Nickel Coated Mica for Conductive Compounds

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Summary: It has been shown that nickel coated mica will function as a conductive filler in ABS compounds. The coating process has been optimised by investigation of $PdCl_2$ (catalyst) concentration, coating temperature and pH and activator. Using a coating temperature of 90°C and a pH of 5, conductive mica powders coated with thin uniform layers of nickel have been produced.

Introduction

With the rapid development of the electronic industry, electromagnetic interference (EMI) is becoming an increasing problem. The USA Federal Communication Commission introduced regulations regarding the immunity and susceptibility of electrical and electronic systems to electromagnetic interference in 1983[1]; in January 1996 new regulations based on these became effective in the European Union [2].

Existing shielding methods include coating/painting of components, the use of conductive polymers, and conductive polymer composites. Coating methods are the predominant choice for EMI shielding operations, accounting for 98% of the market when a review was carried out in 1995[3]. In recent years, considerable research effort has focused on the development of conductive polymers. However, their cost is much higher than commodity polymers, so in the immediate future, these materials are likely to be used in more specialist applications, or blends.

In conductive polymer composite materials, a conductive filler is incorporated into a polymer matrix. The most common conductive fillers are carbon black, carbon fibres, metallic powders, flakes or powders, and fibres coated with metals[2]. Mica was selected for this project as it exists in the form of flakes of high aspect ratio, and acts as a reinforcing filler in polymers. If coated with metal, mica has the potential to retain this advantage and at the same time become a conductive filler. Properties of composites containing such a filler have been reported previously[4-7]. In this study the production of nickel coated mica has been re-evaluated in order to develop a procedure for coating mica particles with thin uniform layers of nickel. In an initial programme, nickel coated mica has been incorporated into ABS[8]. It was found that for 1mm thick samples

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containing 60μm mica particles a filler volume fraction of 0.24 and about 40% of nickel on mica particles, corresponding to 3.6 volume % of nickel was required to produce electrically conductive composites. Increasing the particle size of the mica reduced the critical filler loading required. In this paper, the nickel coating process has been investigated in detail, in order to reduce the amount of nickel required to achieve conductivity.

Experimental

Materials

A phlogopite grade of mica, Mica TK 100C-100201 was supplied by Microfine Minerals Ltd. The average particle size was 100μm, density 2500kg m^{-3}, and surface area 0.0613m^2g^{-1}. The composition of this grade of mica was SiO_2 = 40-42%; Al_2O_3 = 9-11%; Fe_2O_3 = 9-11%; MgO = 22-24%; K_2O = 10-11%.

Lea Manufacturing (UK) provided the Niklad electroless plating solutions. The sensitiser, which contained $SnCl_2$, was Niklad 261. Niklad 262, a dilute solution of palladium chloride was used as activator. The electroless plating solution was Niklad 795, which contained 10-15% nickel sulphate, a reducing agent sodium hypophosphite ($NaH_2PO_2.H_2O$) and a number of other components such as complexing agents and stabilizers. A one-pack activator, Macuplex D-34C, containing both $SnCl_2$ sensitiser and $PdCl_2$ catalyst, supplied by MacDermid was also investigated.

Electroless nickel coating

The Niklad 261 was used to form Sn^{2+} on the surface of the mica. The Sn^{2+} then reduced the palladium chloride in Niklad 262 into metallic palladium, which formed the catalytic sites needed to deposit the nickel metal. The main reaction is as follows

$$Sn^{2+} + Pd^{2+} \longrightarrow Pd^{0} + Sn^{4+} \qquad (1)$$

The nickel was deposited from Niklad 795, and reduced to metallic nickel by the sodium phosphite. The main reactions are as follows[9]

