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Synthesis and Dielectric Characterization of -COOH Functionalized MWCNT Filled PMMA Nanocomposites

Physics

KEYWORDS : COOH-MWCNT, PMMA, in-situ polymerization, dielectric studies

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ABSTRACT

A series of COOH functionalized multiwalled carbon nanotubes (MWCNT) filled polymethylmethacrylate (PMMA) nanocomposites was prepared in the laboratory. The concentration of MWCNT (<3 wt%) was changed in the step of 0.50 wt.% and nanocomposites were prepared by in-situ polymerization of MMA monomer followed by compression moulding. Frequency and temperature dependent dielectric behavior of these nanocomposites were studied to investigate the influence of a polar group functionlised CNT inclusion in a polar polymer (PMMA). It was observed that at all temperatures and frequencies dielectric constant of pure PMMA decreased with low wt% of CNT and then increased with further increase in CNT loading. At room temperature, composite with 1.50wt% of CNT showed a minimum value of dielectric constant at all frequencies. Secondly with increasing temperature dielectric constant increased till it reached glass transition temperature (Tg) and then decreased with further increase in temperature.

1.0 **Introduction**

Carbon nanotubes (CNTs), both single walled as well as multiwalled, have proven to be very effective as nanofillers in improving the electrical and dielectric properties of polymer matrix [1-5]. The only limitation of CNTs as nanofillers is their higher production cost. Therefore, the mass production of CNT based functional composite materials is very difficult as they are not as economically viable as graphene sheets. Secondly, the incorporation of CNTs and their uniform dispersion in the polymer matrix has been rendered difficult due to the strong van der Waals forces between carbon nanotubes which agglomerate and form bundles. Hence, the surface of carbon nanotubes is modified via functionalization to reduce agglomeration [6-12]. In order to achieve uniform dispersion of CNTs in polymer matrix various techniques have been attempted such as sonication [13], in situ polymerization [14] solution mixing [15-17] melt mixing [18,19] compression molding [20] and electrospinning spinning [21] .When present during the addition polymerization of methyl methacrylate monomer, carbon nanotubes were shown to participate in the polymerization process [22]. Hence, in this work it was decided firstly to use polar group functionalized CNT and secondly in situ polymerization and sonication to develop PMMA (polar polymer) based nanocomposites and characterize them for their dielectric behavior.

2.0 Materials and methods

Methyl methacrylate (MMA) (Density = 0.936g/cc and Purity = 99%) was obtained from Sigma Aldrich, Germany. Benzoyl peroxide (Melting point = 54°C) was obtained from Sigma Aldrich, Germany. This was formulated specially for use with Histocryl and LR white acrylic resin. COOH functionalized MWCNT (dia 20-30 nm) and length (10-30 micron) purity (95%) was obtained from Nanostructred and Amorphous Materials, Houston, Texas (US). Firstly, in-situ polymerization of MMA monomer was carried out in test tubes with the help of ultra-sonication under suitable conditions. Exact amount of MWCNT was taken in dry test tubes and then it was sonicated for 5 minutes in dry condition. 10g of MMA monomer and 0.1g of BPO initiator were added to the test tubes. Nitrogen was purged for 1 minute in every test tube to create an inert atmosphere. Test tubes were plugged tightly with cotton and sonicated for 10 minutes at room temperature. Now, these systems were slowly heated to 60°C and sonicated for total 2 hours until the monomer system became viscous and MWCNT got entrapped into the polymer chains. After 2 hours, sonication was stopped and systems were heated for another 2 hours to complete the polymerization under nitrogen atmosphere. After 4 hours polymeric lumps were formed inside the test tube. Test tubes were then broken to take out the polymeric lumps. These polymer lumps were crushed at 20,000 lb pressure in compression moulding machine without heating. Thus, micro cracks developed inside the lumps and then they were granulated. Granules were dried at 60°C under vacuum for 24 hours to remove low molecular weight components. After that, granules were compression moulded to make samples at 165°C and at 15,000 lb pressure. Granules were preheated for 15 minutes and compression moulded for another 15 minutes with a breathing time of 30 seconds. Then, samples were slowly cooled to 65°C by circulating water inside the platen and then they were ejected from the mould. Samples were prepared by varying the weight percentage of CNT. The sample designation and composition is listed in Table1. 2.1

2.1 GPC Analysis of PMMA

Waters 1525, Binary HPLC Pump Instrument having THF as mobile phase, with Viscotek VE 3580 RI Detector was used to determine the molecular weight of pure PMMA (Table 2) using polystyrene as calibration standard with 1 ml/min flow rate when column and detector temperature was at 35°C.Figure 1 shows the molecular structure of PMMA.

