



Graft copolymerization of acrylonitrile onto wheat straw cellulose by silane coupling agent

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Abstract

Cellulosic fibers are finding their applications in many fields ranging from automotive to biomedical purposes. They also have wide applications as the reinforcement component in polymers to add the specific properties in the final product. Wheat straw (WS) cellulose is a low-cost lignocellulosic material. In this study, a grafted copolymer of poly(acrylonitrile-g-wheat straw) [poly(AN-g-WS)] was prepared by applying the alkaline surface modification method to obtain pure cellulose. A silane coupling agent (MPS) was used for the silanization of alkaline treated WS. Acrylonitrile monomer and AIBN initiator were used in the last step for graft copolymerization of poly(AN-g-WS). The poly(AN-g-WS) was functionalized, and characterized by fourier transform infrared spectroscopy (FTIR), and X-ray diffraction spectroscopy (XRD). The results proved the potential of the prepared poly(AN-g-WS) for environmental applications.

Keywords: Wheat straw cellulose, Alkalization, Silane treatment, Graft copolymerization

1. Introduction

Natural polymers based on lignocellulose have attracted the attention of many researchers because of their potential applications for different purposes. Every year, several thousand tons of biopolymeric materials are produced worldwide. However, most of these economic and environmentally friendly biomaterials remain unused. Usually, due to natural or artificial decomposition, their presence could lead to environmental pollution issues. Also, traditional incineration methods of agricultural waste directly increase carbon dioxide and particulate matter in the air, resulting in global warming, which is a major environmental concern [1].

Biomass of agricultural wastes includes cellulose, hemicellulose, lignin, minerals, proteins, oils, waxes, starches, etc., with active functional groups such as alcohol, phenols, carboxylic acids, carbonyl, and ether. Due to the presence of active functional groups, these biological materials can have various applications. Among the different compositions of natural materials, cellulose is widely used as a biopolymer to manufacture paper, cardboard, cellophane membranes, fabrics, water-soluble adhesives, and binders, etc [2,3,4].

Various surface modification methods i.e., alkaline pretreatment, could be applied to biomaterials. Surface modifications lead to changes in the surface of the lignocellulosic material, such as an increase in surface area, average pore volume, and pore diameter. Also, by alkaline modification, ester bonds converts to carboxylates and alcohols. In addition to modification, these methods also could lead to partial hydrolysis of hemicellulose, swelling of



cellulose, decreased degree of cellulose polymerization, increased polysaccharide porosity essentially required for adsorption, and significant removal of lignin-containing polysaccharides resulting in better cellulose access. Alkaline pretreatment is more applicable to biomass containing low amounts of lignin (such as hardwood, crop and agricultural waste) than to softwoods containing large amounts of lignin. This method's advantages include moderate operating conditions (temperature and pressure), minimal degradation of available sugar, easy recovery, and removal of existing alkalis at the end of the pretreatment process. However, some of the disadvantages of this treatment are the long treatment time and the need for highly concentrated alkaline solutions [5,6].

The presence of hydroxyl groups in lignocellulosic fibers would increase their sensitivity to moisture, chemical materials, water, and reduce the fibers' useful properties in contact with environmental conditions. The formation of hydrogen bonds between hydrophilic fibers leads to the formation of agglomerate bunches. As a result, their distribution between the non-polar matrices is heterogeneous and poor adhesion occurs between the phases. Hence, before combining cellulose fibers with polymer matrices to form composites, various physical and chemical modifications could be applied. Applying various chemical modifications to the fibers such as dewaxing, mercerization, benzolation, silanization, and cyanoethylation can increase the chemical resistance, hydrophobicity, and adhesion between natural fibers and the hydrophobic polymer matrix in the interface as shown in Figure 1 [7,8,9].

