PolyCond: electromagnetic shielding with conducting polymers

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From February 2005 to January 2009, about 20 European companies and organisations participated in the European Sixth Framework Programme research project 'PolyCond'. The aim of this project was to develop high-value, environmentally friendly and low-cost conducting composites for protection against the effects of electromagnetic interference and electrostatic discharge. The project partners looked at plastics containing intrinsically conducting polymers such as polyaniline, and at conducting carbon nanotubes as filler in a non-conducting polymer matrix, as well as hybrid systems with combinations of both fillers.

Picture this: your mobile phone is lying on your desk, close to the speaker of your computer system. A few seconds before you receive a call or SMS message on your mobile phone, the speaker makes a buzzing noise. Is this clairvoyance of the speaker? No way. Here, the wire to the speaker acts like an antenna that picks up and amplifies the signal it receives from the mobile phone network. This is a typical example of electromagnetic interference between electronic components, and it shows that electromagnetic fields are all around us.

Electromagnetic interference

Unwanted electromagnetic interference effects occur when sensitive devices receive electromagnetic radiation that is being emitted – whether intended or not – by other electric or electronic devices such as microwaves, wireless computers, radios and mobile phones. As a result, the affected receiving devices may malfunction or fail, of which the malfunction of pacemakers when in the vicinity of certain electronic devices is a striking, yet detrimental, example.

The effects of electromagnetic interference are becoming more and more pronounced, caused by the demand for high-speed electronic devices operating at higher frequencies, the more intensive use of electronics in e.g. computers, communication equipment and cars, and the miniaturisation of these electronics. For example, mobile phones and smartphones are typically operating at 800-1900 MHz, and around 2 GHz for data transmission through Universal Mobile Telecommunications Systems (UMTS). Compact, densely packed electronic components produce more electronic noise.

These trends indicate the need to protect components against electromagnetic interference (EMI) in order to decrease the chances of these components adversely affecting each other or the outer world. The effects of electromagnetic interference can be reduced or diminished by positioning a shielding material between the source of the electromagnetic field and the sensitive component. This protection may be achieved by making the housing of electronic components electronically conducting. 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 conducting shielding material. In turn, these currents generate counteracting fields which weaken - or in the ideal case cancel - the originally applied fields. Ideally, external fields stay outside the shielding material, and internal fields stay inside. As EMI shielding is composed of reflection and absorption contributions, both the conductivity in the volume of the protecting material as well as the thickness of the material may be of importance. In a practical way, the extent of shielding is also subject to the size and shape of openings in the shield. For example, at a frequency of 1 GHz the opening must be less than 12 mm for effective EMI shielding.
Shielding is not only applicable to housings that separate electronic devices from the outside world. Also data cables can be shielded from their surroundings, for example, by a wire mesh encircling an inner core conductor as in an coaxial cable for transmission of radio and television frequency signals.

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. For ESD protection surface conductivity is important, to allow a fast and controlled discharge of static charge.

Materials for electromagnetic shielding

Due to their high electrical conductivity (order of magnitude 10^6 Siemens/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 conducting coating (e.g. nickel) on a supporting material such as plastic. Another option is the incorporation of metal (stainless steel) powder or fibres as conducting 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 where mass should be as low as possible. Furthermore, metals are prone to corrosion. In order to produce metal coatings, at least two processing techniques have to 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.

PolyCond - the basics

A way to overcome the problems mentioned above is by incorporating small volume fractions of non-metal, electrically conducting fillers in a non-conducting plastic matrix by means of compounding (injection moulding or extrusion) as a one-step process. This idea forms the basis of the PolyCond project.

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 electrically insulating properties, as can be seen from their usefulness as insulation for electric wires. With a typical electrical conductivity of less than 10^{-14} Siemens/cm these engineering plastics can not shield electronic devices from electromagnetic radiation. For EMI shielding the conductivity should be higher than 10^{-2} Siemens/cm.

