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Surface modification of cellulose nanowhisker throughout graft polymerization of 2-ethyl-2-oxazoline

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ABSTRACT

The cellulose nanocrystals, prepared by acid hydrolysis of cotton linter, consisted of slender rods with an average length of 173 nm and diameter of 80 nm, respectively. The surface of obtained cellulose nanocrystals was chemically modified using tosyl chloride and then tosylated cellulose nanowhisker was used as macroinitiator for cationic ring opening graft polymerization of 2-ethyl-2-oxazoline monomer. The occurrence of chemical modification was evaluated by FTIR and ^{1}H NMR spectroscopies. Finally cellulose-g-POX was hydrolysed in acidic condition and therefore cellulose nanowhisker-g-PEI was prepared. X-ray diffraction measurements showed that the initial crystalline structure of CNW (Type I_β) was changed during graft polymerization and grafted POX in the surface of CNW was in amorphous form and DLS measurements showed that the hydrodynamic dimension of the resulted product is about 135 nm.

1. Introduction

Poly(oxazolines) have been the subject of a considerable amount of research since the 1960s, with a significant number of papers focusing on the polymerization of 2-substituted oxazolines (Aoi & Okada, 1996; Frump, 1971; Kagiya, Narisawa, Maeda, & Fukui, 1966). Although the use of poly(2-oxazolines) in adhesive and coating formulations, as pigment dispersants in inks, and in drug delivery applications has been documented (Adams & Schubert, 2007; Adeli, Zarnegar, & Kabiri, 2008). The polymers have not found widespread commercial application, as the (batch) polymerizations times range from several hours to several days (Jin, 2004; Lach, Hanselmann, Frey, & Mülhaupt, 1998; Weberskirch, Hettich, Nuyken, Schmaljohann, & Voit, 1999). Recent advances in synthetic technology, notably the advent of microwave reactors, which allow easy access to high-temperature/high-pressure synthesis conditions, have allowed the acceleration of polymerizations by factors of up to 350, when compared with conventional reflux conditions (Hoogenboom, Fijten, & Schubert, 2004; Hoogenboom, Leenen, Huang, Fustin, Gohy, & Schubert, 2006; Wiesbrock et al., 2005).

Another attractive feature of polyoxazolines is the ease of preparation of copolymers, not only block copolymers, but also of star-shaped and hyper branched motives as well as cross-linked networks (Cai & Litt, 1989; Litt & Lin, 1992; McAlvin & Fraser, 1999). Due to the versatility of this class of polymer and their ability to form functional materials and nanostructures, the interest in poly(2-acyl-2-oxazoline)-based materials is rising. Furthermore, this class of materials could be promising for use in biomedical applications (Christova, Velichkova, Goethals, & Du Prez, 2002; Hoogenboom & Schlaad, 2011).

Also as a renewable material, cellulose and its graft copolymers have been widely studied, focusing on their biological, chemical, as well as mechanical properties (De souza Lima & Borsali, 2004). The material based on cellulose and its derivatives have been used for more than 150 years in a wide variety of application, such as food, paper production, biomaterials and pharmaceuticals (Dufresne, 2010; Habibi & Dufresne, 2008). In the 1950s, Rånby reported for the first time that colloidal suspension of cellulose can be obtained by controlled sulphuric acid – catalysed degradation of cellulose fibres (Mukherjee & Woods, 1953; Rånby, 1951). This work was inspired by the studies of Nickerson and Habrle who observed that the degradation induced by boiling cellulose fibres in acidic solution reaction a limit after a certain time of treatment (Nickerson & Habrle, 1947). Transmission electron microscopy (TEM) images of dried suspensions revealed for the first time the presence of aggregates of needle-shaped particles, while further analyses of these rods with electron diffraction demonstrated that they had the same crystalline structure as the original fibres (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011).

Cellulose nanowhisker (CNW) obtained from acid hydrolysis of cellulose fibres has been realized as a new class of nano-materials. Compared to cellulose fibres, CNW possesses many advantages, such as nanoscale dimension, high specific strength and modulus,

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high surface area, unique optical properties, etc. (Moon et al., 2011). These amazing physicochemical properties and wide application prospects have attracted significant interest from both research scientists and industrialists.

