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Cathodic electrografting of acrylics: From fundamentals to functional coatings

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ABSTRACT

Promoting permanent adhesion between so dissimilar materials as polymers and metals is a very challenging target and a severe brake to the implementation of many potential applications. However, synthetic polymers can now be chemisorbed onto a variety of conducting surfaces by cathodic electrografting of acrylic monomers. The first part of this review will focus on the fundamental aspects of this emerging technology, thus from the historical discovery to experimental and theoretical developments, with the purpose to better comprehend the electrografting phenomenon.

Once firmly established, this concept has been exploited in order to make polymeric coatings with specific functionality chemisorbed onto more diversified substrates in more convenient liquid media. This remarkable progress that largely relies on advanced controlled polymerization processes will be the topic of the second part of the review, with a special emphasis on the more recent development of smart coatings, particularly stimuli responsive coatings very well-suited to nanotechnologies.

Contents

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1. Introduction

Permanently adhering organic coatings onto inorganic surfaces is a long-lasting challenge, because, in case of success, the surface properties could have the synergistic benefit of the characteristic features of the substrate and the top coat. So, a tremendous research effort has been devoted to this problem, successfully in case of very specific substrates. For instance, (macro)molecules bearing thiol groups are known for chemisorption onto gold [1]. When glass is concerned, organosilanes $[Cl_n[(OR)_n\text{-Si-}(F)_{4-n}]$ are now available on the market place as adhesion promotors. Indeed, chloro(or alkoxy) silanes easily react with the silanol groups of the glass surface with formation of covalent bonds. The organic functions F, e.g., primary amine and epoxide, are anchoring groups for mutually reactive organic (macro)molecules [2]. Very recently, 3,4-dihydroxyphenylalanine (DOPA), a biomolecule found in the glue of mussels, has been reported as a very promising promotor of strongly adhering biomimetic coatings [3].

Among the high research activity in the area of surface modification, electrografting is a very powerful method which has received comparatively little attention. This is surprising because this technique has many attractive features for modification of conducting or semi-conducting surfaces. The main interest of the electrografting process is to solve the recurrent problem of the organic/metal interface weakness. The electrografting warranties a robust polymer/metal interface and offers the possibility to tailor the functionality of the grafted polymer film opening the door to a wide range of demanding technological applications. This electrochemical process is very easily implemented (only a conventional potentiostat is required) at the lab scale so as at the industrial level and requires commonly used, readily available monomers ((meth)acrylic derivatives). Over the plasma treatment, electrografting has the tremendous advantage to allow the precise control of the chemical composition of the polymer film. The growth of polymer brushes from chemisorbed initiator suffers often from the need to adapt the anchoring chemistry when going from one surface to another. Electrografting can be applied to a wide range of (semi)-conducting surfaces by keeping the same chemistry. Limitations of electrografting were the oxygen and water-free needed environment together with the use of organic solvents such as dimethylformamide to be efficient. Today, this process is thus applied industrially only for the coating of small-size high added value metallic devices such as biomedical implants and electronic circuits. Anyway, as it will be developed in the following paragraphs, recent developments are progressively overcoming these limitations, making electrografting a highly competitive process.

2. Fundamentals of the cathodic electrografting of acrylic monomers

2.1. Characteristic features of electrografting

More than two decades ago, a first report was published about quite a powerful and effective technique of chemisorption of polyacrylonitrile onto metals, such as copper and nickel [4]. This one-step electrografting technique relied on the electroinitiation of the polymerization of acrylonitrile in acetonitrile under a well-controlled cathodic polarization. This pioneering work by Lécayon et al. aroused not only curiosity but also optimistic prospects for the permanent coating of metals, whose surface protection against atmospheric agents is of the utmost importance and hardly achieved satisfactorily.