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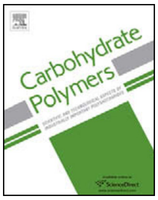

Dendronization of cellulose nanowhisker with cationic hyperbranched dendritic polyamidoamine

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ABSTRACT

Polyamidoamine (PAMAM) dendrimers with active amino group up to the third generation were grafted onto the surface of cellulose nanocrystals (CNCs) by a divergent method. Cellulose nanowhiskers (CNW) are gaining interest as a “green” nanomaterial with exceptional chemical and mechanical properties for high-performance nanocomposite materials. Cellulose nanowhiskers are usually isolated from cotton by sulfuric acid hydrolysis and hydrochloric acid hydrolysis. The grafting of PAMAM dendrimer on CNW surface was monitored using FTIR, ^{1}H NMR, DLS and AFM. The results of FTIR and ^{1}H NMR confirmed the formation of PAMAM on the CNW. AFM images indicated the PAMAM synthesis on CNW through the nano-scale structures of macromolecules. The Zeta-potential value of polymer was found to be around +25 mV, and according to the collected data, the effective diameter of the CNW-g-PAMAM particles measured through DLS technique was found to be 73 nm.

1. Introduction

Dendrimers are practically nanoscale and monodisperse highly branched molecules which have been used broadly for the development of polymeric delivery systems via encapsulation of drug and other small molecules in their interior void spaces or attached to their surface. (Lee, MacKay, Frechet, & Szoka, 2005; Zhu et al., 2010; Tomalia, Naylor, & Goddard, 1990; Tomalia, Hall, & Hedstrand, 1987; Svenson & Tomalia, 2005; Menjoge, Kannan, & Tomalia, 2010). Dendrimers, as a family of macromolecules, were discovered in the late 1970s. Since then, a great deal of research has been conducted into developing new synthetic routes as well as finding new applications for dendrimers. The unique abilities of dendrimers has led to the design of novel dendritic materials for a variety of advanced applications such as bio imaging, drug and gene delivery, cancer diagnosis and sensors (Mintzer & Crinstaff, 2011; Newkome & Shreiner, 2010; Tomalia, 2005; Esfand & Tomalia, 2001).

Dendronized polymers are formally a sub-group of comb polymers, in which the linear chains of the grafts have been replaced by dendrons. The properties of these kinds of polymers are believed to depend on a number of factors such as type of dendron, attachment density along the backbone, end-group functionality, and degree of polymerization. Because of the large number of properties that can be tailored independently in this type of architecture, several novel applications have been proposed, for example building blocks for nanometer sized construction, efficient light-emitting materials, isolating conducting polymers, complexation agents for DNA, degradable drug carriers, and support for catalysts.

Recently, dendronized polymers based on PAMAM have been developed for different applications like gene delivery systems and biopolymers utilization, and oligosacharids such as chitosan and cyclodextrins, as core polymers, have attracted considerable interest due to their appropriate properties (Zhuang et al., 2008; Sarkar & Kundu, 2012; Bertran, Zhang, Schluter, Kroger, & Aleman, 2013; Helms, Mynar, Hawker, & Frechet, 2004; Zhang, Shu, Bo, & Schluter, 2003; Adeli, Beyranvand, & Kabiri, 2013) However, as the most widely available biopolymer having a uniform structure (i.e., a b-1-4-linked polyglucan), cellulose and cellulose derivatives have attracted considerable attention. Cellulose fibers of microfibrils are assemblies with a unique structural hierarchy. They break down into short crystalline rods known as cellulose nanowhiskers through hydrolysis (Osullivan, 1997; Samir, Alloin, & Dufresne, 2005; Dash, Li, & Ragauskas, 2012; Liu, Liu, Yao, & Wu, 2010; Hubbe, Rojas, Lucia, & Sain, 2008; Nishino, Takano, & Nakamae, 1995; Pooyana, Tannenbaumc, & Garmestanib, 2012; Habibi, Lucia, & Rojas, 2010; Bielawski, Bielawska, Muszynska, & Popławska, 2011). Cellulose nanowhiskers (CNWs) have been a subject of intense investigation due to their exceptional physical and mechanical properties, nanoscale dimension, high specific strength,

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availability, biodegradability and ability to be functionalized with specific surface chemistries through a variety of chemical processes (Guo & Catchmark, 2012; Zhang, Wanga, Xu, &Cheng, 2012).

In the present study, the grafting of cationic hyperbranched dendritic PAMAM onto the surface of cellulose nanowhisker was investigated with the purpose of preparing a modified cellulose nanowhisker. First, the cellulose nanowhisker was synthesized via acid hydrolysis process and then the obtained nanowhisker was tosylated. The tosylated cellulose nanowhisker was utilized as a rode-like core nanostructure and denderonized by using PAMAM dendrons up to 3 generation through divergent method. Finally, the obtained cellulose nanowhisker-g-PAMAM was characterized by using FT-IR and NMR spectroscopy. The morphology and size of resulting CNW-g-PAMAM were investigated, using AFM microscopy and DLS technique.

2. Experimental

2.1. Materials

The cellulose material used in this study was commercial cotton linters. *p*-Toluenesulfonyl chloride, urea, ethylene diamine, methyl acrylate, and methanol were purchased from Merck. Ethylene diamine, methyl acrylate, and methanol were purified by distillation before the synthesis of PAMAM branches. The other chemicals used in the study were of analytical grade and used as received.

