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Acid mediated networked cellulose: Preparation and characterization

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ABSTRACT

High-yield networked cellulose (NC) material was prepared by sulfuric acid dissolution of microcrystalline cellulose (MCC) and regeneration in ethanol. The dissolution was studied by varying treatment temperature and time while acid concentration was kept constant at 70%. Dried NC material was studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD data revealed that the material has mainly an amorphous phase with a crystalline portion characteristic of cellulose II. TEM images confirmed the network nature of the produced material. It was noticed that, when dried, the NC material shrinks in volume while maintaining integrity and shape with an improved hardness upon shrinkage. Hardness and elastic modulus were investigated using nanoindentation and tablet hardness testing. Hardness measured via nanoindentation was 801 Pa with an elastic modulus of 9.9 GPa.

1. Introduction

Science and technology continue to move toward renewable, environmentally friendly, and sustainable materials. Cellulose and its derivatives are of growing importance in the development of sustainable polymeric materials (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose is the main component of plants, maintaining their structure, and is also found in bacteria, fungi, algae and even in animals (Sun, Zhou, & Yang, 2007). Cellulose is inexhaustible and biodegradable natural raw material characterized by interesting properties such as hydrophilicity, chirality, broad-chemical modification capacity, and the formation of different polymorphs (Klemm et al., 2006). Even though cellulose exhibits such interesting properties, there are some properties that hinder utilizing cellulose in many applications especially those where solubility and mechanical stability are important (de Souza Lima & Borsali, 2004). Dissolution of cellulose to form a homogeneous mixture with a solvent is seen as a necessary step into cellulose modification. Cellulose is insoluble in water and most organic solvents because of its supramolecular structure (Nevell & Zeronian, 1985). In order to modify its properties, several solvents and solvents mixtures have been developed to dissolve cellulose (Heinze & Koschella, 2005). The structure and properties of cellulose can be engineered and modified through dissolution and regeneration into advanced microstructures. Dissolved cellulose can be precipitated (regenerated) with the addition of an excess of a polar solvent (anti-solvent) like water, ethanol, acetone, or mixtures of them (Pinkert, Marsh, Pang, & Staiger, 2009). Significant studies have been done on the use of organic solvents, ionic liquids and NaOH media to dissolve cellulose and modify it for the development of novel materials and applications. LiCl/DMAC system has been used as solvent for cellulose to obtain functionalized materials via modified wood cellulose (Jing, Liu, Li, Wang, & Pu, 2007). Cellulose hydrogels were prepared by the regeneration of cellulose from its ionic liquid solution of 1-allyl-3-methylimidazolium chloride (Li, Lin, Yang, Wan, & Cui, 2009). Regenerated cellulose from the ionic liquid of 1-butyl-3-methylimidazolium chloride has been studied as pretreatment for enzymatic hydrolysis as a route for biofuels production (Zhao et al., 2009). Zhou and Zhangt (2000) prepared regenerated cellulose membranes having tensile strength of 89 MPa by dissolving cellulose in 6 wt% NaOH/4 wt% Urea solution. The process of cellulose dissolution and regeneration produces cellulose derivatives that can be utilized for specific applications (Akira, 2001). Acids, such phosphoric and sulfuric acid, can be utilized to dissolve cellulose. Acids are generally used to hydrolyze cellulose in order to produce fermentable sugars (Rinaldi & Schüth, 2009). The effects of phosphoric acid concentration on supramolecular structure of cellulose and enzymatic hydrolysis of the treated cellulose have been studied before (Zhang, Cui, Lynd, & Kuang, 2006). Zhan et al. observed that at a certain phosphoric acid concentration (80–86.2%) a phase transition from cellulose swelling to cellulose dissolution occurred. Regenerated amorphous cellulose precipitated from the dissolved homogeneous cellulose upon mixing with anti-solvent (cold water). Helbert and Sugiyama (1998) were able to regenerate cellulose II by dissolving crystalline cellulose (Avicel) in phosphoric acid (83%) followed by slow addition of either water or ethanol. The regenerated cellulose had low degree

