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Polymeric ionic liquid materials derived from natural source for adsorption purpose

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ABSTRACT

Spherical microgel from a natural polymer, Gum Arabic (GA) with a high yield, 78.5 ± 5.0% was successfully synthesized in a single step. Furthermore, a superporous GA cryogel were also prepared under cryogenic conditions. These GA microgel and cryogels were turn into ionic liquid (IL) forms by post modification reactions using triethylenetetraamine (TETA) as a linear amine source, and polyethyleneimine (PEI) as a branched amine source. The modified-GA-PEI (M-GA-PEI) microgel/cryogel were protonated with HCl and treated with $[N(CN)_2]^-$, $[PF_6]^-$, and $[BF_4]^-$ anions to obtain GA based IL microgel and cryogels for the separation of bioactive molecules. The zeta potentials of GA microgel were changed from +52.15 ± 4.8 to −27.30 ± 4.2 mV upon the post modification with PEI. The blood compatibility of the prepared GA based microgel and cryogel were investigated by means of hemolysis and blood clotting tests and found that all types of materials are compatible with blood with 4.89 ± 0.69% maximum hemolysis ratio, and 75.6 ± 5.6 minimum blood clotting index. The antimicrobial properties of GA microgels were determined by disc diffusion method and the quaternized PEI microgel (Q-GA-PEI) were effective in killing *S. aureus* (gram +) and *E. coli* (gram −) bacteria with 13 ± 1 mm inhibition zones. Furthermore, the separation capabilities of bioactive molecules such as ascorbic acid (AA), sodium diclofenac (SDC) and paraquat (PQ) were also determined by using the bare, modified and IL GA cryogel because of their super porous nature.

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1. Introduction

Polymeric ionic liquids (ILs) are composed of inorganic anion and organic cation groups on the polymer structure [1]. They are generally synthesized by directly polymerization of monomers in IL form or by the post modification of already prepared polymeric materials [2–5]. IL have gathered considerable attention because of the wide range of applications including separation and purification of industrially significant chemicals and/or toxic compounds [6–8], acidic gases [9], basic materials in batteries, and due to applications in solar cells, fuel cells, supercapacitors, catalyst for various reactions [10,11], biosensors [11,12], and high performance electrochemical cells [13] because of their high ionic conductivity, low volatilities, non-flammability, and high thermal stability [14,15]. In recent years, the effects of the anionic and the cationic groups on the biological activity were also investigated due to the environmental concerns [16–20]. Various forms of biopolymeric IL materials including film [21], fiber [22], coating, and membrane that are used for potential biomedical applications such as biosensor [23], drug carrier/delivery material, medical dressing material, membrane devices, tissue engineering, implantable devices, and for separation of bioactive molecules [24].

Gum Arabic (GA) is a branched biopolymer consisting of different types of polysaccharides called arabinogalactose, rhamnose and glucoronic acid, and essential amounts of protein [25]. GA microgel, prepared by crosslinking reaction of linear GA has great advantaged as a biomaterial attributed to its unique properties obtained from renewable source, biodegradability, hemocompatibility, cytocompatibility, chemically modifiable surfaces, and tunable charge [26]. Therefore, in this study, polymeric GA based hydrogel materials with different size, shape, and morphologies were prepared the natural sources, GA in the forms of microgel and superporous cryogel were chemically post modified with different modifying agents with cationic structure by means of anion exchange reactions to render IL materials. IL forms of GA microgel

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and cryogel were prepared via post modification reactions with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPACl), triethylenetetramine (TETA), and polyethyleneimine (PEI) to generate positively charged amine groups on the polymeric materials. Moreover, PEI modified GA base microgel/cryogel were protonated with HCl and then further exposed to anion exchange reactions by treatments with sodium dicyanamide (SDC), ammonium hexafluorophosphate (AHFP), sodium tetrafluoroborate (STFB). The characterization of these IL natural polymeric materials was evaluated using SEM, FT-IR spectroscopy, and zeta potential measurements. The blood compatibility and antimicrobial susceptibility of the prepared IL materials were also investigated. Additionally, the separation and purification capabilities of the modified and IL forms of GA cryogels were also investigated for various types of bioactive molecules such as vitamin C, a drug molecule and for a pesticide.

2. Material and methods

2.1. Materials

Gum Arabic from the Acacia tree (Branched polysaccharide, Sigma-Aldrich, Mw: 250,000 g/mol), divinyl sulfone (DVS, 98%, Merck) as chemical cross-linker, sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 98%, Sigma-Aldrich) as surfactant, gasoline (Total, 95 octane, lead free) as solvent, and epichlorohydrin (ECH, >99% Sigma-Aldrich), 3-chloro-2-hydroxypropyl trimethyl ammonium chloride solution (CHPACl, 65%, Fluka), triethylenetetraamine (TETA, 97%, Sigma-Aldrich) and polyethyleneimine (PEI, 50 wt%, Mn: 1200, Sigma-Aldrich) as chemical modifying agents were used as received. Hydrochloric acid (HCl, 36.5–38%, Sigma-Aldrich) was used for protonation process. Sodium dicyanamide ($NaN(CN)_2$, 96%, Aldrich), ammonium hexafluoroborate (NH_4PF_6, 99%, Aldrich), and sodium tetrafluoroborate ($NaBF_4$, 97%, Merck) were used as anion sources to prepare IL microgel/cryogel. Nutrient agar (for microbiology, Merck) and nutrient broth (for microbiology, Merck), potato dextrose agar (Merck) were used as microbial growth media. All the solvents; acetone (99%, BRK), ethanol (99%, Birkim) and DMF (99%, Merck) were used as received. *Escherichia coli* ATCC 8739 and *Staphylococcus aureus* ATCC 6538 strains were obtained from the Microbiology Department of the School of Medicine at Canakkale Onsekiz Mart University. Sodium bicarbonate and calcium chloride were purchased from Sigma-Aldrich. Ascorbic acid (99%, Sigma Aldrich), sodium diclofenac (local vender), 1,10-dimethyl-4,40-bipyridinium dichloride (Paraquat, PQ, Fluka), were used as received. All aqueous solutions were freshly prepared using ultra-pure distilled water (DI) 18.2 M cm (Millipore-Direct Q UV3).