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \longrightarrow Ni + 2H_3PO_3^- + 2H^+ \qquad (2)$$

$$H_2PO_2^- + H_2O \longrightarrow H_3PO_3^- + H_2 \qquad (3)$$

A known amount of mica was stirred for 30min in Niklad 261 (10% weight of $SnCl_2$ in aqueous solution) at room temperature, filtered, rinsed with de-ionized water; then stirred for 30min in Niklad 262 (2% weight of $PdCl_2$ in aqueous solution), filtered, then rinsed again with de-ionized water. The treated mica was dried at 80-100°C in an oven for 2 hours. The weighed catalysed powder was put into Niklad 795 solution diluted by deionized water. After an initial period of inactivity, the nickel coated rapidly onto the mica flakes. The onset of this process was indicated by the appearance of hydrogen bubbles. The effects of solution agitation, palladium chloride concentration (2-10%), reaction temperature (70°C and 90°C) and pH (4-6) were investigated. During reaction the pH value of the electroless plating solution was maintained at the required level by adding 1:1 (volume ratio) ammonia solution.

When the one pack activator was used, mica particles were treated with diluted Macuplex solution for a period of 15 minutes, dried in an air circulating oven at 80 – 100^0C for two hours and then treated with nickel sulphate solution as described above. The mica was weighed before and after coating to determine the weight % coating.

Characterisation of coated filler

Nickel coated mica particles were sputter coated with a thin layer of gold, then examined by Scanning Electron Microscopy in order to observe the nickel coating. It is known that this coating method deposits some phosphorous as well as nickel, so a selection of coated samples were analysed using an Atomscan 25 spectrometer with an inductively coupled plasma (ICP) emission source for accurate determination of nickel and phosphorous concentrations.

Measurement of volume resistivity

To measure the volume resistivity of the various nickel coated mica powders, pellets of known dimensions were produced in a special die by applying a pressure of 1.5 MPa for 10 minutes to samples of each of the powders. These specimens were mounted between custom-made electrodes and values of resistance were measured with a standard multimeter (Beckman Industrial Tech 310). During testing the electrodes needed to be pressed into contact with the pellet to ensure a constant meter reading. An average value of two readings of volume resistivity was obtained for each pellet.

Results and discussion

SEM photographs of nickel coated samples produced with and without agitation of the plating solution demonstrated that a much more uniform coating was produced when the solution was stirred. Agitation increases the rate of diffusion and convection so that the reactants are transferred more efficiently to mica surfaces.

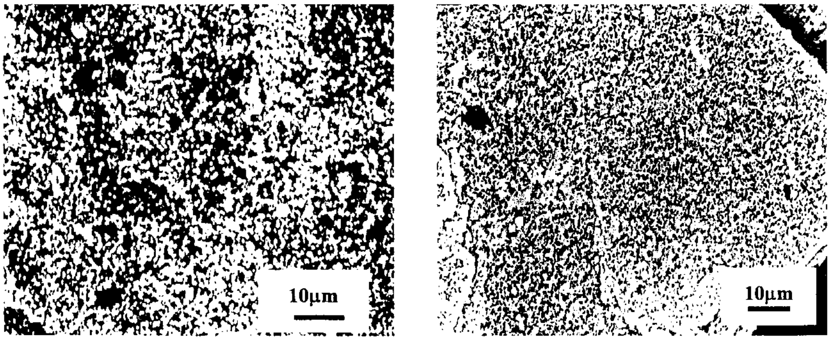
Results obtained for coatings (pH 4, coating temperature 90°C) with the same concentration of nickel in the plating solution, but different concentrations of palladium chloride catalyst show that increasing the concentration of palladium neither increases the amount of nickel deposited, nor reduces resistivity, so 2% $PdCl_2$ was used in subsequent experiments.

Coating was carried out at pH = 4 and 6, and at 70°C and 90°C. Examination of resulting samples showed that less nickel was deposited at 70°C; SEM photographs suggested that coating was incomplete at 70°C, and the resistivities of resulting samples were higher. It was therefore concluded that coating should be carried out at 90°C.

