Carbohydrate Polymers 98 (2013) 562–567

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Preparation and characterization of nano-cellulose with new shape from different precursor

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ARTICLE INFO

Article history:
Received 25 April 2013
Received in revised form 29 May 2013
Accepted 18 June 2013
Available online 26 June 2013

Keywords:
Nano-cellulose
Acid hydrolysis
Differential scanning calorimetry
Thermo gravimetric analysis

ABSTRACT

Three different precursor materials – 1. China cotton, 2. South African cotton, 3. Waste tissue papers were used to produce nano-cellulose by acid hydrolysis route. No chemical pretreatment has been done for the production of nano-cellulose from these precursors. Prepared nano-cellulose and their corresponding precursor materials were characterized by transmission electron microscopy (TEM), particle size analysis, X-ray diffraction (XRD) study, thermo gravimetric analysis (TGA), differential scanning calorimetric (DSC) analysis and Fourier transformed infra red (FTIR) spectroscopy. A comparative study of the characteristics was done with the properties of raw materials and with that of nano-cellulose. Shape and size of the nano cellulose generally depends on nature of the precursor and hydrolysis condition. Morphology study of nano-cellulose from different sources revealed range of length from 50 to 200 nm and diameter from 10 to 90 nm. Higher thermal stability and crystallinity of nano-cellulose were observed compared to that of precursor from TGA/DSC study.

1. Introduction

Cellulose is one of the most abundant and ubiquitous polymers on the planet Earth occurring in wood, cotton, hemp and other plant-based materials and serving as the dominant reinforcing agent in different matrices (Eichhorn et al., 2010; Iwamoto, Abe, & Yano, 2008; Mathew, Chakraborty, Oksman, & Sain, 2006). It has widespread application in biomedical, packaging, automobile sectors in the present age, but also in past for making of ropes, sails, paper, timber for housing and many other applications (Iwamoto, Nakagaito, Yano, & Nogi, 2005). Nano-scale celluloses like cellulose nano-fibrils, nano-whiskers, microfibrillated cellulose, and bacterial cellulose are high-value materials that serve as promising candidates for bio-nanocomposite production (Henriksson, Berglund, Isaksson, Lindstro, & Nishino, 2008; Henriksson, Henriksson, Berglund, & Lindstro, 2007; Iguchi, Yamanaka, & Budhiono, 2000). Nano-scale cellulose has different attractive properties like high strength and stiffness, low weight and biodegradability; thus getting more interest commercially and in research (Janardhnan & Sain, 2006; Klemm et al., 2006) Moreover cellulose nanocrystalls have liquid crystal properties and can show chiral nematic self-ordering in non-polar solvents (Heux, Chauve, & Bonini, 2000). Several processes have been used to extract highly purified nano-cellulose depending on their sources and pretreatment method. These methods include mechanical treatments like high pressure homogenizing (Jonoobi, Mathew, & Oksman, 2012; Qua, Hornsby, Sharma, & Lyons, 2011) chemical treatments like acid hydrolysis (Elazzouzi-Hafraoui, Nishiyama, Putaux, Heux, & Dubreuil, 2008; Habibi, Lucia, & Rojas, 2010) and biological treatments like enzymatic hydrolysis (Paavo et al., 2013). Several researchers prepared conventional nanocellulose from cotton (Das et al., 2009; Das, Ray, Bandyopadhyay, & Sengupta, 2010; Savadekar & Mhaske, 2012). As the content of cellulose in cotton fibres is very high (upwards 90%), generally, there is no need for pretreatment to obtain nano-cellulose.

The geometric properties of the nano-cellulose structures (shape, length and diameter) depend mainly on the origin of the cellulose and the extraction process (Boluka, Roya, & Mark, 2011). Several sources of cellulose have been used to obtain cellulose nanostructures, not necessarily conventional needle-shaped, which have high crystallinity. Recently, spherical

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http://dx.doi.org/10.1016/j.carbpol.2013.06.029

cellulose nanoparticles have been synthesized by several researchers (Haafiz Mohamad, Eichhorn, Hassan, & Jawaid, 2013).