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of polymerization and nano-size dimensions. The work reported on the use of phosphoric acid as a solvent highlighted a relatively low kinetics to obtain efficient dissolution (Zhang et al., 2009). On the other hand, sulfuric acid has been used before as a solvent for cellulose dissolution and hydrolysis (Xiang, Lee, Pettersson, & Torget, 2003). Concentrated sulfuric acid is capable of disintegrating the cellulose chains by breaking the hydrogen bonding between them. However, in parallel with the dissolution and the disruption process of cellulose physical structure, there are hydrolysis reactions of cellulose. Concentrated sulfuric acid has the capability of hydrolyzing cellulose chains by interacting rapidly with the glycosidic oxygen linking two sugar units in a cellulose chain (Rinaldi & Schüth, 2009). The molecular dissolution reaction mechanism of acid-catalyzed hydrolysis of cellulose is described elsewhere (Xiang et al., 2003). The reaction starts with a proton from the acid interacting rapidly with the glycosidic oxygen linking two sugar units. The breakage of the glycosidic bonds is the main step in the hydrolysis of cellulose. This causes a decrease in the degree of polymerization and degradation into sugars. In this paper we introduce an optimized method and conditions to prepare a networked cellulose material by sulfuric acid-dissolution of cellulose and regeneration into suspension. The intent here is to disrupt and introduce changes in the physical structure of cellulose before the hydrolysis chemical reaction takes place. The process of acid dissolution and hydrolysis of cellulose depends mainly on its supramolecular structure that has crystalline areas and amorphous areas (Sjöström, 1993). The selection of acid concentration is a key to the dissolution process. Previous work that investigated sulfuric acid hydrolysis of cellulose reported that acid concentrations below 64% would target the amorphous portion at an accelerated rate and the crystalline portion at a slower rate. This behavior of cellulose/64% acid mixture was utilized in isolating cellulose nanocrystals (Dong, Revol, & Gray, 1998; Revol et al., 1994). Working at higher concentrations would disrupt the crystalline structure and dissolve cellulose chains. As a result, the whole cellulose material becomes equally exposed to hydrolysis. There is a short window between the process of disruption of the crystalline structure (dissolution) and the process of hydrolysis. This process has controlled parameters which are mainly acid concentration, mixing time and temperature. This study focused on developing optimized parameters with the target of getting cellulose chains into solution while minimizing degradation and cleavage of the glycosidic bond. These chains will then be precipitated in a different form using anti-solvent such as water or ethanol. The parameters were optimized to achieve dissolution, avoid degradation and maximize yield of precipitated material. Dried films of the generated material were characterized to identify applicable properties.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC) was provided by FMC BioPolymer (Avicel-PH101). Sulfuric acid, 95–97%, Reagent Grade, was purchased from Scharlau. Ethanol was purchased from Sigma–Aldrich.

2.2. NC suspension preparation

Microcrystalline cellulose (MCC) powder was mixed with 70% (w/w) H_2SO_4 at a ratio of 1 g cellulose/10 ml H_2SO_4 using Varian Dissolution System (VK7010) at different temperatures and for different times with 250 rpm agitation. After mixing, a white material was precipitated by adding either ethanol (−17 °C) or water (4 °C) as anti-solvents. The volume of anti-solvent used was equivalent to the volume of acid used. The product was collected and washed with DI water through centrifugation three times at 4700 rpm for 10 min using Allegra™ 25R Centrifuge. Centrifugation was conducted at 4 °C. The centrifugation process resulted in separating the precipitated cellulose material from the spent liquor. The precipitate was collected again and dialyzed for 3 days until the pH is 6–7. The resultant white suspension was weighed then sonicated using Hieschler Ultrasonic Processor UP400S for 30 min. Portion of the sonicated suspension was freeze-dried using VirTis Wizard 2.0 Freeze Drier. After dialysis the yield was calculated by withdrawing a known amount of small sample and obtaining its oven-dried weight. The yield is calculated based on the solid product weight after hydrolysis and drying compared to the starting weight.

