

Preparation and Characterization of Flexible Polyvinylchloride-Copper Composite Films

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SUMMARY

Flexible PVC films are statically charged due to their low electrical conductivity. This creates fire threat during its handling. Conductive materials are added to films to prevent this. In the present study it was aimed to prepare PVC- copper composite films by sol gel technique and characterize the prepared films. It was aimed to increase the electrical conductivity of the films by adding copper powder. However, the copper particles settled down to bottom instead of forming a conductive network that covers the whole cross section. Thus at the film cross-section a plastic upper phase and a copper rich lower phase were present. The film did not conduct electricity due to this uneven distribution. The minimum volumetric and surface resistivities of the films were at the order of 10^9 ohm-cm and 10^{10} ohm square respectively.

Keywords: PVC, Copper powder, Static electricity, Conductivity

1. INTRODUCTION

Metal filled polymer composites are widely used for electromagnetic interference shielding. They have a lighter weight than metals and are less costly¹. Electrically conductive polymer composites (CPC) are obtained by blending an insulating polymer matrix with conductive fillers like carbon black, copper powder or other metal particles. CPCs exhibit several interesting features due to their resistivity variation with thermal, mechanical or chemical treatments. It was found that morphology and structure of conductive pathways within the composite were key parameters determining most of the electrical properties of the CPC.

When a polymer matrix having conductivity σ_p is filled with dispersed filler having a conductivity σ_f , the composite prepared gains a conductivity value σ . When the volume

filler fraction Φ reaches a critical value Φ_c (so-called percolation threshold), an infinite conductive cluster (IC) is formed and, consequently, the composite becomes conductive². As the filler concentration increases from Φ_c to the filling limit F, the value of σ increases rapidly over several orders of magnitude, from the value σ_c at the percolation threshold to the maximal value σ_m . Below the percolation threshold, the conductivity change is negligible and the conductivity of the composite is equal to the polymer conductivity σ_p or slightly higher. The typical dependence of the logarithm of conductivity on the filler volume fraction is shown in **Figure 1**.

Statistical percolation threshold model predicts the conductivity based on the probability of particle contacts within the composite. By computer simulation it was possible to predict the points and bands in a cluster. McLachlan, proposed the model which takes probability

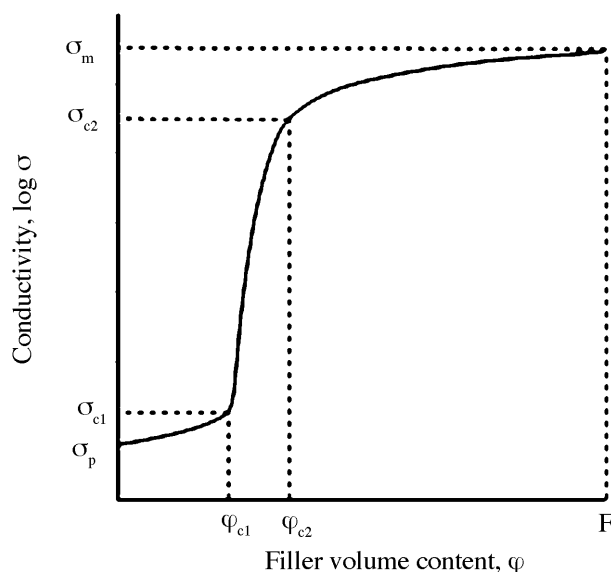
of connection. In this model general effective media theory was used for analyzing the electrical resistivity of the composite. McLachlan suggests this model for conductive particles in an insulating matrix. The goals of the modeling study for McLachlan to determine what factors were critical in controlling conductivity values and to be able to accurately predict and explain the results. The model equation was given in Equation (1) and it describes the conductivity (resistivity) of a wide variety of binary mixtures as a function of the conductivities of the component, the volume fraction of each parameters⁴.

