Preparation and characterization of antibacterial Senegalia (Acacia) senegal/iron–silica bio-nanocomposites

Tuba Şişmanoğlu [a], Selcan Karakuş [a], Özgür Birer [c,d], Gülin Selda Pozan Soylu [b], Ayşen Kolan [a], Ezgi Tan [a], Öykü Ürk [a], Gizem Akdut [a], Ayben Kilislioglu [a,*]

[a] Istanbul University, Faculty of Engineering, Department of Chemistry, 34320 Avcilar, Istanbul, Turkey
[b] Istanbul University, Faculty of Engineering, Department of Chemical Engineering, 34320 Avcilar, Istanbul, Turkey
[c] Koç University, Department of Chemistry, Sarıyer 34450, Istanbul, Turkey
[d] Koç University, KUYTAM Surface Science and Technology Center, Sarıyer 34450, Istanbul, Turkey

ABSTRACT

Many studies that research bio-nanocomposites utilize techniques that involve the dispersion of strengthening components like silica, metal and metal oxides through a host biopolymer matrix. The biggest success factor for the bio-nanocomposite is having a smooth integration of organic and inorganic phases. This interattraction between the surfaces of inorganic particles and organic molecules are vital for good dispersion. In this study, a novel biodegradable antibacterial material was developed using gum arabic from Senegalia senegal (stabilizer), silica (structure reinforcer) and zero valent iron particles. Silica particles work to not only strengthen the mechanical properties of the Senegalia senegal but also prevent the accumulation of ZVI nanoparticles due to attraction between hydroxyl groups and FeO. The gum arabic/Fe–SiO_2 bio-nanocomposite showed effective antibacterial property against the Gram-positive Staphylococcus aureus and Gram-negative Escherichia coli. Using Scanning electron microscopy, homogeneous dispersion and uniform particle size was viewed in the biopolymer. X-ray diffraction studies of iron particles organization in Senegalia senegal also showed that the main portion of iron was crystalline and in the form of FeO and Fe^0. X-ray photoelectron spectroscopy was used to evaluate the chemical composition of the surface but no appreciable peak was measured for the iron before Ar etching. These results suggest that the surface of iron nanoparticles consist mainly of a layer of iron oxides in the form of FeO. Thermal gravimetric analysis was used to determine the thermal stability and absorbed moisture content.

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1. Introduction

Biodegradable materials are versatile in its usage due to its nontoxic and environmentally friendly properties. Natural polymers contain weak mechanical properties that require support through nanoscale blending with other synthetic polymers or inorganic matters. Biopolymers are usually used in these applications as stabilizing matrices. However, the mechanical properties of biopolymers are typically not suitable for demanding applications. It is possible to enhance these properties with a homogeneous dispersion of inorganic nanoparticles into the organic matrix [1–5]. Various inorganic materials have been used as possible additives to enhance the polymer strength. Having two different types of

filler components in the same matrix may play a critical role in preventing agglomeration of the chemical species.

In this study a biodegradable non-toxic biopolymer, gum arabic from Senegalia senegal (Gum arabic), was used as a matrix in developing the new material with an antibacterial property. Gum arabic (GA) is a complex mixture consisting of carbohydrates and glycoproteins [6,7]. The core carbohydrate structures account for 93% of the total components. It has been shown that the majority of the remaining components is arabinogalactan protein with highly branched structure [8,9]. The peptide moieties (2% present in gum arabic) are hydrophobic while the polysaccharide chains are hydrophilic and extend out into the solution. In order to enhance its mechanical, thermal and surface properties a small amount of silica was added and homogeneously dispersed through the biopolymer. The antibacterial properties of the material were achieved by the addition of zero valent iron (ZVI) nanoparticles. Silica served not only to strengthen the mechanical properties of the GA but to also

prevent the accumulation of ZVI nanoparticles by covering the surface of the particles like an envelope.

2. Experimental procedure

2.1. Materials

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (Aldrich), sodium borohydride ($NaBH_4$) (Merck), ethyl alcohol (C_2H_5OH) (Merck), Senegalia senegal powder, silica gel (Merck)

2.2. Preparation

Percentage of the inorganic component in GA/Fe–silica bio-nanocomposite was 1% and prepared in three steps:

i Iron (III) chloride solution was prepared by dissolving 0.54 g $FeCl_3 \cdot 6H_2O$ in 24 mL ethanol and 6 mL distilled water mixture. 0.1 M $NaBH_4$ solution was prepared by dissolving 0.3783 g $NaBH_4$ in 100 mL water. $NaBH_4$ solution was added to iron (III) chloride solution drop by drop and solution was stirred vigorously.
ii 0.5 g gum arabic (Balmumcu) was dissolved in 100 mL water and sonicated for 5 min.
iii 0.5 g silica (Merck, silica gel 60, mesh 70–230) was dispersed in 100 mL water and shaked for 10 min.

