This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of
Macromolecular
Science Part A:
Pure and Applied Chemistry

Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Dielectric Properties of Polymer Composites Filled with Different Metals

Anjum Qureshi[a][b]; Ayhan Mergen[b]; Mehmet S. Eroğlu[c]; N. L. Singh[d]; Arif Güllüoğlu[a]
[a] Department of Physics, Fatih University, Istanbul, Turkey [b] Department of Metallurgical and Material Science Engineering, Marmara University, Istanbul, Turkey [c] Department of Chemical Engineering, Marmara University, Istanbul, Turkey [d] Department of Physics, M. S. University of Baroda, Vadodara, India

Online publication date: 04 January 2011

To cite this Article Qureshi, Anjum , Mergen, Ayhan , Eroğlu, Mehmet S. , Singh, N. L. and Güllüoğlu, Arif(2008) 'Dielectric Properties of Polymer Composites Filled with Different Metals', Journal of Macromolecular Science, Part A, 45: 6, 462 — 469

To link to this Article: DOI: 10.1080/10601320801977756

URL: http://dx.doi.org/10.1080/10601320801977756

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2008) **45**, 462–469

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320801977756

Dielectric Properties of Polymer Composites Filled with Different Metals

ANJUM QURESHI,[1,2] AYHAN MERGEN,[2] MEHMET S. EROĞLU,[3] N. L. SINGH,[4] and ARIF GÜLLÜOĞLU[2]

[1]*Department of Physics, Fatih University, Istanbul, Turkey*
[2]*Department of Metallurgical and Material Science Engineering, Marmara University, Istanbul, Turkey*
[3]*Department of Chemical Engineering, Marmara University, Istanbul, Turkey*
[4]*Department of Physics, M. S. University of Baroda, Vadodara, India*

Received October, 2007, Accepted November, 2007

Electrically conductive composite systems based on polyvinyl chloride (PVC) and polymethyl methacrylate (PMMA) filled with metal powders of Al and Cu have been studied. The composite preparation conditions allow the formation of a random distribution of metallic particles in the polymer matrix. Dependence of the dielectric and conductivity properties of the PVC and PMMA/fillers was studied over a broad range of frequency and volume fraction of metal fillers. The experimental results could be explained by means of the conductivity of fillers and the interface polarization between polymers and fillers. Percolation was also seen in this study when the volume fraction of conducting fillers was close to critical value, in which the composites undergo an insulator-conductor transition. The relation among the dielectric property and the fillers with different conductivity was proposed.

Keywords: polymers; metal fillers; Dielectric properties

1 Introduction

Polymer composites filled with various metals are of interest for many fields of engineering. The interesting properties of such systems make them technologically important and competitive to other alternative materials due to their various behavior and cost effectiveness. Some of the application areas of polymer-metal composites are metal catalysts embedded in polymer electrolytes for fuel cells (1), and prosthetic devices frequently feature acrylic bone cement in contact with metallic implant materials. Electroactive and conductive polymers are another potential application of polymer composites. A remarkable electromechanical response has been discovered in electroactive polymers with high dielectric constant when a low applied field is used (2). Electroactive polymers have potential application in actuators, sensors and power generation. Conductive polymer composites are of great interest because their electrical properties can be tailored by properly choosing the components and their relative concentration. The possible application of conductive polymer composites are capacitors, self-regulating heater, over temperature protection devices, antistatic materials for electromagnetic interference shielding of electronic devices, electrical conductive adhesives and circuit elements in microelectronics (3, 4).

The achievement of metallic properties in polymer composites depends on many factors and it is just the possibility of controlling the electrical and physical characteristics which determines the variety of ranges of their application. Composite materials of an amorphous polymeric matrix and randomly dispersed metal particles are considered as a heterogeneous disordered system (5–7). The electrical properties of these composites is directly related to the permittivity and conductivity of the constituent phase, the size, shape, and the volume fraction of the filler and the adhesion between metals and polymer (7, 9, 10). Some other factors such as preparation method, interface between the fillers and the polymers and possible interactions between the conductive and non-conductive phases are also significant (11, 12).

The concentration of the conductive inclusions has been proved to be a crucial parameter, governing the electrical behavior of the metal-polymer composites. When the filler content is low, the mean distance between metal particles or clusters is sufficiently large and conductance is restricted

---

Address correspondence to: Anjum Qureshi, Department of Physics, Fatih University, Istanbul 34500, Turkey. E-mail: anjumqur@gmail.com and Arif Güllüoğlu, Department of Metallurgical and Material Science Engineering, Marmara University, Istanbul 81040, Turkey. Tel.: +90-212 866 33 00; Fax: +90-212 866 3402; E-mail: gulluoglu@eng.marmara.edu.tr

by the presence of dielectric matrix. However, by increasing phase content, the metal "islands" get closer and at a critical concentration of the filler, a physical path is formed, through which the content can flow percolation the whole system.