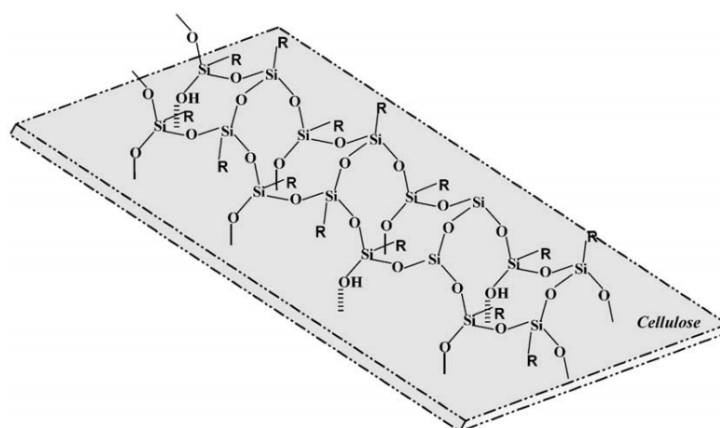


Figure 1. Schematic of the silane structure on the cellulosic substrate [10]

The aim of the present study was to prepare poly(AN-g-WS) via free radical polymerization and by applying alkaline pretreatment to WS and using the silane agent (MPS) as a coupling agent between hydrophilic and hydrophobic matrix.

2. Experimental

2.1. Materials

For the cellulose extraction, wheat straw(WS) was purchased from a local market in Urmia city, Iran. Sodium hydroxide (NaOH), acetic acid (C₂H₄O₂), acrylonitrile (AN) were purchased from Merck Co. (Germany); 3-(Trimethoxysil)propyl methacrylate (MPS), azobisisobutyronitrile(AIBN) were purchased from Sigma-Aldrich Co. (USA); ethanol (C₂H₅OH), methanol (CH₃OH), acetone (C₃H₆O) were purchased from Taghtirekhorasan Co. (Iran). All the chemicals used were of analytical grades. For the preparation of the different solutions, double distilled water was used.

2.2. Alkalization of WS



For alkali pretreatment of wheat straw, a 8% NaOH solution was prepared. The ratio of wheat straw to NaOH solution was selected as 1:20 and mixed completely at a temperature range of 60-70 °C using a mechanical mixer. This step is repeated twice each for 3 hr. After this step, the suspension was smoothed using a vacuum pump, filtered, and the resultant filtered material was washed repeatedly with distilled water until pH 7 was reached. Then, the fibers were dried at 65 °C for 24 hr and alkalinized WS was prepared.

2.3. Silane treatment of alkalinized WS

2 g of alkalinized WS was added to a three-necked flask with 60 ml ethanol and stirred for 2 hr. Then, 3 ml silane agent MPS was added dropwise to the flask. Acetic acid was used to adjust the pH of the solution to 3.5–4. In the next step, the low-pressure nitrogen was applied to the flask for 30 min to prepare an oxygen-free medium. Finally, the reaction performed at 45°C for 16 hr and at the end of the process, the WS-g-MPS was washed and filtered with methanol and oven-dried at 60 °C for 48 hr.

2.4. Graft copolymerization

For graft copolymerization process, 1 g of cellulose was added to a three-necked round-bottom flask with 55 ml of water and acetone solution with ration of 10:1 and stirred for 30 min. Then, 3.8 ml of acrylonitrile (AN) monomer was added to the flask and stirred for 30 min. The AIBN initiator was first dissolved in acetone and then added to the reactor and stirred for 30 min. Afterwards the polymerization reaction started by applying a temperature of 80 °C for 10 hr. Finally, the products were filtered and washed with DMF solvent for six times and then the final product (cellulose grafted copolymer) was placed in the oven at 70 °C for 48 hr until a constant weight of dried products were obtained.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of raw WS, alkalinized WS, silane treated WS, and poly(AN-g-WS) are shown in

Figure 2. According to this figure, there is a peak at 3426 cm^{-1} for raw WS cellulose and alkalinized WS. This peak is related to carboxyl groups (OH) on the cellulose surface, as shown in

Figure 2 (a, b). The sharp peak at around 2897 cm^{-1} is indicative of aliphatic C-H. The peak present in 1735 cm^{-1} in the raw WS, which is disappeared after modification, refers to ester chains. The 1638 cm^{-1} peak refers to a ketone carbonyl group whose intensity decreased after treatment. Mutations at 1430 cm^{-1} and 1374 cm^{-1} refer to asymmetric bending of C-H related to CH_2 , which have been much weakened after treatment. Finally, it should be noted that the peaks at around 1600, 1430, 1336, and 1220 cm^{-1} refer to the lignin group and the peaks at 1058 cm^{-1} , and 897 refer to the hemicellulose group, which has almost disappeared or weakened after alkalization pretreatment. Similar results are also reported in the literature [11,12].