2.2 Dielectric Studies

AC frequency dependent values of parallel capacitance (Cp) and loss tangent or dissipation factor (tanδ or D) of the nanocomposite samples were measured by using Agilent 4263B precision LCR meter. Dielectric constant (ε′) was calculated using the formula:

$$\varepsilon' = C/C0 \quad \text{………………..(1)}$$

where, Co $(=\varepsilon_o A/d)$ is the capacitance with vacuum between parallel plates, and ε_o is the permittivity of free space, A is the area of electrodes, and d is the thickness of the sample. dc conductivity (σ_{dc}) of the nanocomposites was measured using Keithley Electrometer Model No. 6517B. Keithley electrometer.

3.0 Results and discussion

Frequency dependent dielectric behaviour of nanocomposites at room temperature is shown in Fig. 2 (a-d) .Figure 2 (a, b)shows the variation of dielectric constant (ε′) and dielectric loss (ε″) respectively with frequencies at room temperature (26°C) and higher temperatures. It can be seen that with increasing frequency dielectric constant (ε′), dielectric loss (ε″) decreases.

This is because of the available relaxation time of the polymer. In Fig. 2c, room temperature (26°C) dielectric constants at different frequencies are plotted as a function of increasing CNT weight percentage. It is expected that at lower frequencies the values of dielectric constant will be higher due to contribution of both electronic polarization and orientational or dipole polarization. With increase in frequencies orientational polarization is restricted but electronic polarization are not. Here it is observed that with increasing CNT percentage dielectric constant decreases and then reaches to a minimum and then start to increase but after 1.5 wt. % it falls slightly. This is because at a constant frequency when CNT percentage increases then more and more restrictions are applied to the polymer molecule to polarization and consequently the contribution of orientational polarization decreases monotonically. But at very low percentage of CNT the enhancement in electronic polarization is suppressed by the decrease in dipole polarization and thus the overall polarization decreases resulting the decrease in dielectric constant value. But after a certain percentage the contribution of increase in electronic polarization and decrease in dipole polarization counter balance each other and after that the increase in electronic polarization becomes more significant. As a result of this phenomenon, dielectric constant reaches a minimum and then starts to increase. But after 1.5% CNT loading it is observed that dielectric constant starts to decrease slowly and this can be due to stabilization of electronic polarization after a certain concentration. So again the decrease in orientational polarization determines the nature of the curve. It has been reported in the literature that the conductive nature of carbon nanotubes enhances the dielectric response of non conductive polymers [16, 23,24]. Carbon nanotubes (at low concentrations) do not hinder or ease the rotation of the ester side group about the C-C bond that attaches it to the polymer main chain but they provide additional dipoles to the polymer matrix. The experimental data published for polymer-SWNT composites [15, 25-27] exhibit an increase in permittivity for the composite samples as compared to the neat samples. The dielectric data obtained in this study agree with these results. Frequency dependence of ac-conductivity of composites at room temperature is shown in Fig. 2d . Temperature dependent dielectric behaviour of PC100 nanocomposites is shown in Fig. 3 at different frequencies. At all temperatures and frequencies it was observed that dielectric constant increased with temperature till it reached Tg and then decreased with further increase in temperature. All composites showed similar pattern of dielectric behaviour.

4.0 Conclusions

Dielectric studies on COOH functionalized MWCNT filled PMMA nanocomposites prepared via in-situ polymerization showed that the dielectric constant of neat PMMA does not change significantly for CNT loading <3wt%. However, for lower loadings it was found that dielectric constant first decreased (probably due to decrease in dipole polarization) and then increased after a loading of 1.5 wt%. The increase in dielectric constant at a higher loading (>1.5wt%) is attributed to the fact that COOH (polar group) functionalised MWCNT provide additionaldipoles to the PMMA (polar) matrix. The magnitude of dielectric constant did not change appreciably with CNT loading (< 3wt%), but at room temperature dielectric constant (ε′) decreased with increasing frequency.

