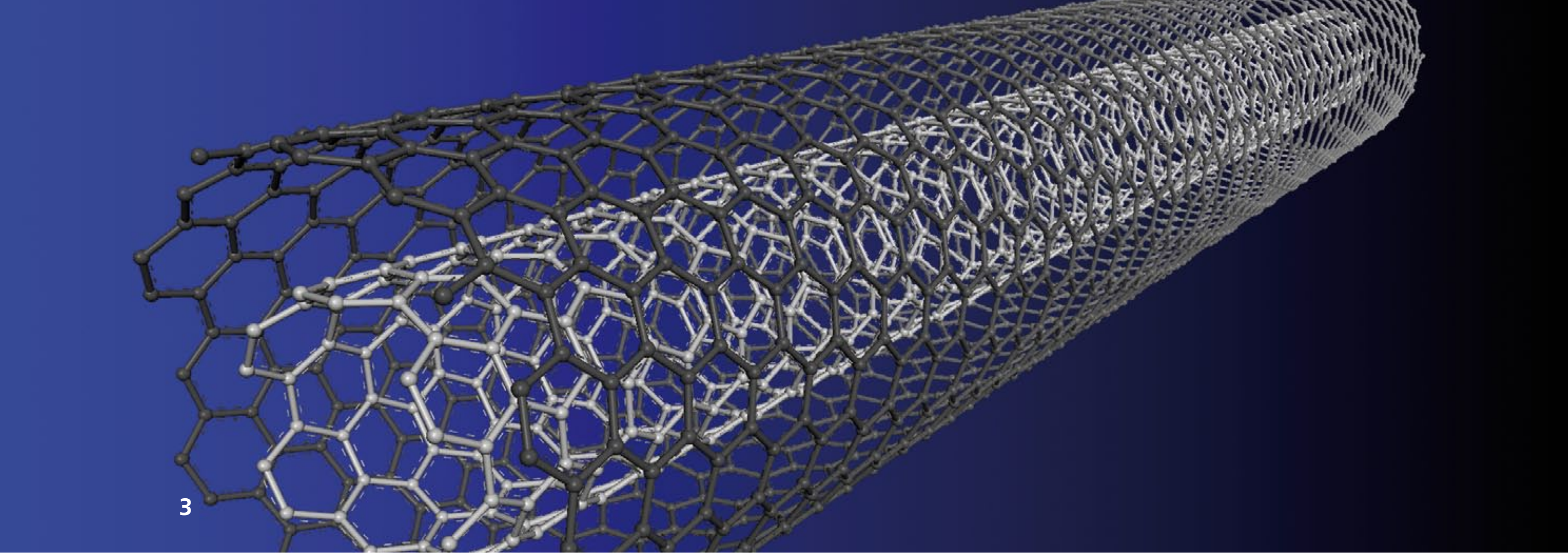
PLASMA TREATMENT OF MICROPARTICLES AND NANOPARTICLES AT ATMOSPHERIC PRESSURE PERMITS NEW MATERIALS AND APPLICATIONS

The name of the group says it all: The section Plasma Technology and Surfaces (PLATO) at the Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM has had many years of success in modifying surfaces by applying plasma treatment methods. Even laymen will under-stand that effective pre-treatment of surfaces is a key issue for using and optimizing materials. Of particular importance here is plasma-polymerization which can be used to generate either insulating, adhesion-promoting, or corrosion-protecting layers. Less well known is that PLATO develops these processes not only for large surfaces but also for microscopic applications: The pre-treatment of particles and their modification with adherent, dense, but also very thin layers in the order of a few nanometers has already been investigated during the last years. This approach is playing an ever more important role for novel materials, for example, in the area of electromobility.