In

Figure 2 (c), which is related to silane treatment, the peak at 660 cm^{-1} is attributed to the Si-C tensile bond. The peak observed near to 1150 cm^{-1} , and 1060 cm^{-1} refers to the asymmetric tensile vibrations of Si-O-Si and Si-O-C [13]. The peak around 1730 cm^{-1} , which was vanished after alkalization pretreatment, reappeared in the silane treatment step and refers to the C=O group related to the used silane factor [14,15]. In



Figure 2 (d), which is related to polyacrylonitrile on cellulose, observing the peak at 2240 cm^{-1} refers to the formation of a $\text{C}\equiv\text{N}$ bond on cellulose [16,17,18]. It should be mentioned that the decrease in the intensity of peak related to the $-\text{OH}$ group in Figure 2 (c, d) indicates the reduction of hydrophilicity of WS due to silane treatment.

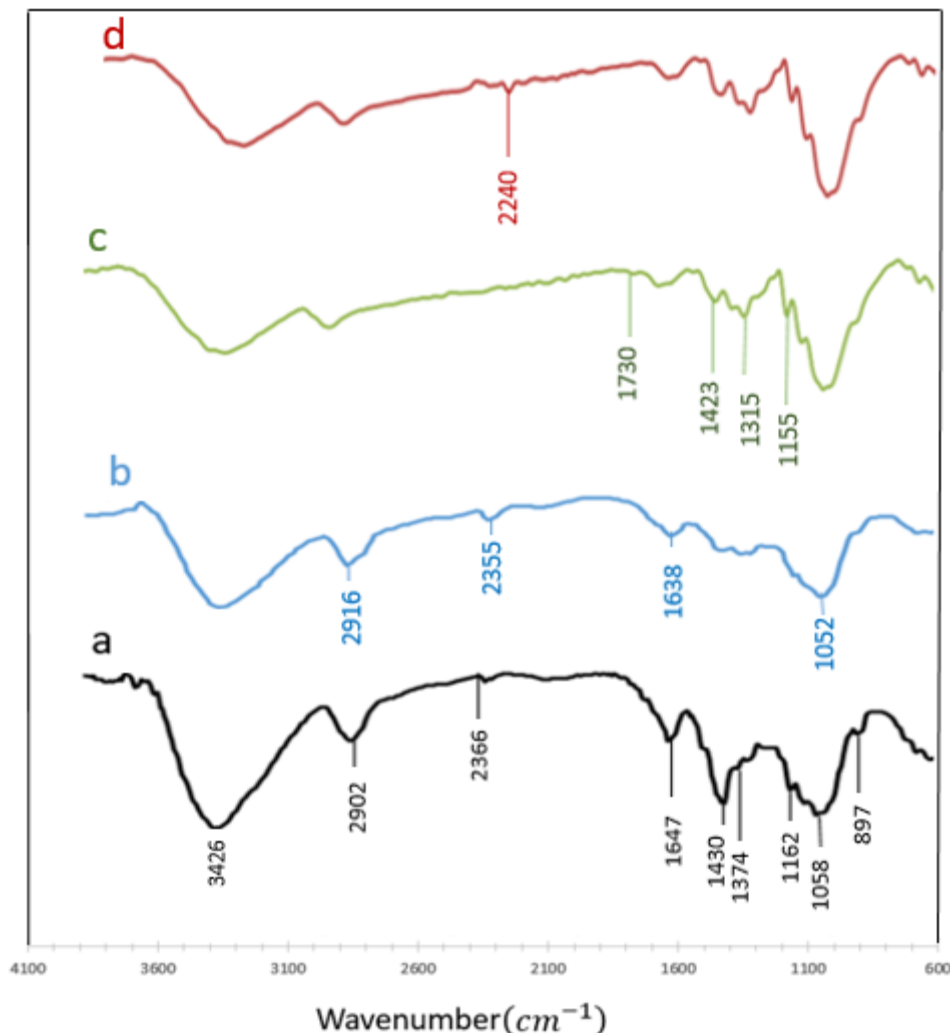


Figure 2. FTIR spectra of (a) pure WS cellulose, (b) alkalinized WS, (c) silane treated WS, and (d) poly(AN-g-WS)

3.2 XRD

The XRD spectra of pure WS cellulose and the prepared poly(AN-g-WS) is presented in Figure 3. The XRD spectrum for pure WS cellulose revealed diffraction peaks at diffraction angles (2θ) = 17.47° , 