2 Conductive Materials

2.1 Conductive Materials to Protect Against Unwanted Electromagnetic and Electric Phenomena

The effects of electromagnetic interference (EMI) between electronic devices can be reduced or diminished by positioning a shielding material between the source of the electromagnetic field and the sensitive component. This protection can be achieved by making the housing of electronic components electrically conductive.

Electrical conductivity is a prerequisite for an EMI-shielding material. This is due to the physical phenomenon that electric fields and varying magnetic fields induce currents in the electrically conductive shielding material. In turn, these currents generate counteracting fields which weaken—or in the ideal case cancel—the originally applied fields (**Figure 2.1**). Ideally, external fields stay outside the shielding material, and internal fields stay inside.

Very much related to EMI shielding is the protection against electrostatic discharge (ESD) in electronic devices. ESD is the uncontrolled transfer of static charge between two objects with different electrical potential. Surface conductivity is important for ESD protection to allow a fast and controlled discharge of static charge.

Due to their high electrical conductivity (~10^6 S/cm), metals are particularly suitable as shielding material against electromagnetic fields. This can be a self-supporting full metal shielding, but also a sprayed, painted or electrolessly applied conductive coating (e.g., nickel) on a supporting material such as plastic. Another option is the incorporation of metal [stainless steel (SS)] powder or fibres as conductive filler in a plastic matrix.

However, there are a few drawbacks to using metal as a shielding material. The weight of the ‘heavy’ metal can be an issue in the case of full metal shielding and plastic matrices with high metal filler content, especially in applications in which mass should be as low as possible. Furthermore, metals are prone to corrosion. To produce metal coatings, at least two processing techniques must be applied—one for the support and one for the coating—which can be costly. It will also be difficult to apply these coatings onto complicated-shaped objects. In addition, the long-term adhesion of the coating to the support has to be reliable.

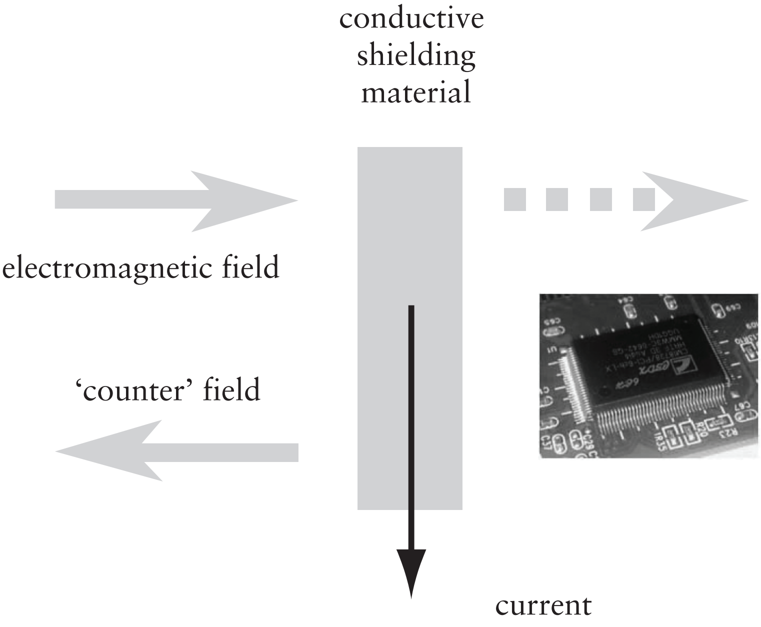

Figure 2.1 Electromagnetic shielding using conductive materials

2.2 Conductive Polymer Composites

A way to overcome the problems mentioned previously is by incorporating small-volume fractions of non-metallic, electrically conductive fillers in a non-conductive plastic matrix by means of compounding as a one-step process. Housings for electronic products (e.g., computers, communication devices) and business equipment (including devices for payment processing) are often made of engineering plastics. A particular problem for shielding is that plastics generally have excellent electrical insulation properties (as can be seen from their usefulness as insulation for electric wires). With a typical electrical conductivity of $<10^{-14}$ S/cm, these engineering plastics cannot shield electronic devices from electromagnetic radiation. For EMI shielding the conductivity should be $>10^{-2}$ S/cm.