Percolation theory describes the transition from state of limited and spatially restricted concentrations of conductive elements to the state of an infinite network of connections. In the vicinity of the transition, transport properties exhibit strongly non-linear behavior which, in the case of electrical conduction, is expressed via a power-law variation of conductivity.

$$\sigma \sim \sigma_0(\varphi - \varphi_c)^t \tag{1}$$

where φ_c is the critical concentration or percolation threshold and t is the critical exponent (13–15). The percolation or volume fraction of the conductive inclusions, is necessary for the onset of conductive behavior. There are numerous studies available in the literature on the electrical properties of polymer-metal filler composites (5, 6, 16, 17). However, much is still not known about the polarization and conducting mechanisms involved in these materials. This lack of information severely inhibits the improvement of new filled polymer composites with excellent property. Therefore, an understanding for the dielectric behavior of the polymer-matrix composites is very important in the engineering application of new materials.

Recently, it has been reported that the characteristic of the fillers and the interfaces between the filler and the polymer matrix would play an important role on deciding the dielectric properties of composites (18, 19). Response of a composite to external fields may depend on the corresponding response of individual phases.

It is well known that the polarizibility of a material is given by its relative dielectric constant ε^*. ε^* is the ratio of the permittivity of the examined material and the permittivity of the vacuum ε_0. To describe storage and dissipation properties, the relative dielectric constant is expressed in its complex form ε^*:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{2}$$

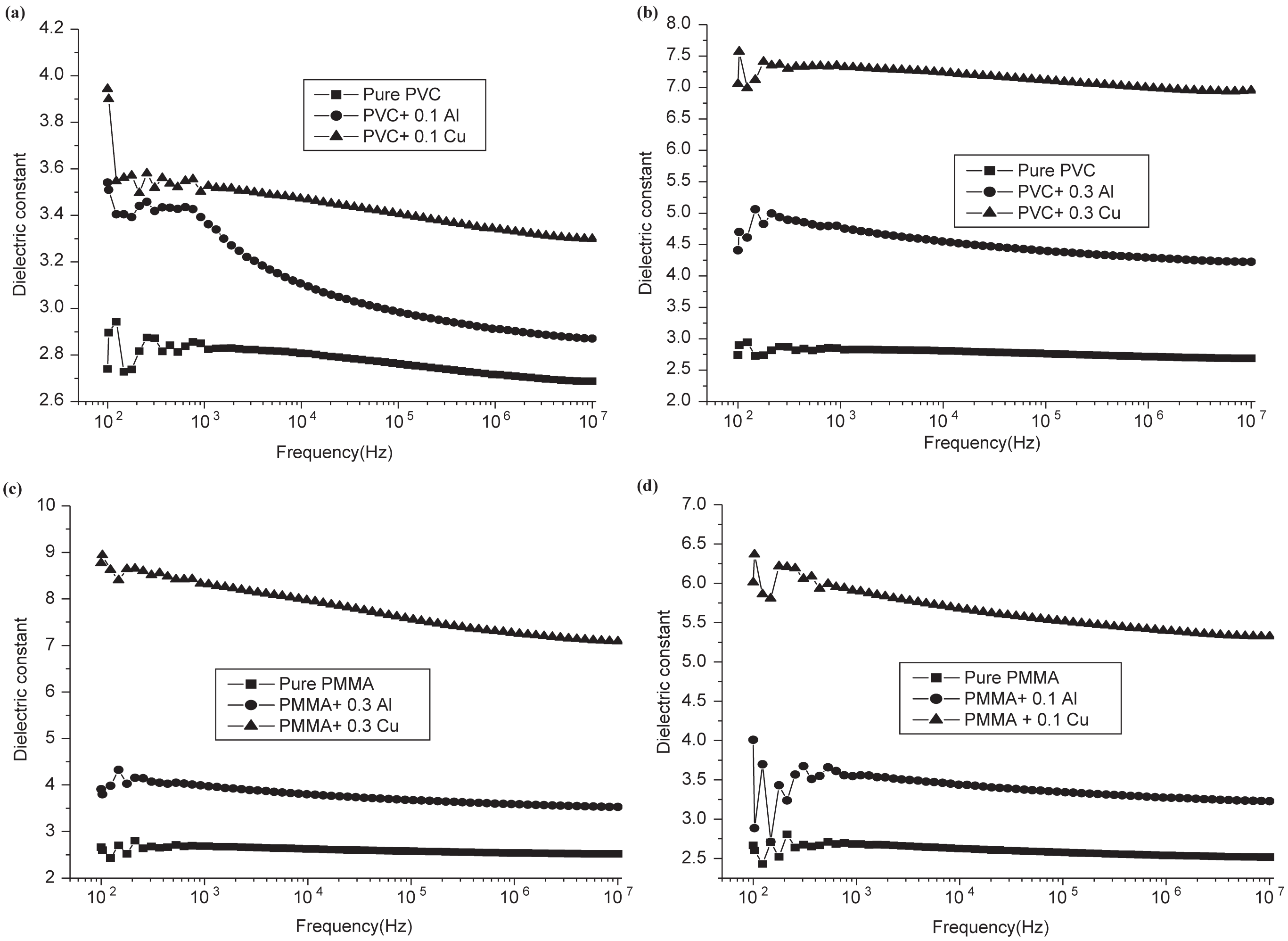

Fig. 1. (a,b,c, and d) Frequency dependence of the dielectric constant of PVC and PMMA composites with conducting fillers at volume fraction of 0.10 and 0.30.

where $\varepsilon^*(\omega)$ is the complex dielectric constant, $\varepsilon'(\omega)$ is the real part of the dielectric constant and $\varepsilon''(\omega)$ is the imaginary part of the complex dielectric constant. The ratio of the imaginary to the real parts ($\varepsilon''/\varepsilon'$) is the "dissipation factor" which represented by tan δ, where δ is the angle between the voltage and the charging current. The angle, δ is known as "loss angle".