22.42° , and 35.52° which correspond to the (101), (002), and (004) diffraction planes, respectively, as shown in Figure 3 (a) [19]. While for poly(AN-g-WS), the resulting XRD pattern shown in Figure 3 (b) is identical to that shown in Figure 3 (a) except that the broad peak at 22.42° for native WS becomes broader which shows the amorphous nature, and intermolecular hydrogen bond of cellulose weakens it and thus, reduces the crystallinity [20].

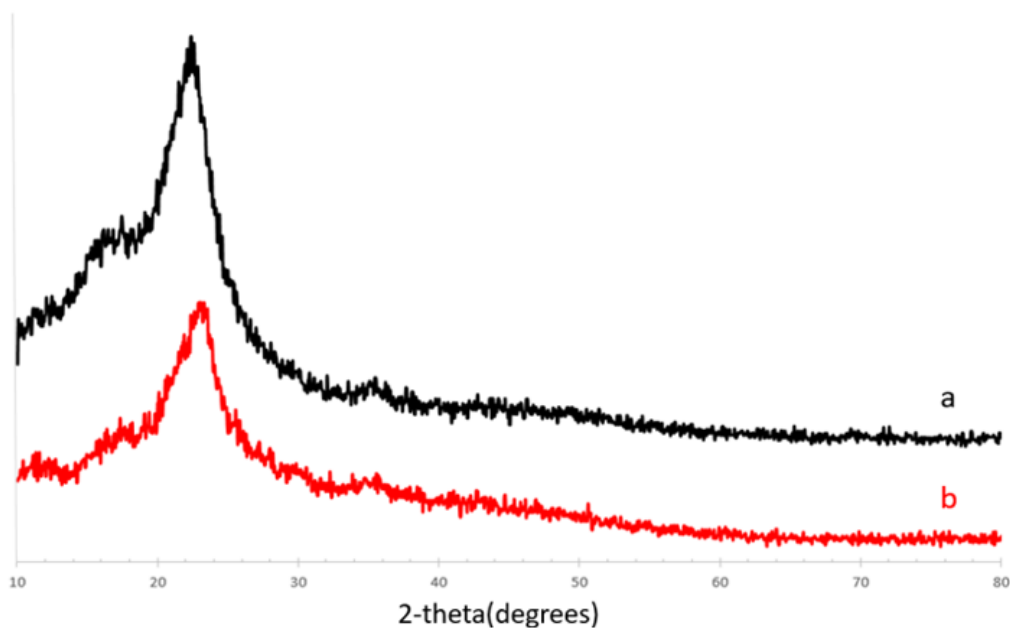


Figure 3. XRD spectra for (a) pure WS cellulose and (b) poly(AN-g-WS)

4. Conclusions

This study demonstrates the alkalization pretreatment and silanization modification of WS, which increased graft acrylonitrile potential of the pure WS cellulose substrate. The prepared poly(AN-g-WS) was characterized and shown good potential for environmental applications. Besides advantages such as availability, biodegradability, waste recycling, and cheapness, by confirming their potential applicability, they can be introduced as a proper replacement for ceramic or metal-based materials in applications such as automotive, electronic industries, marine, etc.

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