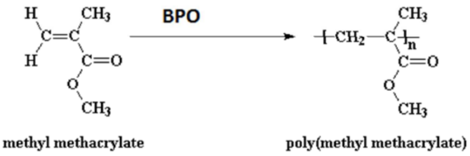

Fig. 1 Polymerisation reaction of MMA monomer to PMMA

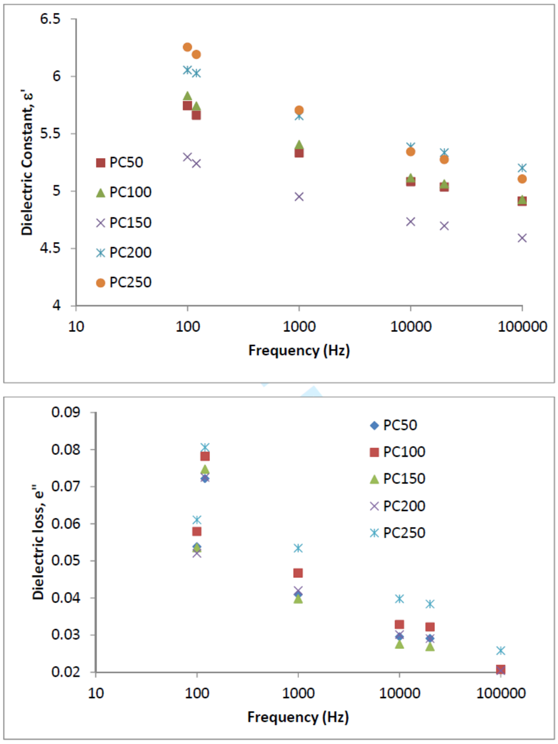

Fig. 2: (a) Dielectric constant and (b) dielectric loss of samples as a function of frequency measured at 50 deg C

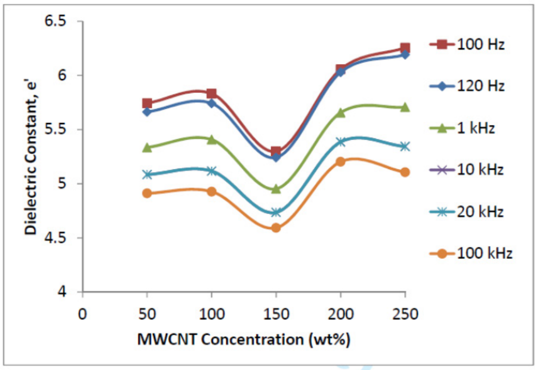

Fig. 2c: Dielectric constant of samples as a function of MWCNT concentration at various frequencies measured at 50 deg C

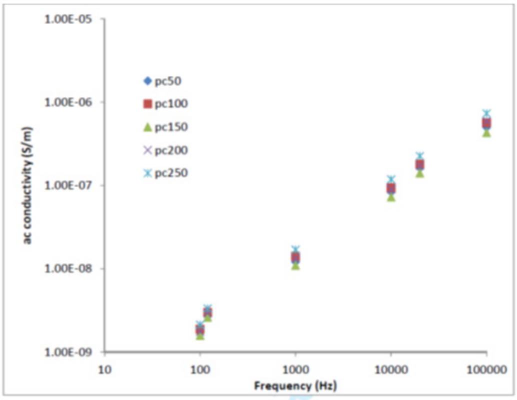

Fig. 2d: Frequency dependence of ac conductivity of all samples at 50 deg C

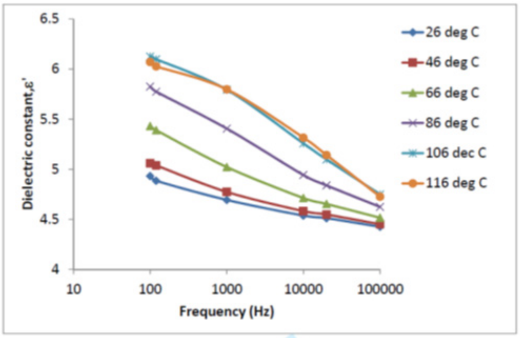

Figure 3a: Dielectric constant of PC100 sample as a function of frequency measured at different temperatures

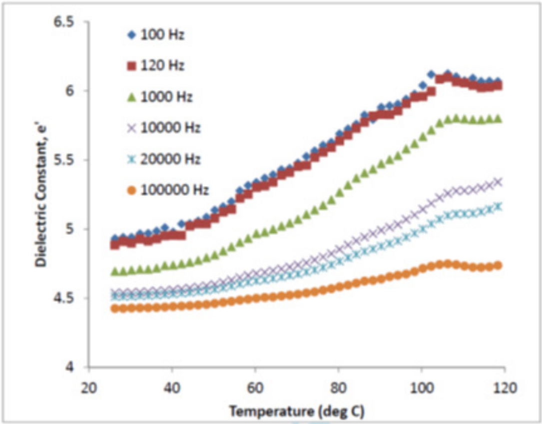

Fig 3b: Temperature dependence of dielectric constant of PC100 sample measured at different frequencies

Table 1. Formulation of Polymethylmethacrylate (PMMA) –MWCNT nanocomposites

Sample Name	Polymethylmethacrylate (wt.%)	BPO (wt.%)	MWCNT (wt.%)
PC000	100	1.00	0.00
PC050	100	1.00	0.50
PC100	100	1.00	1.00
PC150	100	1.00	1.50
PC200	100	1.00	2.00
PC250	100	1.00	2.50

