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An Electroconductive Filler for Shielding Plastics

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Summary: A well characterised grade of mica was used to prepare nickel-coated mica fillers by an electroless coating technique. These fillers were incorporated into polypropylene (PP) and acrylonitrile-butadiene-styrene (ABS) using a Haake Internal mixer and a two-roll mill to produce conducting composites suitable for EMI shielding applications. Compounded polymers were fabricated into sheets of different thickness by compression moulding. The dependence of conductivity on sample thickness was studied and samples were tested for electrical resistivity, shielding efficiency, and thermal and mechanical properties. Reduced sample thickness during compression moulding decreased the electrical resistance of the polymer composites due to orientation and the formation of a good conducting network. Volume resistivity of PP composites was lower than for ABS composites with 50% Ni coating and equivalent filler weight fracions, showing that better conductivity could be achieved in a semi crystalline polymer than in an amorphous polymer. 0.6 weight fraction of 50 wt.% nickel coated mica in ABS showed a shielding efficiency of 16dB compared with 27.8dB in PP.

Keywords: ABS; electroless nickel coating; EMI shielding fillers; polypropylene

Introduction

Plastics capable of conducting electricity offer many advantages. They provide inherent EMI shielding to protect business machines, automotive and aerospace components and computers from electromagnetic interference. In addition to the consideration that a device should not emit radiation that interferes with others, electronic devices must be capable of functioning under EMI from other sources, i.e., they must exhibit electromagnetic compatibility, and must be shielded in such a way so that both incoming and outgoing interferences can be filtered. Plastics are widely used to make shells for electronic equipment. However, their volume resistivities are approximately 10^{13}-10^{17} ohm-cm, so they are transparent to electromagnetic waves.

A range of options is available for introducing conductivity to plastic housings and enclosures: these options broadly fall into three categories. Intrinsically conductive polymers such as polyacetylene, polyaniline, polythiophene and polypyrrole can be produced[1], but these are expensive, and difficult to process. Coating methods are the predominant choice for EMI shielding operations, accounting for 98% of the market in

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1995[2]. However, they have a number of drawbacks as they involve an extra production process, can be subject to delamination, and are difficult to recycle. The third approach is to produce plastic composites containing conductive fillers. In conductive polymer composite materials, a conductive filler is incorporated into a polymer matrix. These materials are relatively cheap and have good processibility. Also, the conductivity of a composite can be adjusted relatively easily to meet product requirements. The most common conductive fillers are carbon black, carbon fibres, metallic powders, flakes or powders, and fibres coated with metals [2].

The electrical resistivity of conductive composites depends on the volume fraction of the conducting filler particles, and is explained by the percolation theory. The conducting filler is required to produce a conductive particle network in the system. Electrical properties depend upon factors such as filler content, aspect ratio, conductivity of filler and the processing conditions. The amount of electrically conductive filler required to impart conductivity to an insulating polymer can be dramatically decreased by selective localisation of the filler in one phase, or better at the interface of a co-continuous two-phase polymer blend[3]. The critical amount of filler necessary to build up a continuous conductive network and accordingly to make the material conductive is referred to as the percolation threshold.

As indicated above, various conductive fillers have been used, but all have some disadvantages[1]. Effective conductive fillers such as nickel-coated carbon fibres are limited to specialist applications due to cost. In this work the use of coated mica has been investigated. Mica is a sheet silicate with a platelet structure having aspect ratios of 20 to 40. Due to its high modulus and flaky shape it is used in plastics to improve rigidity and dimensional stability[4].

If coated with metal, mica has the potential to retain dimensional stability and increase rigidity of the composite used, at the same time become a conductive filler. Properties of composites containing such a filler have been reported. Kortschot and Woodhams[5] emphasised the importance of aspect ratio, and suggested that this could be achieved by using a thin metal coating on a substrate such as mica. Low nickel concentrations could be used if thinner and more uniform coatings could be achieved. Du and Kumagani[6] mixed nickel-coated mica / epoxy and triethylenetetramine at 115 ^{0}C for 30 minutes. It was observed that nickel-coated mica flakes, oriented in the direction parallel to the sheet, which increased contacts between fillers, had a very good shielding effectiveness.