In the present study, the dielectric behavior and conductivities of the PVC and PMMA composites loading with metal fillers of Al and Cu having different conductivity were studied over a broad range of frequencies (100 Hz–10 MHz) and as a function of metal filler volume fractions (0–0.30). The effect of different metal fillers on dielectric property and conductivities of polymer composites matrix has been explored.

2 Experimental

Polyvinyl chloride (PVC) and Polymethyl methacrylate (PMMA) are used as polymer matrix donated by Vesbo Company, Turkey while the Al and Cu metal fillers were purchased from Alfa Aesar and Merck, Germany. The volume fraction of fillers varied from 0 to 0.10, 0.20, and 0.30 in the composites. Filled polymer matrices of PVC and PMMA samples were prepared by solution casting method. Tetrahydrofuran (THF) was used as a solvent to dissolve the polymers. The mixture of polymers and fillers were stirred with different volume fraction of THF at room temperature using a magnetic stirrer at high speed of around 700 rpm until all polymer grains dissolved. After obtaining a homogeneous mixture, the mixture was poured on a clean glass trough. The solvent was evaporated at room temperature (25°C ± 1°C) to get thin films of polymer composites which were then dried in a vacuum oven at 30°C.

Alternating current (ac) dielectric properties of the samples were measured using HP4194A Impedance/Gain-Phase Analyzer in the frequency range 100 Hz–10 MHz at room temperature. The electrodes were painted with silver paste before the measurement.

3 Result and Discussion

3.1 Dielectric Property of the Composites

Figures 1 (a,b,c, and d) show the frequency dependence of the dielectric constant of PVC and PMMA composites containing conducting fillers at volume fractions of 0.10 and 0.30. Composites of PVC and PMMA containing Al and Cu fillers have a higher dielectric constant than either pure PVC or PMMA as expected (12, 20). In addition, composites of PVC and PMMA containing Cu filler have a higher dielectric constant than PVC and PMMA containing Al filler. This is due to higher conductivity of Cu. The dielectric constants decrease gradually with increasing frequency. At low frequencies, the polarization follows the change of the electric field; the loss is minimal and the contribution to the dielectric constant ϵ' is maximal. At high frequencies, the electric field changes too fast for the polarization effects to appear. In this case, the contribution to the dielectric is minimal and there are almost no dielectric losses in the system.

The variation of dielectric constant as a function of filler fraction and filler type in PVC and PMMA matrices at 1 MHz is shown in Figures 2 and 3. In addition, the variation of dielectric constant as a function of volume fraction for each filler type (Al and Cu) in PVC and PMMA at four different frequencies (300 Hz, 10 kHz, 100 kHz and 1 MHz) is also shown in Figure 3 (a, b, c and d). A moderate increase in dielectric constant is observed when the filler content is low in the case of PVC. But in PMMA, a sharp increase in dielectric constant is deduced at low filler content. Both in PVC and PMMA, as the filler content approaches a value which corresponds to the transition region, a large change in dielectric constant is observed. The increase in the dielectric content with filler content is a direct consequence of interfacial polarization effect (21–23) between polymer and the filler particles. As shown in Figures 2a and b, this effect was seen at a concentration level of 0.30 for PVC either filled with Al or Cu. However, the abrupt increase in dielectric constant in PMMA composites filled with Cu and Al is noticed when the volume fraction of the filler is close to 0.10. The value

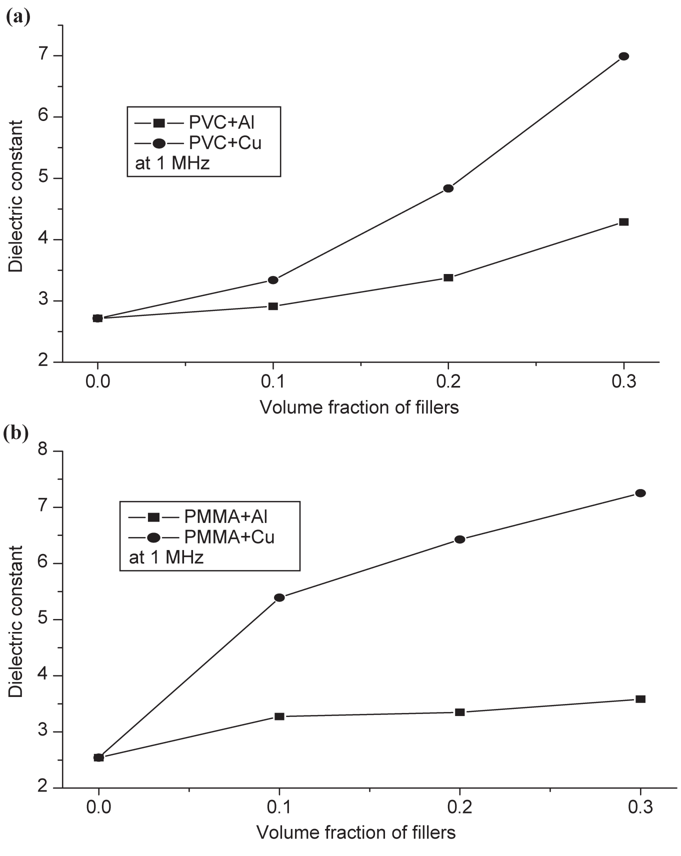

Fig. 2. (a,b) Variation of dielectric constant as a function of fillers fraction and filler type in PVC and PMMA at 1 MHz.

