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PVC-Cu composites with chemically deposited ultrafine copper particles

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PVC–Cu composites with chemically deposited ultrafine (0.1 to 0.3 μm diameter) copper particles were prepared by hot-pressing copper-coated PVC powder (− 106, + 150 μm) at 120° C. Metallic copper in fine-particle form was deposited on the PVC particles by reducing an ammoniacal cupric acetate solution with hydrazine at 85° C. The electrical resistivity (d.c.) and transverse rupture strength of these composites were measured. Measurement of electrical resistivity indicated that in these composites copper particle network formation was initiated at a copper content of about 0.2 vol %; with further increase of copper content the resistivity dropped sharply from about 10^{14} (for pure PVC) to about 10^5 MN m^{-2} Ωcm at a copper content of about 0.5 vol %. Increase of copper loading beyond 0.5 vol % did not decrease resistivity significantly whereas the rupture strength increased continuously from 120 MN m^{-2} (for pure PVC) to a value of about 300 MN m^{-2} with 4 vol % copper loading. This high value of resistivity even after copper particle chain formation and the continuous increase of rupture strength, is thought to be due to formation of a thin layer of polymer film between the copper particles introducing a "quasi-random" character to the otherwise segregated network of copper particles.

1. Introduction

The effects of the metallic fillers in polymeric matrices have been studied by many authors, [1–2] and various models [2, 3] have been proposed to explain quantitatively the phenomenon of endless chain formations taking place by "segregated net-works". It was also found that with increasing ratio of the particle size of polymer and metal phases it was possible to achieve electrical conduction with as low as 4 vol % metal. However, all these investigations considered mechanical mixtures of polymer and metal powders. The present study was undertaken to develop a method of precipitating fine metallic particles on polymer surfaces and to study the properties of the briquettes prepared from these composite powders.

2. Experimental methods

Commercially available PVC powder (grade S-65-211, NOCIL) was sieved and the − 106 to + 150 μm fraction was used in the present study. Metallic copper in fine-particle form was deposited on the PVC particles by reducing an ammoniacal cupric acetate solution with hydrazine at about 85° C into which the polymer powder was added as a substrate. Fig. 1 shows metallic copper deposited in fine crystalline form more or less uniformly over the polymer surfaces. Fig. 2, shows the shape of the individual copper particle. The particle size of the copper varied between 0.1 and 0.3 μm as measured by scanning electron microscopy. Fig. 3 shows the deposited amount of copper estimated chemically as a function of the amount of cupric acetate, added in the original solution (curve A). For comparison, curve B shows the maximum amount of copper that could be deposited. The deposition efficiency was found to vary between 50 and 70%.

Samples were compacted in steel cylindrical dies at a pressure of 45 MN m^{-2}, and a temperature of 120° C to yield briquettes of about 1 cm

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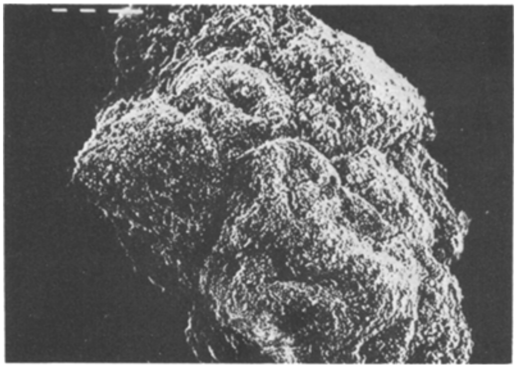

Figure 1 Scanning electron micrograph of PVC particles showing deposited copper on the surface, × 650.

thick and 2.6 cm diameter. Electrical resistivity and transverse rupture strength of the briquettes were measured, the experimental details of which have been reported earlier [3, 4]. The polished and fractured surfaces of the briquettes were studied under optical and scanning microscopes, respectively.

3. Results and discussion

Fig. 4, shows that chemically deposited ultrafine copper particles lead to the formation of well-defined segregated network. Measurement of electrical resistivity (Fig. 5), indicates that the network formation is initiated at a copper content 0.22 vol % (X_A). Addition of higher amounts of copper sharply reduces the resistivity of the sample from 10^{14} to about 10^5 Ωcm. The point of inflection (X_B) is at 0.5 vol % metal loading.

