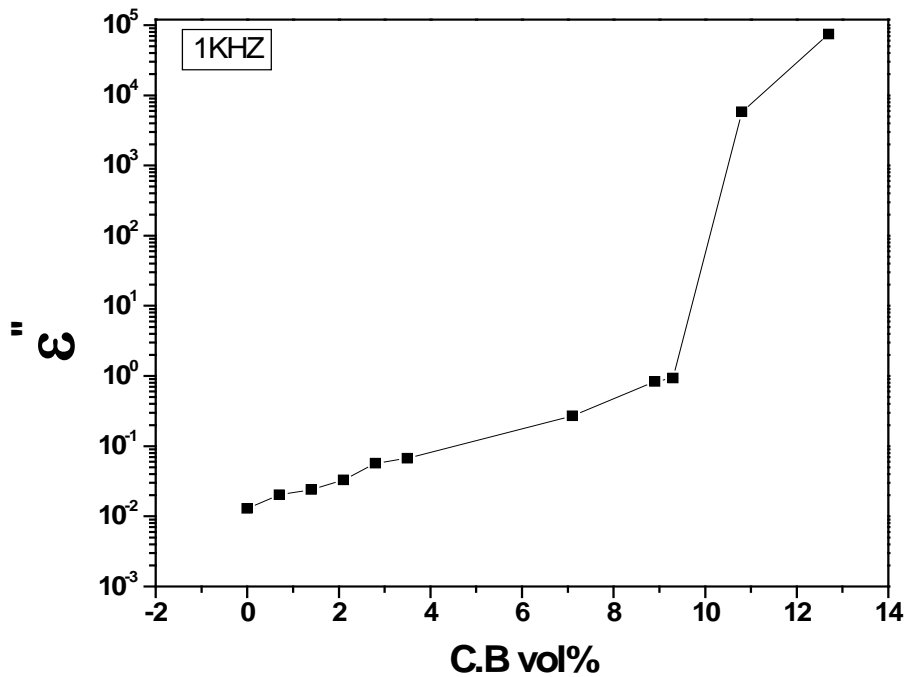


Figure (4): Variation of ϵ'' with CB loading vol% at room temperature and 1kHz frequency.

The frequency dependence of ϵ'' in the rang (1kHz-1MHz) shows a peak values (α -relaxation) which shifts towards lower frequencies as CB loading increases as shown in Fig.(5). This can be attributed to the shift in T_g towards higher temperature with the increase in CB loading as shown in Fig. (6).

(T_g was calculated as a result of DSC thermal analyses according to DSC-60 SHIMADZU Japan measurement as shown in fig.(7-a) and fig.(7-b) for pure PVC and (0,14.6 %) vol CB loaded composite respectively as an example).

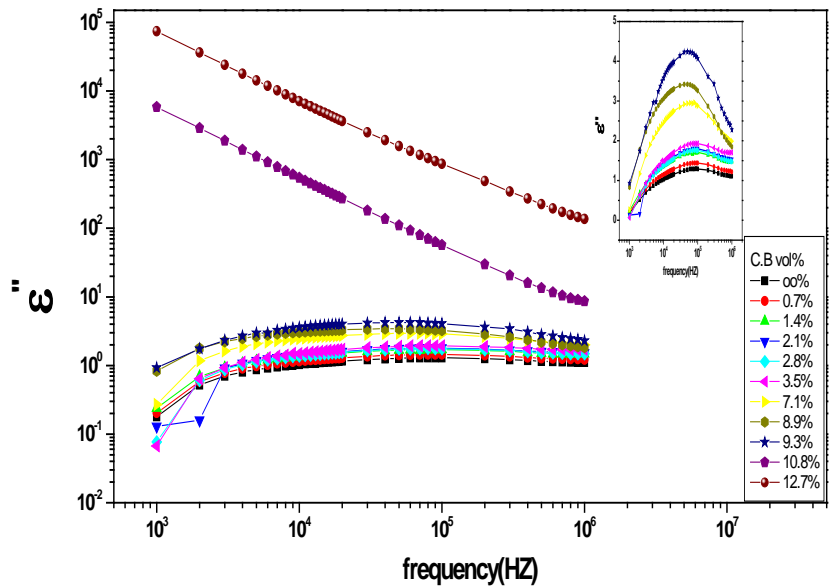


Figure (5) : Variation of ϵ'' with frequency at room temperature for different CB loading .