The main objective of the work is the facile synthesis and characterization of nano-cellulose with different shape which was completely different from conventional nano-cellulose like nano fibrils, nano-whiskers, microfibrillated cellulose. Physical and chemical characterization of this prepared nano-cellulose together with their thermal stability was investigated in comparison with the properties of their raw materials, in order to define their applicability and suitability to develop new fields of research.

2. Experimental

2.1. Materials

Three different raw materials:

1. China cotton (CC)
2. South Africa cotton (SAC)
3. Waste tissue paper (TP)

Sulfuric acid (Merck), NaOH (Merck).

2.2. Preparation of nanocellulose from different sources

Nano-cellulose was prepared from three different sources by acid-catalyzed hydrolysis method (Dong, Kimura, Revol, & Gray, 1996). Acid concentration was 47% sulfuric acid which was optimized by Das et al. (Das et al., 2009). Briefly, the calculated amount of raw materials were mixed with measured amount of sulfuric acid and vigorously stirred at 60 °C for 2 h. An acidic suspension of nano-cellulose resulted. The resulted suspension was centrifuged and washed with deionized water several times to reduce acid concentration. The suspension was finally neutralized with 0.5 N NaOH solutions and again washed with distilled water. The prepared nano-cellulose suspension was freeze-dried to get nano-cellulose powder. Nano-cellulose obtained from China cotton, South African cotton and waste tissue paper was referred as CNC, SANC and TANC respectively.

2.3. Charaterization

TEM analysis: Samples were examined under transmission electron microscopy (TEM, JEOL, Japan) equipment for microscopic analysis. A droplet of diluted suspension of nano-cellulose sample was deposited on a carbon microgrid (400 mesh) prior to examination and allowed to dry.

Particle size analysis: Particle size analysis of the different nano-cellulose was done with a dynamic light scattering particle size analyzer (Yobin Horiba, LB-550). A very dilute solution was made by taking nano-cellulose in deionized water. Then the solution was sonicated for good dispersion. Then, the sonicated solution was placed in the particle size analyzer to get particle size distribution.

XRD study: X-ray diffraction (XRD) analysis of nano-cellulose from various sources were conducted using X-pert PRO XRD Cu K_α radiation (wavelength 0.154 nm), operated at 40 kV/40 mA. The samples were scanned in fixed time (FT) mode with a counting time of 2s under diffraction angle 2θ in the range of 1°–60°.

DSC study: Runs were carried out in a DSC Q2000 V24.4 (TA instrument) from room temperature to 400 °C at a heating rate of 10 °C/min under nitrogen atmosphere at flow rate 50 ml/min. The experiment was done by first heating, cooling, second heating cycles.

TGA: The thermal stability of samples was determined by means of thermo gravimetric analyzer using a TGA Q500 (TA Instruments) at a heating rate of 10 °C under nitrogen atmosphere, from room temperature to 500 °C.

FTIR spectroscopic study: FTIR of the all nano-cellulose samples were done by SHIMADZU instrument. Scans were carried out on wave number from 4000 cm^{-1} to 600 cm^{-1}.

3. Results and discussion

Hydrolytic cleavage of glycosidic bonds between two anhydroglucose units was observed during acid hydrolysis of the precursor material to produce cellulose with nanometric dimension. This action is counteracted by rearrangement of the tangling chain ends, which is favoured by release of internal strain. In this way amorphous portion gets dissolved by the acid hydrolysis, leaving behind the crystalline regions. Acid hydrolysis followed by mechanical treatment results in disintegration of the cellulose structure into nano crystalline cellulose particles. Effective production of nano-cellulose with different shape was resulted due to effective acid hydrolysis with mechanical agitation from different precursor. Rectangular and square shaped nano-cellulose crystals were observed for CNC and TNC samples from TEM analysis (Fig. 1a–c). The approximate ranges of diameter of CNC and TNC were from 30 to 60 nm and 10 and 90 nm respectively. However, TEM image of SANC showed smaller and finer particles of completely different shape from other samples. The diameter range of this sample was from 2 to 10 nm and the shape was irregular. Interestingly, the range of diameter distribution varied considerably among the sources; that is the diameter range of SANC aggregates was from 2 and 10 nm, was smaller than those from CNC and TNC, ranging from 30 to 60 nm and 10 to 90 nm, respectively.