2.3. Microstructure analysis

X-ray diffractograms of the oven-dried samples were obtained on an X-ray diffractometer (PANalytical, X'Pert Pro). Microstructure images were obtained using JEOL 2011 High Contrast Digital Transmission Electron Microscopy (TEM). Samples were prepared by air drying the cellulose suspension on Quantifoil® grids (SPI).

2.4. Hardness using nanoindentation

About 25 ml of the resulting sample was taken in a small beaker and subjected to air drying in a shaker (80 °C) for few hours (~4 h) till a dry thick film was formed. The dry film was used for making samples for nanoindentation. Nanoindentation measurements were carried out at room temperature with an MFP 3D Asylum Research Nanoindenter in an acoustic box. The indenter was a cube corner tip with a spring constant of 3.78 μN/nm.

2.5. Hardness using tablet hardness tester

Tablets were prepared by casting the suspension and leaving it to air-dry for 1 day. The hardness of the resultant tablets was measured using Dr. Schleunger® Pharmaton 8M Tablet Tester.

2.6. TGA

Thermal characteristics of NC material were investigated by using thermogravimetric analyzer (TGA). The sample, 6–10 mg, was analyzed by increasing the temperature at a rate of 10 °C/min in a stream of nitrogen (20 ml/min).

3. Results and discussions

3.1. Acid dissolution and structural change

It is well reported (Hermans & Weidinger, 1946; Xiang et al., 2003) that dissolved cellulose favors regeneration into the more thermodynamically stable cellulose II microstructure. In this work, we used the formation of cellulose II as an indication for dissolution and the yield as an indication to the degree of hydrolysis. In the first set of experiments we studied the effects of acid concentration. We studied the capability of the chosen concentration of 70% to dissolve cellulose (the 70% acid concentration was chosen based on a preliminary work that is not reported here). X-ray diffraction data of the treated, washed, dialyzed and dried material are presented in Fig. 1. The data give an indication of the dissolution behavior of cellulose by clearly showing the phase change from cellulose I to cellulose II. Acid concentration of 70% was able to completely dissolve cellulose. Fig. 1 shows X-ray diffractograms of MCC before treatment compared with regenerated cellulose. The X-ray diffraction pattern of MCC is a typical pattern of crystalline cellulose I. The X-ray diffraction pattern of the regenerated material shows mainly amorphous cellulose with weak peaks characteristic of cellulose

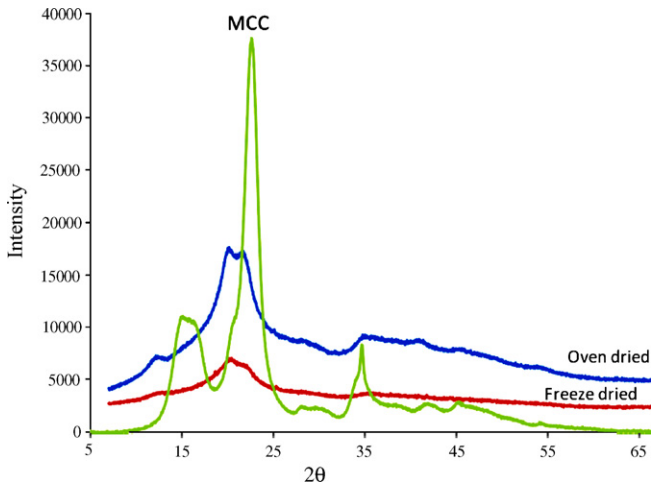

Fig. 1. X-ray diffraction pattern of microcrystalline cellulose before (MCC) and after sulfuric acid (70%) treatment at 5 °C for 30 min.