It has been proposed [3] that for equi-axed particles the following relationship should hold

$$\frac{X_B}{100 - X_B} = \frac{2.99}{r_p/r_m} \qquad (1)$$

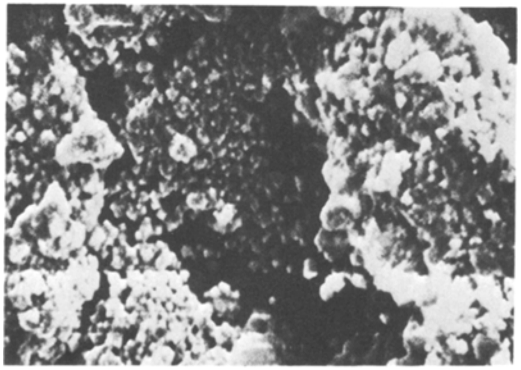

Figure 2 SEM showing dispersion of copper particles on PVC surface, × 5000.

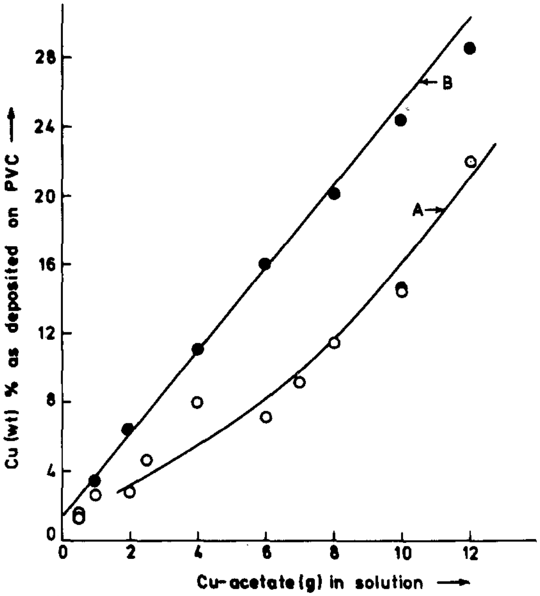

Figure 3 Actual (A) and theoretical (B) amount of copper deposited as a function of amount of copper acetate solution.

where r_p is the average radius of polymer particles in (μm) and r_m the average radius of metal particles (μm). According to Equation 1, r_m should be of the order of 0.18 μm if X_B is 0.5 vol %. The values of r_m obtained by SEM studies fully support this estimation. Furthermore, the value of $X_B/X_A = 2$, closely approximate to the percolation probability parameter linking these two values as established earlier [3].

A distinctive feature of the present experiment is the high value of resistivity (10^5 Ωcm) obtained after the chain formation has been completed beyond X_B. Previous studies with mechanically mixed copper powder [2, 3] mostly reported

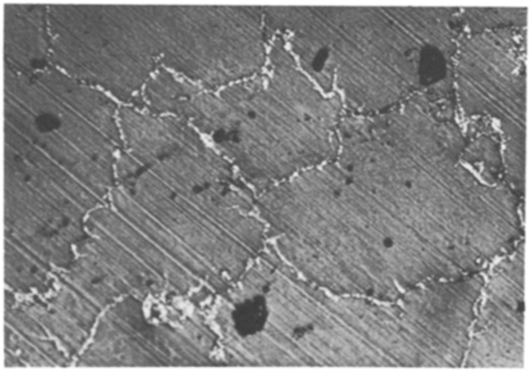

Figure 4 Segregated network of copper in PVC matrix in compression-moulded briquette, × 300.