The particle size and particle size distribution depend on the structure of the source sample, acid concentration, temperature, time, procedure of hydrolysis and the mechanical treatment. Fig. 2 showed the particle size analysis of different nano-cellulose samples. Although the size distribution of each sample varied from ~4 to 15 nm, but the distribution pattern was different. As evident from TEM study (Fig. 1) that SANC showed finer particles, a lower range of distribution for SANC was observed from Fig. 2. The highest volume (%) showed the particle range of 7–9 nm for SANC and 9–10 for CNC and TNC. From TEM study, it was also evident that the particle size was larger for CNC and TNC in comparison to that observed in particle size analysis study. That might occur due to the high agglomeration affinity of CNC and TNC. Similar observation was reported by Das et al. (Das et al., 2009; Das, Ray, Bandyopadhyay, & Sengupta, 2010). The suspension of nano cellulose was dried to nano-cellulose powder and subjected to XRD analysis. The XRD graphs of the precursor and the prepared nano cellulose particles are shown in Fig. 3.

The crystallite size was calculated (Das et al., 2009) by using the Scherrer equation in (1),

$$L_{h,k,l} = K\lambda = \beta \cos\theta \quad (1)$$

where $K = 0.94$, based on the full width at half maximum of 002 reflection. The cellulose I peak responsible for 002 reflections was at $2\theta = 22.2°$. The % crystallinity was also calculated (Das, Ray, Bandyopadhyay, & Sengupta, 2010) as per the formula in (2),

$$\%\,\text{Crystallinity} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100 \quad (2)$$

The changes in the % crystallinity and the crystallite size perpendicular to 002 plane are summarized in Table 1. In case of China cotton, the crystallinity of CNC increased (92.4%) compared to source China Cotton (82.4%), implying that dissolution of amorphous china cotton raised the crystallinity of the CNC particles. In South African Cotton also, removal of amorphous fractions increased the crystallinity of the SANC particles (97.8%) with respect to their source