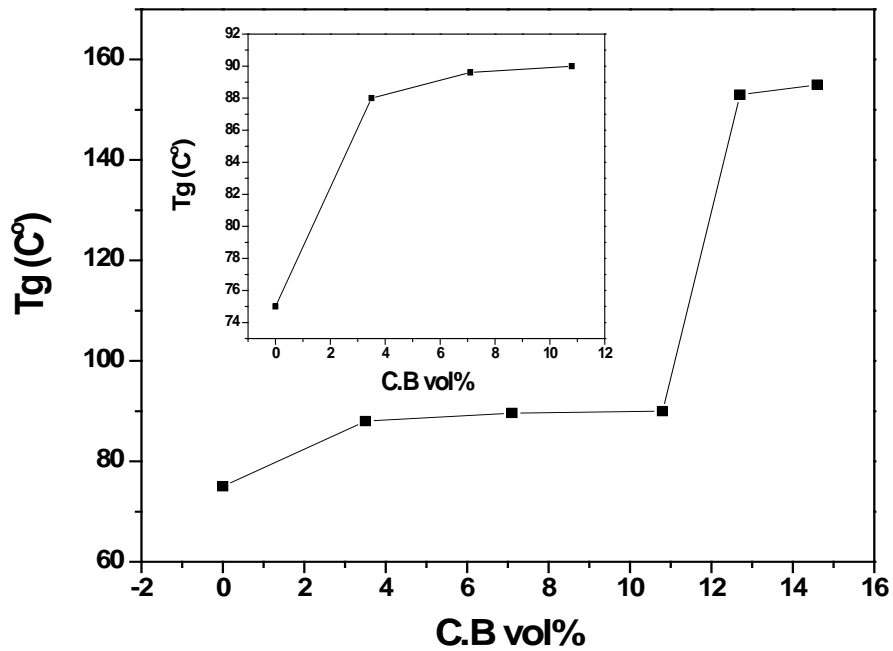


Figure (6) :Variation of T_g with CB loading vol% of CB/PVC composites.