Filling a matrix of engineering plastic with an electrically conducting material combines the availability of a housing made of shielding material with the advantages of traditional compounding of this composite. 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 are possible. Traditionally, metal or carbon black particles have been used as electrically conducting 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. Furthermore, materials which contain carbon black are limited in their colour. Therefore, we aim at developing novel filler materials such as intrinsically conducting polyaniline polymers and conducting carbon nanotubes, with a filler content that is as low as possible. In this way, conductivity will be provided to the material while the original plastic processing properties will remain the same. Table 1 shows a non-limiting range of matrix polymers that has been covered in the PolyCond project.

Conducting polymer composites

When the concentration of electrically conducting particles in a composite exceeds a certain level, the so-called 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 conducting. The conductivity of the filler material will be the upper limit for the electrical conductivity of the entire composite.

The percolation limit depends on the shape of the conducting particles. For traditional spherical shaped fillers at a random distribution, approx. 10 to 20% has to be added before the composite will be electrically conducting. The higher the aspect ratio (length-to-width ratio) of the particles, the lower the concentration for percolation to take place. Carbon nanotubes with a diameter of a few nanometers and a length of micrometers (i.e. a high aspect ratio) can form a conducting network at much lower volume fractions - and potentially lower costs - than cheaper, traditional fillers as carbon fibre and carbon black.

Carbon nanotubes, especially those of a multi-wall composition, which can best be described as multiple layers of graphite rolled in on themselves, are known to conduct electricity. For intrinsically electrically conducting

[Table 1]: Examples of matrix polymers covered in the PolyCond research project

Matrix polymers	Benefits/properties
Polypropylene (PP)	Good toughness possible with polyaniline
Polyamide 12 (PA 12)	Wire coating, high chemical resistance
Polyamide 6/66 (PA 6/66)	Tough, easy to mould, high temperature resistance
Polycarbonate (PC)	Much better properties than obtainable with carbon black
Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS)	Very good toughness and good mouldability
Polycarbonate/Polybutylene terephthalate (PC/PBT)	Very good toughness for housings
Glass filled Polyphenylene sulfide (PPS)	Very high stiffness and very high temperature resistance
Thermoset Polyurethane (PU)	(Very) large mouldings

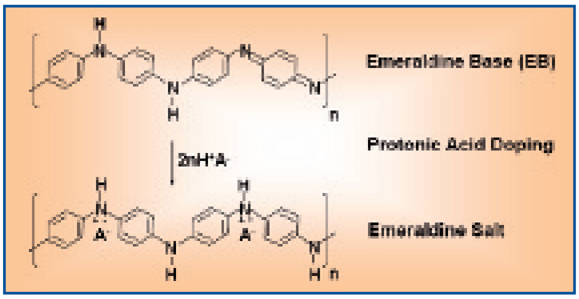
plastics, conjugated polymers form the basis. These are polymers with alternating single and double carbon-carbon bonds in their chains. The electrical conductivity will be realised by doping these polymers. Examples of intrinsically conducting polymers are polyacetylene, polyaniline and polypyrrole.

The aims of the PolyCond project were ambitious: develop large-scale, commercially applicable production processes that allow new products that contain these conducting plastics to perform better than products that are currently available. Better in terms of conductivity, weight reduction, cost reduction and production time, with improved balances of physical and electrical properties. Here we describe the ways in which we tried to reach those aims.

Chemical modification of polyaniline

One approach was to process the inherently conducting polyaniline and the non-conducting polymer matrix at the same time. The problem here is that the well-conducting emeraldine salt form of polyaniline – resulting from an emeraldine base doped with an acid, see Figure 1 – is not meltable (via injection moulding or extrusion), and hence can be dispersed only in the matrix as conducting hard particles with relatively low aspect ratios. To make the final product electrically conducting, this would require a high concentration of polyaniline particles, which was not desirable due to the difficult processing route and high material costs. To overcome these problems, it was anticipated that polyaniline would form better conducting mixtures at lower filler fractions if a continuous network together with the matrix polymer could be established. Within PolyCond, the chemical modification of polyaniline and the use of additives has been investigated, to improve the processability of the conducting polymer with a lower filler content and to result in a higher level of conductivity.