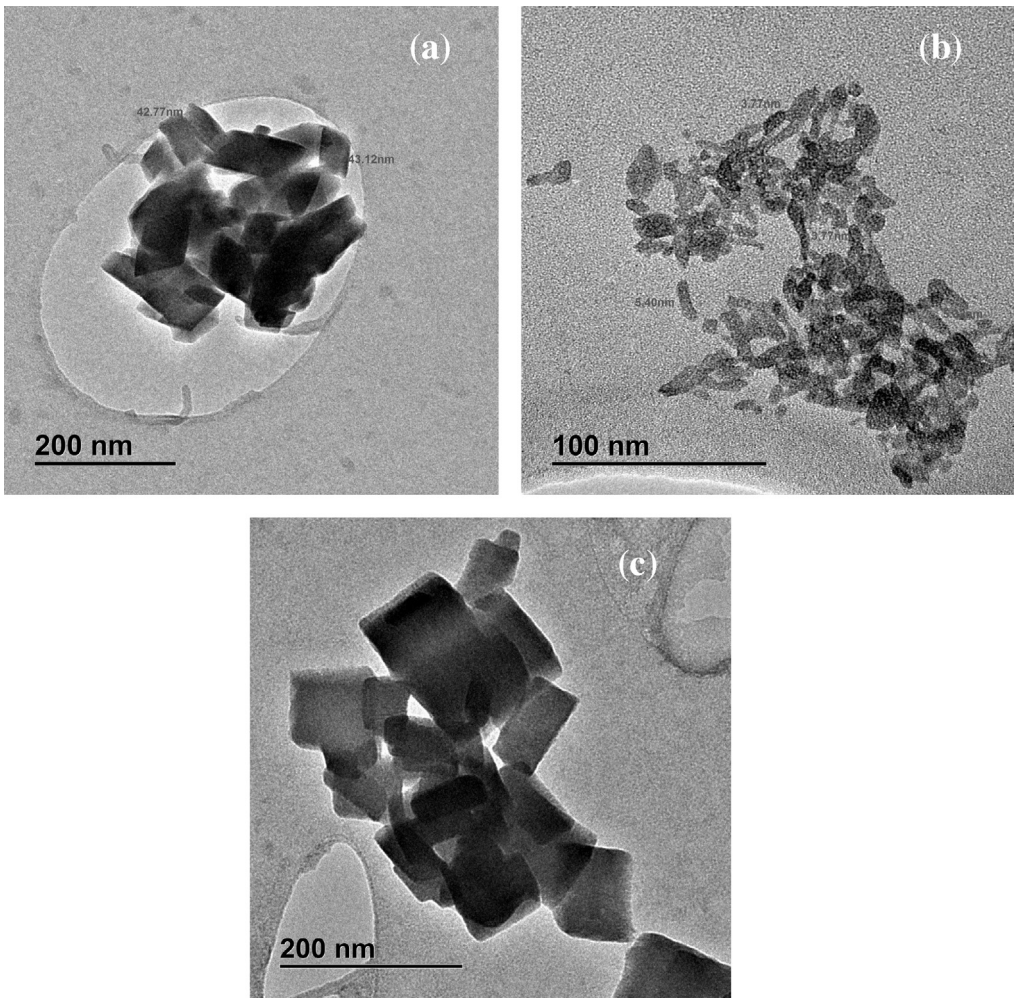

Fig. 1. (a) TEM image of CNC (b) TEM image of SANC (c) TEM image of TNC.

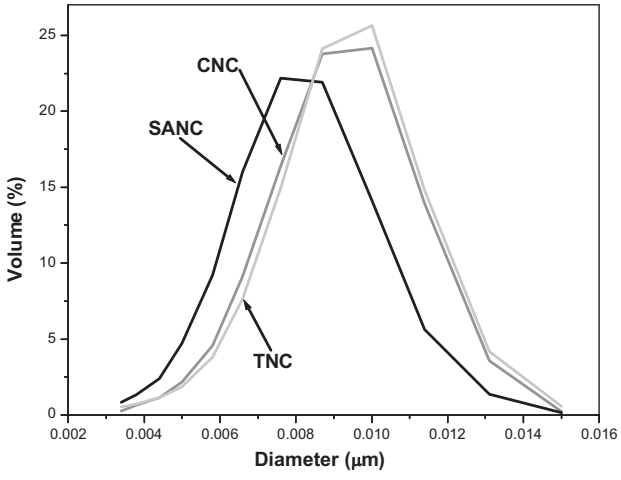

Fig. 2. Particle size analysis of three nanocellulose samples.