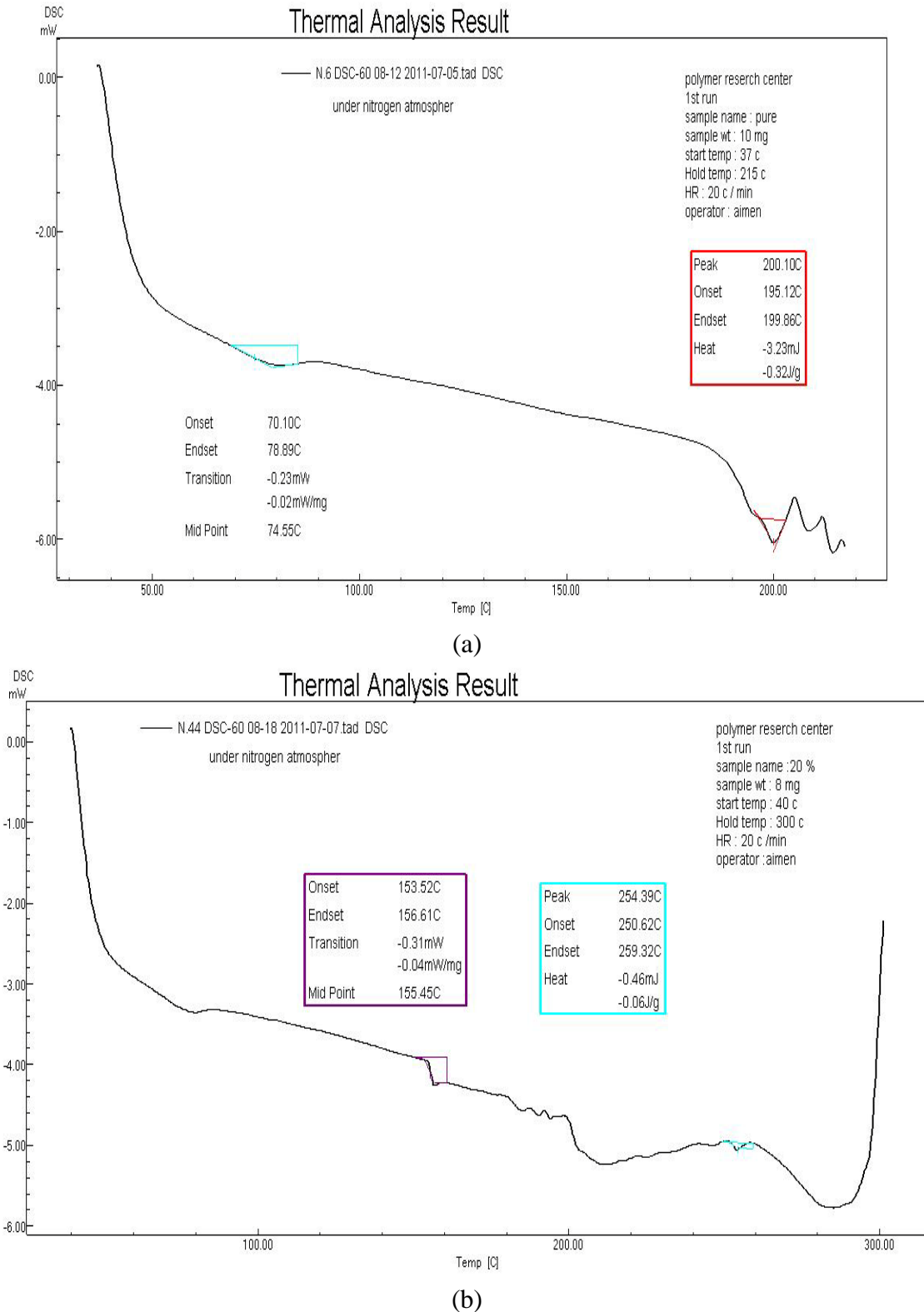


Figure (7): DSC thermal analysis of (a) pure PVC (cement) and (b) (14.6 %) vol CB loaded composite.

Fig. (8) illustrates the variation of ϵ'' versus temperature in the range (30-90 °C) for CB composites. It can be seen that ϵ'' increases with rise in temperature. The increase in ϵ'' for all composites is related to

the increase of segmental mobility and ionic conduction due to the consequence drop in viscosity of the polymer and the thermal dissoiication of the molecules [24].

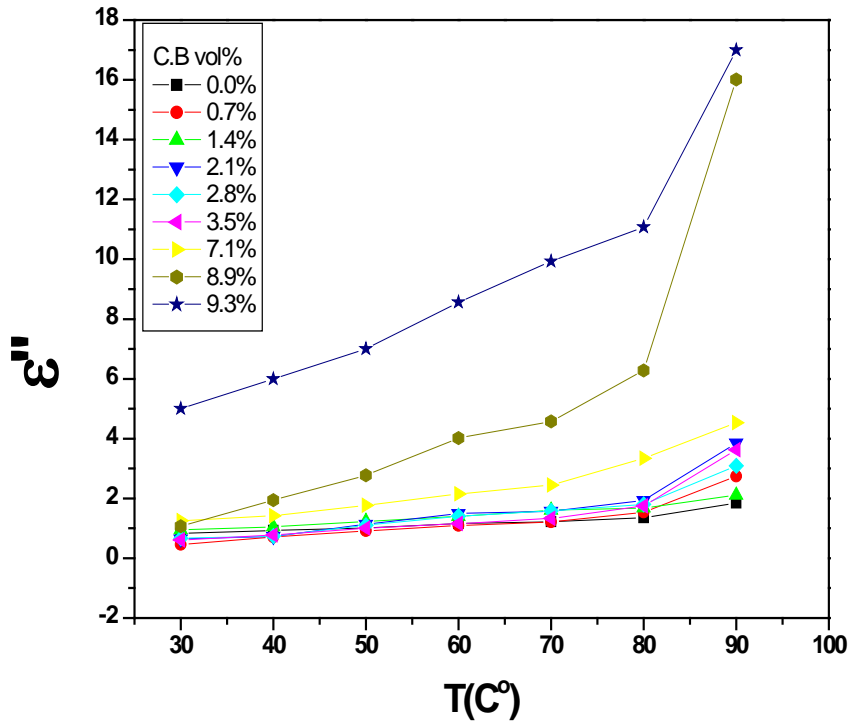


Figure (8): Variation of ϵ'' with temperature at 1KHz frequency for different CB loading .

3.3 A.C conductivity ($\sigma_{a.c}$) :

The loading dependency of $\sigma_{a.c}$ is illustrated in Fig.(9). It can be seen that $\sigma_{a.c}$ increases with the increase of CB loading. At low loading (less than 4%) the conductive CB particles form a finite clusters but are relatively widely separated by the insulating matrix (PVC) so $\sigma_{a.c}$ is limited by polymer matrix . At this stage, charge carrier transport mechanism via hopping or tunneling is unexpected due to the relatively large insulating barriers. A further increase in CB

loading reduces the separation between particles such that, the electric field can assist charge carriers tunneling mechanism. When CB loading reaches a critical value (percolation threshold) a network of conductive paths of physically contacted particles starts to form through the polymer matrix , and $\sigma_{a.c}$ increases continuously with the increase of CB loading . The magnitude of $\sigma_{a.c}$ reaches ($4.4 \cdot 10^{-3}$ S/m) for CB loading of 12.7%.