Filling a matrix of engineering plastic with an electrically conductive material combines the availability of a housing made of shielding material with the advantages of traditional polymer processing techniques. These advantages include the use of existing compounding equipment—so no large new investments have to be made—and the ease of manufacturing small, complex shapes in a one-step process. Several fillers can be used. Traditionally, metal or carbon-black particles have been used as electrically conductive filler materials. A high level of these fillers can be detrimental for the processability, density and surface quality of the material, the costs and mechanical properties of the moulded product, and may cause wear to the processing equipment. Therefore, an interesting solution is to use novel filler materials such as intrinsically conductive polyaniline polymers and conductive carbon nanotubes (CNT) with a filler content that is as low as possible. In this way, conductivity and sufficient mechanical stability will be provided to the material while the original plastic processing properties will remain the same.

When the concentration of electrically conductive particles in a composite exceeds a certain level (the 'percolation limit'), the particles come into contact with each other and form a continuous path in the material for electrons to travel. In this way, the composite material has become electrically conductive. The conductivity of the filler material will be the upper limit for the electrical conductivity of the entire composite.

The percolation limit is dependent upon the shape of the conductive particles. For traditional roughly spherical-shaped fillers at a random distribution, ~10–20% has to be added before the composite will be electrically conductive. The higher the aspect ratio (length-to-width ratio) of the particles, the lower is the concentration for percolation needed to take place. CNT with a diameter of a few nanometres and a length of micrometres (i.e., a high aspect ratio) can form a conductive network at much lower volume fractions—and potentially lower costs—than cheaper, traditional fillers such as carbon fibre and carbon black (**Figure 2.2**).

The incorporation of small volume fractions of novel, non-metallic electrically conducting fillers in a non-conducting plastic matrix by means of compounding as a one-step process forms the basis of conductive polymer composites. The filler materials used here are intrinsically conductive polyaniline polymers and conductive CNT. Conjugated polymers form the basis for intrinsically electrically conductive plastics (e.g., polyaniline). These are polymers with alternating single and double carbon-carbon bonds in their chains. The electrical conductivity will be realised by doping these polymers. CNT, especially, multi-wall carbon nanotubes (MWCNT), which can best be described as multiple layers of graphene rolled in on themselves, are known to conduct electricity.

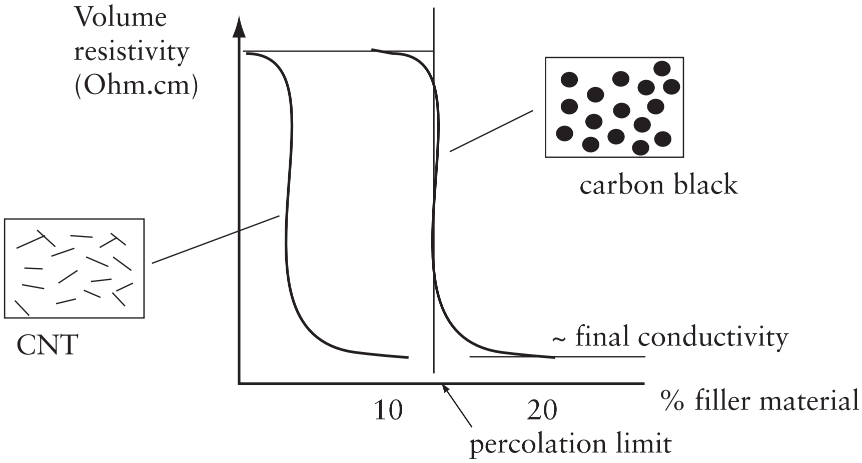

Figure 2.2 A comparable conductivity of CNT with less filler materials compared with carbon black. Note: resistivity is the reciprocal of conductivity.

2.3 Carbon Nanotubes as Conductive Filler Material

2.3.1 Compatibility of Carbon Nanotubes with Polymers

Resistivity data have been obtained for compounds consisting of engineering plastics filled with MWCNT made using a twin-screw extruder. Nanocyl NC7000 is commercial-grade MWCNT; NC9000 is development-grade, polyethylene-coated MWCNT. For NC7000 and NC9000, the lowest volume resistivities—and therefore the best compatibilities—are obtained with resins of intermediate solubility parameter, i.e., polycarbonate (PC), polystyrene-*co*-acrylonitrile (SAN) and polybutylene-terephthalate (PBT). These polymers form percolation networks at a 2.5 wt% MWCNT concentration.