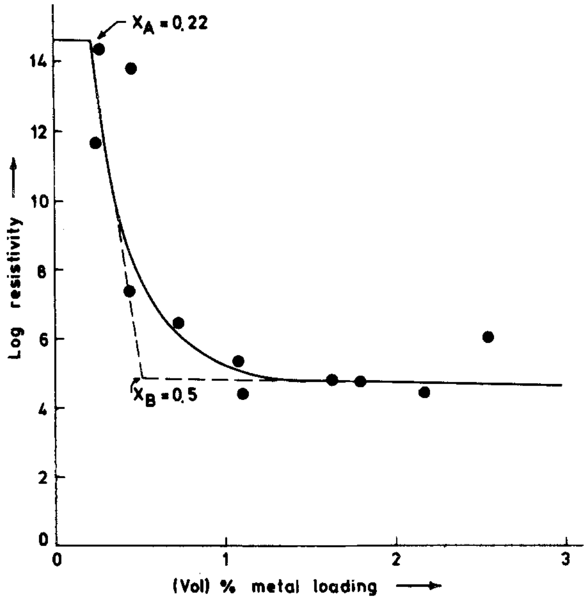

Figure 5 Electrical resistivity as a function of metal loading.

values of ohmic order. These authors have shown [3] that the resistivity at X_B, where the first mono-layer of metal forms around the polymer particle is a direct function of the unit metal contact resistance, R_0. The parameter R_0 was found to depend upon surface conditions such as the thickness of the oxide scales on the metal particles. X-ray and chemical studies of the coated PVC powder revealed that the deposited copper particles were virtually free of oxide. Thus the high value of R_0 may be explained on the basis of formation of thin polymer film around the metal particles during the preparation of briquettes. Analogous results were obtained [5] on PVC–copper composite with plasticizers and stabilizer. The stabilizers formed a coating on the metal surface and raised the value of R_0.

The formation of the thin polymer film between metal particles introduces a "quasi-random" character to the otherwise segregated network. This has a profound influence on mechanical property of the composite as given in Fig. 5, where the transverse rupture strength of briquettes is plotted against metal loading. The strength of the composite is found to increase continuously and reach a value of about 300 MN m^{-2} with only 4 vol % metal loading. Compared to a value of 120 MN m^{-2} for pure PVC [3], this means an increase of about 200% in strength with a very low filler concentration. In spite of the metal network being formed with as low as 0.5 vol % filler loading, the strength of the composite continued to increase with high loadings because of the polymeric film formation on metal surfaces which retained

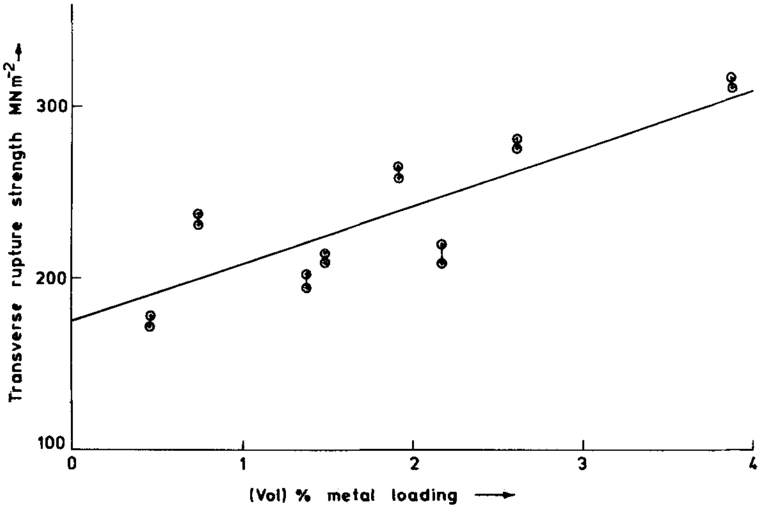

Figure 6 Transverse rupture strength of PVC–copper composite as a function of vol % metal loading.

