www.vbripress.com, www.amlett.com, DOI: 10.5185/amlett.2012.3326 Published online by the VBRI press in 2012

Microhardness and electrical properties of PVC/Cu composites prepared by ball mill

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Received: 28 March 2012, Revised: 24 April 2012 and Accepted: 26 April 2012

ABSTRACT

Polymer matrix composites filled with metals are widely studied for the applications in electrostatic dissipation (ESD) and electromagnetic interference (EMI) shielding. In view of this, the electrical conductivity and the microhardness of the polymer matrix composites based on poly(vinyl chloride) (PVC) as matrix and copper (Cu) as reinforcement were determined. The composites were prepared using ball milling followed by hot pressing. Both constituents PVC and Cu were mixed together in a dry condition at room temperature for 12 h, 24 h and 36 h and then blended powder was hot pressed at 175 °C and 50 MPa. The Cu content was varied from 0 to 40 wt% (9.3 vol%) in the matrix. Optical microscope showed good dispersion of Cu particles in the matrix and the degree of Cu dispersion increased with increasing ball milling time. The electrical conductivity of the composites increased approximately six orders of magnitude for 9.3 vol% Cu composite. A percolation threshold was obtained at 3.7 vol% Cu. The microhardness increased by more than 18 % compared to the pure matrix. For a given loading of Cu, the electrical conductivity and the microhardness of the composites increased with increasing ball-milling time. This was attributed to the better and uniform dispersion of the Cu particles in the matrix at higher ball milling time.

Keywords: Polymer-matrix composites; electrical conductivity; optical microscopy; hardness.

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Introduction

The electrical properties of polymer matrix composites (PMCs) containing metallic particles, carbon black (CB), carbon fibre (CF) and carbon nanotubes (CNTs) are widely studied for the applications in an electromagnetic interference shielding (EMI), *electrostatic dissipation (ESD)*, embedded capacitors and gas sensors **[1-12]**. Owing to good electrical conductivity (~ 6×10^5 S/cm), thermal conductivity (400 W/m.K) and mechanical properties copper (Cu) is used as conductive filler in the polymer matrix **[13]**. Alvarez et al. **[14]** reported a percolation threshold of 10 vol% and 15–30 vol % for submicron and micron sized Cu filled linear low density polyethylene (LDPE) composites, respectively. Mamunya et al. **[15]** investigated the electrical and thermal conductivity of Cu/Ni filled epoxy/PVC composites. The percolation threshold depends upon the size, shape and spatial distribution of the filler in the polymer matrix **[16].** Recently, it has been studied that ball milling strongly influences the mechanical and barrier properties of clay filled polymer nanocomposites. The increasing milling time improve the dispersion of nano-clay into the polymer matrix **[17]** and reduces significantly the crystallite size of

fillers and polymers **[18].** Moreover, ball milling with more than 15 h de-agglomerates and disperses the nano particles into the matrix **[19].**

However, rarely any attention was paid to the effect of ball milling time on the properties of the PVC/Cu composites. In view of this, the main objective of this work is to study the effect of ball-milling time (12-36 h) on the electrical and mechanical (particularly microhardness) properties of PVC/Cu composites. The microstructure, electrical conductivity and microhardness of the composites were investigated using optical microscope, high resistivity meter and Vickers hardness tester, respectively.

Experimental

Materials

The PVC powder was obtained from the commercial source. Electrolytic Cu powder purchased from Otto Kemi, Mumbai was used as filler without treatment. It has density of 8.94 g/cc. Its particle size varies in the range of 10-44 µm. The purity of Cu powder was 99.5 %.

Fabrication of PVC/Cu composites

The well dried PVC and Cu powders were mixed together using ball mill at room temperature for 12 h, 24 h and 36 h. Then, the mixture was again dried in a vacuum oven at 100 °C and finally, it was hot pressed. The appropriate weight of the mixture was filled into a tool steel die of 13 mm in diameter. It was heated at an average heating rate of 10 ºC/min to a maximum temperature of 175 ºC and 50 MPa. The dwell time was about 30 min. Then, the sample was air cooled to a temperature of 65 ºC and finally ejected out from the die cavity. The thickness of each sample was about 3 mm. By using similar processing conditions, five different composites containing 0, 10, 20, 30, and 40 wt% Cu particle in the matrix were fabricated. Composites were coded by C-X, where X indicates weight % of the Cu in the matrix.

