ARTICLE IN PRESS

Journal of Industrial and Engineering Chemistry xxx (2015) xxx-xxx



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry



journal homepage: www.elsevier.com/locate/jiec

Grafting of prepared chitosan–poly(propylene) imines dendrimer hybrid as a biopolymer onto cotton and its antimicrobial property

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ARTICLE INFO

Article history: Received 28 April 2014 Received in revised form 28 January 2015 Accepted 2 February 2015 Available online xxx

Keywords: Cotton Fabric Antimicrobial RSM Chitosan-dendrimer PPI

Introduction

ABSTRACT

Cotton was successfully treated by chitosan--dendrimer PPI hybrid (CS-PPI) using pad-dry-cure method. Scanning electron microscope (SEM), Fourier transform infra red (FTIR) and weight gain analysis clearly confirmed that CS-PPI was grafted on cotton through the formation of new chemical bonds. Due to the presence of CS-PPI on the surface of cotton, the weight gain of cotton was ~6% increased, and consequently the antimicrobial activity of the treated fabrics under optimum conditions was raised. As a worthy phenomenon, the treated cotton with CS-PPI in a concentration of 20% on the weight of the fabric was shown 100% of bacterial reduction.

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Q2 Although, water absorbency, dyeing ability, stability, air permeability, biodegradability, and no static electricity in cotton makes that as a good candidate in textile industry, high holding moisture of cotton makes that susceptible to microbial attack [1,2]. Microbial enzymes can readily hydrolyze the polymer linkages of cotton, and especially attack to the additives of textiles. This attack causes to discoloration and damage of the textile's functional properties such as elasticity and tensile strength [3].

Nowadays, the rising demand of humans for comfortable, clean, and hygienic textile goods with the protected property of the body against fungus and bacteria is an essential requirement for the production of antimicrobial textiles [4–6]. For the achievement of these ideal purposes in textile industry, the following points should be considered for choosing the antimicrobial agents: no adverse effect on the color, compatible with human skin, lack of environmental problems and high operation speed against microorganisms and stability resistant to repeated washing. It is well known that chitosan is one of the best candidates in this scope [7].

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http://dx.doi.org/10.1016/j.jiec.2015.02.002

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Chitosan is a bio-polymer with many distinctive features such 29 as bio-degradability, non-toxicity, cationic nature, and antimicro-30 bial activity [8–10], and has various applications in textile dyeing 31 and finishing processes. Unfortunately, bonding between textile 32 and chitosan in alkaline conditions is weak and provides the loss 33 antimicrobial activity and the poor durability of textile. This 34 problem creates some disadvantages in widespread applications of 35 chitosan [5,7,11]. To overcome these problems, two methods are 36 37 generally applied for using of chitosan on textiles; the first includes the treatment of glyoxal, glutaraldehyde or citric acid as the cross 38 linking agents between chitosan and textiles. These agents 39 increase the durability of chitosan on textile [12,5,13]. In the 40 second procedure; several modifications on chitosan structure is 41 carried out. The modification includes the grafting of attractive 42 multifunctional macromolecules such as sugars, cyclodextrin, 43 crown ether and dendrimer with chitosan. This grafting provides 44 the stronger linkages between chitosan and textiles and enhances 45 the durability and the efficiency of chitosan properties on 46 textiles such as antimicrobial, guest-molecule carriers and 47 chelating [14–16]. 48

Dendrimers, as the mono-disperse building blocks and 49 acceptable bio-compatible materials, are perfect guest-molecule 50 carriers [17,18] and have been recently used for the modification 51 of chitosan in medicine, biology and dye removal applications 52 [19–21]. 53

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54 To our knowledge, no report has been presented on the grafting 55 of CS-PPI on cotton fabric. So, in this study, CS-PPI was applied on 56 cotton fabric according to the pad-dry-cure method for the first 57 time. The effects of the operational parameters such as pH, time 58 processing, CS-PPI and CA concentrations on the grafting process 59 were evaluated by RSM technique. FTIR and SEM analysis were 60 used to confirm the formation of new chemical bonds between CS-PPI and cotton fabric. The antimicrobial properties of treated 61 fabrics were examined by Escherichia coli (E. coli) and Staphylococ-62 63 cus aureus (S. aureus) microorganisms. In addition, based on the 64 finding of this study, some attempts were done to propose a 65 grafting mechanism for this process.