$$\frac{(1-\Phi)(\rho_m^{1/t} - \rho_h^{1/t})}{\rho_m^{1/t} + A\rho_h^{1/t}} + \frac{\Phi((\rho_m^{1/t} - \rho_l^{1/t}))}{\rho_m^{1/t} + A\rho_l^{1/t}} = 0 \quad (1)$$

In Equation (1), Φ was the volume fraction of the filler, A found from the critical percolation threshold value from $A=(1-\Phi_c)/\Phi_c$, ρ_m , ρ_l , and ρ_h was given as resistivity of component, polymer and filler respectively and t was the critical exponent. The equation, was valid for all volume fractions, and is shown to fit a large variety

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Figure 1. Electrical conductivity on conductive filler volume content³**Table 1. Composition of plastisols and volume fractions of copper in plastisols**

Sample Number	Plastisol (g)	Copper (g)	Vol. Fraction of Cu
Reference sample	10.009	0	0
1	10.010	1.004	0.011
2	10.012	4.002	0.053
3	10.012	8.004	0.095
4	10.013	12.000	0.134
5	10.005	16.002	0.187

of experimental data very well. The critical exponent ranges between 1.5 and 3.1. The value of t was varied within these ranges to obtain and determine the sensitivity of the model calculations with changing parameter⁴. As t is increased, the calculated conductivity was decreased by up to several orders of magnitude. In order to accurately predict the conductivity using this model, it was important to pick the correct value for t unless this will lead to significant difference between expected conductivity values and experimental values⁴.

It was aimed to control the conductivity of flexible PVC films by adding conductive copper particles in the present study. The copper particles were mixed to plastisols and the

films obtained by spreading plastisols on glass were gelled by heating. Composites having copper particles in the range of zero and above threshold volume fractions were prepared for this purpose and their volume and surface resistivities were measured.

2. EXPERIMENTAL

2.1 Sample Preparation

Emulsion type PVC powder (PETVINYL 38/74), dioctyl phthalate (DOP) and Viscobyk 5025 were used to prepare the films. Aldrich copper powder which has $1.673 \mu\text{ohm}\cdot\text{cm}$ resistivity, density of 8.94 g/ml , was sieved and particles below $100 \mu\text{m}$ were used in composite preparation⁵. On the other hand different amounts

of copper powder were used to reach different volume ratios of copper in the samples. These volumes were used for preparation of films with different volume and surface electrical conductivities.

3. METHODS

100 g PVC, 80 ml DOP and 5 ml DOP were mixed evenly. Then different amounts of copper powder were mixed with each 10 g of plastisols to prepare the composites. In **Table 1** composition of plastisols and volume fractions of copper in plastisols are shown. The mixtures were spread on glass plates by using Sheen Automatic Film Applicator-1133N, at 100 cm speed. $500 \mu\text{m}$ blade thickness was chosen for films. Plastisol films on glass plates were heated to 140°C in Selectra Vacuum Oven to obtain flexible plastic films by heating.

3.1 Functional Groups in Copper Powder

The impurities in the monodisperse copper powder, which had a size of less than $38 \mu\text{m}$, was determined using FTIR spectrophotometer SHIMADZU FTIR-8201 with KBr disc method.

3.2 Morphology of the Fracture Surfaces of the Films

Plastigel films obtained by the heating process were analyzed with the SEM (Scanning Electron Microscopy). Small size of films was cut from the main plastisol films. All those cut pieces were immersed in the liquid nitrogen. Boiling temperature of nitrogen is approximately -200°C and liquid nitrogen is a good choice to reach brittle samples. The brittle samples obtained by immersing in liquid nitrogen were fractured into two to obtain fracture surfaces. The surfaces were coated with gold by EMITECH K550 X which would help to make them conductive for better resolution at the SEM.

