Structural Changes of Regenerated Cellulose Dissolved in FeTNa, NaOH/thiourea, and NMMO Systems

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ABSTRACT: Regenerated cellulose was prepared from microcrystalline cellulose (MCC) via dissolution in three well-known nonderivatizing systems: ferric chloride/sodium tartarate/sodium hydroxide (FeTNa), sodium hydroxide/thiourea (NaOH/thiourea), and *N*-methylmorpholine-*N*-oxide (NMMO) systems. The effect of regeneration using the different systems on the supramolecular structure of the regenerated celluloses was studied using X-ray diffraction and Fourier transform infrared (FTIR). The effect of regeneration on supermolecular structure, morphology, and thermal stability of regenerated celluloses were studied using scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The effect of regeneration systems used on the chemical reactivity of cellulose toward carboxymethylation, acetylation, and cyanoethylation reactions was briefly studied. The results showed dependence of all the aforementioned properties on the dissolution reagent used in spite of that all studied reagents cause the same change in cellulose crystalline structure (from cellulose I to cellulose II). The degree of polymerization, crystallinity, and thermal stability of the regenerated cellulose (RC) samples were in the following order: NaOH/thiourea RC > FeTNa RC > NMMO RC. SEM micrograph showed unique surface for the NMMO RC sample. The reactivity of the different regenerated cellulose samples toward carboxymethylation, cyanoethylation, and acetylation depended mainly on the reaction system and conditions used rather than on crystallinity of regenerated cellulose. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2862–2871, 2008

Key words: cellulose; dissolution; NaOH/thiourea; FeTNa; *N*-methylmorpholine-*N*-oxide

INTRODUCTION

Cellulose is the most abundant resource in nature. It is renewable, biodegradable, and biocompatible so that it is one of the main chemical resources of the future.[1] Cellulose has not reached its potential applications because it cannot be melted to be fabricated into a desired form or to be dissolved in a common cheap solvent. The strong inter- and intramolecular hydrogen bonding, high degree of polymerization (DP), high crystallinity, and consequently limited reactivity restrict the ability of cellulose to be used in many fields due to its difficult solubility. Thus, for many decades commercial regeneration of cotton or wood cellulose has been mainly based on the xanthate process that creates the problem of the possible discharge of toxic gases from its spinning process.[2]

There are two classes of cellulose solvent systems: derivatizing and nonderivatizing solvent systems. The term derivatizing solvent denotes systems that dissolve cellulose by chemical interaction between cellulose and the solvent, whereas the term nonderivatizing solvent denotes systems that dissolve cellulose by intermolecular interaction only. In case of the derivatizing solvent systems, cellulose derivatives are formed as a result of the reaction between the solvents and cellulose. These derivatives could be easily converted to cellulose or used as intermediates in subsequent homogeneous reactions to prepare other cellulose derivatives. Examples of derivatizing solvent systems[3] include formic acid/zinc chloride, trifluroacetic acid/trifluroacetic anhydride, nitrogen tetraoxide/dimethyl formamide, chlorotrimethyl silane/pyridine, and carbon disulfide/sodium hydroxide. On the other hand, dissolution of cellulose in nonderivatizing solvent systems is an important route for cellulose dissolution and regeneration as well as being one of the approaches to develop advanced and homogeneous cellulose derivatives. Derivatization of cellulose under homogeneous conditions results in uniform distribution of substituents along and between the cellulose chains. Recently, many efforts have been made to explore new nonderivatizing solvent systems[4] such as ammonia/ammonium thiocyanate,[5,6] hydrazine/thiocyanate,[7] calcium and sodium thiocyanate,[8,9] zinc chloride,[10] lithium chloride/*N*,*N*-dimethylacetamide,[11,12] NMMO·H_2O,[13–17] and aqueous solution of sodium hydroxide, NaOH/thiourea, and NaOH/urea.[18–22] The transition metal-complex solvent systems such as copper hydroxide/NH_3, $FeCl_3$/tartaric acid/NaOH, and inorganic mol-