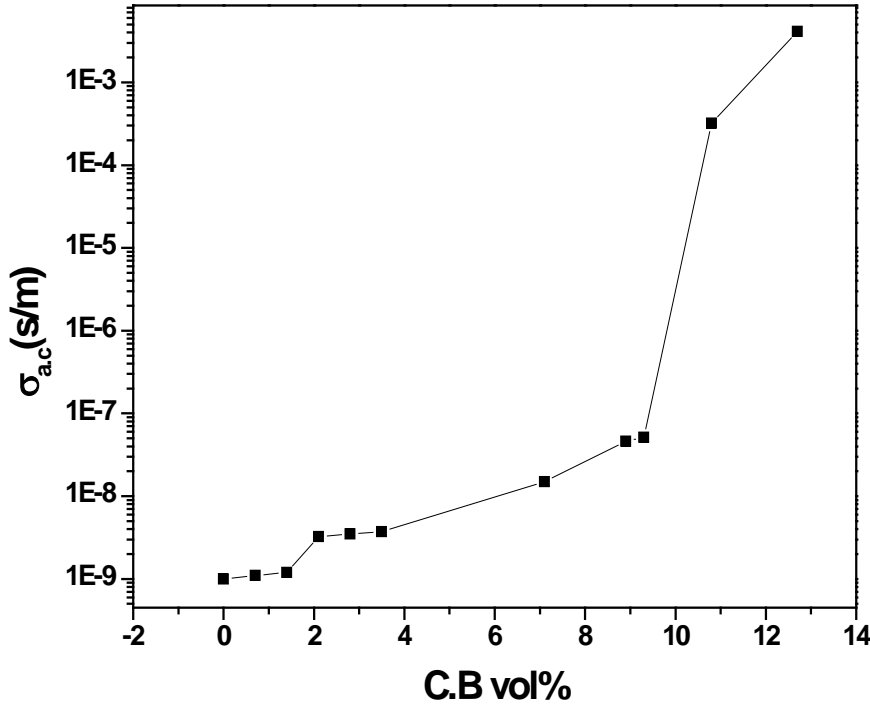


Figure (9) : Variation of σ_{ac} with CB loading vol% at room temperature and 1kHz frequency.

The frequency dependence of σ_{ac} conductivity for various volume percent loading of CB composite is shown in Fig(10). For the composites with relatively low CB loading (≤ 9.3 vol%), there is almost a gradual linear increase in a.c conductivity with increasing frequency. This is a typical behavior for dielectric material, which may be attributed to the thin layer of the insulating phase (PVC), which forms the boundaries between the conductive particles (cluster) of

CB. These boundaries are more active to prevent hopping and tunneling conduction between the insulated conductive particles (in CB composites tunneling conduction was suggested [25-27]). With the increase of loading and frequency the boundaries become less active via charge carriers tunneling between the insulated clusters, therein σ_{ac} increase with the increase of frequency, same behavior has been observed by S. Sindhu and et al [28].

