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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Dendronized polymers are formally a sub-group of comb polymers, in which the linear chains of the grafts have been replaced by dendrons.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

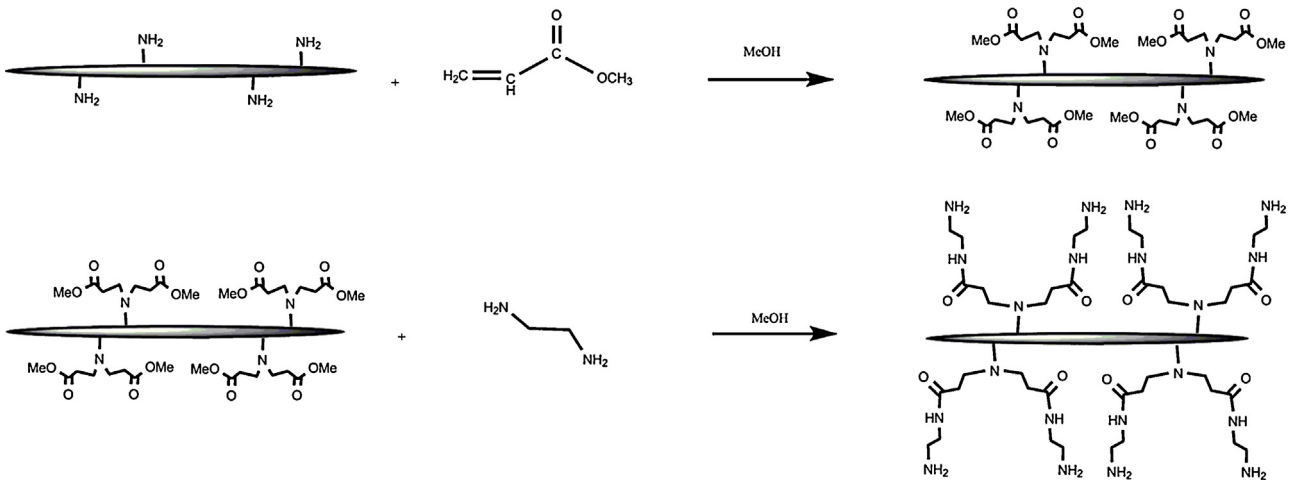
First, second and third-generation PAMAM dendrimers were synthesized on the amino functionalized cellulose nanowhisker. Thus, the G0 CNW obtained was mixed with methanol under a nitrogen atmosphere at 40 °C and an excess of methyl acrylate was slowly added. The mixture was stirred for 24 h, followed 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



Scheme 1. Typical process for preparation of CNW-g-PAMAM.

and chitosan and other high molecular weight compounds (Hasani, Cranston, Westman, & Gray, 2008).

3.2. Characterization

3.2.1. FT-IR analysis

FTIR spectroscopy of the chemical component of PAMAM is a useful tool for the analysis of the chemical components in CNW and dendrimers. Fig. 1 shows the FT-IR spectra of unmodified cellulose nanowhisker (spectrum *a*) and tosylated cellulose nanowhisker (spectrum *b*), respectively. The absorption at 3360, 2900, 1634, 1379, 1114, 1068, and 892 cm^{-1} are associated with native cellulose in the spectrum *a*. The strong absorption at 3360 cm^{-1} and at 2900 cm^{-1} is due to the stretching vibration of OH groups and C—H, respectively. The peak at 1630 cm^{-1} corresponds to the bending mode of the absorbed water (Sun, Sun, & Tomkinson, 2004b). The band at 1371 cm^{-1} is assigned to the O—H bending. The absorption band at 1114 cm^{-1} relates to C—O stretching in celluloses. A strong peak at 1068 cm^{-1} arises from C—O—C pyranose ring skeletal vibration (Sun, Sun, Zhao, & Sun, 2004a). A sharp band at 902 is characteristic of ß–glucosidic linkages between the sugar units (Gupta, Madan, & Bansal, 1987). Commonly, the introduction of functional groups onto cellulose nanowhisker surfaces is made by the reaction of the surface hydroxyl groups. In this method, the introduction of amino groups onto the cellulose nanowhisker surface as grafting sites for PAMAM was achieved by treatment of the cellulose nanoparticle with tosyle chloride and then amination of resulted tosylated cellulose nanowhisker with EDA.