The work presented here involves the chemical modification of cellulose nanowhisker with poly(2-oxazolines) via cationic ring opening graft polymerization of 2-ethyl-2-oxazoline on the surface of cellulose nanoparticles utilizing MW irradiation that can be converted to polyethyleneimine (PEI) through acid hydrolysis process. Polyethyleneimines (PEIs) are a class of cationic polymer which have been proven to be effective nonviral vectors for gene delivery system.

2. Experimental

2.1. Materials

The cellulose material used in this study was commercial cotton linters. P-toluene sulfonyl chloride was purchased from Merck and used as received. 2-Ethyl-2-oxazoline used as the monomer was obtained from Merck. It was purified by distillation and stored over molecular sieves. The other chemicals used in the study were of analytical grade.

2.2. Measurements

2.2.1. NMR spectroscopy

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

2.2.2. FT-IR

The FT-IR analysis was performed using a FT-IR Bruker-Tensor 270 spectrometer. The cellulose nano-whiskers and their derivatives were mixed with analytical grade KBr 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 <10 nm, typical resonance frequency of 325 kHz and force constant of 46 N/m.

2.2.4. Dynamic light scattering (DLS)

The particle size and size distribution of modified cellulose nanowhisker 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 directly placed in the cell. All measurements were carried out at 25 °C.

2.2.5. X-ray diffraction (XRD)

The pattern of X-ray diffraction of the samples was obtained by Siemens diffractometer with Cu-kα radiation at 35 kV in the scan range of 2θ from 2 to 30°.

2.3. Methods

2.3.1. Preparation of cellulose nanowhisker

Briefly, the cotton linter (30 g) was first cut into small fragments, the obtained cellulose was transferred into 2% NaOH solution (100 ml) during which the mixture was stirred vigorously with a mechanical stirrer. The slurry was then filtered and thoroughly washed with DI water until the wash water was neutral pH, the resulting cellulose fibres were air-dried, and then added to 65% H_2SO_4 (35 ml) in a 45 °C water bath for 1 h, after hydrolysis process, the fibre slurry turned into milky colloid suspension, the mixture was then transferred into centrifuge bottles and centrifuged. The fractions were continuously washed by addition of DI water and centrifuged at 2000 RCF. After washing, the products were neutralized with NaOH to PH 7, the neutralized products were sonicated at 80 °C for 5 h, the thoroughly washed products were freeze dried and stored at 5 °C for further testing (Habibi, Lucia, & Rojas, 2010).

2.3.2. Tosylation of cellulose nanowhisker

Cellulose nanowhisker (0.5 g) was placed in 12.5 ml of 36% NaOH aqueous was separated by filtration, washed with methanol until the washing became neutral to phenolphthalein, and dried in a vacuum for 10 h at room temperature. The cellulose nanowhisker thus mercerized and added to 12.5 mL of pyridine then to the mixture, 5.91 g of P-toluene sulfonyl chloride was slowly added below 10 °C. Then, the mixture was stirred for 1 day at room temperature, poured into 60 ml cold water, and separated by filtration. The washing of the tosylated cellulose nanowhisker with cold water was repeated three times. Then, the tosylated cellulose nanowhisker was further purified by extracting with anhydrous methanol in a Soxhlet extraction apparatus for 20 h and dried in a vacuum for 20 h at 50 °C to give 0.478 g of the tosylated cellulose nanowhisker.

2.3.3. Preparation of CNW-g-POX under microwave irradiation

Tosylated cellulose nanowhisker (initiator, 0.5 g) and 2-ethyl-2-oxazoline reagent (1 ml) were added in microwave vial then reaction mixture was heated for 13 min to 360% MW power. After heating, the polymerization mixture was quenched by addition of water finally the polymerization mixture was cooled to room temperature and purified with methanol then dried in a vacuum. The CNW-g-POX copolymer was obtained as a light-yellow powder: yield 0.5 g. The resulting CNW-g-POX copolymer was analysed by ^{1}H NMR spectroscopy.

