



Synthesis of antibacterial surfaces by plasma grafting of zinc oxide based nanocomposites onto polypropylene

Yoann de Rancourt, Benoit Couturaud, André Mas, Jean Jacques Robin *

Institut Charles Gerhardt, Montpellier, UMR5253 CNRS-UM2-ENSCM-UM1, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier 2, cc1702, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

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ABSTRACT

Antibacterial polymer surfaces were designed using ZnO nanoparticles as a bactericide. Mineral encapsulated nanoparticles were grafted onto activated polymer surfaces through their shells. Polypropylene (PP) surfaces were treated using an innovative process coupling core-shell technology and plasma grafting, well-known techniques commonly used to obtain active surfaces for biomedical applications. First, ZnO nanoparticles were encapsulated by (co)polymers: poly(acrylic acid) (PAA) or a poly(methyl methacrylate-co-methacrylic acid) copolymer [P(MMA-MA)]. Second, PP substrates were activated using plasma treatment. Finally, plasma-treated surfaces were immersed in solutions containing the encapsulated nanoparticles dispersed in an organic solvent and allowed to graft onto it. The presence of nanoparticles on the substrates was demonstrated using Fourier-Transform Infrared Spectroscopy (FTIR) analysis, Scanning Electron Microscopy (SEM)/Energy-Dispersive X-ray (EDX), and Atomic Force Microscopy (AFM) studies. Indeed, the ZnO-functionalized substrates exhibited an antibacterial response in *Escherichia coli* adhesion tests. Moreover, this study revealed that, surprisingly, native ZnO nanoparticles without any previous functionalization could be directly grafted onto polymeric surfaces through plasma activation. The antibacterial activity of the resulting sample was shown to be comparable to that of the other samples.

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1. Introduction

Aside from the interesting properties of bulky polymers, polymer surfaces remain relatively inert toward chemicals. Consequently, their modification remains a great challenge in the design of functional polymers for specific applications. In recent years, Considerable interest has been focused on tailoring polymer surfaces by grafting suitable nanostructured particles for various applications [1–3].

Plasma treatment is an attractive technique to graft complex macromolecules onto various supports to develop nanomaterials for biotechnology [4,5]. Gas-plasma-containing activated species are generated from electric discharge inside the gas or monomer vapors, leading to the formation of intermediate radical species and polar groups being grafted onto the material surface. The selection of the treatment parameters, such as the nature of the gas flow, the pressure in the reactor, and the power and time of discharge, allows for control over the surface modification while reducing the use of solvents and the production of chemical waste. Argon, oxygen, helium, water, carbon dioxide, nitrogen, and ammonia are the most commonly used gases for the introduction

of hydroxyl, carbonyl, peroxide, carboxyl, amine, and amide groups.

Core-shell methodologies applied to mineral particles have been widely studied in recent years and show great potential as a route to tailor the chemical and physical properties of a broad variety of metal oxide particles and of nanoparticles. Core-shell refers to multilayer wire or particle-shaped materials. For instance, silica, TiO₂, magnetite, and ZnO are commonly used to manufacture core-shell nanocomposites with various applications such as photonic crystals, solar cells, anti-UV coatings, and sensors [6–9]. ZnO is known to have an anti-UV effect, and this property has been widely investigated. This mineral also exhibits an additional but less described property; its bactericidal activity when in nanoscale form makes it useful in the design of antibacterial materials [10–16]. Even if the mechanism is not fully understood yet, it is believed that factors such as UV sensitivity and the nanoscale size have an important influence on the antibacterial activity. According to the studies about antibacterial effects of ZnO, two different mechanisms seem to act in synergy. The first one has been described by Seil while synthesizing ZnO-containing PVC films [13]. The release of Zn²⁺ from the nanoparticles into the bacterial culture media was related to an antibacterial effect. The explanation proposed is that these ions could interfere with bacteria functions. But more investigations have been carried out on a bacterial

* Corresponding author. Fax: +33 4 67 14 40 28.

E-mail address: Jean-Jacques.Robin@univ-montp2.fr (J.J. Robin).

photoinactivation effect of ZnO, with a mechanism comparable to the well-known photocatalytic activity of TiO₂ [17]. Akhavan, in a study about ZnO nanorods, highlighted factors like high surface area and hydrophilicity as well as smaller optical band-gap energy, to explain an increase in antibacterial efficiency [11]. Such observations comfort the photocatalytic mechanism for ZnO antibacterial property. Tang also showed a clear evidence of the action of light, and especially UV of increasing activity of nano-ZnO in Polystyrene films [14]. The explanation given for this antibacterial activity is the oxidation of bacteria by active oxygen, obtained by redox reactions of adsorbed water and oxygen with photoactivated ZnO surface. Finally, further experiments made by Akhavan and Karunakaran allowed to demonstrate this photocatalytic process [10,12]. It is described that electron–hole pairs are created by electron transition, induced by light activation. Oxygen molecules are reduced by electrons coming from the conduction band of ZnO to form superoxide radicals. These radicals also produce other reactive species like H₂O₂ or hydroxyl radicals. Meanwhile, adsorbed water and surface hydroxyls are oxidized by holes from the valence band and also form radical hydroxyls. All these reactive species may finally degrade bacteria cell membranes, which result in their death by leakage. Typical core–shell methods have been used to functionalize ZnO nanoparticles and insert them into polymer films to obtain antibacterial coatings [14].