Table 2 GPC analysis of pure PMMA (PC000)

Sample	Property	Value
PC000	M_n (g mol^{-1})	2,68,021
	M_w(g mol^{-1})	8,33,736
	PDI (M_w/M_n)	3.111

REFERENCE

1] Ziad Khattari, Mufeed Maghrabi, Tony McNally, Saadi Abdul Jawad, Physica B, 406 2565 (2011) [2] E. Kymakis, I. Alexandou, G.A.J. Amaratunga, Synthetic Metals 127, 59 (2002) [3] Grimes, C.A. C. Mungle, D. Kouzoudis, S. Fang, P.C. Eklund, Chemical Physics Letters, 319, 460 (2000) [4] J.M. Yeh, K.C Chang, C.W Peng, M.C Lai, S.S Hwang, H.R Lin, S.J. Liou, , 11(8), 6757 (2011) [5] S. Kumar, T. Rath, B.B. Khatua, A.K. Dhibar, C.K. Das, J Nanosci Nanotechnol., 9(8), 4644 (2009) [6] A. Hirsch, Angew. Chem. Int. Ed. 41, 1853 (2002) [7] CNR Rao, B.C. Satishkumar, A. Govindaraj, M. Nath, Chem Phys Rev, 2, 78 (2001) [8] J.N. Coleman, A.B. Dalton, S. Curran, A. Rubio, A.P. Davey, A. Drury, B. McCarthy, B. Lahr, P.M. Ajayan, S.R. Roth, R.C. Barkle, W.J. Blau, Advanced Materials 12 (2000) [9] J. Chen, M.A. Hamon, H. Hu, Y. Chen, A. Rao, P.C. Eklund, R.C. Haddon, Science, 282 (1998) [10] M.A. Hamon, J. Chen, H. Hu, Y. Chen, M.E. Itkis, A. Rao, P.C. Eklund, R.C. Haddon. Advanced Materials, 11 (1999) [11] I.W Chiang, B.E. Brinson, R.E. Smalley, J.L. Margrave, and R.H. Hauge. J. Phys. Chem. B 105 (2001) [12] W. Huang, Y.Lin, S. Taylor, J. Gaillard, A.M. Rao, Y. Sun. 2002. Nano Letters 2, 231 (2002) [13] A Koshio, M. Yudasaka, M. Zhang, S. Iijima, Nano Letters 1, 361 (2001) [14] C Park., Z. Ounaies, K.A. Watson, R.E. Crooks, J. Smith, S.E. Lowther, J.W. Connell, E.J. Siochi, J.S. Harrison, T.L. St. Clair. Chemical Physics Letters 364, (2002) [15] J.P. Harmon, P. Muisener, L. Clayton, J. D' Angelo, A. K. Sikder, A. Kumar, M. Meyyappan, A. M. Cassell. Material Research Society Symposium Proceedings, 697 (2001) [16] S. Tatro, L.M. Clayton, P.A. Muisener, A.M. Rao, J.P. Harmon, Polymer 45, 1971 (2004) [17] L.M. Clayton, T. G. Gerasimov, M. Cinke, M. Meyyappan, J.P. Harmon, Polymer Bulletin, 52 (2004) [18] P. Potschke, T.D. Fornes, D.R. Paul, Polymer (2002) [19] Y. Zou, Y. Feng, L. Wang, X. Liu, Carbon 42 271 (2004) [20] R. Haggenmueller, H.H. Gommans, A.G. Rinzler, J.E. Fischer, and K.I, Winey, Chemical Physics Letters 330, 219 (2000) [21] R. Sen, B. Zhao, D. Perea, M. Itkis, H. Hu, J. Love, E. Bekyarova, and R. Haddon, Nano Letters 4, 459 (2004) [22] Z. Jia, C. Wang, Xu, J Liang, B. Wei, D. Wu, S. Zhu, Materials Science and Engineering A A271 395 (1999) [23] L.M. Clayton, A. Sikder, A. Kumar, M. Cinke, M. Meyyappan, T. Gerasimov, and J.P. Harmon, Advanced Functional Materials 15 (2005) [24] Zhao, Q., J. Wood, and H.D. Wagner, J. Polymer Sci: Part B: Polym Phys 39, 1492, (2001) [25] P. Muisener, L. Clayton, J.D'Angelo, J. Harmon, A.K. Sikder, A. Kumar, M. Meyyappan, B. Chen, and A. Cassell, J. Mater. Research 17, 2507 (2002) [26] C. Brosseau, A. Beroual, A. Boudida, Journal of Applied Physics, 88, 12 (2000) [27] R.P Kusy, J.Q. Whitley, S. Kalachandra, Polymer, 42, 2585 (2001)