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ten salts such as $LiClO_4 \cdot 3H_2O$, NaSCN/KSCN/$LiSCN \cdot 2H_2O$, and $LiCl/ZnCl_2/H_2O$ are added to the category of nonderivatizing solvents.[2,23] From all of the aforementioned solvent systems, *N*-methylmorpholine-*N*-oxide (NMMO) is the only currently used system at the industrial level for spinning of cellulose; the product is called Tancel and Lyocell. The spun fibers are characterized by high strength as well as high fibrillation tendency. The advantage of this solvent is its ability to attain exceedingly high concentration of cellulose (e.g., 35% w/w in DP 600). However, the NMMO system has some disadvantages associated with its use such as the high temperature required for dissolution, the degradation of cellulose, the side reactions of the solvent itself without an antioxidant, and its high cost. To overcome the degradation during dissolution, propyl galate is usually used as an antioxidant.[24,25]

Although different nonderivatizing cellulose dissolving systems have been discovered, no studies have been carried out to compare these different systems to each other on cellulose of the same origin regarding the effect on DP, supramolecular structure, morphology, thermal stability, and chemical reactivity. The aim of this work is to study the effect of regeneration of microcrystalline cellulose using three dissolution systems that are known to cause the same change in cellulose crystalline structure. These systems were ferric chloride/sodium tartarate/sodium hydroxide (FeTNa), sodium hydroxide/thiourea (NaOH/thiourea), and NMMO. NMMO is the recent industrial cellulose dissolution reagent. FeTNa is one of the early discovered cellulose complex-forming dissolving reagents and has the ability to dissolve high-DP cellulose. Regeneration using NaOH/urea or thiourea is recently reported as a convenient method for dissolution that utilizes the mercerization reaction between cellulose and alkali. The effect of dissolution and regeneration using different regeneration systems used on chemical reactivity of cellulose toward carboxymethylation, acetylation, and cyanoethylation reactions was briefly studied.

EXPERIMENTAL

Materials

Reagent grade microcrystalline cellulose, *N*-methylmorpholine-*N*-oxide monohydrate ($NMMO \cdot H_2O$), ferric chloride, tartaric acid, sodium hydroxide, thiourea, monochloro acetic acid, glacial acetic acid, acrylonitrile, and sulfuric acid were used as received.

Dissolution of MCC

Dissolution and regeneration of MCC in FeTNa, NaOH/thiourea, and $NMMO/H_2O$ systems were carried out according to the optimum conditions of previously published methods.[20,26,27] In case of FeTNa system, the concentrations of sodium hydroxide, sodium tartarate, and ferric chloride were 2.4, 1.1, and 0.3*M*, respectively. In case of NaOH/thiourea, the concentration of NaOH and thiourea were 1.5 and 0.65*M*, respectively. In case of $NMMO/H_2O$ system, a 50 : 50 water/NMMO mixture was used. The regenerated cellulose (RC) samples were oven-dried at 65°C under vacuum. The DP of regenerated cellulose was determined by viscosity measurement of the samples dissolved in copper hydroxide-ethylene diamine solution.[28]

Characterization of regenerated cellulose

X-ray diffractometery (XRD) was carried out using a Phillips X-ray diffractometer. The diffraction patterns were recorded from $2\theta = 5$–50 using Cu Kα radiation at 40 kV and 25 mA. The samples were pressed into pellets (25-mm in diameter) by compression of 0.25 g in a mold under a pressure of 50 MPa. The crystallite size of MCC was measured using the half-height width of the 002 reflection. Crystallinity index (CrI) was calculated as follows[29]:

$$\mathrm{CrI} = [(I_{002} - I_{\mathrm{am}})]/I_{002}$$

where I_{002} is the intensity of the 002 peak (at about $2\theta = 22$) and I_{am} is the intensity corresponding to 101 peek.

FTIR was carried out using a JASCO 300-E Fourier transform infrared spectrometer; KBr disc technique was used. A Perkin–Elmer thermogravimetric analyzer was used to study the thermal stability of the different regenerated cellulose samples. The heating rate was set at 10°C/min over a temperature range of 50–800°C. Measurements were carried out in nitrogen atmosphere with a rate of flow of 50 cm^3/min. Scanning electron microscopy (SEM; gold coating, Edwards Sputter Coater, UK) was performed using a JEOL 6310 (Joel Instruments, Tokyo, Japan) system running at 5–10 keV.