Table 1 Volume resistivities of Ni coated micas (two-pack activation)

%Coating	Solution pH	Volume resistivity (ohm cm)
29.0	6	6.8×10^7
28.0	4	5.2×10^7
36.0	4	4.5×10^7
55.0	4	42.9
36.0	5	334.6
43.0	5	17.2
50.0	5	8.7
53.0	5	7.2
56.0	5	5.8

For coating a solid substrate, increasing pH is known to increase deposition rate of nickel and reduce the amount of phosphorous in the resultant coating[10]. Some coating



(a) (b)

Fig 1. SEM photos of nickel coated mica (49% coating) at 90°C, and (a) pH = 4, (b) pH = 5

experiments were carried out at pH 6, but at higher nickel concentrations, instability of the bath was observed. The effect of varying nickel concentration and pH are shown in Table 1, and SEM micrographs of samples coated with approximately 49% Ni at pH values of 4 and 5 are shown in Fig 1.

Inspection of this data shows that coating is optimised using a pH of 5. It is also seen that the amount of nickel deposited increases as the nickel concentration increases. The mica is coated with small nodules of nickel about 0.5µm in diameter, suggesting that coating thickness should be of this magnitude if a single layer of nickel is deposited.

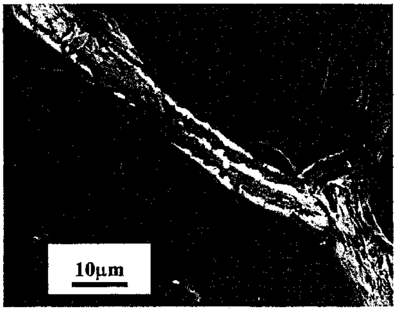


Fig 2. Cross section of coated mica particle mica

Fig 3.SEM photos of nickel coated (25% coating, one-pack activator)

An SEM photograph showing the edge of a coated mica flake is shown in Fig 2. It is seen that coating (which appears white on the photogarph) occurs on the surface of the mica, and also at internal surfaces where edges of platey mica flakes are exposed. It

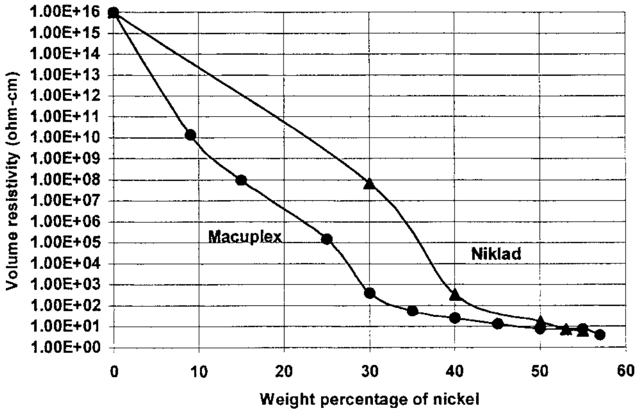


Fig 4.Volume resistivity as a function of Ni concentration

appears to be about 0.7μm thick, but further optimisation produced thinner coatings. Nickel and phosphorous concentrations were measured for samples with various nickel concentrations, and the two activator systems. The amount of phosphorous formed along with nickel was found to be minimum when the reaction was carried out at pH of 5. (e.g. for samples shown in Fig 1, 13.74%P in coating at pH 4 and 10.18%P at pH 5). Fig 3 shows an SEM photograph with 25% coating using the one-pack activator. This is very similar to Fig 3b with a 49% coating obtained using the two-pack activator. Volume resisitivity of the two series of samples is plotted against actual nickel concentration in Fig 4, confirming the benefits of the two-pack system.

Conclusion

For best results, electroless nickel coating of mica should be carried out at 90°C, using a stirred solution and a pH of 5. Uniform coatings about 0.5μm thick, consisting of a network of nodules, can then be produced. The amount of nickel required to produce a conductive filler is lower when a one-pack activator is used.

Acknowledgements

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