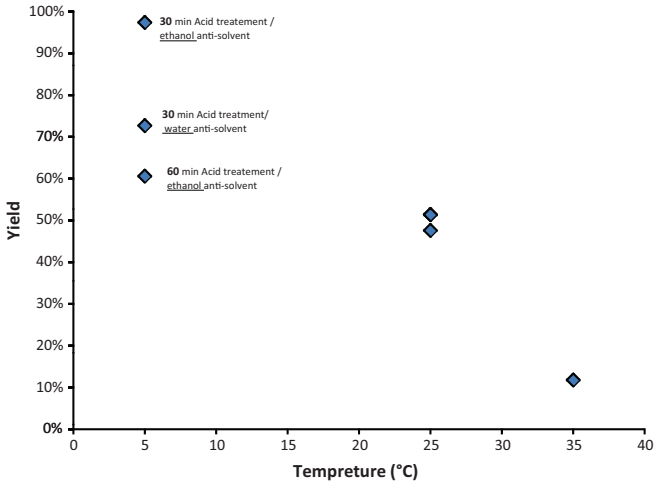

Fig. 2. Yield values of regenerated NC material as a function of temperature, data from Table 1.

II. The treatment process modified cellulose crystallinity. Cellulose was regenerated into a new, less ordered structure. A significant portion of the regenerated material is amorphous. We assume that re-crystallization occurs within the suspension at the moment of introducing the anti-solvent. Since cellulose II peaks intensity in the oven dried samples are stronger than those for the freeze dried ones, there is the possibility of cellulose II structure formation upon drying as well. It could also be possible that the freeze drying process disrupts the order in the sample and reduce its crystallinity.

3.2. High yield production

According to Table 1, different suspensions were prepared at different conditions. The data in Table 1 and Fig. 2 suggest that temperature is the main factor that affects the yield. Using conditions of NC5 (in Table 1), high yield values of 97.4% were obtained at low temperature (5 °C). Other factors such as time and anti-solvent (water or ethanol) can affect the yield as well, especially at low temperature. The results revealed that high yield values can be achieved at low temperature and short time with ethanol as a precipitating agent. We have used ethanol as a precipitating agent for two main reasons. First, it can be efficient in stopping the hydrolysis reaction by quenching and dilution. Ethanol can be cooled to low temperatures below its freezing point (−114 °C). In our work we used ethanol at regular freezers temperature of (−17 °C). The second reason for using ethanol is that future process development for mass production of acid treated cellulose will benefit from the use of ethanol as anti-solvent. Ethanol is a light material which can be easily separated from the concentrated acid upon treatment with cellulose. There are different available technologies for low cost-efficient separation of ethanol from concentrated sulfuric acid. The challenge would be to perform this separation process in an energy efficient way focusing on recovering the initial acid concentration to be recycled for cellulose treatment. One example technique for efficient separation is by using humidified air saturated with ethanol at 40 °C to strip out the ethanol from the acid mixture (Lightner, 2002).

Using the conditions of NC5 is the most efficient for the production of NC suspension because of the high yield that can be obtained by these conditions. Five replicate experiments were conducted at the same conditions as NC5 and all gave an average yield of 97.1% (SD = 0.22). The temperature and the time were optimum for the cellulose to modify and form special arrangement of its hydrolyzed chains that can be precipitated in high yield. We can also notice that despite of the identical conditions for NC5 and NC6, the yield is different. It is expected to have low yield from NC6 since water is not good as a precipitating agent. Some of the material were lost because it stayed soluble in water and then washed out.

3.3. Hardness and nanoindentation

The hardness of the resultant NC material was measured in two different ways; using tablet hardness tester and using nanoindentation. Tablets were prepared by simple casting of the suspensions and tested using Dr. Schleunger® Pharmaton 8M Tablet Tester. All the suspensions' tablets needed more than the maximum limit of the instrument, i.e. 450 N, to disintegrate. This is a high hardness value of a cellulosic material.

For measuring the hardness via nanoindentation, oven-dried samples of all suspensions were indented to a displacement of 400 nm with displacement velocity of 40 nm/s. The hardness and the elastic modulus were calculated after analyzing the resultant force–displacement curves by Oliver–Pharr model. Fig. 3 shows a sample of force–displacement curves obtained by multiple indentations to 400 nm for one of the oven-dried NC suspensions. The elastic modulus and hardness values are given in Table 2. The results of the mechanical properties of NC material support the fact that NC5 conditions are optimum. The conditions of NC5 produced hard material with an elastic modulus of 9.9 GPa.

Table 1
Different conditions for the preparation of different NC suspensions.