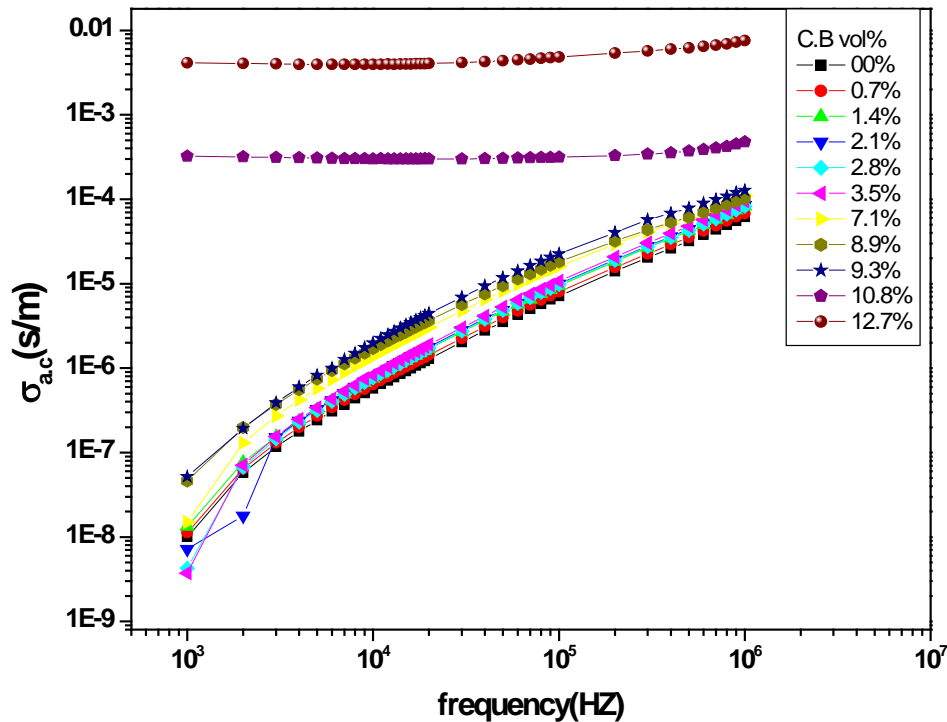


Figure (10): : Variation of $\sigma_{a.c}$ with frequency at room temperature for different CB loading .

For higher CB loading, $\sigma_{a.c}$ is almost frequency independent taking as a limit the D.C value ($\sigma_{d.c}$) (i.e. the composite behaves like a single phase conductor). It can be also seen , that , at a critical loading(≈ 10.8 vol%) percolation threshold occurs . This means that the CB clusters get closer and form physically contacted linkage , which results in an initial conducting path through the composite (insulator – conductor transition).

Form the figure of $\sigma_{a.c}$ frequency dependence , it is clear that the percolation

threshold is reached at ≈ 10.8 vol% and the bulk conductivity reaches value as high as ($4.4 * 10^{-3}$ S/m) for CB loading percentage of 12.7% .

Fig (11) shows the variation of a.c conductivity with temperature . The influence of temperature on $\sigma_{a.c}$ has been explained by considering the mobility of charge carriers responsible for hopping [29]. As temperature increases the mobility of hopping ions in PVC also increases thereby increases conductivity .

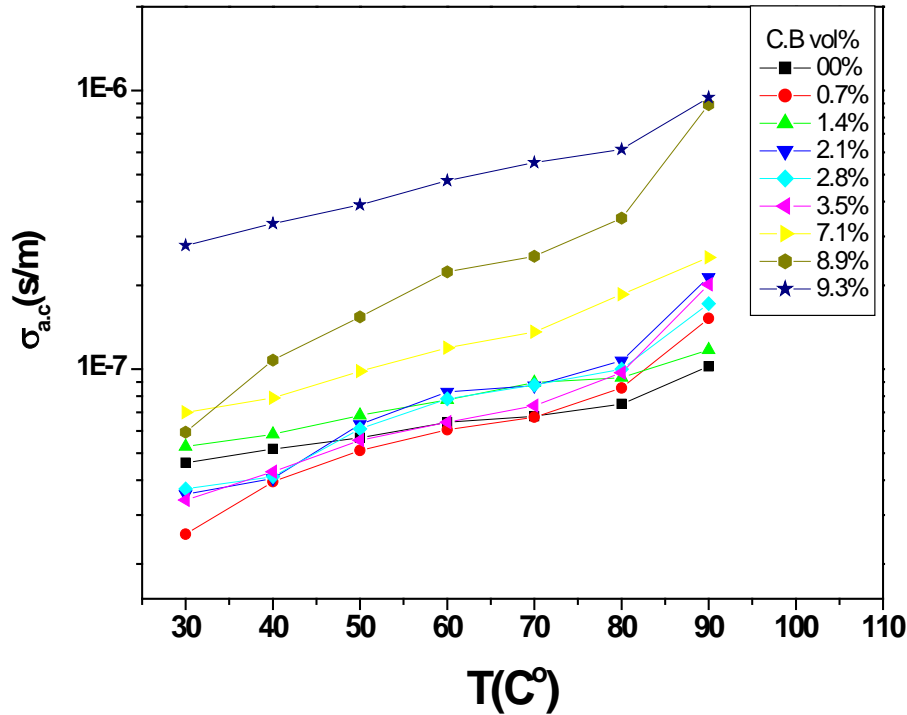


Figure (11): Variation of σ_{ac} with CB loading vol% and temperature at 1kHz frequency.