is just the percolation thresholds of these composites. Such high percolation thresholds are fancy in the composites with different conducting fillers. The dielectric constant of the composites is also a function of its capacitance, which is proportional to the quantity of charge stored on either surface of the sample under an applied electric field (20, 24). In the case of PVC and PMMA composites filled by conducting fillers, the quantity of the accumulated charge will increase because of the polarization of the PVC and PMMA/filler at interfaces. The polarization makes an additional contribution to the charge quantity. From this point of view, the dielectric constant of the composites will be higher than that of the pure polymers, and it will also increase with increasing the filler content. The experimental results in Figures 2 and 3 just support this explanation. Therefore, the materials with high dielectric constant could be prepared by adding the conducting fillers.

At the same content of the fillers, the dielectric constant of the composites with Cu fillers is higher than those of the composites with Al fillers. This result is attributed to the effect of the different conductivity of fillers.

Figure 4 (a, b, c, and d) shows the frequency dependence of the dielectric loss of the composites in PVC and PMMA with conducting fillers at volume fraction of 0.10 and 0.30, respectively. The dielectric loss decreases first then less dependent of frequency. This is because the induced charges gradually fail to follow the reversing field causing a reduction in the electronic oscillations as the frequency is increased.

The value of dielectric loss as a function of filler fraction at 1 MHz for PVC and PMMA composites are presented in Figure 5 (a and b), respectively. Moreover, the dielectric loss of PVC and PMMA composites containing different volume fraction of fillers (Al and Cu) are also indicated at four different frequencies (300 Hz, 10 kHz, 100 kHz and 1 MHz) in Figure 6 (a, b, c and d). The increase in dielectric loss with increasing filler contents may be attributed to the interfacial polarization mechanism of the heterogeneous system.

Cu containing PVC and PMMA composites have higher dielectric losses due to its higher conductivity. PMMA composite containing Al has very low dielectric loss until filler

