



Novel hybrid coatings with controlled wettability by composite nanoparticle aggregation



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ABSTRACT

The aim of this study is to evaluate novel hybrid materials as potential candidates for producing coatings with hierarchical roughness and controlled wetting behaviour.

Magnetite (Fe_3O_4) nanoparticles obtained by co-precipitation were embedded in matrices synthesized by radical graft co-polymerization of butyl acrylate (BA), butyl methacrylate (BMA), hexyl acrylate (HA) or styrene (ST) with ethylene glycol di-methacrylate (EGDMA) onto previously modified chitosan bearing surface vinyl groups. The resulting composite particles were characterized regarding their average size, composition and magnetic properties. Hybrid thin films containing suspension of composite particles in ethanol and pre-hydrolysed hexadecyltrimethoxysilane (HDTS) as a coupling/crosslinking agent were deposited by spin coating or spraying. The films were cured by heating and subsequently characterized regarding their morphology (scanning electron microscopy), contact angle with water and adhesion to substrate (scratch test). The structure-property relationship is discussed.

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1. Introduction

The design of synthetic surfaces with controlled wettability involves a fine balance between hierarchical morphology with micro and nanoscale features and the low surface energy of the material, properties inspired by the naturally occurring superhydrophobic materials [1,2]. Such surfaces offer extensive potential applications, among which self-cleaning, anti-corrosion or anti-fouling coatings and microfluidic devices [3,4]. Over the past decades, various methods have been reported for fabricating superhydrophobic surfaces, such as chemical vapour deposition, etching, templating, lithography, sol-gel processes or layer-by-layer assembling method, mainly through two different processes: producing a micro-nanostructured coarse morphology on low surface energy materials or obtaining a rough layer first and then chemically modifying it with low surface energy materials [5,6]. Although great progress has been made on the fabrications of such surfaces, many of these methods involve multistep procedures and difficult process controls. Recently, a number of studies have been devoted to the use of controlled assembly of micro- and nano-sized particles that is known to be facile and cost effective, to manufacture coatings with hierarchical roughness. For example, superhydrophobic

Co_3O_4 films with micro-nanostructure prepared via a solvothermal procedure possess excellent anti-icing properties and outstanding mechanical stability [7]. Hydrophobic surfaces prepared via colloidal assembly of silica microspheres and gold nanoparticles displayed hierarchical superstructures due to a suitable combination of small and large scale roughness [8]. Superhydrophobic polypropylene/zinc oxide nanocomposites have been prepared by simple solution casting [9]. Thin films with hierarchical structure exhibiting large contact angles with water drops were obtained by using silica nanoparticles dispersed in poly(dimethylsiloxane) [10]. Anti-icing coatings that use polymer modified fossil diatomaceous earth particles (natural silica particles) have recently been reported [11]. Iron oxides nanoparticles attract increasing attention due to their broad range of applications and their unique properties: strong response in magnetic field, biocompatibility, durability, low toxicity and low cost [12]. Superhydrophobic surfaces induced by magnetic particles open up new areas of applications [13]. Inspired by the so called lotus effect, a simple procedure to produce magnetic superhydrophobic superparamagnetic nano-composite from $\text{Fe}_3\text{O}_4@SiO_2$ core-shell nanoparticles modified with 3-glycidoxypropyltrimethoxysilane and grafted with polystyrene via covalent bond is reported by Zhang and Lei [14]. Coatings prepared with Fe_3O_4 nanoparticles modified with fluoroalkyl silica produced temporary superhydrophobic surfaces with the aid of a magnetic field [15]. Ding et al. [16] reported the prepara-

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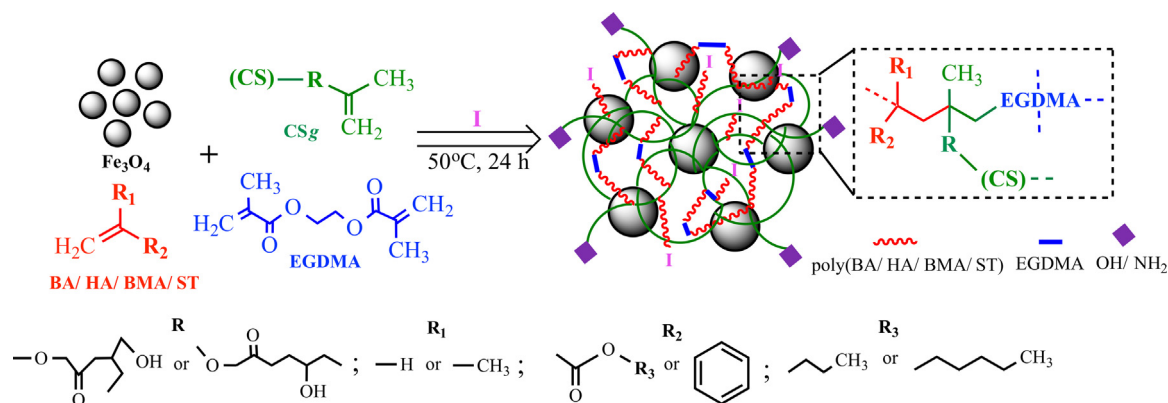


Fig. 1. Composite particles synthesis.

tion of superhydrophobic coatings containing Fe_3O_4 nanoparticles, silicone resin and aminopropyltriethoxysilane.