2.2. Measurements

2.2.1. NMR spectroscopy

NMR spectra analysis were performed on a Bruker 250 MHz for a proton isotope at room temperature with a pulse angle of 30°, a delay time of 10 s and an acquisition time of 2 s. Samples were dissolved in DMSO-d_6 with a concentration of 15% w/v at 60 °C. Also, HMDS was used as the internal standard for NMR, and all of the chemical shifts were reported in parts per million (ppm).

2.2.2. FT-IR spectroscopy

All FT-IR spectra were collected with a FT-IR Bruker-Tensor 270 spectrometer. The cellulose nano whiskers and their derivatives were prepared as potassium bromide pellets at a weight ratio of 5/200 mg.

2.2.3. Atomic force microscopy (AFM)

Atomic force microscope (AFM) imaging was performed using a Dimension 3100 series Scanning Probe Microscope (Veeco Metrology Inc., Santa Barbara, CA). The AFM was operated in tapping mode using a rectangular silicon cantilever NSC 15/AIBS (Mikro-Mash Wilsonville OR) with a tip radius of <10 nm, a typical resonance frequency of 325 kHz, and a force constant of 46 N/m.

2.2.4. Dynamic light scattering (DLS)

The particle size and size distribution of modified cellulose nano-whisker was determined by dynamic light scattering (DLS) using a 90 Plus particle size analyzer equipped with diode laser operating at 658.0 nm. The sample of modified cellulose nanowhisker was diluted with distilled water to adjust the solid content to 0.05 wt% and was directly placed in the cell. All the measurements were carried out at 25 °C.

2.3. Method

2.3.1. Preparation of the cellulose nanowhisker

The Cellulose nanowhiskers were prepared following the reported hydrolysis procedure in the literature (Habibi et al., 2010). In brief, the cotton linter (30 g) was cut into small fragments, treated with sulfuric acid 64% (35 ml) at 45 °C for 1 h, and stirred vigorously. The reaction was rinsed by adding 7-fold of DI water, and the sediment was centrifuged at 10,000 rpm. The precipitate redispersed in DI water. The fractions were washed by adding DI water and centrifuged at 10,000 rpm several times. Then, the resulting neutralized product was sonicated. The obtained products were freeze dried and kept in the refrigerator until they were used.

2.3.2. Tosylation of cellulose nanowhisker

The tosylated cellulose nanowhisker was prepared according to the authors' previous study (Dadkhah Tehrani, & Neysi, 2013). Briefly, 0.5 g Cellulose nanowhisker was merserized in 35% NaOH and dried in a vacuum over night at room temperature. The merserized cellulose nanowhisker was added to 12.5 ml of pyridine and then, 5.91 g of *p*-toluenesulfonyl chloride was slowly added to the mixture below 10 °C. The reaction mixture was stirred at room temperature for 1 day. Afterwards, it was poured into 50 ml cold water and filtered. The tosylated cellulose nanowhiskers were washed with cold water three times. Then, they were further purified by extracting with anhydrous methanol in a Soxhlet extraction apparatus for 25 h and dried in a vacuum over night at 50 °C.

2.3.3. Preparation of amino functionalized cellulose nanowhisker

The tosylated cellulose nanowhisker mixed with ethylenediamine in methanol solution under a nitrogen atmosphere at 45 °C for 24 h. The obtained product was washed three times with methanol to gain the amine-functionalized CNW (termed G0 CNW).

2.3.4. Preparation of CNW-g-PAMAM

First, second and third-generation PAMAM dendrimers were synthesized on the amino functionalized cellulose nanowhisker. Thus, the G0 CNW obtained was mixed with methanol under a nitrogen atmosphere at 40 °C and an excess of methyl acrylate was slowly added. The mixture was stirred for 24 h, followed by three washes of the resulting ester-functionalized CNW (G0.5 CNW) with methanol. The G0.5 CNW obtained were mixed with an excess of ethylenediamine in methanol and stirred for another 24 h at 70 °C, and the resulting G1 CNW were washed three times with methanol. Michael addition reaction of amine with methyl acrylate and aminolysis of the obtained product was repeated to synthesize higher generation PAMAM dendronized CNW. The dendrimer-modified CNW was then washed three times with methanol.

3. Results and discussion

3.1. Graft polymerization

By the development of nanotechnology, surface modification of nanoparticles through surface graft polymerization, which leads to production of materials with new properties, and the application of the resulting polymer-grafted particles, have aroused great interest. The present study reported successful surface grafting of polyaidoamine onto nano-sized cellulose nanowhisker via dendrimer synthesis methodology. The grafting of hyperbranched PAMAM onto the cellulose nanowhisker surface was achieved by repeating the following two steps in a methanol as a solvent: (1) Michael addition of amino groups to MA, and (2) Amidation of the obtained terminal ester groups with ethylenediamine (Scheme 1).

Chemically modified polysaccharides with enhanced properties are gaining increasing importance not only because they are inexpensive but mainly because polysaccharide segment of the product is biodegradable (Ljungberg et al., 2005; Barikani & Mohammadi, 2007). For the last few decades, graft polymerization of monomers has been one of the common, efficient and available approaches of chemical modification of natural polymers such as starch, cellulose