4. Conclusions

CB / PVC (cement) composites is easily processed from PVC solution, and CB. The composites permittivity ϵ' shows a strong dependence on CB loading and increases as CB loading increases until percolation at (~13% vol) loading is reached. Frequency dependency of ϵ' shows dependence on filler loading, at low CB loading percentages, ϵ' is nearly stable versus frequency. ϵ' increases

with the temperature rise of the composites. The dielectric loss ϵ'' values increase with the increase of CB loading, and the frequency dependency shows a peak values (α -relaxation) which shifts towards lower frequencies as CB loading increase. The a.c conductivity increase with the increase of loading and temperature, and shows frequency independency at higher loading.

References:

- 1- Y.Xu, D.D.L Chung, C. Morz, Composites, Part A 32(2002)1749.
- 2- R. Strumpler, J. Glatz- Rechenbach, J Electrocerm, 3(1999)329.
- 3- S. Toshikawa, T. Oata, R. I. Newnham, J. Am. Ceram. Soc. 73, (1990) 263.
- 4- S.K. Bhattacharya, Metal-filled polymers, (Properties and Applications) New York: Marcel Dekker: (1986).
- 5- B.Weidenfeller, M. Hofor, F. Schilling , Composites, Part A 33 (2002) 1041.
- 6- Y. P. Mumuny, V. V. Pavydenko, P. Pissis, E. V. Lebeder, European Polymer Journal, 38 (2002) 1887.
- 7- W. Thongruang, R. J. Spontat, C. M. Balik, Polymer, 43 (2002) 3717.
- 8- P. K. C. Pillai, G. R. Narula, A. K. Tripathi, Polymer, J, 16(1984)575.
- 9- V. Singh, A. R. Kulkarni, T. R. Rama Mohan, J. Appl. Poly. Scie, 90 (2003) 3602.
- 10- A. Moulart, C. Marrett, J. Colton, Polymer Engineering and Science , March 44, 3 (2004).
- 11- Ou. Runging, R. A. Gerhardt, C. Marrett, A.Moulart, J.S. Colton, Composites, Part B 34 (2003) 607.
- 12- K. T. Chung, A. Sabo , A. P. Pica, J. Appl. Phys, 53 (10) (1982)6867.

- 13- Y. Chekanov, R. Ohnogi, S. Asai, M. Sumita, *J. Material Science*, 34 (1999) 5589.
- 14- J. Xu, M. Wong, C.P. Wong, *Electronic components and Technology Conference*, (2004) 536.
- 15- L. Ramajo, M. Catro and M. Reboredo, *J. Appl. Sci. Manuf.*, 38, 1852-1959, (2007).
- 16- N. Chand, D. Tain, *Bull Matter Sc*, 273 (2004) 227.
- 17- R. V. Rao, M. H. Shridhar, *Materials letters*, 55, 1-2 (2002)34.
- 18- G. C. Pasarras, E. Manolakaki, G. M. Tsangaris, *composites, Part A* 33 (2002) 375.
- 19- H. S. Gohturk, J. J. Fiske, D. M. Kalyon, *J Appl Poly. Sci.* 50(1993) 1891.
- 20- A. A. Hussain, W. A. Hussain, *J. Basrah Researches (Science)* 36 No. 3 (2010).
- 21- D. M. Grannan, J. C. Garland, D. B. Tanner, *Phys. Rev. lett.* 46 (1981) 375.
- 22- C. H. Kim, J. S. Shin, *Bull, Korean Chem. Soc* 23,3(2002)413.
- 23- S. Nakamura, T. Tomimura, G. Sawa, *Conference on Electrical Insulation and Dielectric Phenomena* (1999) 298.
- 24- B. Tareev, *Physics of dielectric materials.* Mir Puplications Moscow (1975).
- 25- T. A. Ezquerra, M. Kulescza, C. S. Cruz, F. J. Batta-Calleja, *Adv. Mater* 2, (1990) 597.
- 26- M. T. Connor, S. Roy, T. A. Ezquerera, F. J. Batta- Calleja, *Phys. Rev. B* 57 (1998) 2286.
- 27- K. M. Jager, D. H. Mequeen, J.A. Tchmutin, N. G. Ryvkina, M. Kluppel, *J. Phys.D: Appl. Phys.* 34(2001) 2699.
- 28- Yu Chao Li, Robert Kwok Yiu Li, and Sie Chin Tjong, *J. Nanomaterials*, Volume (2010), Article ID 261748, 10 pages.
- 29- S. Sindhu, M. R. Anantharaman, B.P. Thampi, K. A .M Alini, P. Kurian, *Bull Mater. Sci.* 25 (2002) 599.