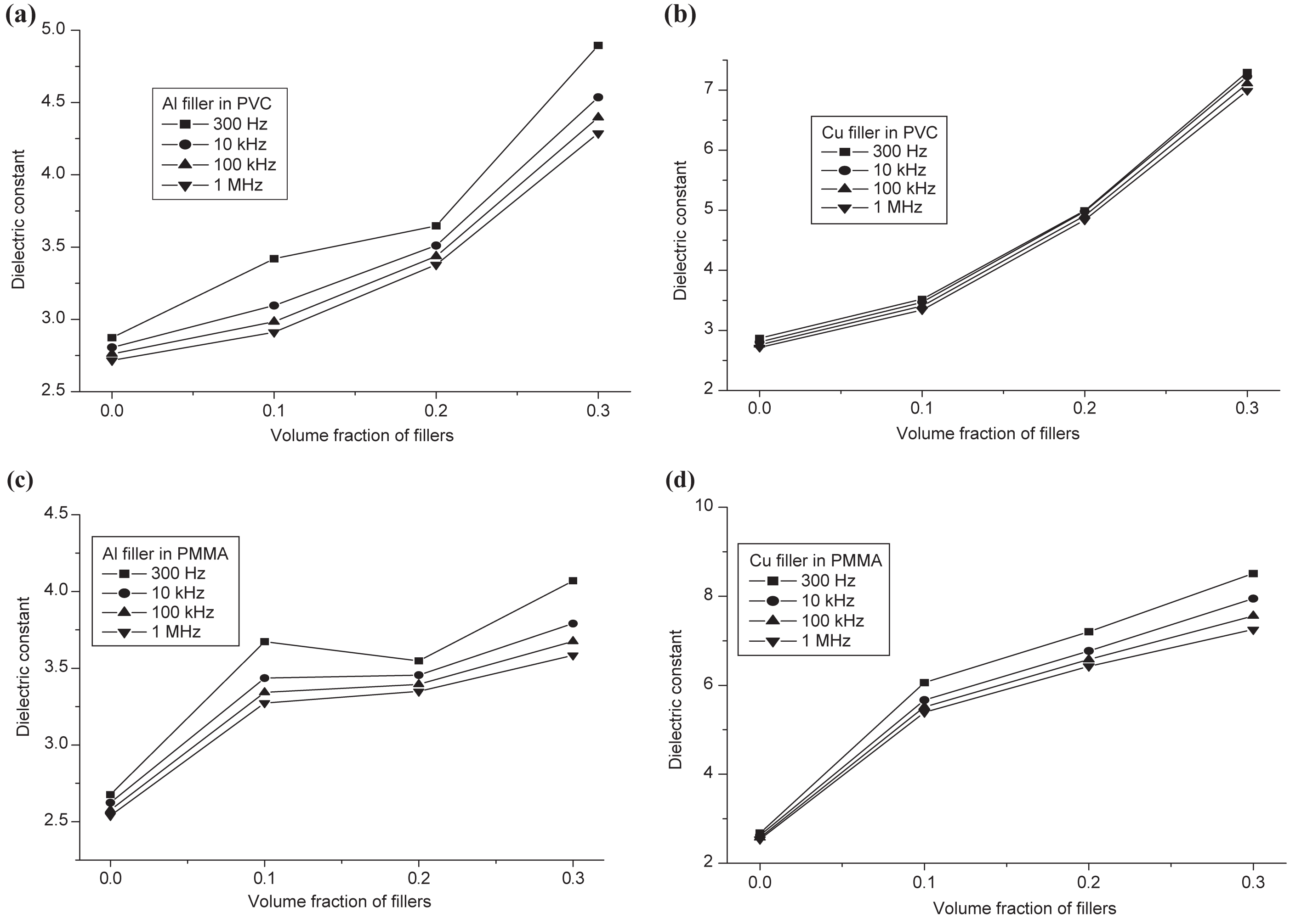

Fig. 3. (a,b,c, and d) Variation of dielectric constant of PVC and PMMA composites as a function of volume fraction for each filler type (Al and Cu) at different frequencies (300 Hz, 10 kHz, 100 kHz, and 1 MHz).

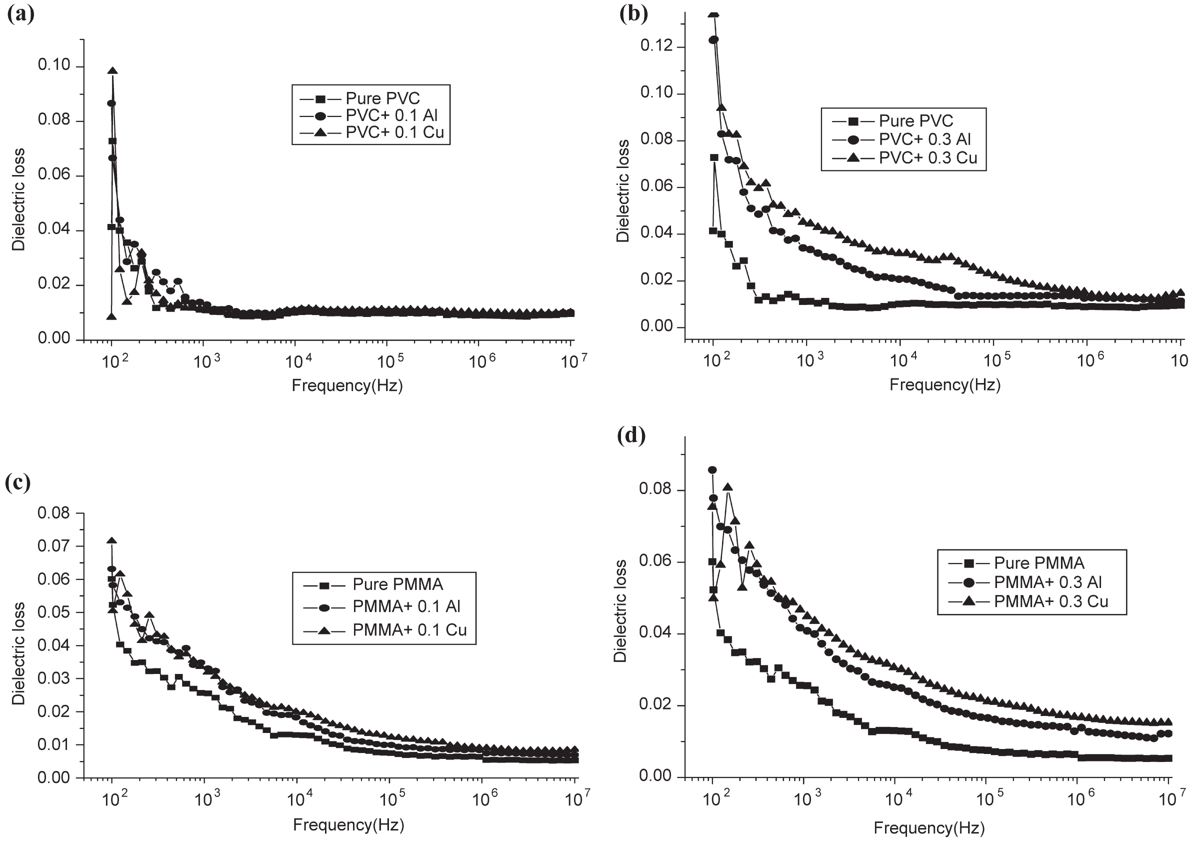

Fig. 4. (a,b,c, and d) Frequency dependence of the dielectric loss of PVC and PMMA composites with conducting fillers at volume fraction of 0.10 and 0.30.

volume fraction of 0.20, but a sharp increase was observed after this value (Figures 5(a) and 6(a)). In the case of PVC containing Al and Cu fillers, the dielectric results were parallel to each other until filler content of 0.20 where the dielectric losses were low, but increased sharply at 0.30 (Figures 5(b) and 6(b)).