Run	Mass cellulose (g)	Acid volume (ml)	Acid concentration (%)	Treatment temperature (°C)	Time (min)	Precipitating agent	Yield (%)
NC1	20	200	70	35	20	Water	11.8
NC2	10	100	70	25	10	Water	47.6
NC3	10	100	70	25	10	Ethanol	51.4
NC4	50	500	70	5	60	Ethanol	60.6
NC5	50	500	70	5	30	Ethanol	97.4
NC6	50	500	70	5	30	Water	72.7

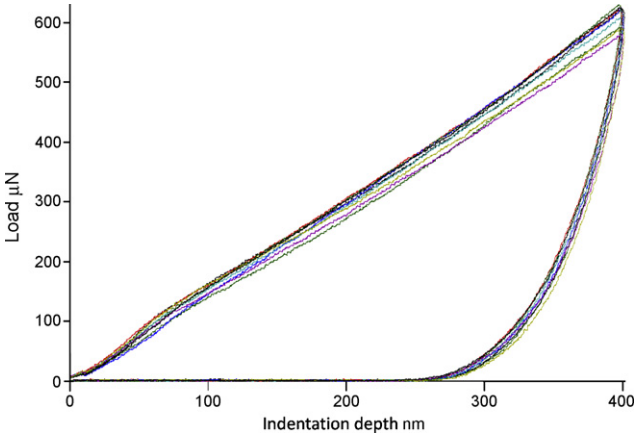

Fig. 3. Force-displacement curves for 400 nm indentations for NC material.

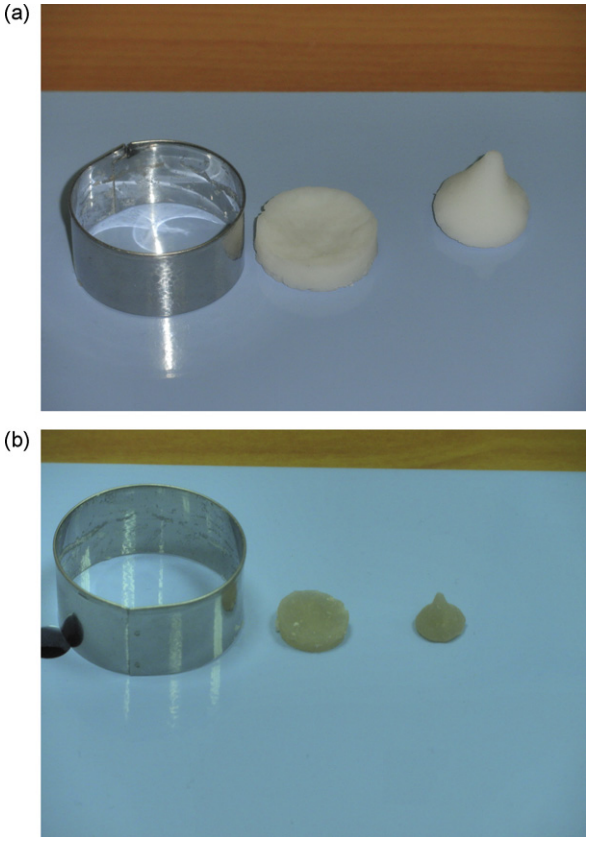

Fig. 4. Shrinkability of networked cellulose: (a) before drying, (b) after drying.

3.4. Shrinkability

The new material seems to gain significant hardness compared to starting MCC. In order to understand the reason behind this significant increase in hardness, it is worth mentioning here that, when dried, the sample shrinks significantly in volume. The sudden precipitation using the anti-solvent caused cellulose chains to connect in different ways to form a three dimensional network. The formation of this network changes the cellulose crystallinity, microstructure, morphology and as a result its properties. Shrinkability is an indication of the network nature of the material. When dried to gel form, and upon further drying, the prepared suspension shrinks while maintaining its integrity as can be seen in Fig. 4.