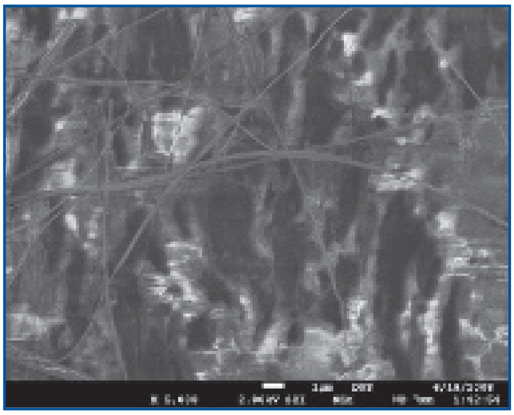
In practice, a reactive extrusion process was used to dope the non-conducting emeraldine base with organic (acidic) compounds in order to disperse it to a very small scale, possibly nano-scale. This resulted in a polyaniline complex that was subsequently compounded with non-conducting polymer matrix materials such as polypropylene by means of a twin-screw extruder. In the best case, polypropylene compounds could be manufactured with a volume conductivity of close to 10^{-2} Siemens/cm.



[Figure 1]: Polyaniline doping process

Compounding and moulding with carbon nanotubes as conducting filler

Lab-scale trials have been conducted using carbon nanotubes from various suppliers in combination with polymer matrices with a wide range of polarity, from polyolefins to polyamides. The non-polar matrices were found to give compounds with the lowest levels of conductivity. It was inferred that matrices of low polarity had the poorest compatibility with carbon nanotubes.



[Figure 2]: Carbon nanotube (CNT) network

The production method used to make the carbon nanotubes also affected the mixing with the polymer matrix resins, probably because the cleaning and purification methods, where used, after synthesis of the carbon nanotubes influence the surface characteristics of the carbon. The optimum compounding formulations have been used in pilot plant-scale moulding trials where surface resistance and shielding performance have been assessed on industrial products. A balance of mechanical properties and electrical properties was achieved. Following the achievement in producing the industrial products for EMI shielding and ESD protection applications from pilot plant-scale compounding and moulding trials, a range of multi-wall carbon nanotube (CNT) filled and CNT/steel fibre hybrid thermoplastics have been developed and produced in production scale quantities.

As a result of the intensive investigation in compounding trials and moulding trials, a 'Best practice guide for PolyCond materials' has been set up as summarised in the appending box 'Design, moulding and processing issues'. PolyCond materials can be compounded and injection moulded into industrial products using existing equipment. 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.

[Box1] Design, moulding and processing issues

With respect to the PolyCond range of conducting polymers, the following general remarks on design, moulding and processing should be taken into account. These 'best practice points' are based on our general experiences during the PolyCond research project.

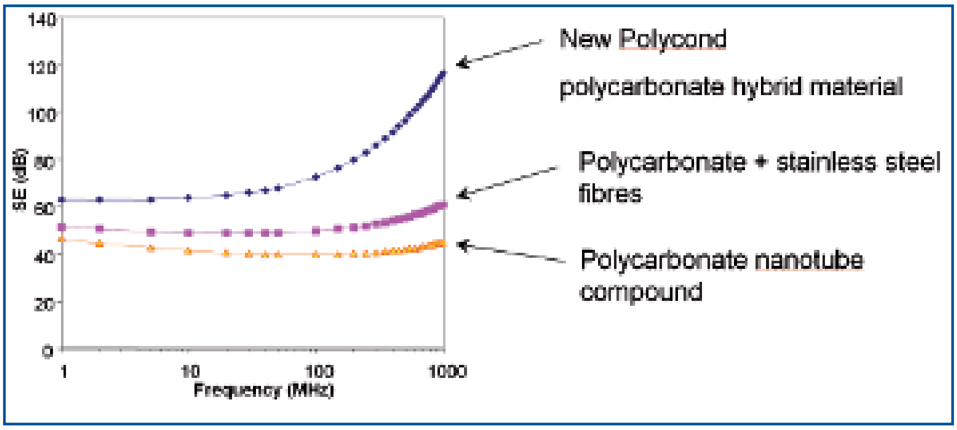
- It is possible to mould PolyCond material to the normal range of thicknesses used in the thermoplastic moulding industry.
- In order to maximise the conductive properties, it is important to keep shear stress to a minimum, hence any sharp corners should be given a generous radii to ease the flow path. For the same reason, it is preferable to use low injection velocities.
- Mould temperature and holding pressure do not appear to affect final conductive properties of the moulded part.
- A 'skin layer' effect has been observed which can result in higher conductivity within the core and lower at the surface. This effect is influenced by melt temperature and injection velocities, and has only a small effect on shielding characteristics.