Initially, the silica and gum arabic solutions were mixed under constant stirring. Finally, the iron solution was added to the mixture under vigorous stirring. The bio-nanocomposites were dried at 100 °C to a constant weight. Thin films of the bio-nanocomposite materials were prepared by casting the solutions on clean glass petri dishes and evaporating the solutions at 100 °C.

2.3. Material characterization

X-ray diffraction (XRD, PANanalytical Xpert-Pro, Cu Kα: 1.5406 Å, 40 kV, 40 mA), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha), scanning electron microscopy (SEM, Quanta FEG 450). The specimen was coated with a thin conducting (tens of nanometers) layer of gold. Fourier transform infrared spectroscopy (FTIR, Nicolet ATR) in ATR mode techniques were used to perform a structural characterization of the materials. Thermal gravimetry analysis (TGA, Shimadzu TGA-50) was used to determine thermal characteristics of GA/Fe–Silica nanobiocomposite to determine degradation temperatures and absorbed moisture content. A 12.4 mg sample was heated at a rate of 10 °C/min starting at room temperature until a temperature of 1000 °C under nitrogen atmosphere.

2.4. Antibacterial tests

A zone inhibition test was performed on an agar plate to test the antibacterial properties of the newly synthesized material. In this experiment, the bacteria strains used were the Escherichia coli and the Staphylococcus aureus. Cultures containing Endo rich agar was used. The Müller hinton medium was used on two separate petri dishes. The first dish, labeled A, contained an 8x8 mm amount of GA while the second dish, labeled B, contained the same amount of GA but with Fe–silica nano particles. The dishes were incubated at 37 Müller hinton medium was used on two separate petri dishes. The first dish, labeled A, contained an 8 mm × 8 mm amount of GA while the second dish, labeled B, contained the same amount of GA but with Fe–silica nano particles. The dishes were incubated at
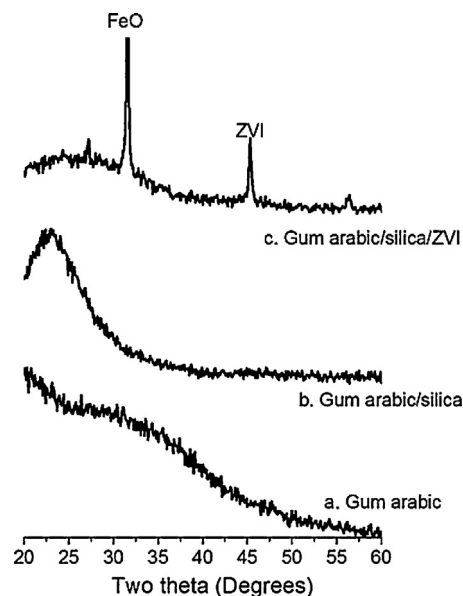

Fig. 1. XRD pattern of (a) Gum arabic, (b) GA/silica and (c) GA/silica/ZVI nano-biocomposite.

37 °C for one day. After the 24 h, E. coli bacteria in petri dish B were only present in the center of the dish as well as on the perimeter.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD patterns of the GA, GA/Silica and GA/Fe–silica bio-nanocomposite are presented in Fig. 1(a), (b) and (c). The GA is amorphous with no distinct peak structure. The silica is in amorphous form and presents the characteristic broad peak at 23° [11,12]. The integrated organic and inorganic phases of the bio-nanocomposite was shown using an X-ray diffraction (XRD). The addition of ZVI changed the XRD pattern from a single broad peak to several sharp diffraction peaks indicating a high degree of crystallization. A sharp peak observed at 2θ value of 45.2° corresponds to the crystal-structure of ZVI nanoparticles [10]. Peaks observed at 2θ values of 31.5° was assigned to the iron oxide [13].

3.2. X-ray photoelectron spectroscopy analysis

The high resolution XPS spectra of the bio-nanocomposite for the carbon, silicon and iron regions are presented in Fig. 2. The top spectra belong to the as prepared sample. The bottom row spectra were recorded after a 30 s argon ion etch at 1000 eV. We removed the surface layers using argon etching. The intensities of spectra of same elements can be compared with each other. The carbon region of as is gum arabic can be deconvoluted into four species, the aliphatic carbon at 285.0 eV, etheric/amine carbon (C–O/C–N) at 286.5 eV, carbonyl carbon at 288.2 eV and carboxyl carbon at 289.4 eV. The silicon region is deconvoluted to a single doublet pair with $2p_{3/2}$ positioned at 102.1 eV. The iron region shows a weak $2p_{3/2}$ peak at 711.2 eV which can be tentatively assigned to Fe^{2+} species. Following a mild etching with 1000 eV argon ions for 30 s, the carbon intensity decreased with a change in the peak envelope shape. Deconvolution shows that the peaks broaden and intensity distribution changes due to the change in surface structure. The Si $2p_{3/2}$ peak shifted to 102.5 eV and gained some intensity. The iron region shows great enhancement in intensity. The peak maximum at 710.7 eV and the weak satellite at 716.2 eV identifies the species as Fe^{2+}, due to surface oxidation of the ZVI nanoparticles.