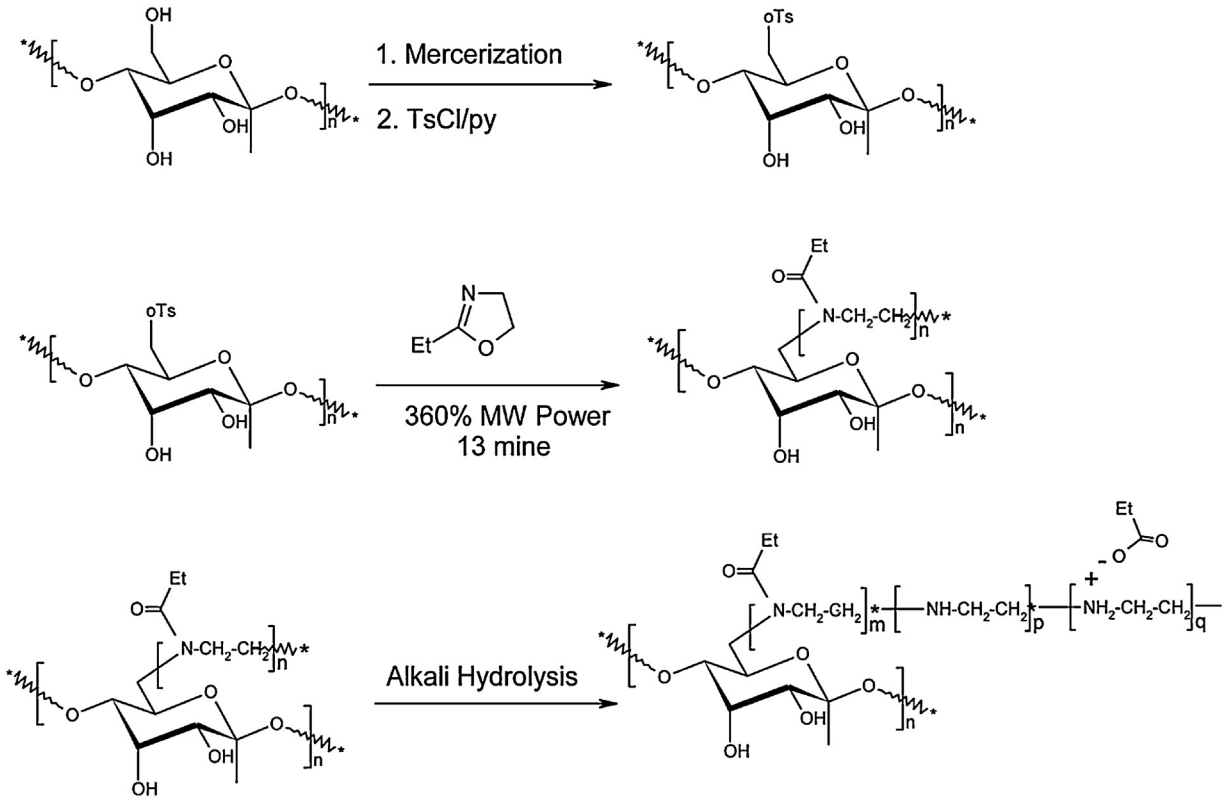
2.3.4. Preparation of CNW-g-PEI

To 0.05 g of resulted (CNW-g-POX) copolymer was added 0.5 ml of a 0.1 N solution of HCl in H_2O the hydrolysis mixture was kept at 98 °C for 3 h. After 3 h the pH of mixture was neutralized to pH 7.1 with use of NaOH solution, finally the obtained CNW-g-PEI dialysis in deionized water and dried in a vacuum.

3. Results and discussion

3.1. Graft polymerization

Chemically modified cellulose and cellulose nanowhiskers with improved properties are gaining increasing importance not only because they are low in cost, but also mainly because polysaccharide portion of the product is biodegradable (Ljungberg et al., 2005). For the last few decades, graft polymerization of monomers is one of the universal, effective and accessible methods of chemical modification of high molecular weight compounds, and natural polymers in particular (Hasani, Cranston,



Scheme 1. Typical process for preparation of CNW-g-PEI from cellulose nanowhisker.