Table 1. The weight % and volume % of the Cu particles added to the PVC matrix.

Samples Code		C-0	C-10	C-20	C-30	C-40
% Cu in the	Weight	0	10	20	30	40
matrix by	Volume	0	1.69	3.72	6.21	9.33

Characterizations

The volume fraction (**Table 1**) of the Cu particles added to the PVC matrix was calculated from its weight fraction using Equation; $V_f = W_f / [W_f + W_m.(\rho_f/\rho_m)]$, where, V_f, W_f and ρ_f are the volume fraction, weight fraction, and the density of the Cu particles. The W_m and ρ_m are the weight fraction and density of the PVC matrix, respectively. Five different composites containing 0, 10, 20, 30, and 40 wt% Cu particles in the matrix were fabricated. The theoretical density (ρ_{th}) of the composites was calculated using the rule of mixtures (ROM) with the density of PVC 1.38 g/cc and of Cu 8.94 g/cc. The experimental density of the composites was determined using the Archimedes's Principle. Optical microscope was used to examine the dispersion of Cu particles in the PVC matrix. Before observation, samples were well polished on successive emery papers and subsequently lapped to remove all scratches. For the measurement of electrical conductivity, samples were coated with a thin coating of silver paste to avoid contact resistance. The volume resistance of samples was determined by using high resistance meter (Keithley 6517B). However, when the volume resistance is below 10^6 Ω, an Agilent 6½ digital multi meter (Agilent 34401A) was used. Then, the volume resistivity was measured by the relation $\rho = R (A/L)$, ρ is the resistivity in Ω-cm, R is resistance in ohm, L is the sample thickness in cm and A is the cross sectional area (cm^2) of sample. The electrical conductivity was reported as the reciprocal of the volume resistivity. The microhardness was measured using Vickers hardness tester (Future Tech FM-700, Tokyo, Japan) at a constant load of 100 g and dwell time of 15s. Three readings were noted at different locations and average value is reported as the microhardness of the composites.

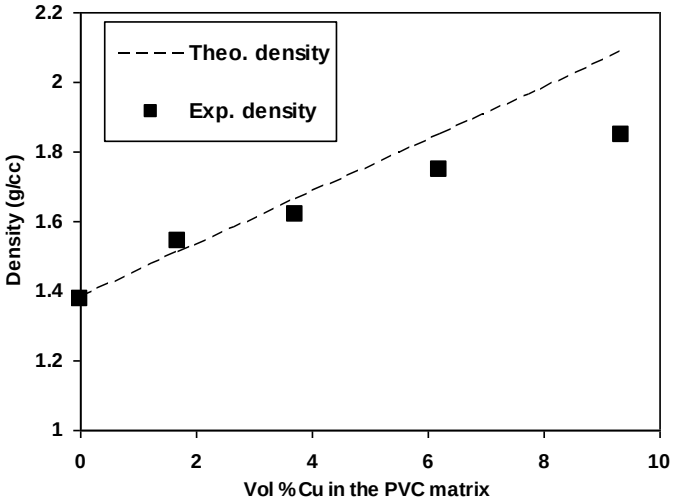

Fig 1. Theoretical and experimental density for the PVC/Cu composites.

Results and discussion

Density

Fig. 1 shows the theoretical and experimental densities of the composites. The pure PVC has experimental density of 1.38 g/cc. The density of the composites increased with increasing Cu content. It is due to the higher density (8.94 g/cc) of Cu than that of PVC. The experimental density of the composites containing up to 3.7 vol% (C-20) Cu is close to that of theoretical density. It indicates that the prepared composites are almost porosity free. However, the experimental density of the 6.2 vol% (C-30) and 9.3 vol% (C-40) composites is lower than that of the theoretical density by approximately 5.4 % and 11.4 %, respectively. This is due to the formation of Cu aggregates which hinder the infiltration of molten polymer through the aggregates during hot processing.