The dielectric loss results indicated that PMMA composite containing 0.10 volume fraction of Al and Cu fillers and PVC 0.20 volume fraction of Cu filler could be employed as dielectric materials in capacitors. The effect of matrix (PMMA and PVC) on the dielectric properties and percolation threshold of Al and Cu filler content in PMMA than PVC can be

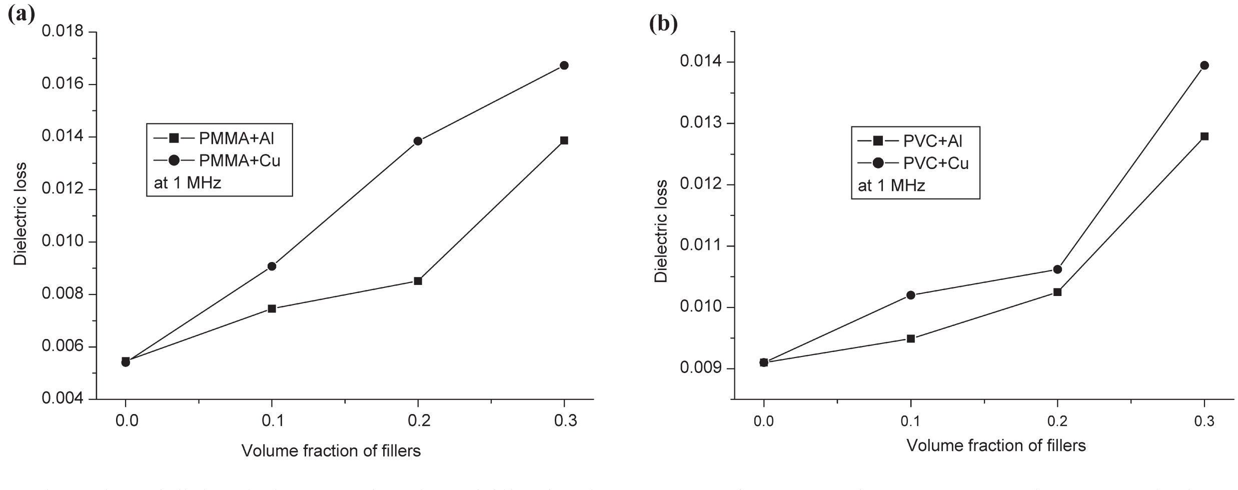

Fig. 5. (a,b) Value of dielectric loss as a function of filler fraction at 1 MHz for PVC and PMMA composites, respectively.

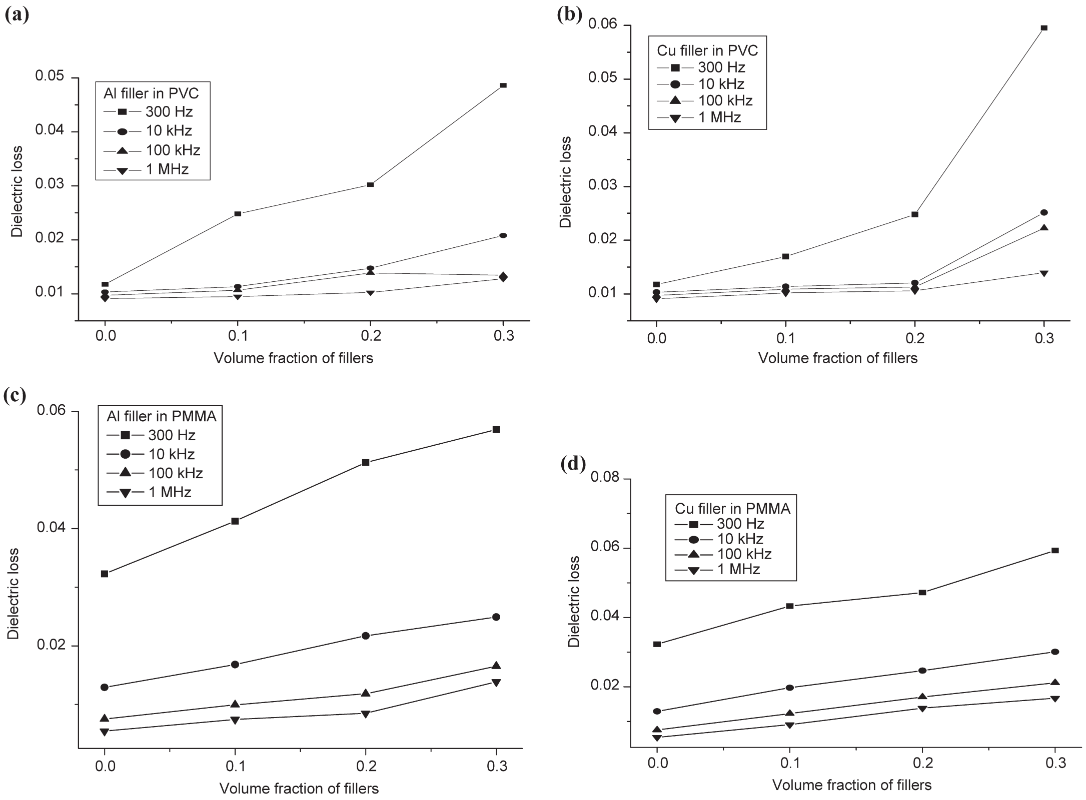

Fig. 6. (a,b,c, and d) Dielectric loss of PVC and PMMA composites containing different volume fraction of Al and Cu at different frequencies (300 Hz, 10 kHz, 100 kHz and 1 MHz).