Previous work[7,8] has identified optimum conditions for the electroless coating of mica, and shown that conductive compounds can be produced using nickel coated mica. In this paper, coating has been carried out on a larger scale to enable composites to be produced.

Experimental

Materials

Mica TK 100C-100201, run number 595, phlogopite grade with layered profile supplied by Minelco Specialities Ltd., UK was used the investigation. The properties of mica are shown in Table 1. The compositional details of the mica are SiO_2 = 40 - 42%, Al_2O_3 = 9 - 11%, Fe_2O_3 = 9 - 11%, MgO = 22 - 24%, K_2O = 10 - 11%.

Table 1. Properties of mica.

Mica grade	Density (gcm^{-3})	Average particle size (μm)	Average particle thickness (μm)	Refractive index	Surface area (m^2g^{-1})	Average aspect ratio*
TK 100C	2.50	100	1	1.58	0.0613	37: 1

* Obtained from direct measurement of thickness (interferometry) and diameter (Carl Zeiss photpmeter) on about 200 particles

Electroless plating solutions used were Macuplex^R Activator D-34C, which is a liquid catalyst system containing both the sensitiser and the activator in a single system for pre-treatment of the specimens before electroless nickel or copper coating, and ELNIC 204, a stable electroless nickel solution. The process is used to deposit an ultra bright, low-medium phosphorous content coating on a variety of substrates. This solution consists of two process components ELNIC 204 A and ELNIC 204 B. ELNIC 204 A is the nickel component and ELNIC 204 B is the reducer and complexing component.

Polymers were used for this work were Escorene PP 7034 P1, a heterophasic polypropylene copolymer supplied in the form of granules by Exxonmobil with a melt flow rate of 12dg min^{-1} at 230 ^{0}C and 2.16kg, and the acrylonitrile-butadiene-styrene resin (Cycolac T ABS) from GE Plastics. Its composition is 25% acrylonitrile, 20% butadiene, 55% styrene with melt flow index of 26dg min^{-1} at 220 ^{0}C and 10kg load.

Chemistry of electroless coating process

This consists of three steps, described in detail previously[7,8].

Step 1. Sensitisation. Treatment with stannous chloride sensitises the surface of mica with Sn^{2+}.

Step 2. Activation. Sensitised mica particles were treated with a 2% solution of palladium chloride. Pd^{2+} is reduced to Pd and acts as the catalytic site for electroless nickel coating.

Step 3. Nickel coating. Pre-treated mica was then treated with different concentrations of nickel solutions based on the weight percent of nickel required. The coating was carried out between 85-90°C, using a pH of 5.

Processing

PP, ABS and nickel coated mica were dried for two hours in an oven at 100°C. These fillers were tumble blended with the resins. Compounding was done using a Haake internal mixer (screw speed 50rpm, mixing for 10 min at 210°C) and a two-roll mill (milling temperatures PP 170°C; ABS 180°C).

The compounds from the Haake mixer and two roll mill were compression moulded for 5 min to prepare 50 mm square test coupons of 1 mm thickness, unless otherwise stated. The moulding pressure was 5MPa; moulding temperatures were 230°C (PP) and 220°C (ABS).

Testing and Characterisation

Testing. Tensile properties were determined for samples cut from 1mm test sheets according to BS 903: Part A: 1971 using a Lloyd Tensile testing machine, type L200R fitted with a 500N load cell. The grip separation speed was 10mm min^{-1} at room temperature. The average of five results was reported. Flexural testing was carried out, according to ISO 178 with a test speed of 10mm min^{-1} using the same Lloyd tensile test machine. The Dapmat computer programme software calculated all flexural properties automatically. The average of five samples per formulation was reported.

Volume resistivity. The prepared test coupons were used to measure volume resistivity as described previously[8]. Resistivity was measured by a super-Megohmmeter type electrometer (Model RM 170) with a DC power supply source. When the applied voltage is small there is no current through the sample. As voltage increases there is a point (described as the break-through voltage of the sample) at which there is apparent current through the sample. One hundred volts, well above the breakthrough voltage of all samples in this study, was used for the measurement of volume resistivity. Reported values are the average values of the resistivity (ohm cm^{-1}) obtained from five measurements on each composite. For thinner samples, it was necessary to reduce the applied voltage to 10V; at higher voltages the current was too high to be measured with the equipment used[7].