Apart from the coating of particles, this also concerns the cleaning and pre-treatment of particles. A plasma, namely a reactive gas containing electrons, ions, and reactive molecule fragments, is able, for example, to clean surfaces: Organic contaminants can be removed. A plasma can also be used to functionalize surfaces: For example, water-repellant (hydrophobic) surfaces can be made hydrophilic, or particles which are difficult to disperse in liquids can be converted to particles that are much easier to process. The latter is achieved by using the plasma treatment to reduce the agglomeration of particles.

In plasma-polymerization, liquid or gaseous starting materials are converted into coatings that are less than a thousandth of a millimeter thick. These layers exhibit an excellent adhesion, even on very small particles, and provide them with, for example, good electrical insulation, thermal conductivity, anti-aging properties, or many other characteristics. Especially the development of atmospheric pressure plasma treatment technologies for particles has been actively improved by PLATO during the last years.


3

First experiences on functionalization of carbon black particles

The first experiences on the modification of particle surfaces were achieved with carbon black particles. Such particles can be produced in ovens and are a mass industrial product. The specialists at the Fraunhofer IFAM have worked with carbon black particles for a long time. This compound can be used as a filler in paints as well as for improving the mechanical and electrical properties of materials. For example, conducting paints or adhesives can be produced via the introduction of the carbon black, which alters the resistance of the polymer. Such a development can be used for lightning protection or for anti-static coatings of aircrafts (Fig. 5). For example, tailfins of aircrafts are coated with an anti-static paint so that electrical charge can be better dissipated.

Carbon black additives can, however, have undesired effects if too much is added or if there is inadequate dispersion, because they can adversely affect the stability of the coating. The PLATO section has therefore developed a method for the effective pre-treatment of carbon black particles, leading to a material that can be more effectively processed and distributed in coatings. This gives a more stable product and faster production times (Fig. 1 and 2). In addition, the use of pretreated carbon black particles allows conducting, stable adhesives to be produced.

Particle treatment – worthwhile for carbon nanotubes

Although industrial carbon black is an advanced material, there are only few niche applications for which the modification of this product using the plasma technology developed at the Fraunhofer IFAM is economically viable. The reason for this is not least the favorable price of carbon black, which only justifies the modification costs in exceptional cases. In contrast, the PLATO treatment method lends itself for high-tech novel developments – for example for carbon nanotubes (CNTs); these are microscopic tubes made of carbon (Fig. 3 and 4). Nanotubes can be used, for example, to generate highly conducting, high-strength polymers and adhesives. This is attributed to the very low electrical resistance of CNTs, meaning a current readily flows along the tubes. The addition of CNTs, however, also allows very high strength polymers to be produced, similar to the use of hollow bamboo to generate very strong structures. One application area that has already been explored for CNTs is the fabrication of special polymers for aerospace applications: In order to make materials very strong and resistant to radiation in space, nanotubes are incorporated into the materials.

In recent years the interest in carbon nanotubes has increased enormously due to their unique properties. They can be used to produce novel composite materials with extraordinary properties.

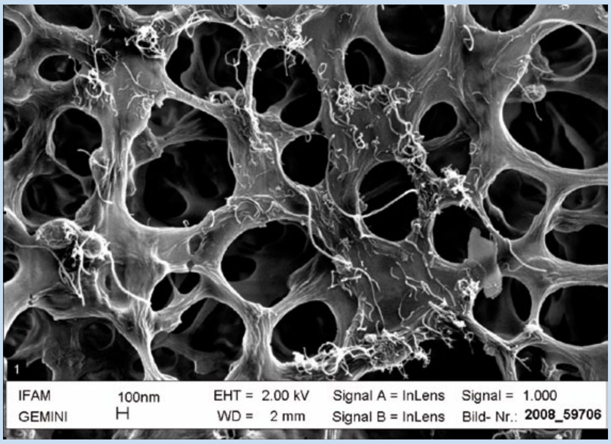


Fig. 4: Scanning electron micrograph of pretreated CNTs on filter material.