Polyesters and acrylic have the best compatibility with CNT. They therefore give the finest mixes and consequently the most complete percolation networks at lower filler loadings. This is the result of the polarisability of the conjugated –C-C=C-C=C-network in the nanotubes. Polarisation of the carbon surface in the presence of acrylic and polyesters results in relatively good compatibility with these matrices and hence the CNT can be taken up into the matrices. Non-polar polypropylene (PP) with a low solubility parameter and polyamide 6 (PA6) with a high solubility parameter give compounds with the poorest electrical performance. **Figure 2.3** shows volume resistivity data of several engineering plastics with their corresponding solubility parameters filled with 2.5 wt% CNT.

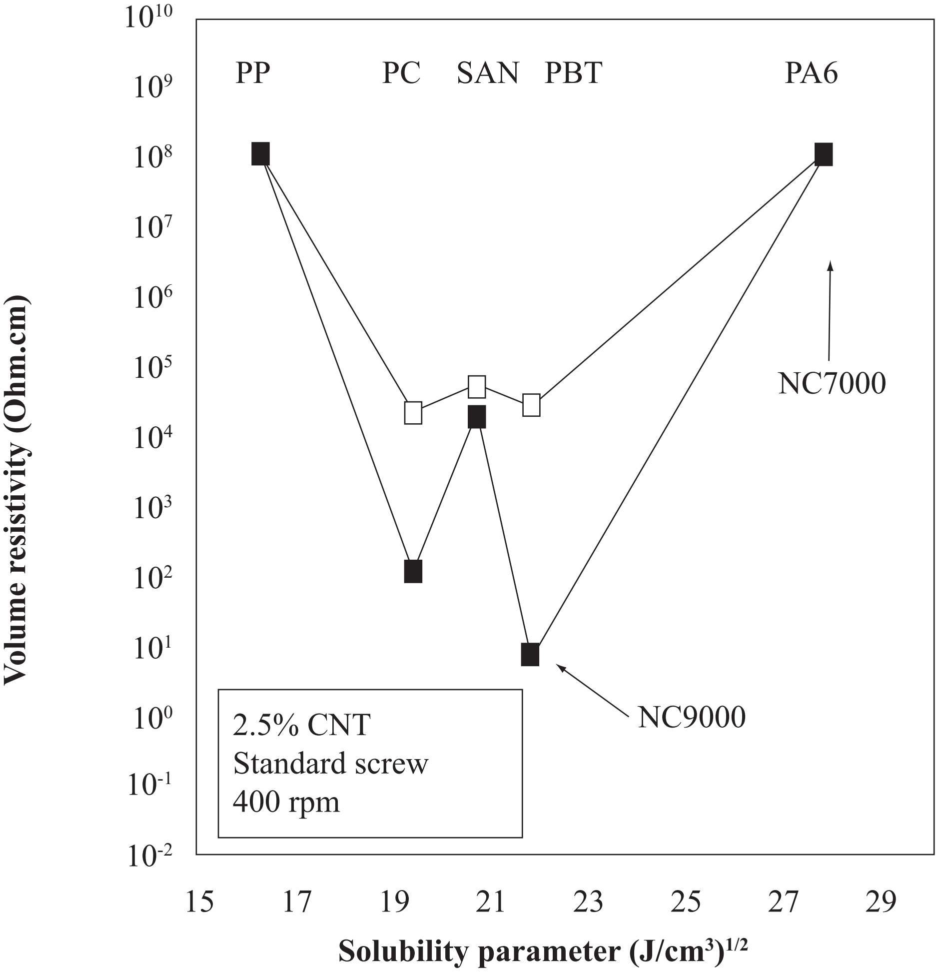

Figure 2.3 Volume resistivity *versus* solubility parameter of several engineering plastics filled with 2.5 wt% NC7000 and NC9000

The production method used to make CNT affects the mixing with the polymer matrix resins. This is most probably caused by the cleaning and purification methods. These methods influence the surface characteristics of the carbon.

Attempts to manufacture moulded parts of polyurethane filled with CNT with good electrical properties have not been successful. The high viscosity of the material sets a limit to the amount of CNT that can be added, which limits the conductivity. At a content of 1.96% CNT, the conductivity obtained is only 1.7×10^{-3} S/cm.