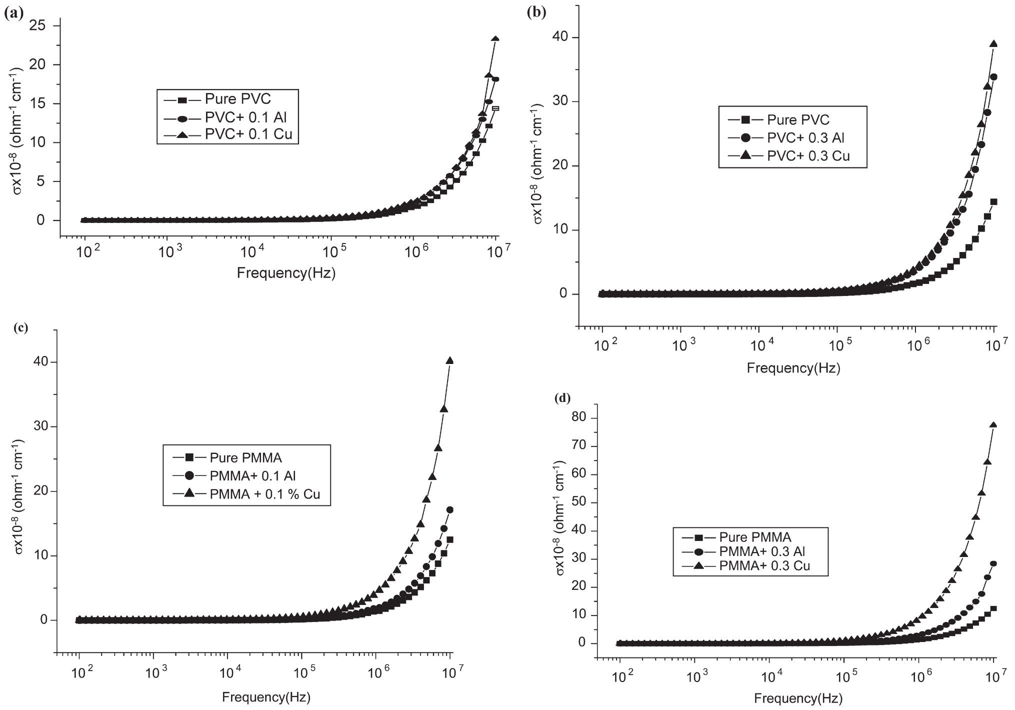

Fig. 7. (a, b, c, and d) Frequency dependence of the conductivity of PVC and PMMA composites containing different volume fractions of conducting fillers (0.10 and 0.30).

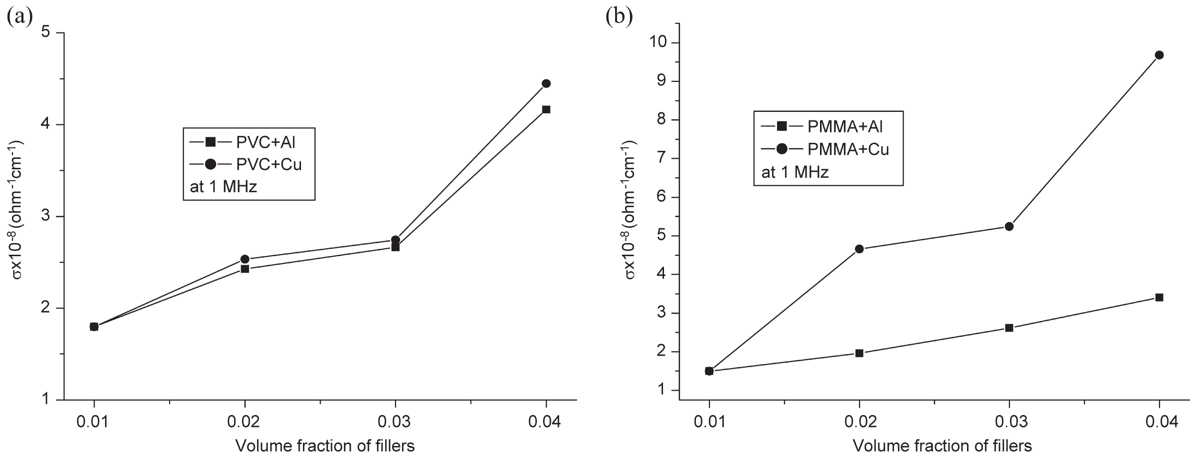

Fig. 8. (a,b) Variation of conductivity at different volume fraction of fillers.

understood in terms of structure and characteristic parameters of the conductive polymer system (25).

3.2 *Conductivity of the Composites*

The ac conductivities of the composites as a function of the frequency and volume fraction of the fillers are shown in Figures 7 (a, b, c, d) and 8 (a, b), respectively. The ac conductivity of the composites increases with increasing frequency and with volume fraction of fillers. It is assumed that an electrical conducting path and network of connections could be formed in the composites with increasing the content of fillers. The conductivity of PVC and PMMA composites with Cu filler is higher in any case due to its higher conductivity (Figure 8). In addition, in PMMA matrix, high conductivity levels were observed at low filler content of Cu (Figure 8b). The fillers with high conductivity could produce the conducting network at low contents. The same results were also found in the literature (24, 26–30). In the case of PMMA, the distribution of fillers is more packed than PVC which employed the difference in the value of percolation threshold.