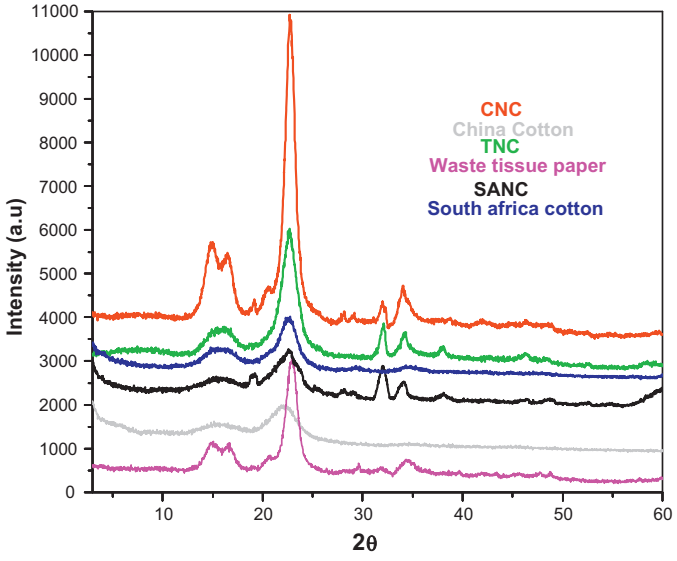

Fig. 3. Comparative X-ray diffractograms of three different kinds of nano-cellulose with corresponding precursor.

South African Cotton (90.2%). But crystallinity decreased in TNC (89.9%) compared to that of waste tissue paper (90.7). Waste tissue paper is generally made from paper pulp. This paper pulp was used to undertake several chemical processes to remove the amorphous portion. Due to removal of this amorphous portion of that paper pulp by means of different chemical processes high crystallinity was observed in case of waste tissue paper. But when waste tissue paper was subjected to acid hydrolysis for the generation of TNC, the highly ordered crystalline structure was affected and that resulted in a little lower crystallinity (Das et al., 2009; Das, Ray, Bandyopadhyay, & Sengupta, 2010) Comparative XRD of the

Table 1
The % crystallinity and apparent crystallite size of nano-cellulose samples obtained from XRD study.

Sample	% crystallinity	Apparent crystallite size (nm) (perpendicular to 002 plane) $2\theta = 22.2^{o}$
China cotton	82.4	3.9
CNC	92.4	8.73
South african cotton	90.2	4.9
SANC	97.8	3.95
Waste tissue paper	90.7	6.8
TNC	89.9	5.81

precursor and the corresponding nano cellulose were also presented in the Fig. 3. Development of new crystalline peaks at $2\theta = 14–16^{\circ}$ and $2\theta = 30–34^{\circ}$ (Fig. 3) were also the evidences of improvement of the crystallinity of the nanocellulose. A significant increase in the crystal size was observed in case of CNC samples, but not in SANC and TNC (Table 1). Similar increase in crystal size on acid hydrolysis was reported by some researchers (Das, Ray, Bandyopadhyay, & Sengupta, 2010; Tang et al., 1996). They concluded that celluloses with loose structure favour the changes in the size of the crystallites during acid hydrolysis. Tang et al. (Tang et al., 1996) explained that both the degradation of smaller crystallites and the growth of the defective crystallites were responsible for the change in crystallite size during acid hydrolysis.

Fig. 4 showed the heating curve of DSC study of the precursor and the corresponding nano cellulose. All the three DSC heating thermo grams (Fig. 4) of the nano cellulose (CNC, SANC, TNC) exhibit distinct endothermic changes within the range of temperature studied. The nature of endotherms, however, is quite characteristic of the composition of the material and differs from each other. The endotherm in each of the three cases is an indication of the course of fusion or melting which gives an idea of the nature of crystalline packing, the extent of which gradually increase or prominent in going from precursor to the corresponding nanocellulose, the nature of amorphous regions during the fusion process. The melting peaks of the crystalline nano cellulose were observed in the temperature range 230 °C–250 °C. But this was not observed in case of any precursor. This fact can be explained by the removal of the amorphous portion by chemical treatments improves the crystallinity of the nanocellulose (Das et al., 2009; Das, Ray, Bandyopadhyay, & Sengupta, 2010). This is also well corroborating our previous XRD

