

Corrosion protection with graphene

B. Munzing

Abstract

Graphene, theoretically the atomic layer of graphite, can now be produced on large industrial scale. Most of these processes generate few layer graphene. The Sixth Element has established a proprietary process to manufacture different types of graphene with specific designed properties for different applications. Research on how to use graphene in coatings started already 2013 with the focus to reduce zinc in solvent based corrosion protection coating systems. In standard primers with high zinc content, zinc acts as cathodic sacrifice layer, as zinc is more ignoble metal, therefore protecting the underlying metal substrate. When the zinc is more and more oxidized, the resulting zinc oxide is building up a barrier, which prevents the attack of the surrounding media (water, salt) to the metal substrate. The idea now was to design a graphene type, being electrical conductive enough to support any cathodic function of the system and being able to act as a barrier without producing a battery cell. A further requirement was that such a graphene can be processed with standard equipment used in the coating industry. Cooperating with an industrial partner in China, Toppen Co, the graphene type SE1132 was developed. It is a few layer graphene with medium conductivity. Addition of 1 % SE1132 to an epoxy primer system and reducing the zinc content to 25 % (based on dry substance) show significant improvements in salt spray testing and water condensation testing compared to a standard zinc rich epoxy primer. The results have been confirmed by measuring the corrosion current of such a system. Sixth Element had been granted a patent in China and US for this development. Based on independent tests of Chinese authorities the system is approved for off-shore applications, first applied to protect the steel construction of an off-shore wind energy tower in 2015.

Recently, new primers have been introduced that contain zinc along with additional pigments. These primers aim to fulfil the latest requirements for corrosion protection, which are set out in an international standards document (ISO 12944-2018).

Unfortunately, zinc products, such as the commonly used zinc powder, are highly toxic to aquatic life. Users in marine environments are therefore increasingly demanding primers with a much reduced zinc content.

This is where graphene, the monolayer form of graphite, comes into play. This material was first detected in 2004, and its exceptional mechanical strength, along with its excellent

electrical and thermal conductive properties, make it attractive for a range of applications. Graphene can also absorb atoms or molecules and can be functionalized by bonding different chemical groups to its carbon atoms.

Over the past 15 years, scientists and engineers have established several routes for producing graphene industrially. For applications in the electronics industry, chemical vapour deposition (CVD), which starts with a carbon-rich atmosphere and deposits a single layer of carbon atoms onto a substrate, is normally used to create graphene sheets with a high electrical conductivity. Another common route is to use a modified Hummers method, in which graphite is first oxidized, and then, through reduction steps carried out in an inert atmosphere, different graphene types are produced. Other methods include peeling off, or exfoliating, layers of graphene using a proprietary electrochemical process.

With the exception of CVD, these methods tend to produce few-layer graphene products, which are available either as a powder or dispersed in solvents, water and polymer systems. The primary particles of a few-layer graphene product might have lateral sizes of 1 μm to more than 50 μm , with a thickness of up to a few nanometers, depending on the number of layers. Even though these products are not pure graphene, their electrical and thermal conductivity and their mechanical properties are very similar to those of the pure material. Crucially, they are close enough for corrosion-protection purposes.

Corrosion, in the most common use of the word, is the electrochemical oxidation of metal (usually steel) with an oxidant such as oxygen, sulphates or chlorides to form chemically stable metal salts – that is, rust. Being a conductive material, graphene is able to influence the electrochemical reaction (together with the second complementary anti-corrosion pigment) in a favourable way, meaning less rust. The barrier properties of graphene support this effect.

Additionally, graphene can strengthen the adhesion of the binder in the coating system to the substrates. This helps to prevent the (salty) water, which attacks the substrates, from separating the protective coating from the substrate.

Biography

Bernhard Münzing started his career at BASF selling fibre reinforced prepregs mainly to the aerospace and sports industry. He then joined L. Brüggemann, a medium sized chemical company, responsible for materials management and

B. Munzing

The Sixth Element (Changzhou) Materials Technology Co, Ltd, China

market introduction of new products. After short period as Sales Manager for a small paint company, he worked for more than 17 years for GELITA, the leading gelatine manufacturer. Covering all potential applications areas for gelatine, he helped customers to adopt the product during the critical phase of the BSE disease, followed by a position in business development for more than 10 years, introducing a new product line to the food market, establishing a new production technology for a special gelatine and launching gelatine based formulations into the metal processing industry. Since July 2016 he is with The Sixth Element, a leading supplier of graphene products responsible for all markets outside China with focus on EMEA region.

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