The main idea of the present study was to combine two different technologies, core–shell modification of nanoparticles and plasma activation, to graft ZnO particles onto polymer surfaces. This innovative process led to functional surfaces. The literature reports a chemical route where nanoparticles were activated by plasma and then reacted with a polymer surface [3], but to the best of our knowledge, the opposite method has never been published. The question to be answered was whether the mineral nanoparticles would be anchored to the polymer surface due to the chemical reaction between the corona of the particles and the activated surfaces. Consequently, a PP substrate was chosen due to its simple chemical structure, low price and ability to be plasma-treated and was activated using plasma treatment. At the same time, ZnO nanoparticles were functionalized according to the core–shell technique. In a final step, these nanoparticles were dispersed in an organic solvent (acetone or methanol) to allow them to graft onto the PP activated substrate, creating an antibacterial coating.

The synthesis method chosen for the manufacture of ZnO nanocomposites was an in situ emulsion radical polymerization inspired by Zhang and Tang [16,18].

First, the ability of surface hydroxyl groups of ZnO particles to react with carboxylic acids in a poly (methyl methacrylate-co-methacrylic acid) (PMMA-co-MA) copolymer was investigated in a one-pot synthesis. In this reaction, MA units of the obtained copolymer shell acted as a coupling agent due to plasma grafting onto PP, as it is assumed carboxylic acids play a crucial role in this process. A molar ratio of approximately 4:1 methyl methacrylate/MA was used to avoid having too much MA in the shell and thus avoid agglomeration of the nanocomposites.

Three other samples were tested in the plasma grafting process: native ZnO, ZnO coated with poly(acrylic acid) chains thanks to the hydroxyl-acid reaction, and ZnO particles bearing a PMMA shell obtained by a core–shell process. These last particles were synthesized by means of two successive steps. In the first step, MA was allowed to graft onto ZnO to act as a coupling agent, and for the second step, the encapsulation of MA-grafted ZnO particles by PMMA. This sample with a PMMA shell was used to prove that PMMA does not play any role in the plasma grafting process and consequently was not expected to graft onto PP substrates.

For antibacterial applications, Nano-ZnO particles exhibit several advantages in comparison with well-known nano-silver particles: low prices and availability. These criteria are crucial for the

manufacturing of mass-market products [19,20]. The process developed in this study using nano-ZnO nanoparticles could be used to modify polymer surfaces for aseptic applications such as medical devices to protect them from bacterial contamination.

2. Materials and methods

2.1. Materials

ZnO nanopowder (<50 nm) was provided by Sigma–Aldrich. Sodium dodecylbenzene sulfonate (SDBS) and potassium persulfate (KPS) were purchased from Sigma–Aldrich and used as received, without any further purification. Methacrylic acid (MA) and methyl methacrylate (MMA) from Sigma–Aldrich were purified over activated alumina columns to remove inhibitors before use. Degacryl 4779L[®] polyacrylic acid (PAA) was supplied by Röhm GmbH. Polypropylene microplates (PP) were purchased from Greiner Bio-one (96 Well, F-bottom, Chimney Well).

2.2. Preparation of the nanoparticles

2.2.1. ZnO coated by (PMMA-co-MA) copolymer (named ZnO-P(MMA-MA))

The ZnO-P(MMA-MA) core–shell nanocomposites were synthesized in a round bottom flask. First, 0.1 g of nano-ZnO was dispersed in 100 ml of MilliQ water. Then, 0.02 g of SDBS was added to reach a concentration lower than the critical micelle concentration (CMC). 0.1 g of MA and 0.4 g of MMA were added, and the mixture was dispersed for 10 min with an ultrasonic bath. After the addition of 5 mg of KPS, the flask was flushed with nitrogen for 15 min to avoid the presence of oxygen. Finally, the reaction was performed by heating to reflux at 80 °C for 5 h under nitrogen and with vigorous stirring (500 rpm). At the end of the reaction, the sample was washed by multiple centrifugation/redispersion cycles in MilliQ water, a 1:1 mixture of acetone and methanol, to remove the free chains of P(MMA-MA) copolymer, and finally pure acetone. After purification, the sample was dried in a vacuum oven at 70 °C for 24 h.

2.2.2. ZnO coated by MA and MA-PMMA (named ZnO-MA and ZnO-MA-PMMA, respectively)

First, 0.2 g of ZnO powder was dispersed in 100 ml of MilliQ water, and MA was added in a large excess (0.1 g). The dispersion was placed in an ultrasonic bath for 15 min and then left to react at room temperature under vigorous stirring for 24 h. The same purification procedure as above was used but with water. The obtained sample was named ZnO-MA nanoparticles. The same synthesis process as for the ZnO-P(MMA-MA) sample was performed, with the following quantities: 30 mg of the previously synthesized ZnO-MA, 100 ml water, 7 mg SDBS, 0.3 ml MMA, and finally 3 mg KPS. The sample was cleaned with water, acetone, and chloroform.

2.2.3. ZnO coated by polyacrylic acid (named ZnO-PAA)

For this sample, 0.1 g of ZnO was added to 0.1 g of PAA previously dissolved in 50 ml of methanol. After 15 min of ultrasonic treatment, the mixture was left to react at room temperature under vigorous stirring for 24 h. The sample was rinsed with methanol.

2.3. Plasma grafting

The treatment of polypropylene was conducted under argon plasma. The effect of plasma treatment with different gas fluxes and pressures inside the reactor, times of exposure, and powers was studied. The plasma reactor consisted of two cylindrical, parallel aluminum electrodes (diameter: 13 cm, distance between

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