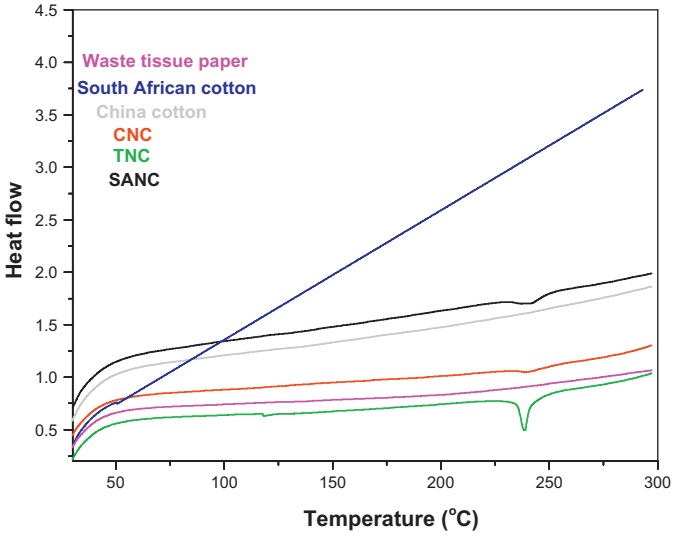

Fig. 4. DSC thermograms of three nano-cellulose with corresponding precursor samples.

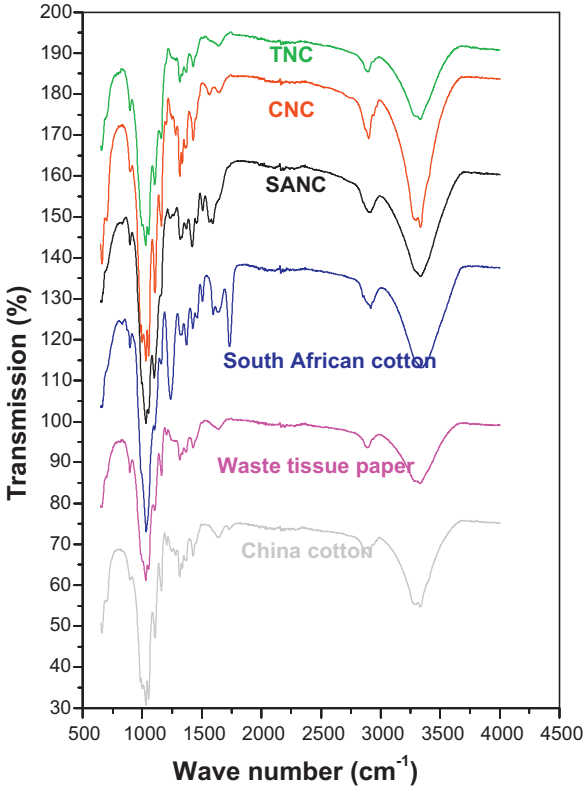

Fig. 5. FTIR diagram of three different nano celluloses with their precursor.

observation. Similar observation was also reported by Mandal et al. (Mandal & Chakrabarty, 2011).

The FTIR spectra of the precursor and the corresponding nano cellulose are shown in Fig. 5 The spectra of the precursor and the corresponding nano cellulose exhibited a broad band in the region 3500–3200 cm^{-1} that indicates the free O—H stretching vibration of the OH groups in cellulose molecules. Moreover, the spectra of all samples showed the characteristic C—H stretching vibration around 2894 cm^{-1} (Mandal & Chakrabarty, 2011). Besides, the transmittance peaks observed in the spectra of nano-cellulose obtained after chemo-mechanical treatments in the region 1649–1641 cm^{-1} are attributed to the O—H bending of the adsorbed water (Mandal & Chakrabarty, 2011). The peak observed in the spectra of the all samples at 1050 cm^{-1} is due to the C—O—C pyranose ring (antisymmetric in phase ring) stretching vibration. The most significant absorption band which continually prominent on acid hydrolysis, respectively, of all the nano cellulose is that of around 900 cm^{-1} (associated with the -glycosidic linkages between glucose units in cellulose) which stands for cellulose, the content of which increases progressively from precursor to nano cellulose. The C—C ring breathing band at 1150 cm^{-1} and the C—O—C glycosidic ether band at 1100 cm^{-1} both of which arise from the polysaccharide component is getting gradually lost or merge with 1050 cm^{-1} peak in nanocellulose because of hydrolysis and reduction in molecular weight (Mandal & Chakrabarty, 2011). This observation was also well corroborating our previous XRD and DSC results.