Westman, & Gray, 2008). Grafting can be carried out in such a way that the properties of the side chains can be added to those of the substrate polymers without greatly changing the latter (Habibi et al., 2008). In this study at first cellulose nanowhisker was prepared and then the macroinitiator, tosylated cellulose nanowhisker, was prepared by the tosylation of the surface hydroxyl groups of the CNW with tosylchloride. The resulted macroinitiator was used for cationic ring opening polymerization of 2-ethyl-2-oxazoline monomer utilizing MW technique. Finally CNW-g-PEI was prepared from acidic hydrolysis of CNW-g-POX. Pathway was used, as represented by the reaction shown in Scheme 1.

3.2. Characterization

3.2.1. FT-IR analysis

Fig. 1a shows the FT-IR spectrum of pure cellulose nanowhisker (CNW), where the % of transmittance is plotted as a function of wave number (cm^{-1}). The wide peak around 3411 cm^{-1} is attributing to the O—H stretching vibrations of CNW. The peaks from the FTIR spectrum of tosylated CNW at 1173 cm^{-1} and 1361 cm^{-1} attribute to the sulfone symmetrical and unsymmetrical stretching vibration, respectively and showed the presence of tosyl groups (Fig. 1b). In this case, the peaks at 1450 cm^{-1} and 1598 cm^{-1} related to aromatic groups are also the strong evidence of the presence of tosyl group.

Fig. 1c and d displays the FTIR spectra of the CNW-g-POX before and after hydrolysis respectively. In Fig. 1c the characteristic peaks of the C=O stretching vibrations of the —CONH group of POX appeared at 1641 cm^{-1}. In addition, bands at 1000–1300 cm^{-1} in the spectrum of the graft copolymer were due to the C—O—C stretching vibrations of the glucose unit of CNW. The result indicated that the product was composed of POX and CNW. Also the peaks at 1450 cm^{-1} and 1598 cm^{-1} related to the aromatic ring of tosyl group have been disappeared, which confirmed the successful graft polymerization.

After hydrolysis process the POX moieties in the graft copolymer (CNW-g-POX) will convert to polyethyleneimine. Fig. 1d is corresponded to CNW-g-POX after Hydrolysis. The absorption peak at

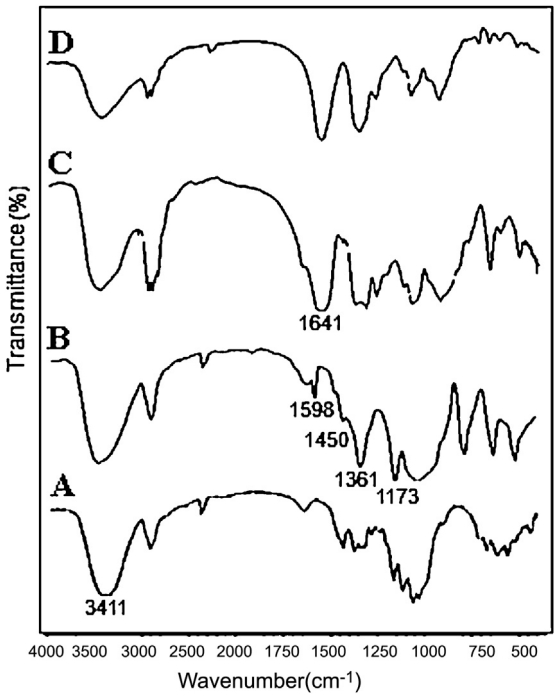


Fig. 1. FT-IR spectrum of (A) cellulose nanowhisker, (B) tosylated cellulose nanowhisker, (C) CNW-g-POX and (D) CNW-g-PEI.