3.3 Measurement of Volume and Surface Resistivities of the Films

Volume resistivity is defined as the electrical resistance through a one-centimeter cube of insulating material and is expressed in ohm-centimeters. Volume resistivity is measured by applying a voltage potential across opposite sides of the insulator sample, measuring the resultant current through the sample. Surface resistivity is defined as the electrical resistance of the surface of an insulator material. It is measured from electrode to electrode along the surface of the insulator sample. Since surface length is fixed, the measurement is independent of the physical dimensions of the insulator sample. Surface density is measured by applying a voltage potential across the surface of the insulator sample, measuring the resulting current. The electrical resistivity of the samples were analyzed typically at constant polarity voltage applied to the molded specimen. The resistivity of the samples was measured according to ASTM D257 using Keithley 6517A Electrometer/High Resistance meter and an 8009 Resistivity Text Fixture. This system was automated using Keithley 6524 test software which displays the resistivity value after each test.

Volume resistivity is measured by applying a voltage potential across opposite sides of the insulator sample and measuring the resultant current through the sample. The Model 6517A automatically performs the calculation by using Equation (2) and displays the volume resistivity reading:

$$\rho_v = \frac{K_v R}{\tau}$$

ρ_v = Volume resistivity
 K_v = The effective area of the guarded electrode for particular electrode arrangement employed
 τ = Average thickness of the sample (mm)
 R = Measured resistance in ohms (V/I)

(2)

All resistivity calculations were done under 10 V alternative voltages.

3.4 Measurement of the Thickness of the Films

Thickness of the samples was only important in volume resistivity calculations. Because of that all the samples were measured 10 different points by using a micrometer.

3.5 Density of the Samples

Archimedes' Principle says that the apparent weight of an object immersed in a liquid decreases by an amount equal to the weight of the volume of the liquid that it displaces. Densities were measured with Archimedes Principle. **Table 2** shows the measured densities of film samples.

The theoretical densities were calculated using Equation (3):

$$\rho_1 \cdot \phi_1 + \rho_2 \cdot (1 - \phi_1) = \rho_c$$
(3)

Where ρ_1 is the density of the copper powder = 8.92 g cm⁻³

ϕ_1 is the volume fraction of copper powder

ρ_2 is the density of composite without copper = 1.221 g cm⁻³

ρ_c is the density of the sample.

Geometric densities were calculated using Equation (4):

$$d = m/V$$
(4)

where: d is density of film

m is mass of film

V is volume of film

Mass was measured by the balance (Sartorius GD603), volume was calculated with measuring of diameter, length and thickness.

4. RESULTS AND DISCUSSIONS

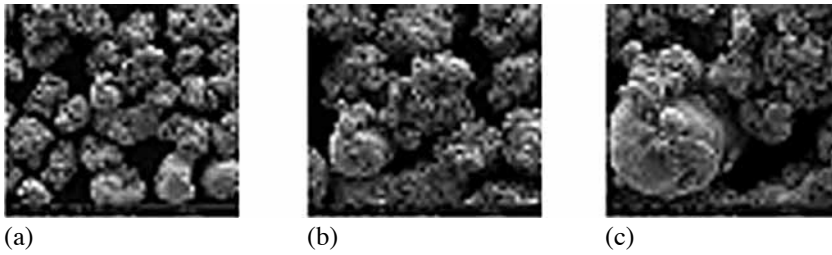
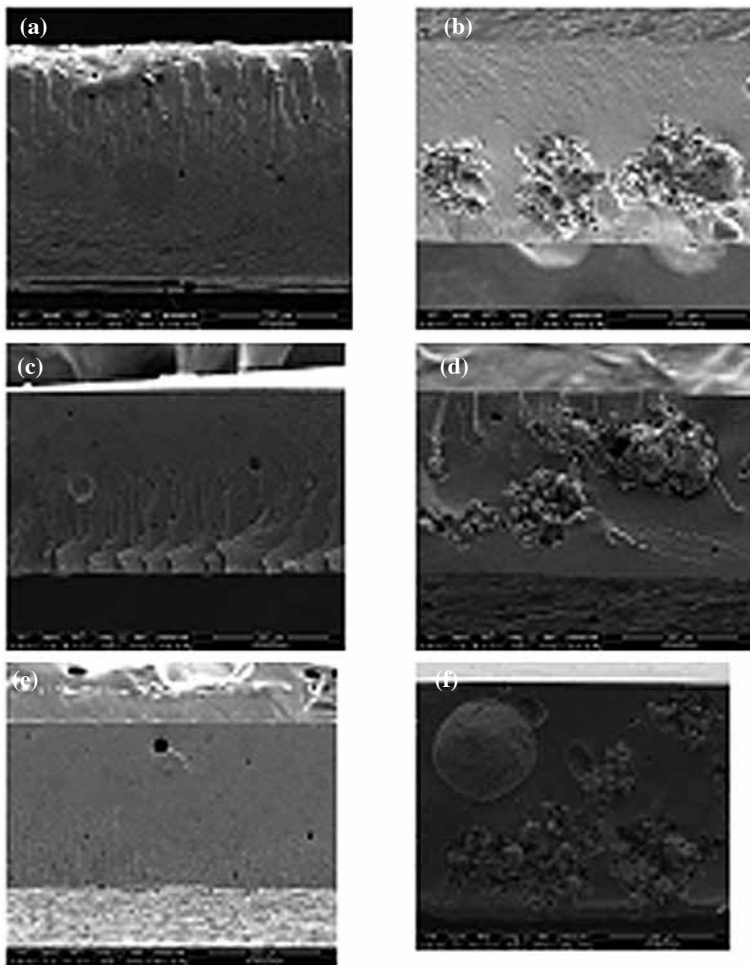
4.1 Copper Powders