Chaotic mixing

'Chaotic mixing' is a novel mixing method that has been investigated. Here, polymers or particles in a polymer can be mixed very efficiently without the presence of large shear forces. This method especially favours nanotubes with long aspect ratios, as they will be disentangled from nanotube aggregates without breaking these aggregates apart. In addition, it was anticipated that it would be possible in this way to form a network out of mixtures of conducting and non-conducting polymers. In a chaotic mixing device, the clearance between the two independently driven rotors (with different rotor speeds possible) is larger than usually found in compounding extruders.

Hybrid materials

Within PolyCond, the advantages of using both polyaniline and carbon nanotubes as conducting fillers were also investigated. The idea here was 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. Hybrid materials of polyaniline complex and carbon nanotubes, having surface resistances lower than 50 ohms, were obtained by in-situ synthesis of the complex. Chemical and physical methods were used to modify the carbon nanotubes prior to compounding with resin systems such as polyurethane thermosetting resin, polyester thermoplastic and acrylic coating resins.



[Figure 3]: EMI shielding results of several filled polycarbonate materials

Figure 3 shows EMI shielding results of PolyCond polycarbonate hybrid material compared to polycarbonate filled with stainless steel fibres and polycarbonate filled with carbon nanotubes. PolyCond polycarbonate hybrid material shows a very high shielding effectiveness of 93% reflection, corresponding with 63 dB shielding. Data of other PolyCond materials are given in Table 2.

[Table 2]: Physical properties of PolyCond materials

Matrix	Conducting material	Code	Volume resistivity (ohm.cm)	Surface resistance (kohm/sq)	Shielding effectiveness
PP	CNT hybrid	9104	7 x 10^{-3}	100	76% reflection 37 dB SE @ 100 MHz 40 dB SE @ 1 GHz
PC/ABS		9303	700	10-1000	69% reflection 34 dB SE @ 100 MHz 34 dB SE @ 1 GHz
PC/PBT	CNT	9603	320	900	61% reflection 31 dB SE @ 100 MHz 29 dB SE @ 1 GHz
PC/PBT	CNT hybrid	9604	6	10-50	86% reflection 47 dB SE @ 100 MHz 57 dB SE @ 1 GHz
PC	CNT	9703	90	20-200	61% reflection 31 dB SE @ 100 MHz 29 dB SE @ 1 GHz
PC	CNT hybrid	9704	8 x 10^{-1}	10-50	89% reflection 53 dB SE @ 100 MHz 64 dB SE @ 1 GHz
PC	CNT	9705	1000	20-2000	62% reflection 31 dB SE @ 100 MHz 29 dB SE @ 1 GHz

Additional information to Table 2:
Volume resistivity (in units ohm.m or ohm.cm) is the resistance of a volume of material (for example a wire) to electric current, corrected for the cross sectional area of the material and the length of the material.
Volume conductivity (in units Siemens/m or Siemens/cm, where the unit Siemens is the reciprocal of the unit ohm) is the inverse of resistivity.
CNT = carbon nanotube
Data are based upon our general experiences during the PolyCond research project. More physical properties of the PolyCond materials can be found in the material data sheets published on the PolyCond website, www.polycond.eu.