2.3.2 Conductivity and Shielding Properties

Optimum compounding formulations have been used in pilot plant-scale moulding trials in which surface resistance and shielding performance have been assessed on the industrial products. For hybrid materials with CNT and SS fibres as filler materials, reflection values ≤93% (equating to 63 dB attenuation at 100 MHz) in injection-moulded PC/acrylonitrile-butadiene-styrene (ABS) can be obtained. These shielding levels compare favourably with steel-filled mouldings in which typical reflections of 83% (corresponding to 42 db attenuation at 100 MHz) are obtained. Similar results were also found in PC with a combination of CNT and SS fibres as conductive filler material, where ≤94% reflection has been measured. There is evidence of synergism between CNT and steel fibre. Moreover, it was found that the hybrid materials showed more even conductivities throughout the bulk and surfaces of the mouldings. This is important for applications in which shielding and surface protection from ESD is required. If only steel fibres are used as conductive filler material, the mouldings tend to have very large differences in resistance from point to point over the surface. This can lead to local charging of the surface and makes quality control of the moulded products uncertain because of local variation in measured resistance.

Following the achievement in producing industrial products for EMI shielding and ESD protection applications from pilot plant-scale compounding and moulding trials, a range of MWCNT filled and combined (CNT and steel fibre) thermoplastics have been developed and produced in production-scale quantities. Conductive polymer composite materials can be compounded and injection-moulded into industrial products using existing equipments. These products give the level of electrical properties matched with the requirements of the final applications and can substitute a multi-stage manufacturing process. **Table 2.1** shows an overview of typical resistivity and shielding properties of conductive polymer composite materials. Here, volume resistivity (in ohm.m or ohm.cm) is the resistance of a volume of material (e.g., a wire) to electric current corrected for the cross-sectional area of the material and the length of the material. Volume conductivity (in Siemens/m or Siemens/cm, where the unit Siemens is the reciprocal of the unit ohm) is the inverse of resistivity.

Table 2.1 Typical resistivity and shielding properties of conductive polymer composite materials

Material	Volume resistivity (Ω.cm) [a]	Surface resistivity (kΩ/sq) [b]	Reflection (%) [c]	Shielding efficiency at 100 MHz (dB) [d)]
9104 PP + CNT/hybrid	7 x 10^{-3}	100	76	37
9303 PC/ABS + CNT	700	10-1000	69	34
9603 PC/PBT + CNT	320	900	69	34
9604 PC/PBT + CNT + SS	6	10-50	86	47
9703 PC + CNT	90	20-200	61	31
9704 PC + CNT + SS	0.8	10-50	89	53
9705 PC + CNT flame retarding	1000	20-2000	62	31

Test methods:
[a] BS 2044: 1984 method 3 at 23 ± 2 °C – this standard has now been superseded by BS 7506-2 [1];
[b] Megohmmeter at 23 ± 2 °C;
and [c] Bekaert Reflectometer

2.3.3 Mechanical Properties

Using standard measuring procedures, the mechanical properties of conductive polymer composite materials have been determined, of which typical values are shown in **Table 2.2**.

Compounds containing CNT in PC and PC/ABS have been prepared, to which SS fibre masterbatch was added. PC/ABS did not lead to any problems with the injection-moulding process. No changes of parameters compared with the unfilled reference polymer were necessary to produce a good product. However, the PC composites had to be modified by using a higher M_w PC resin, dried PC and dried CNT. In this way it was possible to obtain non-brittle conductive polymer composites.

Table 2.2 Typical mechanical properties of conductive polymer composite materials

Material	Tensile stress at break (MPa) [a]	Tensile strain at break (%) [a]	Tensile modulus (MPa) [b]	Flexural modulus (MPa) [c]	Impact strength (kJ/m^2) [d]
9103 PP + CNT	20.6	80	1010	942	42
9104 PP + CNT/hybrid	15.9	20.3	990	1020	9.3
9303 PC/ ABS + CNT	41	18.9	2633	2075	21.1
9603 PC/ PBT + CNT	47.9	13	2520	2339	36.7
9604 PC/ PBT + CNT + SS	60.3	4.3	2450	2840	10.1
9703 PC + CNT	61.9	8.0	2570	2703	7.1
9704 PC + CNT + SS	64.9	7.1	2700	3020	8.8
9705 PC + CNT flame retarding	65.0	12	2700	3100	11.0