The FTIR spectrum of the copper powder indicated that it was not pure, it contained a small amount of hydrocarbon and the surface of the particles was coated with copper oxide⁶. As seen in the SEM micrograph in **Figure 3** 5-100 μ m copper particles were stuck to each other to form agglomerates.

4.2 Composite Films Morphology

Reference sample did not have any copper powder in it but some air bubbles were seen in **Figure 3a**. **Figure 3b** shows the fracture surface of the sample which has 1 vol.% copper. There are strips formed during fracturing. A small size of air bubble is clearly shown.

Figure 3e shows SEM images of sample which has 13 vol.% copper. The copper powders in PVC film can be seen. There was polymer phase between the particles. **Figure 3f** shows the fracture surface of the film with maximum copper content, 18 vol.%. Agglomerated copper particles are clearly seen in the images. There are no air bubbles in the samples. However copper particles were present at the bottom of the films and there was a polymer phase at the upper layer. This could be due to settling of copper

Figure 2. SEM images of copper powders (a) 250x, (b) 500x, (c) 1000x magnification**Figure 3.** SEM micrographs of composites with (a) 0, (b) 0.01, (c) 0.05, (d) 0.09, (e) 0.13, (f) 0.18 volume fraction of copper**Table 2.** The measured density and resistivity values for different copper volume fractions

Φ	ρ (g cm ⁻³)	Average Thickness (mm)	Surface resistivity Ohm square	Volumetric resistivity (ohm-cm)
0	1.22	0.335	9.44E+10	2.10E+10
0.01	1.33	0.369	1.76E+09	2.46E+10
0.05	1.57	0.321	1.49E+09	3.46E+10
0.09	1.84	0.339	1.90E+11	2.76E+12
0.13	2.32	0.477	2.75E+11	2.06E+12
0.18	2.39	0.497	8.75E+11	2.10E+12
1.00	8.92	-	-	1.67E-6

particles in PVC plastisol due to its high density.

4.3 Density of Composites

The measured, theoretical and geometric density values are not identical but they were close to each other as seen in **Figure 4**. As reported in **Table 2** when amount of copper powders increased, the density of plastigel was also increased as expected. All the samples were prepared with using film applicator blade with 500 μ m thickness. However the thickness of the composites were not the same in all films. Thickness also increased with the copper volume fraction as seen in **Table 2**.