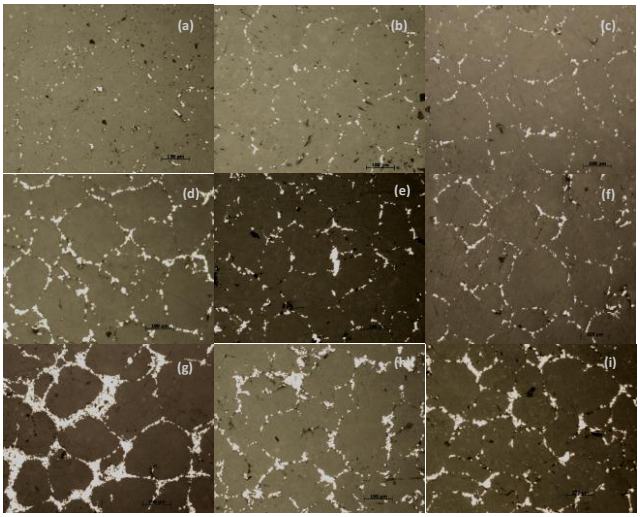

Fig 2. Optical microscopy images of composites containing (a-c) 20 wt%, (d-f) 30 wt% and (g-i) 40 wt% Cu after 12 h (a, d & g), 24 h (b, e & h) and 36 h (c, f & i) ball milling time.

Microstructure of PVC/Cu composites

The influence of dry ball milling time after 12 h, 24 h and 36 h on the dispersion of Cu particles in the matrix is shown in **Fig 2**. **Fig. 2(a-c)** shows the dispersion of Cu particles in the C-20 composite prepared after ball milling time of 12 h, 24 h and 36 h, respectively. It can be seen that dispersion of Cu improved with increasing ball milling time and the size of Cu aggregates also decreased. Moreover, the PVC particles are surrounded by the Cu particles making garland-type structure. The thickness of the garland decreased with increasing ball milling time. However, in case of C-30 and C-40 composites, the tendency for Cu aggregates was increased due to the decreased inter-particle distances between the Cu particles. It can be clearly seen that the size of aggregates decreased with increasing ball milling time as shown in **Fig 2i**.

Vickers microhardness of PVC/Cu composites

Fig. 3 shows the microhardness of composites as a function of Cu content. The microhardness of the composites increased significantly with increasing content of Cu in the matrix. The microhardness increased from 13.9 kg/mm^2 for pure PVC to 16.4 kg/mm^2 (after 36 h) for C-40 composite. It increased due to the resistance to the plastic deformation of the PVC matrix from comparatively hard Cu particles. The significant improvement in microhardness may be attributed to the better distribution of Cu powder and good adhesion between the PVC and Cu particles. **Fig. 3** also correlates the experimental microhardness with the values predicted from the rule of mixtures (ROM) and modified-ROM (M-ROM). The ROM and M-ROM for the microhardness can be expressed by Eq. (1) and Eq. (2), respectively.

$$H_c = H_m(1-V_f) + H_f V_f \quad (1)$$

$$H_c = H_m(1-V_f) + \beta.H_f V_f \quad (2)$$

where, H_c, H_m and H_f are the microhardness of the composite, matrix and Cu filler, respectively. It can be seen that there is wide gap between the experimental data and the values predicted from the ROM. To bridge the gap, the M-ROM was used which uses the strengthening efficiency factor (β), the value of β varies between 0 and 1 [20]. We can see that M-ROM with β=0.5 nicely fits the data of the composites mixed for 12 h while its value increased to about 0.6 with increasing ball milling time to 36 h. It is due to the better dispersion of the Cu particles in the matrix as confirmed from optical microscope.