Shielding efficiency. The electromagnetic shielding efficiency of the polymer composites was carried out at QinetiQ Ltd., Farnborough. The sample geometry is shown in Fig 1. Samples were prepared by machining from compression moulded sheet. A washer shaped sample is electrically connected between the inner and outer conductor of a specially designed coaxial fixture, which is placed between the signal source and the detector. The ratio of the power of the signal received with the sample present to the power received with no sample is the shielding effectiveness of the sample. The sample must make good electrical contact at both the inner and outer surfaces, or the measured shielding effectiveness will be lower than the sample is capable of providing. The microwave transmission losses of the filled plastic materials within the range of 0.1-20 GHz, were measured at room temperature. A major drawback of this test is that it would not identify any property anisostropy which is common in filled polymer composites.

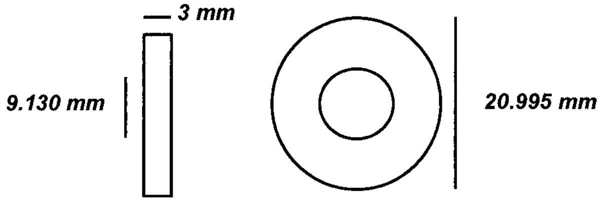

Fig. 1. Sample Dimensions for EMI test.

Results and discussion

Properties

Tensile and flexural data for the composites produced are shown in Tables 2 and 3. Both tensile strength and elongation decrease with increase in filler loading, but also as the % coating increases. No reinforcement is being provided by the mica as observed by Yang et al[9] who incorporated nickel-coated carbon fibre into ABS. The decrease in tensile strength as the amount of nickel coating increases suggests that the nickel is impeding polymer filler interaction. It has been demonstrated that in filled composites[10] stress concentration points are introduced through dewetting of the filler from the polymer and these will create discontinuities in the structure rendering it weak.

Flexural modulus increases with filler concentration due to the introduction of a highjer modulus filler as expected, but also slightly as the amount of nickel coating increases, presumably because of the high modulus of the nickel coating itself. The effect of the coated nickel has been investigated, and will be reported in a future publication.

Table 2. Mechanical properties of polypropylene composites.

Filler loading in composite (Wt.Frac.)	**% Ni coating on mica**	**Tensile Strength (MPa)**	**Elongation (%)**	**Flexural modulus (MPa)**
PP	-	30.8	45.5	679
0.1	30	27.3	22.5	869
0.2	30	22.8	13	1050
0.3	30	19.9	10.5	1188
0.4	30	15.5	4	1276
0.5	30	11.1	3.5	1401
0.6	30	9.4	3	1646
0.1	40	22.8	20.5	1161
0.2	40	19.6	11	1385
0.3	40	17.9	6	1629
0.4	40	15.3	3.5	1840
0.5	40	10.1	3	1969
0.6	40	8.9	2.5	2021
0.4	45	13.8	3	1888
0.5	45	9.5	2.5	1989
0.6	45	7.9	2.5	2086
0.4	50	10.2	2.5	1965
0.5	50	7.2	2	2123
0.6	50	5.9	1.5	2145

Volume resistivity

Table 4 and Fig 2 show volume resistivities for 1mm thick composite samples produced using a pressure of 5 tonnes. The volume resistivity of composites containing conductive filler depends on the proximity of neighbouring conductive particles. Table 4 shows that volume resistivity depends on both the amount of nickel on the mica, and the weight fraction of the coated filler. No significant change in resistivity was observed when the mica was coated with 30% nickel.

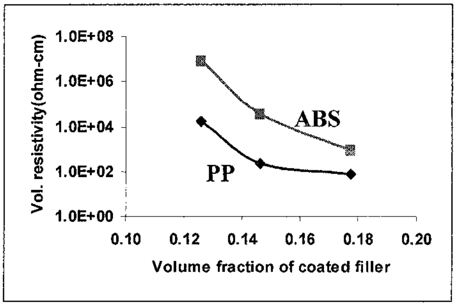

Fig 2. Comparison of resistivities of PP and ABS.

Table 3. Mechanical properties of ABS composites.