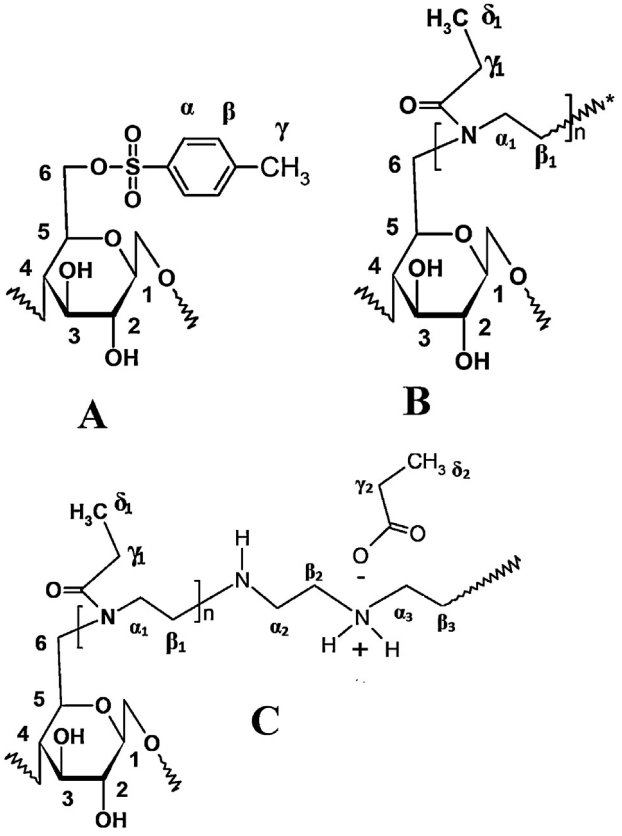


Fig. 2. Molecular structure of (A) tosylated CNW, (B) CNW-g-POX and (C) CNW-g-PEI.

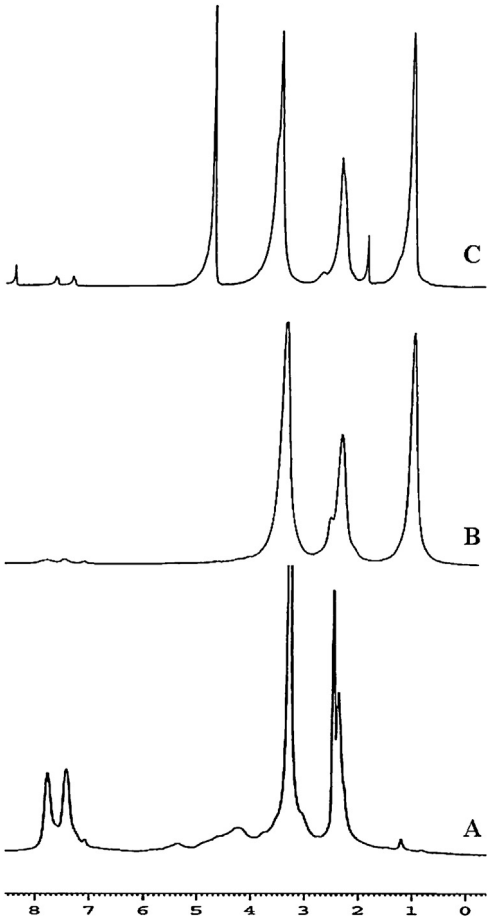


Fig. 3. ^{1}H NMR spectrum of (A) tosylated cellulose nanowhisker in DMSO-d6, (B) CNW-g-POX and (C) CNW-g-PEI.

1641 cm^{-1} related to the C=O stretching vibrations of the —CONH group of POX in this spectrum has been reduced significantly that confirms the hydrolysis of POX has been done.

3.2.2. NMR analysis

The structure of synthesized tosylated CNW, CNW-g-POX and CNW-g-PEI was confirmed by ^{1}H NMR. Numbers 1–6 denoted the protons in the glucosidic rings of CNW and the Greek symbols indicate the Protons in tosylate group, POX and PEI units as illustrated in Fig. 2.

Standard ^{1}H NMR spectrum of the tosylated CNW was measured in DMSO-d_6. Fig. 3a shows a representative ^{1}H NMR spectrum of tosylated CNW. As shown in Fig. 2a, the signals of the cellulose backbone chain (signals at 3–5 ppm) obviously, indicate that the structure of the original polysaccharide remained; new peaks due to tosyl group are all detectable, as evidence of the formation of tosylated CNW in agreement with the above-mentioned FT-IR results. The resonance signal at 2.38 ppm (γ protons) was ascribed to methyl protons attach to aromatic ring of tosyl group and the aromatic region between 7.4 and 7.7 clearly exhibits two signals (α and β protons) of the tosylated CNW. All the evidences from the spectra of FTIR and NMR indicate that tosylated CNW was synthesized successfully.