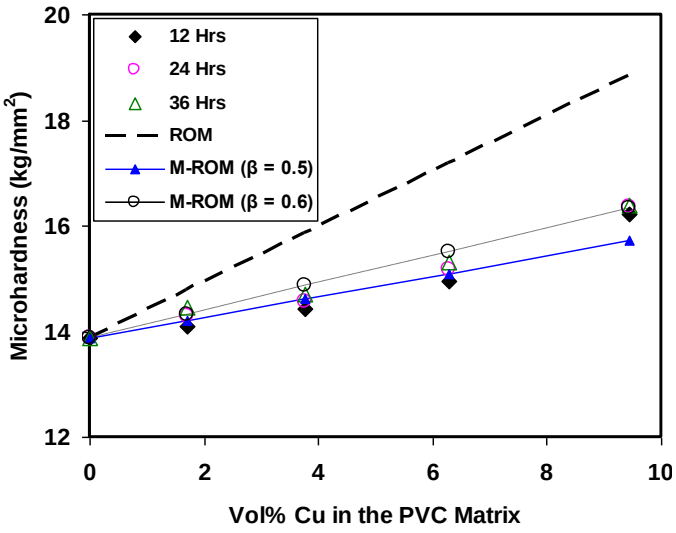

Fig 3. Microhardness of the PVC/Cu composites as a function of vol% of Cu.

Electrical conductivity

Fig. 4 shows the volume electrical conductivity of the composites prepared after mixing for three ball milling times (12, 24 and 36 h) as a function of Cu content. The electrical conductivity of the pure PVC is about 10^{-8} S/cm. The conductivity of the composites increased with increasing Cu content. The increase in conductivity does not exhibit a linear additive characteristic. A drastic increase in the electrical conductivity (i.e., percolation threshold) was observed between 3.7 vol% (20 wt%) and 6.2 vol% (30 wt%) Cu content. It is due to the formation of the three-dimensional conductive network of Cu particles through the polymer matrix and thus, composite becomes conductive [**2**].

These conductive networks have either physical contact between Cu particles and/or they are separated by a very small distances across which electrons can tunnel. Interestingly, as shown in **Fig 4**, the conductivity of the composites increased approximately one-order of magnitude with increasing ball milling time. This may be attributed to the homogeneous distribution of Cu particles and the formation of more number of three-dimensional networks at higher ball milling time. However, the

percolation threshold is almost independent on the ball milling time.

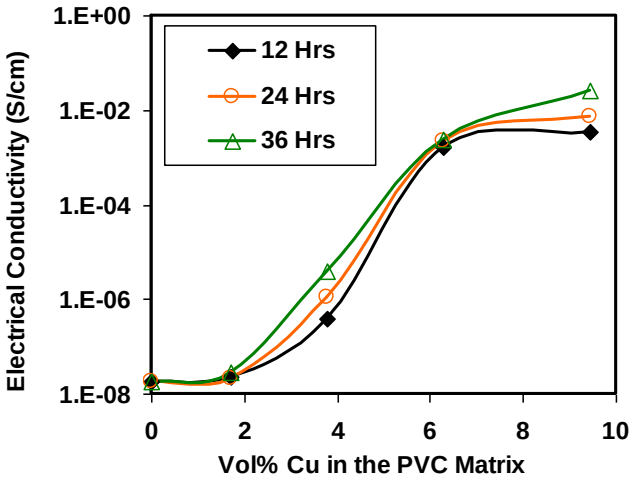

Fig 4. Electrical conductivity of the PVC/Cu composites as a function of vol% of Cu.

Conclusion

A series of PVC/Cu composites were prepared using ball mill followed by hot pressing. It was found that the dispersion of the Cu particles in the matrix increased with increasing ball milling time from 12 h to 36 h. It is due to the decreased size of Cu dendrites and hence, more number of three-dimensional conductive networks of Cu particles is formed in the matrix. The percolation threshold of the composites was about 3.7 vol% Cu. The electrical conductivity increased approximately six orders of magnitude for the 9.3 vol% composite. The microhardness of the composites was increased with increasing Cu content and the ball-milling time.

Acknowledgement

One of the authors Ms Kulthe wishes to acknowledge financial support (Grant No.: 40-26/2011 (SR)) under the scheme of support for major research project from the University Grants Commission (UGC), India.

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