Chemical modification of regenerated cellulose

Regenerated cellulose samples prepared using the different dissolution reagents were acetylated, carboxymethylated, or cyanoethylated using the previously published methods.[28] Chemical analysis was carried out for the determination of degree of substitution in case of cyanoethylation and carboxymethylation, and the acetyl content in case of acetylation according to the standard methods for each of these derivatives.[28]

RESULTS AND DISCUSSION

During the course of dissolution and regeneration of cellulose using different solvent systems, cellulose fibers are exposed to variable conditions. For example, cellulose is exposed to high temperature in case of using NMMO/H_2O system while it is exposed to high alkalinity in case of using NaOH/thiourea and FeTNa systems. These harsh conditions may result in degradation of cellulose, change of its crystallinity, and the reactivity of cellulose toward chemical modification. The following parts discuss the effect of regeneration using the three aforementioned systems on DP, crystallinity, morphology, thermal stability, and chemical reactivity of cellulose. In this study, cellulose of low molecular weight (microcrystalline cellulose of DP $\sim$ 300) was used. The use of microcrystalline cellulose in dissolution studies is common due to easier solubility and the more pronounced effects due to possible changes in structure. The same trends of the results are expected to be obtain in case of using cellulose of high DP. The ease of solubility of low DP cellulose in solvents, especially aqueous NaOH-based solvent, has become the basis of an alternative process for cellulose fiber spinning but so far, it has not been practiced in industry.

Effect of regeneration on degree of polymerization of regenerated cellulose

The dissolution mechanism of cellulose in the nonderivatizing solvents, e.g., FeTNa, NaOH/thiourea, and NMMO/H_2O depends on destruction of the strong hydrogen bonding system between cellulose chains. However, degradation of cellulose during dissolution using the different cellulose solvents has been reported. Degradation of cellulose during dissolution in NMMO system has been reported, and the addition of an antioxidant such as propyl galate is of industrial practice to minimize cellulose degradation.[24–25] Also, degradation of cellulose by NaOH, especially in the presence of air, is known and it increases as the temperature increases.[30]

The effect of dissolution using the FeTNa, NaOH/thiourea, and NMMO/H_2O systems on DP of MCC was tested and the results are shown in Table I. As it is clear from the table, the NaOH/thiourea system had the lowest degradation effect on DP followed by FeTNa system, whereas the NMMO system had the highest degradation even in the presence of propyl galate. These results indicate that temperature plays a major role in degradation during dissolution, since dissolution using NaOH/thiourea, FeTNa, and NMMO systems are carried out at $<10^{\circ}C$, room temperature ($\sim$ 25°C), and at 115°C, respectively. In addition, the alkali concentration used in case of FeTNa system is higher than that of NaOH/thiourea system ($\sim$ 2.4 and 1.5*M* NaOH were used in case FeTNa and NaOH/thiourea systems, respectively).

TABLE I
Effect of Regeneration System on Degree of Polymerization of Regenerated Cellulose

Solvent system used	DP
None (MCC)	299
FeTNa	275
NaOH/thiourea	281
NMMO	264

Effect of regeneration on morphology of regenerated cellulose

The effect of dissolution on the microstructure of regenerated cellulose was studied using SEM. As shown in Figure 1(a), microcrystalline cellulose has a short fibrous structure with fibrils on its surface. In case of NaOH/thiourea and FeTNa systems [Fig. 1(b,c)], regeneration of cellulose resulted in lamellar structure. On the other hand, a porous structure with many fibrils on the surface of regenerated film was produced in case of using NMMO. The characteristic porous structure in case of using the NMMO system could be attributed to crystallization of the NMMO during cooling of cellulose/NMMO solution and consequently affecting the microstructure of regenerated cellulose.[31,32] The change in the microstructure will have significant effect on the properties and application of these regenerated fibers or films. For examples, lamellar structure with very low porosity could be useful for films used in packaging products; porous structure is useful in membranes; and regenerated fibers with many fibrils on the surface is useful in high-strength composites because of the higher fiber/matrix interaction.

Effect of regeneration on supramolecular structure of cellulose

X-ray diffraction of regenerated cellulose

Because of their chemical constitution and spatial conformation, cellulose chains form aggregate of highly ordered structures. Cellulose exists in several crystal modifications, differing in unit cell dimensions and possibly, in chain polarity.[33] In wood and cotton, native cellulose (cellulose I) has mainly a monoclinic unit cell with probably parallel cellobiose chain segments running in opposite directions along the fiber axis. The antiparallel chain packing in cellulose I is also supported by some authors. Another commercially important cellulose crystalline modification is cellulose II, which is formed by precipitating