Fig. 3b shows the ^{1}H NMR spectrum of the CNW-g-POX in DMSO-d_6. In this spectrum signals related to aromatic group are disappear and signals related to polyethylene oxazoline at 1.1 ppm (δ1), 2.42 ppm (γ1) and around 3.4 ppm (α1 and β1) are appear that this signals confirm the successful synthesis of CNW-g-POX.

Fig. 3c shows the ^{1}H NMR spectrum of the partially hydrolyzed CNW-g-POX (CNW-g-PEI) in D_2O. In this spectrum signals at 3–5 ppm related to the cellulose nanowhisker protons and proton peak in ethyleneimine unit was appeared at 3.4 ppm. Residual amount of hydrolysis product, propionic acid, which might be ionically bound to protonated secondary amine group, was also detected (peak at 1.1 ppm corresponding to δ3 and peak at 2.2 ppm corresponding to γ3). Even after extensive dialysis and purification with anion-exchange resin, a residual amount of propionic acid could not be fully removed. This observation was in agreement with literature and confirms partial hydrolysis of CNW-g-POX. Also it must be mentioned that the solubility of resulted CNW-g-PEI in water has improved significantly through hydrolysis process that it can be another evidence of partial hydrolysis of POX moieties and formation of N-propionyl ethyleneimine unit.

3.2.3. AFM analysis

The cellulose nanocrystals were characterized by atomic force microscopy. A typical AFM image obtained from the concentrated and dilute suspension of hydrolyzed cellulose (CNW) is shown in Fig. 4a and b respectively. The AFM micrograph of cellulose nanocrystals in dilute solution indicates that they exhibit a whisker like morphologies with sizes ranging from 80 to 150 nm and the suspension contains cellulose fragments consisting of both individual and aggregated nanocrystals. One problem here is the whiskers' tendency to aggregate to form bundles, as seen in Fig. 4b in more concentrated solutions the cellulose nanowhiskers could be aggregated and therefore particles with higher size will be formed.

Also the typical height profiles of the cellulose whiskers in concentrated and dilute solution were shown in Fig. 4a and b respectively. As shown in Fig. 4a in dilute solution the difference between the lowest and the highest point to give a height of 16.1 nm which is in agreement with others observations (Lahiji et al., 2010).