66 Experimental

Materials and equipments 67

68 Plane cotton fabrics with weft/cm: 36 and warp/cm: 32 69 (density: 150 g/m^2) were utilized in this study. Chitosan was 70 received by Kitotak Co. (degree of deacytilation (DD): 85%, M_W: 71 1000 kDa, Iran). Nonionic detergent (Lotensol, Hansa) was used to 72 scouring fabrics. All other chemicals were used in their laboratory-73 grade (analytical reagents, Merck).

74 SEM graphs were prepared using the AIS-2100 scanning 75 electron microscope (Seron Technology Co). All the samples were 76 coated with gold before SEM testing. FTIR spectra were recorded on 77 a Nicolet Nexus 670 instrument using KBr pellets under standard 78 operating conditions. The measurements were performed at 20 °C 79 and a relative humidity of 65%.

80 Preparation of CS-PPI

81 Chitosan was dissolved in aqueous solution, containing acetic 82 acid and water/methanol. Ethyl acrylate was added to the solution. 83 After stirring at 50 °C for 10 days, the reaction mixture was quenched and then was precipitated in acetone which was 84

saturated with NaHCO₃. The precipitate was collected by filtration, 85 and then the filtrates dispersed in saturated H₂O with NaHCO₃. 86 The resulting mixture was dialyzed against H₂O, and lyophilized to 87 give N-carboxyethyl chitosan ethyl ester. For the preparation of N-88 carboxyethyl chitosan, the prepared ethyl ester was added to 89 NaOH solution; the mixture was stirred for 2 h, dialyzed, and 90 lyophilized as above. The precipitated powders were obtained in quantitative vield (95%).

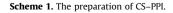
N-carboxyethylchitosan was dispersed in methanol. PPI (G = 2) was added to the prepared suspension and the mixture was stirred at room ambient. After three days, the mixture was evaporated to dryness, dispersed in NaOH solution at room temperature for 2 h, dialyzed, and lyophilized to give CS-PPI. The summarized preparation of CS-PPI is illustrated in Scheme 1 and was described in detail in our previous work [22].

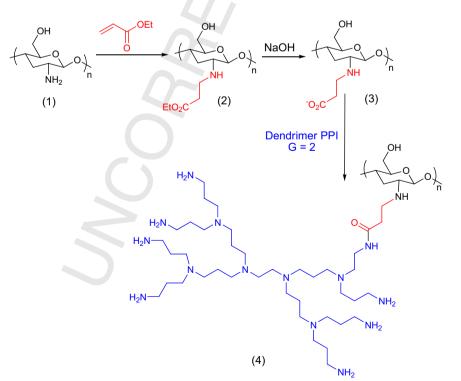
CS-PPI grafting on fabric

The cotton fabric used in this work was desized, mercerized and 101 washed. The fabrics washed using 2 g/L nonionic detergent 102 (Lotensol, Hansa) for 30 min at 60 °C with L.R 40:1. Then, fabrics 103 rinsed and dried. The grafting of CS-PPI as an antimicrobial agent 104 in various concentrations (5-25% owf) on the washed fabrics was 105 performed using CA (2.5–12.5% owf) as a cross-linking agent in 106 different concentrations and sodium hydrogen phosphate (SHP) as 107 a catalyst at a concentration of 10% (owf). This process was carried 108 out in different time (6–30 h) and pH (4–12), and then fabrics dried 109 at 70 °C for 5 min and cured at 110 °C for 3 min. Afterwards, fabrics 110 weight gain was calculated from the difference in weight of the 111 cotton fabric before and after the CS-PPI grafting reaction for three 112 times and the average weight was reported. 113

RSM analyses

The effects of variables such as pH, time processing, CS-PPI and 115 CA concentrations on finishing process were investigated by RSM 116





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