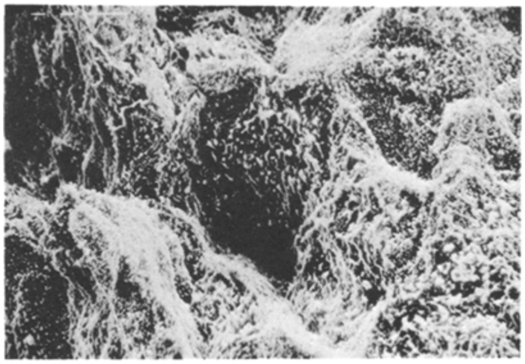

Figure 7 SEM fractograph of PVC–Cu composites showing interparticle fracture and fine flow lines.

matrix continuity. Similar results were obtained in the studies with plasticizer [5]. SEM fractographs show the rupture surfaces were principally interparticle in nature but with fine flowlines possibly caused by the ruptured polymer films on metal surfaces (Fig. 7). The straight line passing through the points in Fig. 6, has the least square fit of the data with a slope of 32.8 and an intercept of 178.6 $\mathrm{MN\,m^{-2}}$. The relation between composite strength and interparticle distance (d_m) has been studied [5–7]. Two models have been proposed to estimate d_m:

(a) in the case of segregated nature [4] of the filler particles

$$d_m = r_m\,3.95(r_p/r_m)^{-\frac{1}{2}}\,V_p^{\frac{1}{6}}\,V_m^{-\frac{1}{2}} - 2; \quad (2)$$

(b) in the case of random distribution of the filler particles

$$d_m = \frac{(1-V_m)}{3V_m}4r_m, \quad (3)$$

where V_p and V_m are volume fractions of polymer and metal phases, respectively.

Equation 2 has been found to be valid for unplasticized PVC–copper composites [4]. The interparticle distance, d_m, calculated by this relation was found to approach zero with onset of monolayer formation, i.e. with the metal loading of X_B (Fig. 5). Beyond this value of metal loading, d_m was found to be negative and the strength of the composite dropped markedly because of ease of crack propagation through metallic contacts [4]. With the addition of plasticizer the picture changed [5]. The thin plasticized polymer film between metallic particles retained matrix continuity and the strength continued to rise beyond the point X_B. This was referred to as quasi-randomness of the network. In this condition, the strength values were found to follow a linear relationship with $d_m^{-1/2}$ as calculated from Equation 3. A very similar result is obtained in the present case. The presence of the polymer film around metal particles (as discussed before) leads to a quasi-randomness in the network; d_m as calculated from Equation 2 becomes negative beyond 0.5 vol% metal loading (X_B in Fig. 5), but strength values continue to increase with higher metal loading d_m calculated from Equation 3 gives an estimation of interparticle distance for an equivalent dispersed system and this is found to follow the inverse square root relationship with composite strength as postulated [6] for particulate composites (Fig. 8).

4. Conclusions

(1) A method has been developed to prepare PVC–copper composite powder with ultrafine

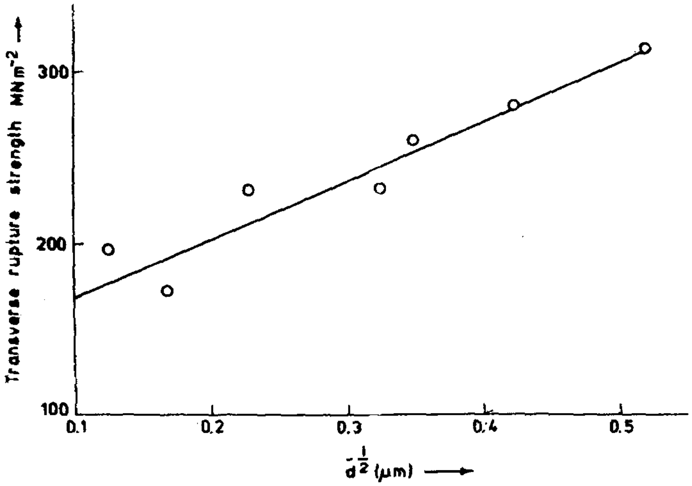

Figure 8 Plot of transverse rupture strength as a function of d_m.

copper particles deposited chemically on polymer surfaces.

(2) The new composite powder allows formation of a segregated network with accompanying conductivity with only 0.5 vol % metal loading.

(3) The formation of a thin polymeric barrier at the metallic contact point raises the composite resistivity and causes a continuous increase in strength.

(4) About 200% increase in strength of PVC is obtained by this method and the strengthening mechanism appears to follow the inverse square-root law linking interparticle distance with composite strength.

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