4 Conclusions

The dielectric properties of the PVC and PMMA matrix composites with Al and Cu conducting fillers were studied over a broad frequency range and volume fraction of fillers. The dielectric constants decrease slowly with increasing frequency. The dielectric constant values of composites indicated that although PVC composites have a threshold at volume fraction of 0.30 either for Al or Cu, PMMA composites containing Al and Cu has a sharp increase at volume fraction of 0.10. In addition, the dielectric constants of the composites with Al fillers are lower than that of Cu fillers. The dielectric loss decreases first, then is less dependent on frequency. It also increases gradually with a rise of the volume fraction of fillers. The conductivity of the composites increases with an increase in frequency and the content of fillers.

5 Acknowledgements

We would like to give our great thanks to The Scientific and Technological Research Council of Turkey (TUBITAK) for financial support of this investigation under the project grant number B.02.1.TBT.0.06.01.216.01-234-1237.

6 References

1. Kumar, G.S., Raja, M. and Parthasarathy, S. (1995) *Electrochim. Acta*, **40**, 285–290.
2. Zhang, Q.M., Li, H., Poh, M., Xia, F., Cheng, Z.Y., Xu, H. and Huang, C. (2002) *Nature*, **419**, 284–286.
3. Cole, D.H., Shull, K.R., Rehn, L.E. and Baldo, P. (1997) *Phy. Rev. Lett.*, **78**, 5006–5009.
4. Delmonte, J. *Metal/Polymer Composites*; Van Nostrand Reinhold: New York, 1990.
5. Roldughin, V.I. and Vysotskii, V.V. (2000) *Progress Org. Coatings*, **39**, 81–100.
6. Strümpler, R. and Glatz-Reichenbach, J. (1999) *J. Electroceram.*, **3(4)**, 329–46.
7. Dyre, J.C. and Shrøder, T.B. (2000) *Rev. Modern Phys.*, **72(3)**, 873–92.
8. Xiao, P., Xiao, M. and Gong, K.C. (2001) *Polymer*, **42**, 4813–4816.
9. Ho, P.S., Height, R., Silverman, R.C.B.D. and Faupel, F. In *Fundamentals of Adhesion*; Lee, L.H. (ed.); Plenum Press: New York, 383, 1991.
10. Qureshi, A., Singh, N.L., Rakshit, A.K., Singh, F., Avasthi, D.K. and Ganesan, V. (2006) *Nucl. Instr. & Meth B*, **244**, 235–238.
11. Brosseau, C., Queffelec, P. and Talbot, P. (2001) *J. Appl. Phys.*, **89**, 4532–4540.
12. Singh, N.L., Qureshi, A., Singh, F. and Avasthi, D.K. (2007) *Mat. Sci. Eng. B*, **137**, 85–92.
13. Zallen, R. *The Physics of Amorphous Solids*; Wiley: New York, 2004 (Chapt. 4).

14. Lux, F. (1993) *Polym. Eng. Sci.*, **33**, 334–42.
15. Bunde, A. and Havlin, S. *Fractals and Disordered Systems*; Springer-Verlag: Berlin, 1991 (Chapt. 2–3).
16. Flandin, L., Prasse, T., Schueler, R., Schulte, K., Bauhofer, W. and Cavaille, J.Y. (1999) *Phys. Rev. B*, **59**, 14349–55.
17. Barrau, S., Demont, P., Peigney, A., Laurent, C. and Lacabanne, C. (2003) *Macromolecules*, **35**, 5187–94.
18. Zewdie, H. and Brouers, F. (1990) *J. Appl. Phys.*, **68**, 713–718.
19. Ahmed, S. and Jones, F.R. (1990) *J. Mater. Sci.*, **25**, 4933–4942.
20. Dang, Zhi-Min, Zhang, Yi-He and Tjong, S.-C. (2004) *Synth. Met.*, **146**, 79–84.
21. Psarras, G.C., Manolakaki, E. and Tsangarris, G.M. (2002) *Composites A*, **33**, 375–384.
22. Ghany, S., Salam, A.E. and Nasr, G.M. (2000) *J. Appl. Polym. Sci.*, **77**, 1816–1821.
23. Foulger, S.H. *J. Appl. Polym. Sci.*, **72**, 1573–1582.
24. Yu, D., Wu, J., Zhou, L., Xie, D. and Wu, S. (2000) *Comp. Sci. Technol.*, **60**, 499–508.
25. Mamunya, Y.E.P., Davydenko, V.V., Pissis, P. and Lebedev, E.V. (2002) *Euro. Polym. J.*, **38**, 1887–1897.
26. Tchoudakov, R., Breuer, O., Narkis, M. and Siegmann (1996) *Polym. Eng. Sci.*, **36**, 1336–1346.
27. Mamunya, Y.E.P., Muzychenko, Y.U.V., Pissis, P., Lebedev, E.V. and Shut, M.I. (2002) *Polym. Eng. Sci.*, **42**, 90–9.
28. Dang, Z.M., Fan, L.Z., Shen, Y. and W-Nan, C.W. (2003) *Chem. Phys. Lett.*, **369**, 95–100.
29. Taipalus, R., Harmia, T., Zhang, M.Q. and Friedrich, K. (2001) *Comp. Sci. Technol.*, **61**, 801–814.
30. Kuo, D.H., Chang, C.C., Su, Te-Yeu, Wang, Wun-Ku, Lin and Bin-Yuan (2001) *J. Euro. Ceram. Soc.*, **21**, 1171–1177.