The thermal stability of a polymeric material depends on the inherent characteristics of the samples as well as on the molecular interactions between the different macromolecules. The chain cleavage or the bond dissociation of the macromolecules takes place when the supplied thermal energy exceeds the bond dissociation energy of the respective chemical bonds.

The nano cellulose particles were subjected to TGA. The loss in weight of the nano cellulose particles with the rise in

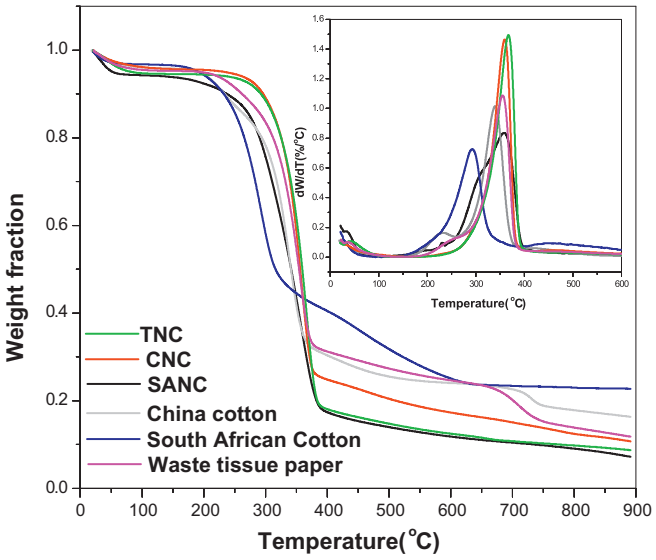

Fig. 6. Comparative TGA and DTGA of nano-cellulose samples with their corresponding precursor.

temperature and their rates of degradations are shown in Fig. 6. It was observed that major degradation temperature shifted to higher range of temperature in case of nano cellulose than corresponding precursor. The higher thermal stability of the nano cellulose can be ascribed to their higher flexibility, hence higher possibility of entanglements of the nano fibril. Similar increase in thermal stability due to tangling effect of flexible microfibrils has been reported by Das et al. (Das, Ray, Bandyopadhyay, & Sengupta, 2010). Thermogravimetric analysis also showed the increased thermal stability for all samples in comparison to their respective raw materials. The higher crystallinity of the nano-cellulose samples compared to that of their raw materials might be the reason for increased thermal stability. DTGA graphs clearly showed the shifting of major degradation peak to a higher one. The major degradation peak temperatures were observed at 360 °C, 358 °C and 367 °C for CNC, SANC and TNC respectively which appeared as higher than the values of their respective raw materials i.e. 338 °C, 290 °C and 353 °C respectively. The activation energy for thermal degradation also revealed information about the nature of thermal degradation and their crystalline packing. The present calculation is based on the Eq. (3) derived by Broido (Ray et al., 2009).

$$ln\left[\ln\left(\frac{1}{y}\right)\right] = \frac{E}{R}\left[\frac{1}{T} + K\right] \quad (3)$$

where $y = w_t/w_0$, w_t = weight remaining at time 't' w_0 = initial weight, T = temperature in Kelvin scale. From the residual weight of the sample ln[ln(1/y)] was plotted against 1/T to get Fig. 7 From the slope of the linear plot which is '$-E/R$' (R = universal gas constant), the activation energy (AE) 'E' was calculated. Activation energy (AE) was also improved in the nano cellulose than their corresponding precursor. But, the only exception was observed in case of TNC due to decrease in crystallinity after acid hydrolysis of TNC as stated in XRD study.