3.5. Microstructure imaging

Fig. 5 shows TEM images of the dried material. The images reveal a network structure. The images suggest that chains bundle together randomly. This indicates that during the regeneration process of cellulose from solution, the chains are bonded to neighboring chain when the acid solvent is withdrawn (diluted) by the addition of ethanol. However, due to the randomness and the quick precipitation, the joining of chains is limited to short lengths. Networking occurs when chains are split to join different bundles.

3.6. Thermal degradation

Thermal stability of the different NC freeze-dried samples was studied using thermogravimetric analysis. The TG and DTG curves of freeze-dried samples of cellulose (treated at conditions NC5) compared with MCC are shown in Fig. 6. From the DTG curves it is observed that, the temperature at which the maximum weight loss is triggered is 324 and 348 °C for NC and MCC respectively. The degradation behavior and drop in the weight is mainly caused by the degradation of the cellulose chains and the evolution of non-combustible gases (carbon dioxide, carbon monoxide, formic acid, and acetic acid). In addition, pyrolysis and evolution of combustible gases occur (LeVan, 1989). The degradation behavior of the NC material was different than that of MCC and showed lower degradation temperature. The onset degradation temperature for NC was 225 °C with about 20% residual weight at the end of the heating cycle. The low degradation temperature for NC is an indication that the treatment process introduced a greater number of free end chains due to hydrolysis. These end chains start to decompose at lower temperature (Staggs, 2006). Also sulfate groups, introduced during hydrolysis, can work as flame retardant in such a way they cause an increase in the char fraction (Roman & Winter, 2004). It is also observed that NC material exhibits a small peak at about 50 °C due to the evaporation of adsorbed water. The amount of adsorbed water is related to the amorphous nature of NC material. Previous study by Roman and Winter (2004) on the thermal degradation of sulfuric acid hydrolyzed cellulose suggested that sulfation is the reason the observed thermal behavior of low degradation temperatures. We tend, however, to believe that the decrease in thermal stability of the acid treated material is due to the increase in amor-

Table 2
Mechanical properties of the NC material measured via nanoindentation.

Experiment	Preparation conditions			Responses	
	Temperature (°C)	Time (min)	Precipitating agent	Hardness (Pa)	Modulus (GPa)
NC4	5	60	Ethanol	351	3.3
NC3	25	10	Ethanol	299	3.3
NC5	5	30	Ethanol	801	9.9
NC6	5	30	Water	468	7.2
MCC				434	4.2

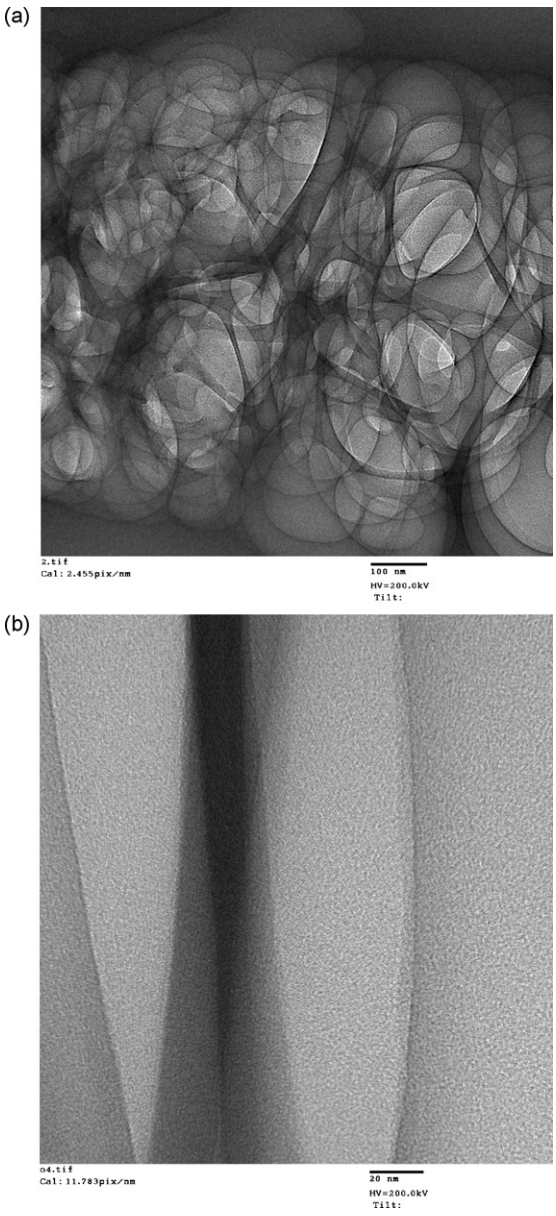

Fig. 5. TEM images for regenerated NC showing the network structure: (a) low magnification, (b) higher magnification.