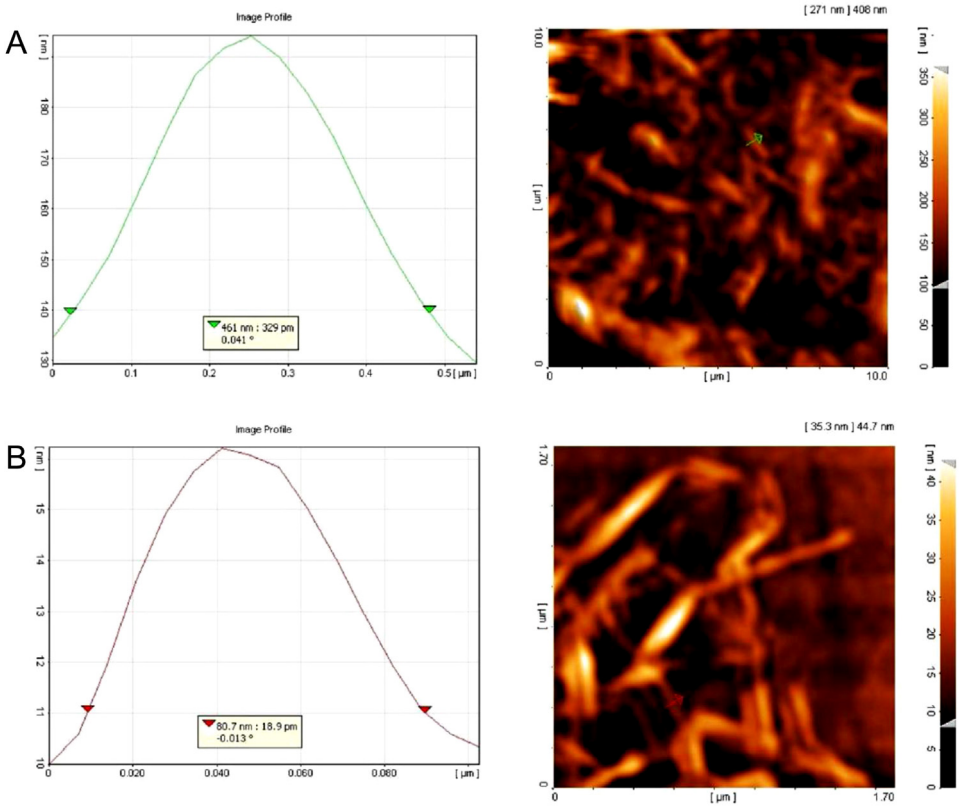


Fig. 4. AFM image and height profile of (A) concentrated aqueous solution of cellulose nanowhisker and (B) dilute aqueous solution of cellulose nanowhisker.

However in concentrated solution of cellulose nanowhiskers as shown in height profile in Fig. 4b the difference between the lowest and the highest point to give a height of about 65 nm which is due to aggregation of cellulose nanowhiskers in concentrated solution.

3.2.4. X-ray diffraction

The crystallographic nature of the CNW, CNW-g-POX and CNW-g-PEI were further investigated by X-ray diffraction. XRD provides evidence of the crystal morphology. As shown in Fig. 5, the diffractogram of CNW shows a clear cellulose I_β polymorph with the 0 0 2 diffraction centred around 22.7°, and the double peak signal at 14.5° and 16° for 1 1 0 and respectively. A small peak around 20° due to 1 0 2 diffraction is also noticed. The intra and intermolecular hydrogen bonds were responsible for the highly ordered crystalline structure.

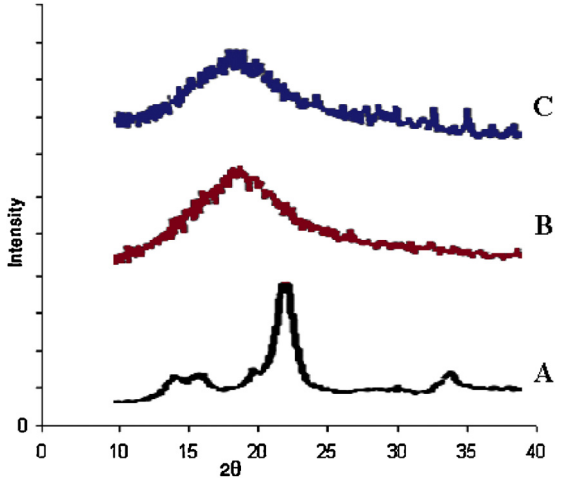


Fig. 5. X-ray diffraction patterns of (A) unmodified cellulose nanocrystal, (B) CNW-g-POX and (C) CNW-g-PEI.

The lateral crystallite size (L(0 0 2)) corresponding to the structural order of the 0 0 2 reflection was calculated from the integral breadth of the peak according to Scherrer's equation (Patterson, 1939). Also the value of the interplanar spacing between the atoms in the crystal, d, can be calculated using the Bragg equation. Crystallite size of 0 0 2 reflection (L(0 0 2)) and the calculated interlayer distance (d(0 0 2)) for cotton cellulose whiskers were 7.82 Å and 65.54 Å respectively. In fact, each cellulose nanowhisker is consist of several aggregation of crystalline parts that connected by small domains of amorphous sections therefore the observed size of cellulose nanowhiskers by AFM technique is larger than calculated size by mean of XRD data.

The XRD patterns of CNW-g-POX before and after hydrolysis are shown in Fig. 5b and c respectively. Comparison of the XRD pattern in Fig. 5b and c with that for cellulose nanowhisker in Fig. 5a reveals that the XRD pattern of the cellulose nanocrystals has been changed after chemical modification via graft polymerization. After graft polymerization, only a main broad diffraction pattern of CNW at around $2\theta = 20°$ was found and the count rate of pure CNW was further reduced. It can, therefore, be inferred that polymer side chains replaced some of the hydroxyl groups on CNW, reducing the formation of intermolecular hydrogen bonds and thereby the destruction of the ordered crystalline structure or the dehydration during vacuum drying at 60 °C. However, in the XRD pattern of cellulose nanoparticles, no peak was observed after modification corresponding to crystalline phase of POX (crystalline POX shows two main diffraction peak at $2\theta = 21.5°$ and 23.9°) that is due to amorphous nature of POX moiety in graft copolymer. XRD pattern of CNW-g-PEI (Fig. 5d) is similar to XRD pattern of CNW-g-POX that is in agreement with NMR result and solubility behaviour of