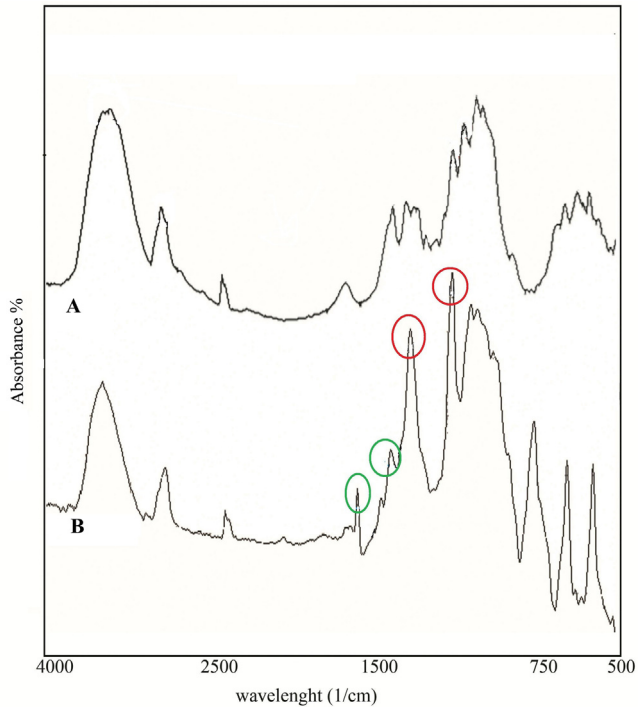


Fig. 1. FT-IR spectrum of (a) cellulose nanowhisker that preparation by sulfuric acid hydrolysis from cotton (b) tosylated cellulose nanowhisker.

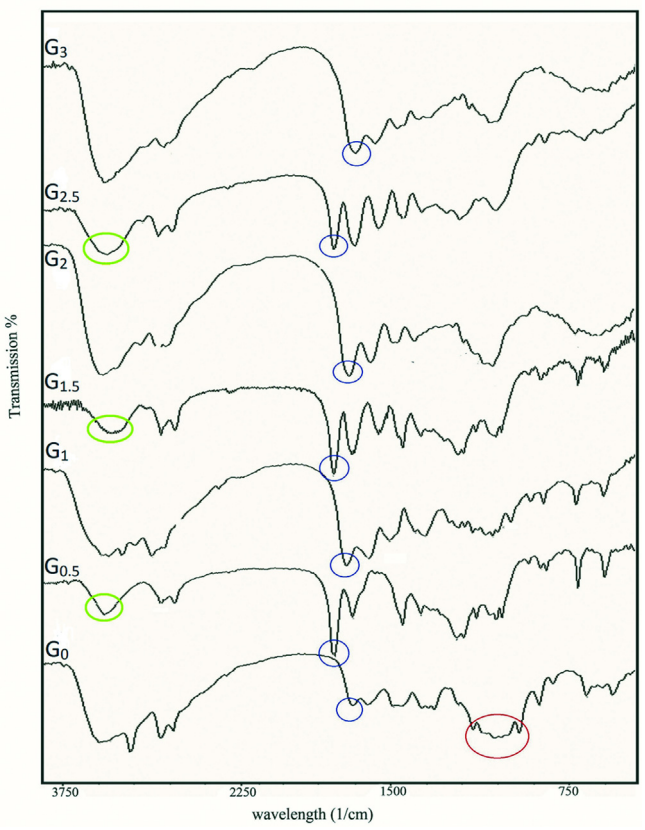


Fig. 2. FT-IR spectrum of cellulose nano whisker-supported dendrimer (G0 up to G3).