In order to utilize these benefits, the federal ministry of education and research helped to set up the Innovation Alliance CNT (Inno.CNT; www.cnt-initiative.de). Its objective is to establish a key future market for materials technology in Germany, which can act as a worldwide leader for novel carbon nano-materials. A very large group of about 80 competent partners from industry and science have become part of Inno.CNT. This includes the Fraunhofer IFAM.

PLATO activities in the sub-project CarboFunk

The PLATO specialists at the Fraunhofer IFAM play a key role in the sub-project CarboFunk. Together with industrial and scientific institutions, work is being carried out on the customized modification of CNTs – because non-treated CNTs have only limited use for manufacturing high-performance composites. Only after surface modification it is possible, for example, to effectively incorporate CNTs in the non-agglomerated state into reactive polymers or other materials in order to mechanically strengthen these composites for lightweight structures and applications.

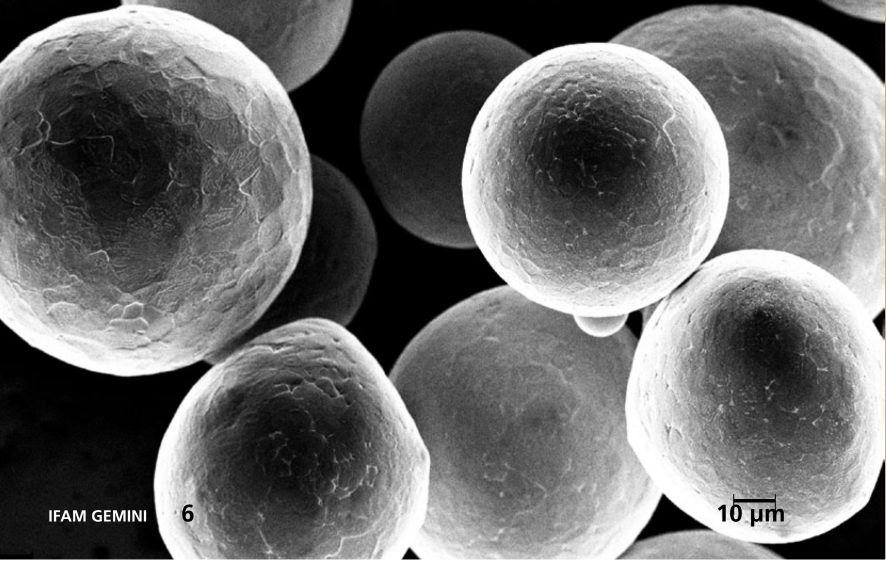
As the health risks associated with carbon nanotubes have not yet been adequately studied, processes and methods must be developed which allow harmless processing of the particles by users. One of the tasks of the CarboFunk project is hence the development of methods which allow CNTs to be safely incorporated into a solid or to be pre-dispersed in a liquid. In this context a long-term stable bond between the CNTs and matrix material is desired, as this prevents the release of CNTs during processing and handling.

Although originally developed by PLATO for the functionalization of carbon black, a low-budget product, the adapted pre-treatment method can be effectively used for CNTs, a high-end product. In the device developed at the Fraunhofer IFAM, CNTs can be functionalized in a closed system in which they are introduced as agglomerated starting products. Using ultrasound, the agglomerated CNTs are then separated from each other, mixed with a liquid, and injected into the plasma. This is carried out in a closed reactor system so that no persons come into contact with the particles. The result is a liquid suitable for further processing – for example, water or an alcohol – in which the particles are dispersed.

The advantages compared to other pre-treatment methods, which are also being studied in the CarboFunk project, include the closed process, the dispersion in a liquid, the degree of automation, and the transfer to industrial production. The PLATO method also involves no chemical baths and acids, meaning there is no chemical disposal issue. In general, nitrogen gas and water are used. The treatment process is also at atmospheric pressure, meaning that a narrow, enclosed, and environmentally-friendly apparatus can be used. This system is highly attractive to be integrated at companies into production processes. The promising PLATO method has in the meantime been applied for a patent.