Summary of technical results

Within the PolyCond research project, a range of conducting plastics have been developed. A number of case studies are shown in the appending box ‘Case studies’ to illustrate the range and flexibility of the properties and potential savings in a variety of applications. Some highlights of the materials developed are:

- Plastics with an improved balance of electrical and mechanical properties have been produced.
- High levels, over 60 dB, of (EMI) shielding have been reached.
- Surface resistance values of less than 10 kohms have been reached.
- With new polyaniline complexes, the electrical conductivity was tuneable in the ESD range.
- Polypropylene compounds had up to 2 decades reduction in volume resistivity.
- Improved performance has been reached with polyaniline/carbon nanotube and stainless steel/carbon nanotube hybrid mouldings.
- Many PolyCond materials can now be produced on a large scale.

[Box2] Case studies

To illustrate the range and flexibility of the properties and potential economic benefits of the PolyCond materials, a few case studies have been developed. A comprehensive description of these case studies can be found on the PolyCond website, www.polycond.eu. These applications are not limiting, due to the versatility of the PolyCond materials. Other applications include the replacement of casings and covers from polyurethane (mainly in electronic applications).

	Application: **Automotive part with EMI shielding properties** Original housing: Metal (high shielding level, expensive in production, heavy, design limitations) Our solution: Polypropylene with polyaniline and carbon nanotubes, with the required EMI shielding protection Improvements: Design flexibility, weight reduction, 25% cheaper, recyclable
	Application: **Blood pressure monitoring device** Original housing: Stainless steel fibre filled PC/ABS (difficult to manufacture, final product failed due to poor physical properties) Our solution: PC/ABS filled with carbon nanotubes, with at least 30 dB shielding Improvements: Toughness, recyclable, ease of manufacture, better surface quality
	Application: **Military radio with high level EMI shielding** Original housing: Metal (high shielding level, expensive in production, heavy, design limitations) Our solution: PC/PBT with carbon nanotubes and stainless steel fibres, with 60 dB shielding Improvements: Toughness, easily moulded, 60% weight reduction, 40% cheaper
	Application: **Grounding plug earth pin** Original: Brass grounding pin (expensive, specialist product) Our solution: Polycarbonate with carbon nanotubes Improvements: Ease of manufacture, 80% weight reduction, plug is 40% cheaper, recyclable

[Box3] Project information

PolyCond was a European Sixth Framework Programme research project in which SMEs, research organisations and trade associations from the Netherlands, Belgium, United Kingdom, Finland, Hungary and Spain participated, with financial support from the European Commission. Aimplas (Spain) was project co-ordinator.

SMEs

Colorex (Netherlands) http://www.colorex.nl;
Faperin (Spain) http://www.faperin.com;
Intermedic (Spain) http://www.inter-medic.net/eng/home.html;
Molespol (Spain) http://www.molespol.abgp.net;
Panipol (Finland) http://www.panipol.com;
Promolding (Netherlands) http://www.promolding.nl;
Rondol Technology (UK) http://www.rondol.com;
TBA - Electro Conductive Products (UK) http://www.tbaecp.co.uk;
Whitaker Technical Plastics (UK) http://www.whitakertechnicalplastics.co.uk

Research Organisations

Aimplas (Spain) http://www.aimplas.es;
Chemical Research Centre - Hungarian Acad. of Science (Hungary) http://www.chemres.hu;
HUT (Finland) http://www.tkk.fi/English;
Smithers Rapra (UK) http://www.rapra.net;
TNO (Netherlands) http://www.tno.nl;
VTT (Finland) http://www.vtt.fi

Trade Associations

BPF (UK) http://www.bpf.co.uk;
Bond voor Materialenkennis (Netherlands) http://www.materialenkennis.nl;
EuPC (Belgium) http://www.plasticsconverters.eu;
Mavesz (Hungary) http://www.mavesz.hu

More information, including data sheets of the PolyCond materials and extended case studies, can be found on the PolyCond website www.polycond.eu.
For further information, please contact each of the project partners via the internet addresses given here, or the project leader via gfoster@rapra.net, or the author of this publication via info@materialenkennis.nl.