However, the preparation of superhydrophobic materials from renewable and environmentally friendly materials by a simple and fast procedure is still challenging. Chitosan is an extremely promising biopolymer that possesses a number of valuable properties, such as non-toxicity, biocompatibility, biodegradability, and cost effectiveness, resulting in a wide range of applications [17]. Moreover, new properties may be imparted to chitosan through its chemical modification via incorporation of corresponding substituents, properties that are of great importance with respect to the development of new materials. Spano et al. have reported the control of the wetting angle of chitosan films by in-situ formation of gold nanoparticles, produced by laser irradiation [18]. The suggested application is in microfluidics. Spirk et al. prepared chitosan-silane hybrid films by sol-gel processes [19]. The highest wetting angles reported by both authors are 60–70°.

In this work we attempt to fabricate novel hybrid thin films containing magnetite-grafted chitosan composites that are able to assemble in a controlled manner to produce hierarchical roughness resulting in water repellent properties. Magnetite nanoparticles were embedded in a shell obtained by solution radical graft copolymerization of butyl acrylate (BA), butyl methacrylate (BMA), hexyl acrylate (HA) or styrene (ST) with ethylene glycol dimethacrylate (EGDMA) onto previously modified chitosan bearing surface vinyl groups. In the hybrid films, chitosan was used as the polymeric binder and partially hydrolysed alkoxy silane was introduced as a coupling agent.

2. Material and methods

2.1. Materials

Analytical grade chemicals were used as received, without further purification. Iron(III) chloride hexahydrate p.a. ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron(II) chloride tetrahydrate p.a. ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), GMA and EGDMA (both stabilized with hydroquinone monomethyl ether) were purchased from Merck, Germany. Low molecular weight chitosan (CS) (Mw = 50–190 kDa; degree of deacetylation 84.5%), BA, BMA, HA, 2,2'-azobis(2-methylpropionamide) dihydrochloride (I), ST (stabilized with 4-*tert* butylcatechol), HDTs (technical grade, 85%), sodium hydroxide p.a. grade and acetic acid were obtained from Sigma-Aldrich, Germany; hydrochloric acid (1N), ammonia, ethanol and acetone were procured from Chemical Company (Iasi, Romania). All solutions were prepared with ultrapure water.

2.2. Synthesis of magnetic chitosan-g-acrylate/styrene composite particles

The magnetic-chitosan g-acrylate/styrene composite particles were obtained in three steps, as follows:

2.2.1. Magnetite nanoparticles preparation

Magnetite nanoparticles were prepared by the standard method of Fe^{2+} and Fe^{3+} ions co-precipitation (molar ratio of 2:1) in alkali solution as previously reported [20]. Typically, the solutions of iron (III) chloride hexahydrate (0.0551 mol) and iron (II) chloride tetrahydrate (0.0275 mol) in ultrapure water (120 mL each) were vigorously stirred (500 rpm) under nitrogen protection in a temperature controlled water bath (65 °C). Then, aqueous sodium hydroxide solution (0.32 mol in 120 mL water) was added (10 mL/min) into the reaction mixture and allowed to react under the same conditions for 1 h. The obtained Fe_3O_4 nanoparticles (batch denoted Mag) were separated in magnetic field, washed with ultrapure water until neutral pH and stored in the refrigerator for the next step.

2.2.2. Synthesis of GMA modified chitosan (CSg)

Modified CS bearing surface vinyl groups was synthesized by GMA coupling in acidic aqueous solutions through an epoxide ring opening reaction, based on a previously published method [21]. Briefly, GMA was added (11.74×10^{-3} mol) to 100 mL CS solution (1% in 1 M aqueous acetic acid) with pH adjusted to 4 using 1N NaOH and the reaction mixture was maintained overnight at 50 °C with stirring at 150 rpm. The resulting mixture was brought to pH=6 and the polymer precipitated in acetone and ethanol to separate the unreacted products, dried in oven at 50 °C and stored for next step.

2.2.3. Synthesis of magnetic-chitosan g-acrylate/styrene composite particles

The process is summarized in Fig. 1.

The magnetic-CS-g-acrylate/styrene composites were prepared by graft radical co-polymerization of BA, BMA, HA or ST with EGDMA as a crosslinker onto the modified CS bearing vinyl groups (CSg), using a water soluble initiator, with addition of magnetite nanoparticles in suspension. The ratio of magnetite to modified CS plus monomers mixture was optimized in preliminary experiments to yield composite particles with an average size of less than 1 μm . The optimal procedure is described below:

In a typical experiment, 0.2 g of CSg dissolved in 80 mL aqueous acetic acid (0.5 M) was thermostated at 50 °C in a tightly closed flask under continuous shaking (150 rpm). A mixture of alkyl acry-

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