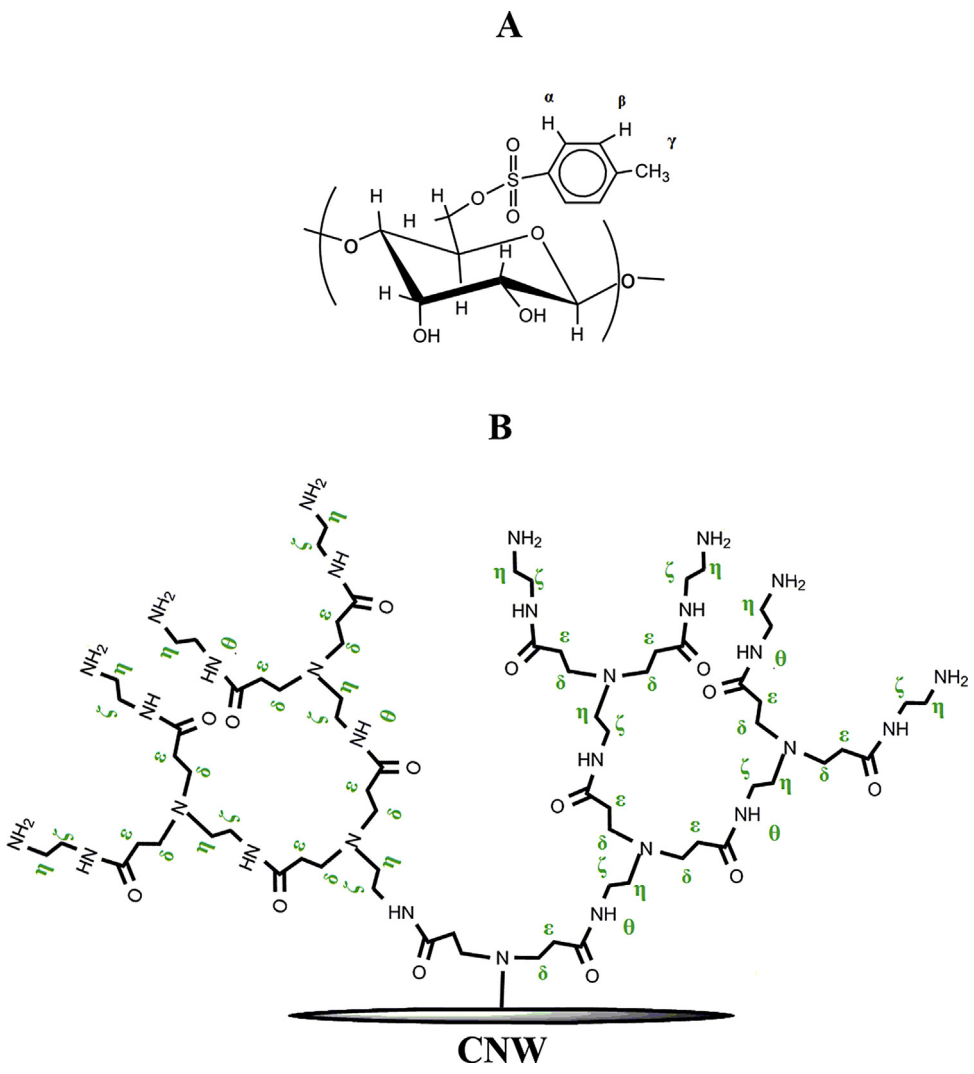


Fig. 3. Molecular structure of (a) tosylated cellulose nanowhisker (b) G3 of PAMAM dendrimer that grows on cellulose nanowhisker.

FTIR spectrum of tosylated CNW is shown in Fig. 1b. As presented in Fig. 1b, the peaks at 1172 cm^{-1} and 1361 cm^{-1} are related to the sulfone symmetrical and unsymmetrical stretching vibration, respectively. Also, the peaks at 1450 cm^{-1} and 1598 cm^{-1} are attributed to aromatic groups and provide strong evidence for the presence of tosyl group. After the amination process, the surface hydroxyl groups converts to amino groups. Fig. 2a displays the FTIR spectrum of the aminated CNW. As shown in the figure, the peaks attributed to the aromatic ring of tosyl group at 1450 cm^{-1} and 1598 cm^{-1} have disappeared, confirming the successful substitution of tosyl groups.