Microparticle coating process for electromobility

The experience of the PLATO section with particle treatment has also become of interest for the area of electromobility, in which the Fraunhofer-Gesellschaft created a trend-setting area of focus via the project "Fraunhofer System Research for Electromobility FSEM" (www.forum-elektromobilitaet.de). In this way, the Fraunhofer-Gesellschaft wants to assist the German car manufacturing industry to safeguard a long-term, leading position in this sector. Fraunhofer specialists are working on solutions for many aspects of electromobility – ranging from new drive system concepts to energy generation and component design. In this context, all the value-



added steps involved in electromobility must be adapted to each other. The objective is to develop fundamental building blocks for electromobility in just two years.

In this area the Fraunhofer IFAM is involved, amongst other things, in the development of new processes for making innovative polymer composites. These composites should reduce the electromagnetic losses in electrical machines. The problem here concerns eddy currents in the soft magnetic components of electrical machines, leading to losses via heat. The current solution for this problem is relatively complex and consists of a multilayered, modular structure made of electrically insulated, assembled sheets. There are numerous disadvantages – including the complicated manufacture, material losses during sheet punching, and design limitations.

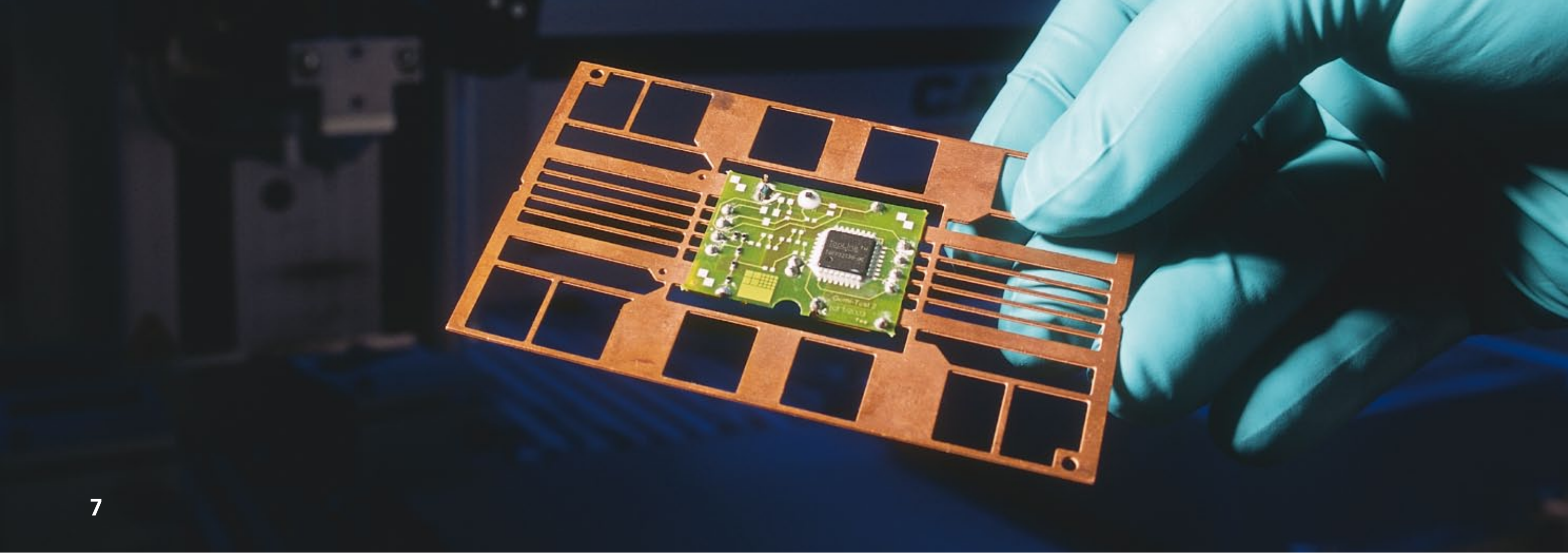
Electrical insulation of metallic fillers