phous content. The increase in amorphous material content in the sample is evidenced from XRD data and the water desorption peaks at 50 °C. Cellulose has an amazing capability of catching and holding on to water which is bound by hydrogen bonding. At the same time, water cannot penetrate cellulose if it is crystalline (Muller, Czihak, Schober, Nishiyama, & Vogl, 2000). The increased capacity of the treated samples to hold into water is a clear indication of increased amorphous portion.

3.7. Network formation mechanism

The schematic in Fig. 7 summarizes the proposed acid dissolution mechanism and possible pathway toward network formation. Due to the crystalline nature of cellulose where individual crystals consist of layers of cellulose chains bound to each other by hydrogen bonding, the concentrated acid starts by opening up this structure. When treating cellulose with concentrated sulfuric acid, dissolution occurs by disrupting the hydrogen bonds linking two chains together. Individual cellulose chains become soluble in the acid. The extent of hydrolysis (breakdown) of the acid-soluble cellulose chains will then depend on the reaction time at the given 70% acid concentration and temperature. The low temperature of 5 °C seems to be good enough to slow the hydrolysis reaction. Adding anti-solvent in which cellulose is not soluble while sulfuric acid is soluble will withdraw the acid from between cellulose chains and results in cellulose chains touching, bundling and re-crystallizing into the more stable cellulose II. Due to the randomness that occurs through mixing, bundling and re-crystallization occur in a random three-dimensional way. Significant portion of the chains do not have the conditions to re-crystallize and as a result the percentage of re-crystallization is low and is distributed throughout the sample. This is confirmed by XRD data where the bulk of the sample is amorphous with weak crystalline peaks.

3.8. Future perspective and applicability

The developed high-yield material has interesting mechanical integrity and strength that make it suitable for different applications. Currently, we are investigating its application as a pharmaceutical excipient and as a reinforcing material in polymeric composite electrolytes. In addition, the disordered microstructural