Fig. 2b–g displays the FTIR spectra of the half and full generations of PAMAM grafted CNW (3 Generation), respectively. The bands between 3100 cm^{-1} and 3600 cm^{-1} are related to stretching vibrations of —NH and —OH groups. The absorption band at 1734 cm^{-1} is related to the CO stretching of the ester groups, which evidently appears in all half generation products. After the reaction of the half-generation products with ethylenediamine, the corresponding full generation is formed and the peak at 1732 cm^{-1} disappears, signifying that the reaction has taken place. Also, in the FT-IR spectra of full generations, the peaks at 2922 and 2850 cm^{-1} correspond to the C—H stretching, the strong bands at 1635 cm^{-1} could be assigned to the C=O stretching of amide groups (—CONH—), and the peaks at 1550 cm^{-1} are related to the N—H bending of the secondary amide groups. Also, the increase in the relative intensity of the above peaks could be verified by the successful growing of PAMAM dendrimers on the surface of CNW.

3.2.2. NMR analysis

The structures of the synthesized tosylated cellulose nanowhisker and cellulose nanowisker-g-PAMAM were confirmed by ^1H NMR. The ^1H NMR spectrum assignments of tosylated cellulose nanowhisker and cellulose nanowisker-g-PAMAM (G3) are shown in Table 1. The Greek symbols indicate the protons in tosyl group and PAMAM unit, as illustrated in Fig. 3.

Table 1
Chemical shift assignments for ^1H NMR of cellulose nanowhisker and CNW-g-PAMAM.

Tosylated cellulose nanowhisker		CNW-g-PAMAM (G3)	
^1H NMR assignment	Chemical shift (ppm)	^1H NMR assignment	Chemical shift (ppm)
Hα,	7.2	Hδ	2.59–2.53
H_β	7.4	H_ε	2.35–2.33
H_γ	2.38	H_ζ	3.23–3.16
		H_η	2.76–2.71
		H_θ	7.6–7.8
Glucopyranan protons	3.5–5	Glucopyranan protons	3.5–5