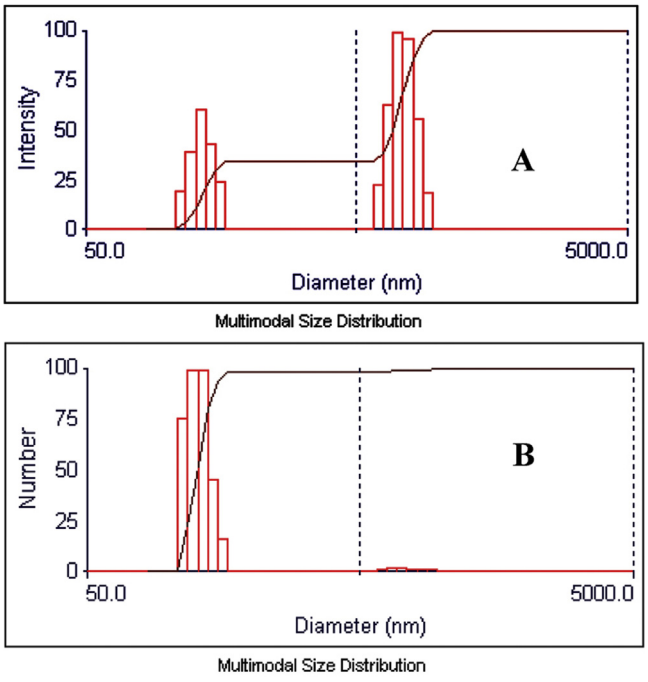


Fig. 6. DLS diagram of CNW-g-PEI (A) intensity distribution and (B) number distribution.

CNW-g-PEI confirms that hydrolysis carried out only partially because fully hydrolysed POX is in crystalline form and therefore insoluble in water.

3.2.5. DLS data

In order to determinate the hydrodynamic dimensions of the resulted product (CNW-g-PEI) in solution, dynamic light scattering (DLS) measurements were performed. This technique was also used to investigate the ability of aggregates formation in solvents. There are two different distributions which can be obtained with this type of DLS measurements (Fig. 6):

Number distribution from which it is possible to determinate the number of molecules of different sizes.

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).

As shown in Fig. 6, are presented number and intensity distributions of the CNW-g-PEI, determined with DLS technique in water as a solvent. In the graphics which represent number and intensity distributions of the different sizes of product at 132 nm and 709 nm, the presence of the aggregates at 709 nm can be detected. The absence of the peaks corresponding to the aggregates (709 nm) in Fig. 6b is due to their very low amount in this product. On the other side, the presence even of the small amount of the aggregates leads to the high scattering of the light which further induces the appearance of the second distribution of the peaks in the graph for the intensity distribution. Associations between molecules in the aggregates probably arise from intermolecular hydrogen bonding between end —OH and —NH groups.

4. Conclusion

Cellulose nanowhiskers (CNW) dispersion was prepared from native cellulose cotton linter (NCL) by hydrolyzing with sulphuric acid. The size of resulted CNW was in the range of 30–80 nm by AFM. Resulted CNW was tosylated and used as macroinitiator for cationic ring opening polymerization of 2-ethyl-2-oxazoline monomer utilizing MW irradiation. The evidence of occurrence of chemical modifications was checked by FTIR and ^{1}H NMR spectroscopies. Also it was checked from X-ray diffraction analysis that the initial crystalline structure of CNW (Type I_β) was changed during graft polymerization and grafted POX in the surface of CNW was in amorphous form. Finally the side chains of obtained graft copolymer (CNW-g-POX) were hydrolyzed in acidic condition and converted to polyethyleneimine.

DLS measurements showed that the hydrodynamic dimensions of the resulted product are about 135 nm. Briefly water soluble modified cellulose nanowhisker (CNW-g-PEI) prepared from water insoluble unmodified cellulose nanowhisker which has potential application as gene delivery system.

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