Filler loading in composite (Wt.Frac.)	% Ni coating on mica	Tensile Strength (MPa)	Flexural modulus (MPa)
0	-	51.6	1742
0.4	50	31.5	2458
0.5	50	16.2	5532
0.6	50	12.1	7481

Table 4. Volume resistivities of polypropylene containing nickel coated mica.

Filler loading in composite (Wt.Frac.)	% Ni coating on mica	Volume resistivity (ohm-cm)
PP	-	10^{16}
0.1	30	8.72 x 10^{11}
0.2	30	7.24 x 10^{11}
0.3	30	7.03 x 10^{11}
0.4	30	6.86 x 10^{11}
0.5	30	6.51 x 10^{11}
0.6	30	6.23 x 10^{11}
0.1	40	6.89 x 10^{11}
0.2	40	5.62 x 10^{11}
0.3	40	4.26 x 10^{11}
0.4	40	3.66 x 10^{9}
0.5	40	2.90 x 10^{9}
0.6	40	9.55 x 10^{8}
0.4	45	8.62 x 10^{8}
0.5	45	6.91 x 10^{8}
0.6	45	7.55 x 10^{6}
0.4	50	5.62 x 10^{4}
0.5	50	6.91 x 10^{2}
0.6	50	9.60 x 10^{1}

At higher Ni levels, resistivity started to decrease as filler loading increased. At very low filler loading, the resistivity of the composites is nearly equal to that of the base polymer as the conductive particles are surrounded by the insulating polymer. The resistivity starts to fall rapidly when the nickel-coated mica content reaches a particular value, known as the percolation threshold. After this transition, the rate of change of resistivity with filler concentration will reduce. At the percolation point continuous contacts are made between adjacent particles to form conductive network, which facilitate the electrical conduction through the composites. In order to obtain conductive composites, the filler itself must be conductive, so that an adequate amount of nickel should be present. Mica coated with ≥ 40% Ni had a volume resistivity of approximately 1 ohm-cm. Clearly a resistivity of this order is necessary for it to function as a conductive filler. The performance of nickel-coated mica flake with 50 wt% Ni was almost identical to that of commercial aluminium flakes. This is expected since the aspect ratio of the coated mica is quite similar to that of aluminium flakes, both being about 20 to 50[5,11].

Fig 2 compares data for PP and ABS at equivalent volume fractions of filler. In semi-crystalline polymers small fillers can be segregated into amorphous regions. In such polymers the critical concentration required to achieve network formation is less than in a purely amorphous polymer where uniform dispersion is achieved. The PP composites based on PP have lower resistivities, suggesting that in this case a conductive network is formed by the concentration of filler in amorphous regions, while in amorphous ABS the nickel coated mica will be distributed throughout the polymer matrix as explained by Reboul et al[12]. The effect of sample thickness was also investigated, and results are shown in Table 5. It is seen that resistivity decreases as samples are pressed to make thinner sheets, due to improved contact between the mica plates.

Table 5. Effect of sample thickness on volume resistivity of PP composites containing 0.6 weight fraction of 60% Ni coated mica.

Sample thickness (mm)	0.2	0.3	0.5	1.0
Volume resistivity (ohm-cm)	4.1×10^1	5.6×10^1	7.2×10^1	9.6×10^1

Volume resistivities of composites of PP and 40% nickel-coated mica fabricated by two different techniques are shown in Table 6. The samples fabricated using a two-roll mill showed better conductivity than samples produced with the Haake mixer. Figures 3 and 4 compare the appearance of the composite with 40% nickel-coated mica using different processing techniques. It is seen that the partcle size of nickel-coated mica was reduced when the composite was compounded in a Haake batch mixer due to the higher shear experienced, but more larger particles with higher aspect ratio are present after mixing on a two roll mill, explaining the better conductivity of this compound[7]. The average particle size of ashed polymer composite processed in the Haake batch mixer was 37.5 μm compared to 75.1 μm for the filler compounded in a two roll mill. Micrographs showed no evidence of adhesion between the mica flakes and the PP matrix.

Table 6. Effect of processing technique on volume resistivity of PP composites containing 40% Ni coated mica.