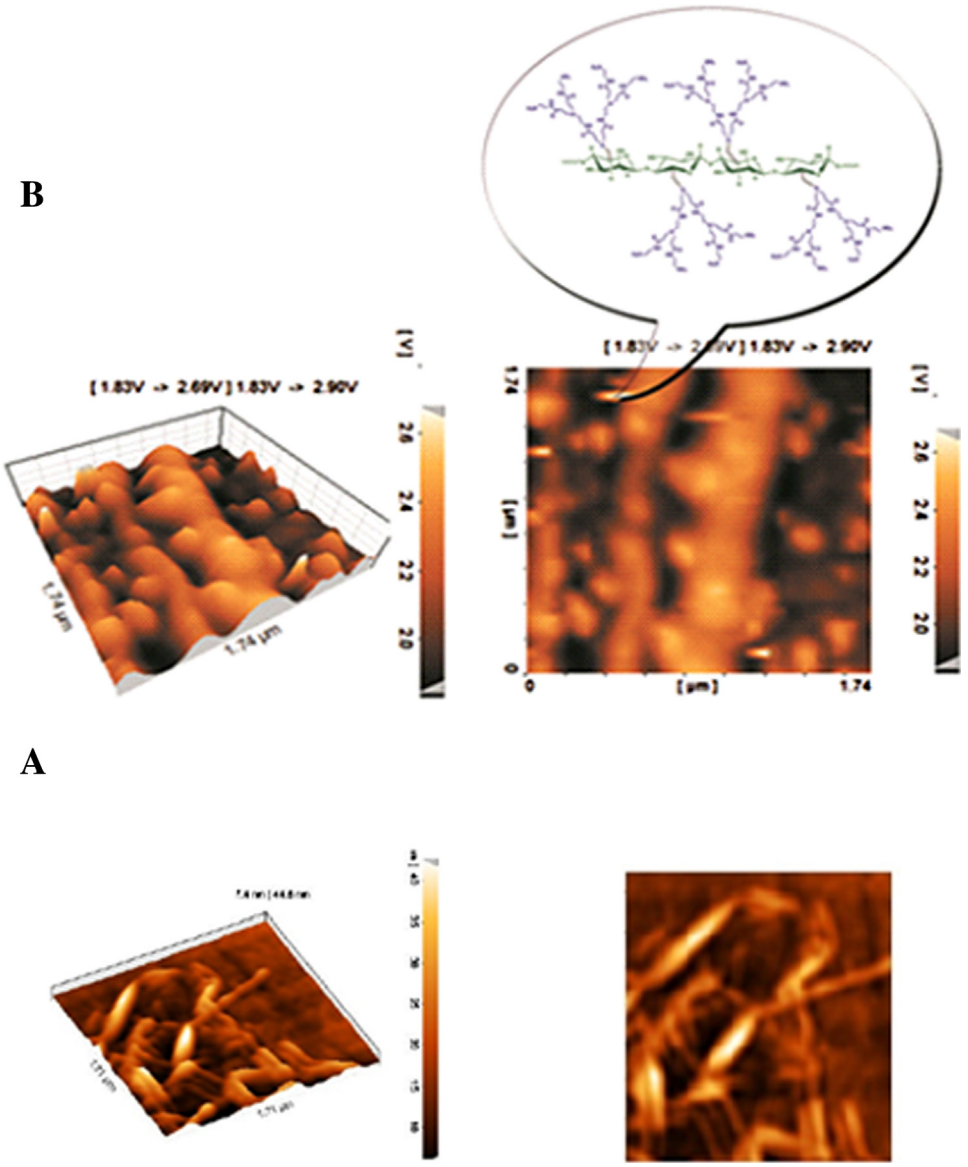


Fig. 4. AFM image of (a) aqueous solution of cellulose nanowhisker and (b) CNW-g-PAMAM (G3).

Standard ^{1}H NMR spectrum of the tosylated CNW and cellulose nanowisker-g-PAMAM were measured in DMSO-d_6 and $CDCl_3$, respectively. As listed in Table 1, the signals of the cellulose backbone chain (signals at 3.5–5 ppm) clearly indicate that the structure of the original polysaccharide remain intact. New peaks are clearly visible due to tosyl group, giving evidence for the formation of tosylated CNW. The peaks at 2.38 ppm (γ protons) are related to methyl protons of tosyl group and the aromatic region between 7.2 and 7.4 clearly shows two signals (α and ß protons) of the tosylated CNW. All the pieces of evidence from the spectra of FTIR and NMR indicate that the synthesis of the tosylated CNW was successful. Also, from the data in Table 1, it could be implied that after grafting of PAMAM moiety onto the surface of tosylated cellulose nanowhiskers the signals related to tosyl group disappear and signals related to branched PAMAM at 2.59–2.53 ppm, (δ protons), 2.35–2.33 ppm (ε protons), 3.23–3.16 (ε protons), 2.76–2.71 (δ protons) and 7.6–7.8 ppm (θ protons) appear, confirming the successful synthesis of CNW-g-PAMAM.

3.2.3. AFM analysis

The nanoscale morphology of the cellulose nanowhisker was studied using atomic force microscopy. The micrograph of cellulose nanowhiskers is given in Fig. 4a. The AFM image of a dilute suspension of CNW shows that the suspension contains cellulose fragments consisting of both individual and aggregated nanocrystals. The shape of the whiskers appears to be needle-like and have a broad distribution in size. They have lengths (L) ranging from 100 to 500 nm and widths (D) ranging from 10 to 30 nm. The exact determination of the width of the nanocrystals is very difficult because of tip broadening effect. However, this effect does not influence measurements of the cellulose whisker height, which can be determined through the whisker surface above the level of the mica surface. Furthermore, these height measurements can be used to estimate the cellulose whisker width with the assumption that the CNWs are cylindrical and their width is estimated through the height difference between mica surface and the nanocrystals (Samir et al., 2005). AFM was also successfully used to characterize G3-NH2 PAMAM dendrimers graft onto cellulose nanowhisker. As shown in Fig. 4b, after surface grafting with PAMAM, it seems that the whisker-like geometrical form of cellulose nanocrystals is preserved. In addition, it seems that the outline of the residues is covered with small spherical shape particles attributed to PAMAM moiety. The overall results of these experiments suggest that tosylation is an