4. Conclusion

Nano cellulose with different shapes has been synthesized successfully from different precursor. Nano crystalline cellulose with different shapes is a versatile reinforcement for the development of bionanocomposite. Now a day's their suitable diversification can able to produce smart materials for high end application. In this work, three different cellulosic materials like China cotton, South African cotton and waste tissue paper were used as a precursor for generating nano cellulose. The CNC, TNC and SANC particles showed a diameter around of 10–90 nm under TEM. The TEM studies have given supporting evidences for the formation of nanocellulose with some unique shape. The XRD results revealed

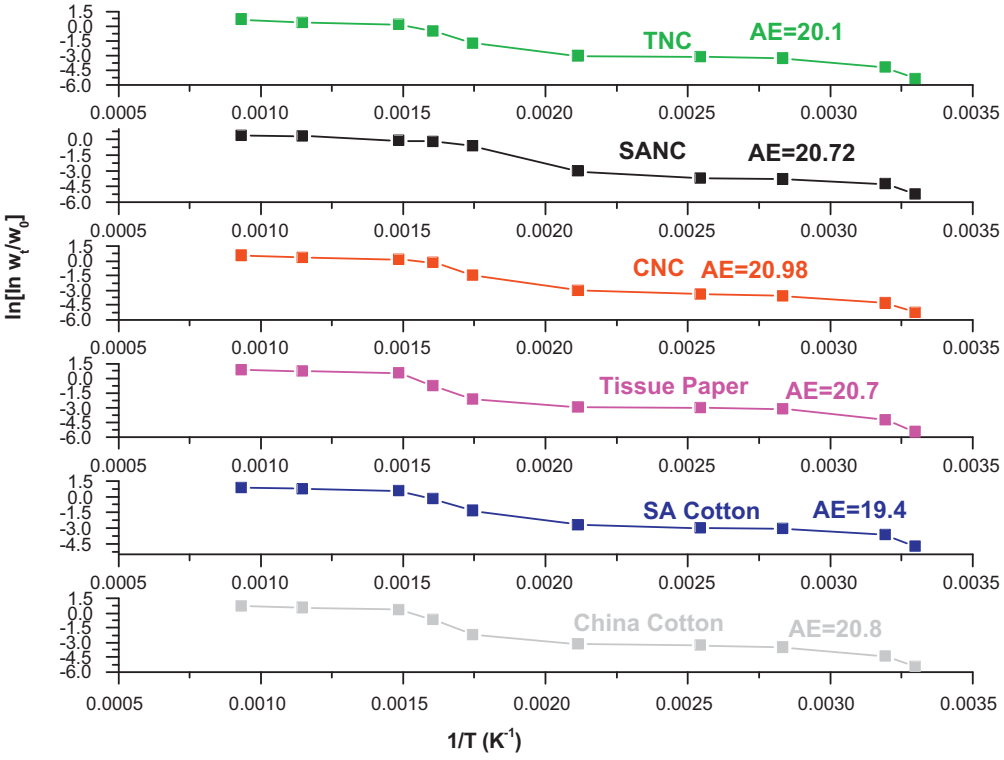

Fig. 7. ln[ln w_t/w_0] vs. 1/T plot of three different nano cellulose with corresponding precursor.

the higher crystallinity of the nano cellulose than the corresponding precursor. Higher thermal stability of the nano cellulose might due to be the tangling effect of the flexible fibrils. The experimental observations revealed that China cotton, South African Cotton and Waste tissue paper can be used to generate nano cellulose, which possess their unique combination of properties and can be used as reinforcing filler in bionanocomposites.

Acknowledgements

The authors (S.S.R. and KD) very much thankful to the Department of Chemical Technology, University of Johannesburg, Doornforntein 2018, Johannesburg, South Africa for financial support. The authors SM and KD also very much thankful to the Department of Chemistry, Nanjing University of Information Science and Technology, Nanjing, China

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