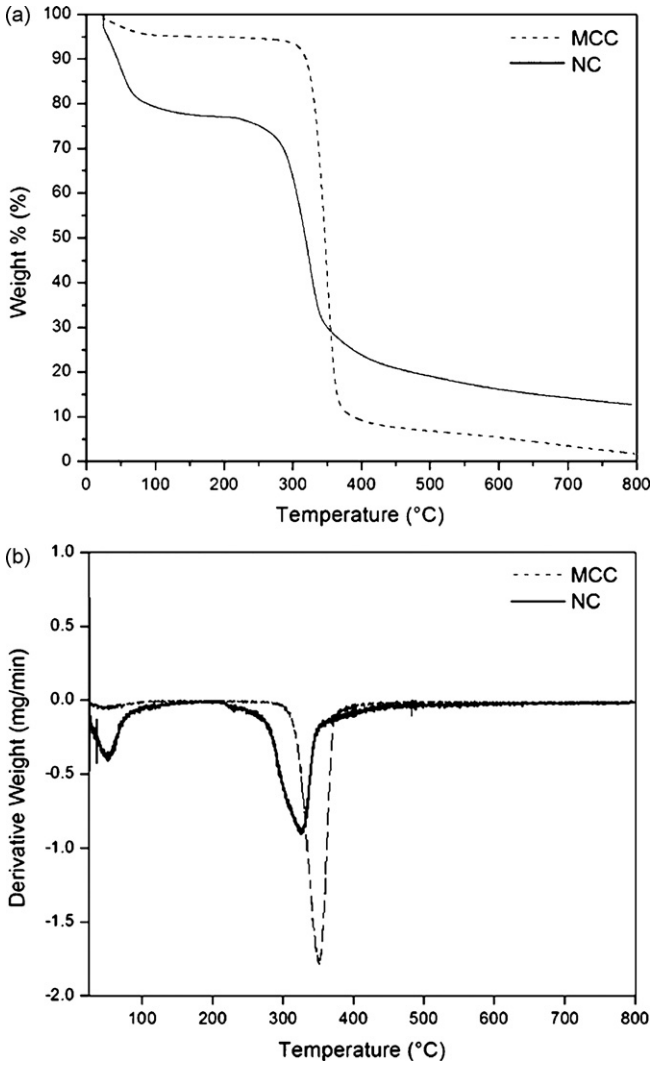

Fig. 6. Thermogravimetric analysis (a) heating curves, and (b) their first derivatives for NC and MCC.

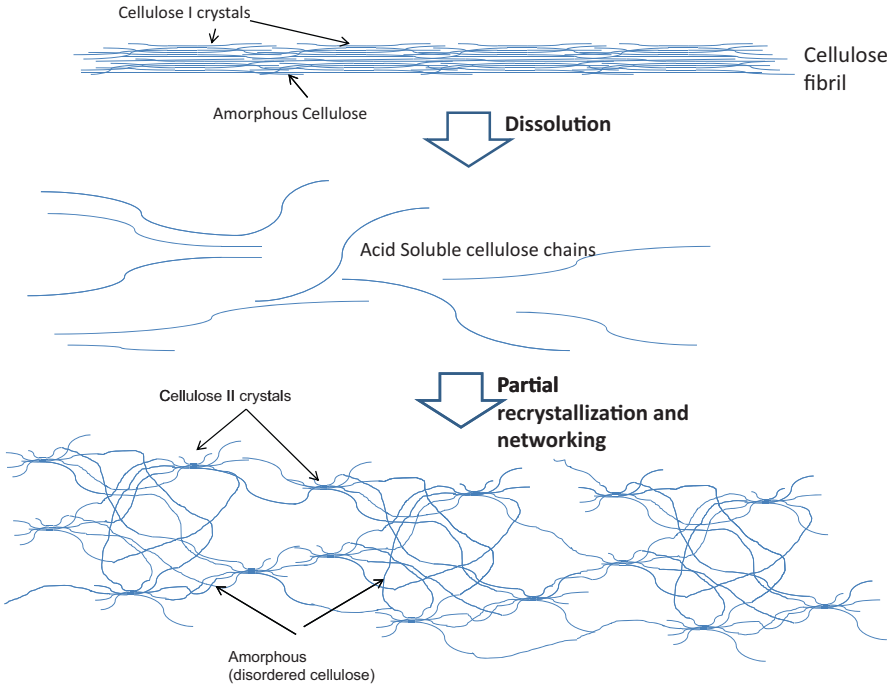

Fig. 7. Schematic representation of suggested network formation mechanism of acid mediated cellulose through partial re-crystallization.

nature of the material showed improved enzymatic hydrolyzability compared to native cellulose (Hashaikeh & Cooney, 2010) which promotes it as a pretreatment method for cellulosic biofuels production. Effective hydrolysis of cellulose into glucose can contribute to utilizing cellulosic waste as a renewable biofuels. Further investigations are in progress to evaluate the material's encapsulation capabilities to host nanoparticles and develop advanced functional composites.

4. Conclusions

Modified cellulose material was prepared via treatment with 70% sulfuric acid and then regeneration in ethanol. The treatment process was fast and efficient. Conditions were optimized to obtain almost complete recovery of the starting material with an average yield of 97.1%. The prepared suspension shows a networked fibers behavior and characteristics. The crystallinity of the starting MCC was modified from cellulose I into cellulose II. We propose that the cellulose II crystal structure occurs at the joining bundles of the network with a random distribution across the network. The NC material maintained a high thermal stability that is less than that of MCC; however, its mechanical stability is much higher. These properties make such material suitable for many applications where biocompatibility, biodegradability, sustainability, and mechanical integrity are important concerns.

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