Test methods
[a] ISO 527-2:1997 [2], 50 mm/min;
[b] ISO 527-2:1997, 1 mm/min;
[c]ISO 178:2003, 2 mm/min;
and [d] ISO 179-1:2010 [3] Izod/Charpy impact strength, notched at 23 ± 2 °C

According to the above (see also **Chapter 4**), conductive polymer composite materials can be compounded and injection-moulded into industrial products using existing equipment. As can be seen above, these products give the level of electrical properties matched with the requirements of the final applications and can substitute a multi-stage manufacturing process. They give a significantly better balance of mechanical and electrical properties than the current generation of commercially available ESD protection and EMI-shielding compounds.

2.4 Polyaniline as Conductive Filler Material

The approach here is to process the inherently conductive polyaniline and the non-conductive polymer matrix simultaneously. A challenge is that the very conductive emeraldine salt form of polyaniline—resulting from an emeraldine base doped with an acid—can be dispersed only in the matrix as conductive hard particles with relatively low aspect ratios. To make the final product electrically conductive would require a high concentration of polyaniline particles, which is not desirable due to the difficult processing route and high cost of materials.

To overcome these problems, it is anticipated that polyaniline will form better conductive mixtures at lower filler fractions if a continuous network together with the matrix polymer can be established. The chemical modification of polyaniline and the use of additives have been investigated to improve the processability of the conductive polymer with a lower filler content and to result in higher conductivity.

A reactive extrusion process is used to dope the non-conductive emeraldine base with organic (acidic) compounds to disperse it to a very small (possibly nano)-scale. This results in a polyaniline complex that is subsequently compounded with non-conductive polymer matrix materials such as PP by means of a twin-screw extruder. Process parameters such as temperature were optimised. However, due to the limitation of the processing temperature for the polyaniline complex, the use of this inherently conducting polymer in a matrix of engineering plastics cannot be achieved. As such, composites with polyaniline as filler material are not yet commercially available. Polyaniline may well be suitable for use in coatings.

2.5 Combinations of Carbon Nanotubes and Polyaniline as Conductive Filler Materials

Further improvement in electrical performance can be found in the hybrid system of a PP matrix with a combined filler consisting of CNT and the polyaniline complex. The idea is that the carbon provides long, continuous electrical conducting pathways, and the small contact surfaces between the nanotubes would be increased by using the conducting polymer as ‘glue’ at the contact points between the nanotubes. This would provide good conductivity at low filler fractions. The polyaniline complex reduces the volume resistivity and surface resistivity of the hybrid, but shows no effect on the shielding effectiveness compared with a PP/CNT compound. This hybrid material gives 75% reflection (~ 37 dB shielding effectiveness at 100 Hz).

Hybrid polyaniline-based complex materials have been synthesised and assessed as melt-processable additives in PP at the laboratory scale. Characterisation work has led to understanding of the process of hybrid formation and the interaction between polyaniline and various types of carbon filler. The *in-situ* synthesis of polyaniline in the presence of NC7000 CNT yielded hybrid materials with resistances as low as 5 Ω; this material was found to give the lowest electrical resistance to PP blends. Blends of PP with this type of hybrid were prepared and the structure-property relationship and the effect of heat treatment on the electrical property of the compounds extensively investigated. The results showed a dramatic decrease (over four decades) of surface resistance during heat treatment. The change in crystalline structure of PP in the presence of CNT or *in-situ* CNT-polyaniline hybrid was found to cause a decrease in surface resistance during heat treatment.

2.6 Conclusions

Conductive polymer composites give a significantly better balance of mechanical and electrical properties than some of the current generation of commercially available ESD protection and EMI-shielding compounds. The best EMI-shielding compounds developed in such a PC hybrid material give 94% reflection (~63 dB shielding effectiveness at 100 MHz). The great advantage of this material over the commercial one that gives an identical level of shielding is that it has much lower filler content. This leads to improvement of the mechanical properties of the final products.

References

1. BS 7506-2, Methods for Measurement in Electrostatics—Test Methods, 1997.
2. ISO 527-2, Plastics—Determination of Tensile Properties—Test Conditions for Moulding and Extrusion Plastics, 1997.
3. ISO 179-1, Plastics—Determination of Charpy Impact Properties—Part 1: Non-Instrumented Impact Test, 2010.