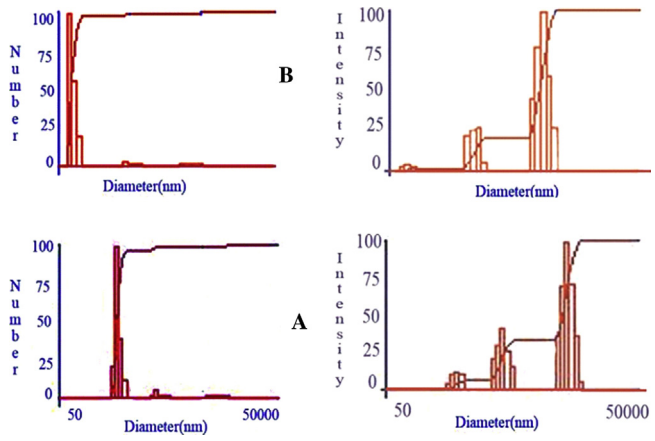


Fig. 5. DLS diagram of (a) cellulose nanowhisker and (b) cellulose nanowhisker after grafting with PAMAM dendrimer (3 generations).

effective technique for grafting PAMAM on cellulose nanocrystal.

3.2.4. DLS data

Light scattering provides additional data to describe the polymer behavior in solution. Fig. 5a and b display the DLS diagrams of the CNW before and after grafting PAMAM dendrimer (third generation), respectively. Number and intensity distributions of CNW-g-PAMAM, determined by DLS technique in water as a solvent, are shown in Fig. 4b. This technique was also used to investigate the ability of aggregates formation in solvents. There are two different distributions which can be obtained through this type of DLS measurements (Fig. 5):

(1) Number distribution by which it is possible to determinate the number of molecules of different sizes.
(2) Intensity distribution, which can give more information about aggregates formation, since large particles scatter much more light than small ones (the intensity of the scattered light is proportional to the sixth power of the particle diameter according to the Rayleigh's approximation). Intensity distribution of CNW-g-PAMAM showed three broad peak ranges from 73 nm to 2.6 μm with more intensive peak located at 2.6 μm. However, in the diagram representing the number intensity distributions, a mono modal distribution is seen. The effective diameter of the unmodified cellulose nanowhisker particles, calculated according to the collected data, was 73 nm with a narrow distribution. The chemical grafting of CNW with PAMAM most probably reduced the physical interaction of cellulose nanoparticles because of the chemical surface modification of hydroxyl groups located at the surface of the nanocrystal. Associations between molecules in the aggregates form through intermolecular hydrogen bonding between sides —OH groups, and therefore, with the decrease of surface hydroxyls groups, the particle size will decrease. Also, the absence of the peaks corresponding to the aggregates in the number distribution diagram of CNW-g-PAMAM is due to their very low amount in this product in the aqueous solution. Small quantity of the aggregates causes high dispersion of light. Accordingly, the comparison of the particle size with number and intensity indicates the possible aggregation of particles.

3.2.5. Surface charge properties

The type and number of surface functional groups play a critical role in the surface charge of the polymers. Zeta-potential of the CNW and CNW-g-PAMAM were also examined by Zeta-sizer. The Zeta-potential value of polymer was found to be around +25 mV. The first obtained unmodified CNW have a negative charge surface about −30 mV. Positively charged surface of polymer is considered to be important for their adsorption to negatively charged particles and thus for their potential application as gene delivery systems.

4. Conclusion

In the present study, cellulose nanowhiskers (CNW) dispersion was prepared from native cellulose cotton linter (NCL) by hydrolyzing with sulphuric acid. The size of resultant CNW was in the range of 30–80 nm by AFM. The obtained CNW was tosylated and used as a nano scale core for grafting PAMAM dendrons onto the cellulose nanowhiskers through divergent synthesis method. CNW-g-PAMAM up to three generations were synthesized successfully and the evidence of occurrence of chemical modifications was checked by FTIR and ^{1}H NMR spectroscopies. DLS measurements showed that the hydrodynamic dimensions of the CNW-g-PAMAM (third generation) were about 73 nm. The comparison of the particle size with number and intensity indicated the possible aggregation of particles. Zeta-potential value of the resultant product was found to be around +25 mV, while the Zeta-potential value of the native CNW is −30 mV. Also, AFM observations showed that whisker-like geometrical form of cellulose nanocrystals was preserved, and after denderonization of CNW, the presence of grafted PAMAM, as small globular residues covering the surface, is detectable.

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