2.2. Synthesis of GA microgel and cryogel

GA microgel and cryogel were synthesized by crosslinking of GA with DVS in a single step by modifying the previously reported methods [26]. To prepare GA microgel, 0.1 g/mL concentration of GA prepared in 0.5 M NaOH solution were suspended in 30 mL 0.2 M AOT-gasoline solution under 1000 rpm mixing rate at room temperature, and immediately, the crosslinker, DVS (100% relative to the repeating unit of GA) was added to medium and mixing continued for 10 min at the same condition. At the end of the crosslinking reaction, GA microgel was collected by centrifuge under 35544*g* for 5 min and washed with ethanol:water mixture (80:20 by volume) three times, and finally with acetone three times more to clean unreacted chemicals and solvent residue. GA microgel were dried with a heat gun, and stored in a closed container for further use. In order to prepare GA cryogel, 0.04 g/mL of GA solution in 0.2 M NaOH solution were placed in a deep freezer at −20 °C for 2 min. Then, DVS (225% relative to the repeating unit of GA) was added to the chilled GA solution. Immediately, the solution was mixed, and put into 8 mm diameter of plastic pipes. These pipettes were placed in a freezer at −20 °C for 24 h. At end of the cryogellation reaction, GA cryogel was cut into cylindrical shapes and washed with water several times. The GA cryogel were dried in an oven at 50 °C.

2.3. Modification and protonation of GA microgel and cryogel

GA microgel and cryogel were modified by three different modifying agents such as 3-CHPACl, TETA and PEI that are possessed different number of amine groups. In the modification of CHPACl, 0.5 g GA microgel/cryogel were treated with 0.2 M 30 mL NaOH solution for 30 min. Separately, 1.5 mL of CHPACl was added in 0.2 M 30 mL NaOH solution and mixing for also 30 min. These two mixture were mixed, and the reaction was carried out for 12 h at room temperature. Modified (M-) GA-CHPACl microgel/cryogel were taken from the reaction medium by centrifuge under 35544*g* for 5 min, and washed with water:ethanol mixture several times. Finally, M-GA-CHPACl microgel/cryogel were washed with acetone, and dried in an oven at 50 °C. In the modification reaction of GA microgel and cryogel with TETA and PEI, 0.5g GA microgel and/or cryogel were suspended into 0.2 M 30 mL NaOH solution for 30 min. Then, washed with water one time, and placed into 20 mL of DMF at 90 °C under 800 rpm mixing rate. Immediately, 2 mL ECH was added to the medium. After 1 h, 1.5 mL of TETA or PEI was added to the reaction mixture and the reaction was carried out for 1 h more. M-GA-TETA or M-GA-PEI microgel/cryogel were washed with ethanol three times, and dried in an oven at 50 °C.

2.4. Preparation of GA ionic liquid microgel and cryogels

To prepare GA IL microgel and cryogel, 1 g M-GA-PEI microgel or cryogel was protonated with 1 M 30 ml of HCl solution for 2 h at 300 rpm mixing rate, and the protonated (Q-) GA-PEI microgel/cryogel were washed with DI water several times by using centrifuge under 35544*g* for 5 min for the microgel and dried in an oven at at 50 °C. The anion exchange of Q-GA-PEI microgel/cryogels were done by reacting with 0.1 M 30 mL $Na[N(CN)_2]^-$ (SDC), $NH_4[PF_6]^-$ (AHFP) and $Na[BF_4]^-$ (STFB) aqueous solution for 24 h at room temperature. The anion exchanged SDC-GA, AHFP-GA and STFB-GA IL microgel/cryogel were washed with water for three times, and with acetone two times by using centrifuge under 35544*g* for 5 min for the microgel. GA IL microgel/cryogel were dried in an oven at 50 °C, and stored in closed containers for further use.

2.5. Characterization of GA based microgel and cryogels

The morphology visualization of GA microgel and cryogels were done by using scanning electron microscope (SEM, Jeol, JSM-5600 LV) operating at 20 kV. The microgel or cryogel were put on carbon tape that are attached onto aluminum stubs and coated with a few nm thicknesses of gold under vacuum. The functional groups of GA microgel and cryogel were analyzed by using FT-IR spectroscopy (Nicolet IS10, Thermo). Zeta potential (mV) measurements of the microgels were determined by using Zeta Potential Analyzer (Brookhaven Inst. Corp.).

2.6. Blood compatibility of GA microgel and cryogels

Hemolysis and blood compatibility tests were used to determine *in vitro* blood compatibility of GA microgel and cryogel. The tests were done with permission and affording to the procedure recognized by the Human Research Ethics Committee of Canakkale

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