Weight fraction of filler	Volume resistivity (ohm-cm)	
	Haake	Two roll mill
0.4	4.01×10^9	3.21×10^9
0.5	3.96×10^9	3.11×10^9
0.6	9.97×10^8	1.71×10^8

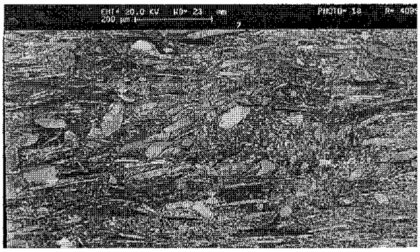

Fig. 3. PPcompounded with Ni coated mica in Haake.

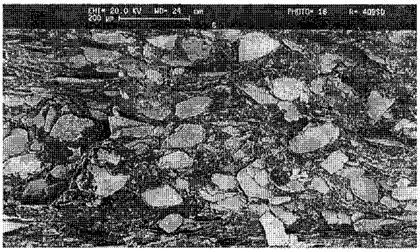

Fig. 4. PP compounded with Ni coated mica using two roll mill.

Shielding efficiency

Shielding efficiency data for samples with the lowest resistivities are shown in Figure 5. The test samples are assumed to be isotropic and homogeneous. The shielding effectiveness of 0.6 weight fraction of 40% nickel coated mica with PP was found to be 9.1dB for the frequency range of 750 – 2000MHz. The value was found to be consistent across this frequency range. 0.6 weight fraction of 45% nickel coated mica had shielding efficiency of 10.1dB. This result was consistent between 500 to 2000MHz. 0.6 weight fraction of 50% nickel coated mica showed the maximum value of shielding efficiency of 27.8 dB at 1000MHz, but, there was a variation observed as a factor of frequency. In line with the resistivity data, the equivalent ABS composite had a lower shielding efficiency of 16dB.

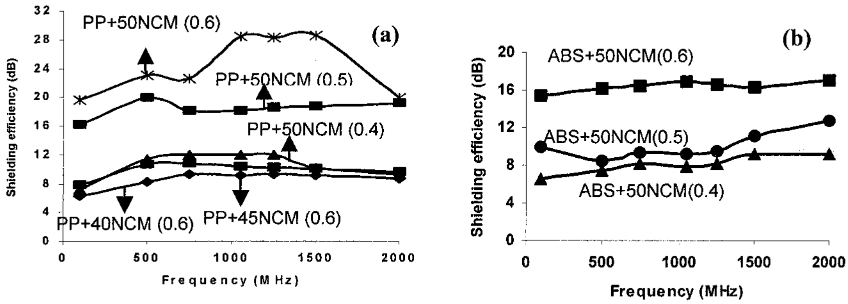

Fig. 5. Shielding effectiveness of composites (a) polypropylene; (b) ABS.

The effect of processing method is illustrated in Figure 6. The composite produced using the two-roll mill had a shielding efficiency of 9.1dB when compared to 7.5dB for the Haake mixed system prepared with different processing techniques The reduction in the particle size of nickel-coated mica clearly reduces the effectiveness.

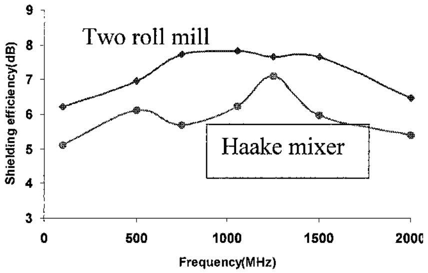

Fig. 6. Shielding effectiveness for composites processed using different techniques.

Conclusions

Tensile properties deteriorated when nickel coated mica was added to PP and ABS, while modulus increased as expected. Micrographs suggested that the interfacial adhesion between the polymer and nickel coated mica is poor, which will explain the poor properties. Conductivity increased with both filler concentration, and the amount of Ni on the mica. 40 – 50 wt % of coating is necessary to produce conductive compounds. Better conductivity and shielding efficiency was achieved in PP than in ABS, probably because the filler is confined to amorphous regions so that a conductive path is established more easily. Conductivity increased as sample thickness decreased because of improved contact between the conductive flakes. Compounds produced on a two roll mill had lower resistivity than those using a Haake rheometer; in the latter case the filler underwent attrition because of the higher shear forces during mixing. The highest shielding efficiency of obtained was 27.8dB for the PP based composite with 0.6 weight fraction of 50% nickel coated mica. The volume fraction of Ni in this composite was 0.06, so conductivity had been achieved at a low nickel concentration.

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