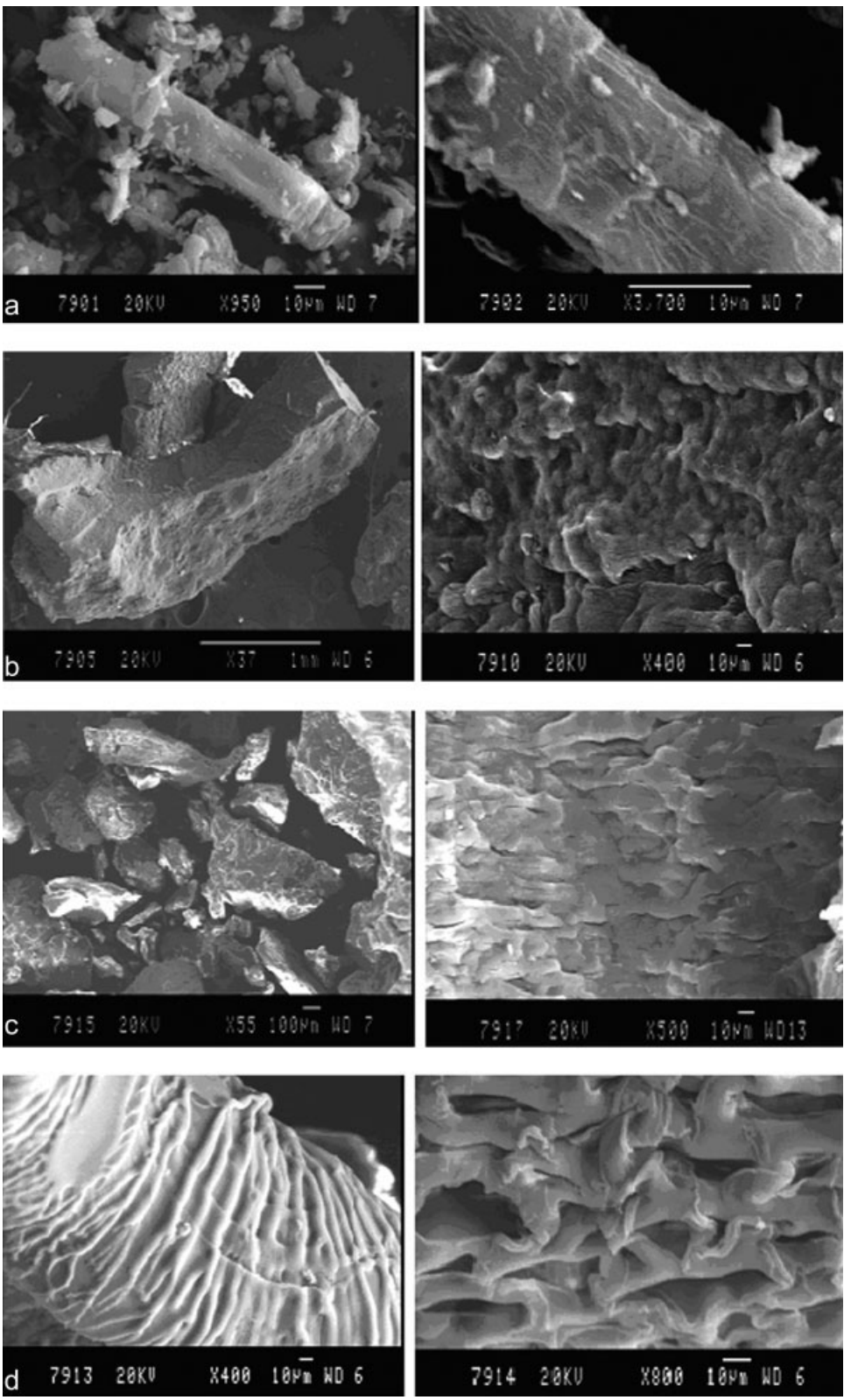

Figure 1 SEM micrographs of MCC (a), FeTNa regenerated cellulose (b), NaOH/thiourea regenerated cellulose (c), and NMMO regenerated cellulose (d).

cellulose from solution into an aqueous medium. The crystal structure of cellulose II is also represented by a monoclinic unit cell, consisting of two antiparallel running cellulose chain segments. But the lattice dimensions of cellulose I and cellulose II are different, especially the lattice angle. In addition, the hydrogen