4.4 Resistivity of Composites

Under normal conditions resistivities of the samples should increase with increasing amount of copper. **Table 2** shows measured surface and volume resistivities of copper powder films.

All of the results were measured three times and these results are the average values. Vol.% copper versus Log of volumetric conductivity was sketched using values predicted by Equation (1) in **Figure 5**. The resistivity of copper was taken as 1.68×10^{-6} and resistivity of PVC was taken 2.1×10^{10} . 't' critical exponent values was selected as 2.5. A in the Mclachlan model was found from the critical percolation threshold value (Φ_c) from $A = (1 - \Phi_c) / \Phi_c$. Φ_c value was selected as 0.16 as reported in reference [1]. To find the composite resistivity value that make the Mclachlan model equation (Equation (1)) close to zero, Goal and Seek application was used. According to the Mclachlan model, log conductivity increases with increasing vol.% of copper, but according to experimental values log conductivity decreased with vol.% of copper. Thus the data did not fit to Mclachlan model. Powders also had lower conductivity than copper. This also effected the conductivity of the composites.

Figure 4. Measured, geometric and theoretical densities versus volume fraction of copper

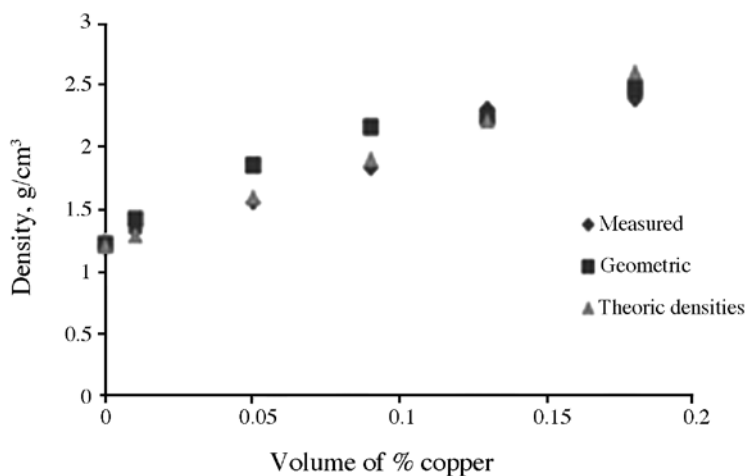
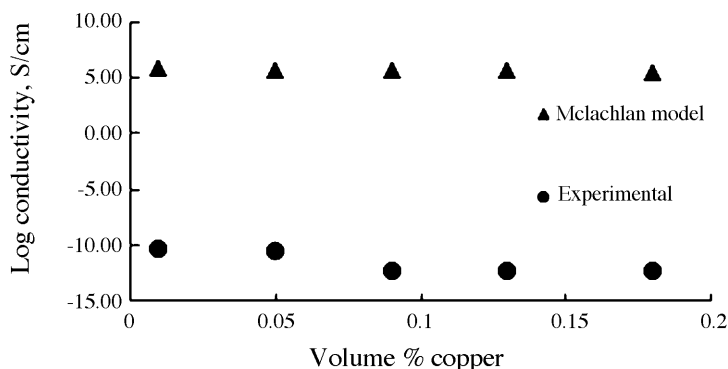


Figure 5. Volumetric conductivity of copper films McLachlan model and experimental values



5. CONCLUSIONS

The copper particles were also in agglomerated state in flexible films. They were not dispersed evenly in the film to create a conductive path. The change of the density of the films with volume fraction of the copper in the films fit to theoretical values. The electrical resistivity did not have the expected values that decrease with increasing copper volume fraction. On contrary to expectations it increased with increasing volume fraction. It was thought that the copper particles having higher density than liquid plastisol sank to the bottom during spreading and fusion of the films. Thus the copper particles could not form a conductive network that covers the whole cross section. Thus at the film cross section a plastic upper phase and a copper rich lower phase were present. The film did not conduct electricity due to this uneven distribution.

Further studies are being made to prepare nanosized copper powders and disperse them evenly in PVC plastisols.

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