The solution of the Fraunhofer IFAM: The coating of metallic fillers at the micrometer level provides mutual electrical insulation. The PLATO section can already realize this particle coating using a plasma-polymer and thereby achieving a very good electrical insulation (Fig. 6). The second main area of work of the Fraunhofer Electromobility Project is "Energy Generation, Distribution, and Conversion" and involves the further development of processes for coating soft magnetic powders. The aim is to use atmospheric pressure plasma-coating to coat soft magnetic powders having different particle size distributions. The Fraunhofer Institute for Integrated Systems and Device Technology (IISB) then performs the further processing with thermoplastic polymers or thermosets. The in-depth experience of PLATO in the area of particle coating and the close collaboration with specialists from other Fraunhofer institutes have already resulted in first successes. The polymer-bound soft magnetic materials, due to their versatile shaping properties, open up totally new opportunities for manufacturing electromagnetic components. As a result there are new technical concepts for the integration of high-performance electronics into complex-shaped spaces.

IPANEMA – new packaging materials for components

A further, promising application for plasma-polymerized micro-particles has been targeted by PLATO since autumn 2007 in the IPANEMA project (funding reference: 01RI0716B). Partners from industry and science are working together on a joint project in order to develop insulated particles for new materials in the field of electronic and electrical engineering. As innovative packaging materials – namely materials that can be used for protection against environmental influences – they should allow the manufacture of new electronic and electrical engineering products. The aim of this project is to improve the competitiveness of various sectors of industry. The unique, heat-conducting properties of these metallic particles and materials, due to the thin, insulating plasma-polymer layers, allow these products to be used as electrically insulating materials. This enables the design and construction of totally new components and systems, as current design methods have reached their limits (Fig. 7).

The background of this project is the fact that increasing miniaturization and integration of chips and assemblies is allowing ever higher power densities, with the result that operating temperatures are also constantly increasing. Other problems arise due to the fact that electronic assemblies are being used at higher ambient temperatures – for example in cars – or at higher humidity, for example, in the Asian marketplace. Where can the heat go? That is one of the key questions that has to be answered in this age of increasing miniaturization, increasing power as well as multifunctional



7

technical and electronic products. Important to recognize in this context is that more than half of the failures of active components are due to excessive temperature.

The objective of the IPANEMA project is therefore to improve the thermal conductivity of the packaging materials in order to dissipate the heat as effectively as possible. This will be achieved by developing thin, electrically insulating plasma-polymer coatings for metallic particles, so that new hybrid polymers with high packing densities can be realized. In addition to aluminum and magnesium, copper particles are of growing interest due to the very high thermal conductivity of this material. The particle coating method developed by the PLATO section has also shown much promise in this project. The objective is to develop polymers containing embedded e.g. copper particles that are coated with insulating layers produced via the low temperature plasma-polymerization. These coatings dissipate the heat very effectively, but hinder electrical contact. If desired, additional functions can be given to the heat-conducting polymer layers, for example for the supplemental application as a filler or a sealant.

CONTACT

Dr. rer. nat. Jörg Ihde
Phone +49 421 2246-427
joerg.ihde@ifam.fraunhofer.de

Dr. Ralph Wilken
Phone +49 421 2246-448
ralph.wilken@ifam.fraunhofer.de

Institute
Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM,
Department of Adhesive Bonding Technology and Surfaces,
Bremen

1 | 2 *Plasma-pretreated colored pigments and carbon black: untreated (left), treated with different treatment intensities (center and right).*
3 *Schematic representation of a multi-walled carbon nanotube (CNT).*
5 *Conducting lacquers and adhesives for high-tech applications containing functionalized carbon nanotubes (CNTs; image source: MEV-Verlag).*
6 *Plasma-treated micro metallic powders for applications in the area of electromobility.*
7 *Heat-conducting packaging materials for innovative production concepts (Image source: MEV-Verlag).*