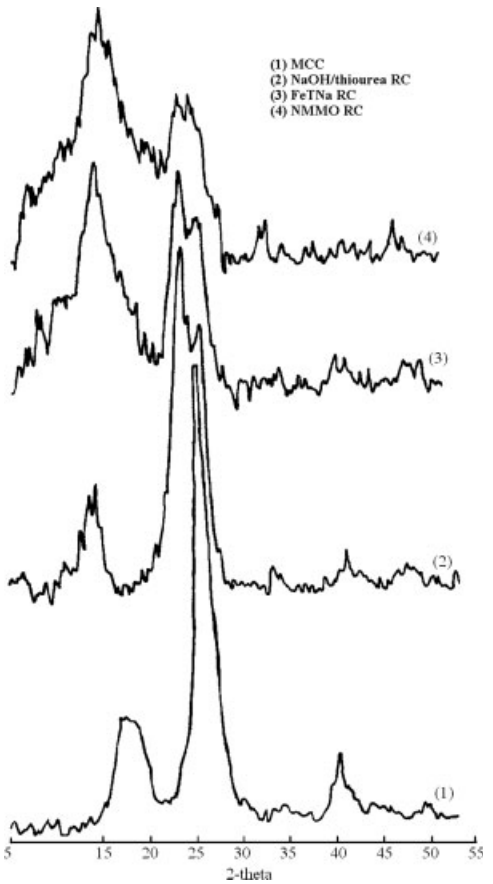

Figure 2 X-ray diffraction of regenerated cellulose (RC) samples.

bonding system of cellulose II appear to be more complicated than that of cellulose I.

In this work, the change in crystalline structure of cellulose because of its regeneration from the three chosen solvent systems was followed using XRD (Fig. 2). The CrI, crystallite size, and the *d*-spacing of the regenerated samples calculated using the XRD data are reported in Table II. The results showed that regeneration of cellulose resulted in significant change in crystallinity, XRD pattern, and crystallite size. MCC showed typical cellulose I structure with reflections at about $2\theta = 27$ and $2\theta = 15$. The reflection peak at $2\theta = 27$ is derived from the 002 plane of the cellulose I lattice, whereas the peak around $2\theta = 15$ is assigned to the reflection of the 101 and 101′ lattice planes of cellulose I. Although both NaOH/thiourea and FeTNa systems are basically alkaline and are known to result in transformation into cellulose II structure, the regenerated cellulose derived from these systems showed different crystallinity. Higher crystallinity was recorded for the regenerated cellulose of the NaOH/thiourea system; the XRD pattern was of sharper peaks than that of FeTNa system. This means that the mechanism of dissolution affects the reordering of cellulose chains upon their precipitation and crystallization. In case of NaOH/thiourea system, the interaction between cellulose and aqueous alkali hydroxide is characterized by an uptake of alkali hydroxide and water onto the fibers resulting in a decrease of NaOH concentration in the surrounding medium. In addition, lateral swelling of the fibers and a change in the lattice dimensions in the ordered regions take place above a specific NaOH concentration.[33] The presence of thiourea enhances significantly the solubility of cellulose in NaOH aqueous solution and reduces the formation of cellulose gel.[20,34] On the other hand, dissolution of cellulose by FeTNa solvent system is caused by complex binding of the anhydroglucose unit to the central Fe atom.[27] It is important to note that dissolution of cellulose in the NaOH/thiourea system is carried out at low temperature (<10°C) using 1.5*M* NaOH/0.65*M* thiourea solution. In case of FeTNa system, the dissolution is carried out at room temperature and the concentration of the alkali in the solution used is $\sim$ 2.4*M*. Regenerated cellulose prepared from NMMO system showed the lowest crystallinity and broadening of the cellulose II X-ray pattern as well as the smallest crystallite size. A recent study on the NMMO/cellulose dissolution showed that amorphous cellulose and cellulose II structure were obtained when cellulose was precipitated from NMMO/H_2O/cellulose solution by adding excess water.[16] Crystallization of NMMO during cooling of cellulose/NMMO mixture could be the reason of the low crystallinity of the obtained regenerated cellulose when compared with the regenerated cellulose obtained using the other two systems.

TABLE II
Effect of Regeneration System of Degree of Crystallinity, *d*-Spacing, and Crystalline Size of Regenerated Cellulose

	Crystallinity index[a]	Relative crystallinity[b] (A_{1370}/A_{2900})	Crystallite size (nm) (D_{002})	*d*-Value	
				From 002 band	From 101 band
FeTNa	0.46	0.18	3.65	4.44	7.26
NaOH/thiourea	0.75	0.22	3.65	4.43	7.24
NMMO	0.39	0.11	3.04	4.47	7.0
MCC	0.80	0.26	6.8	3.94	5.91

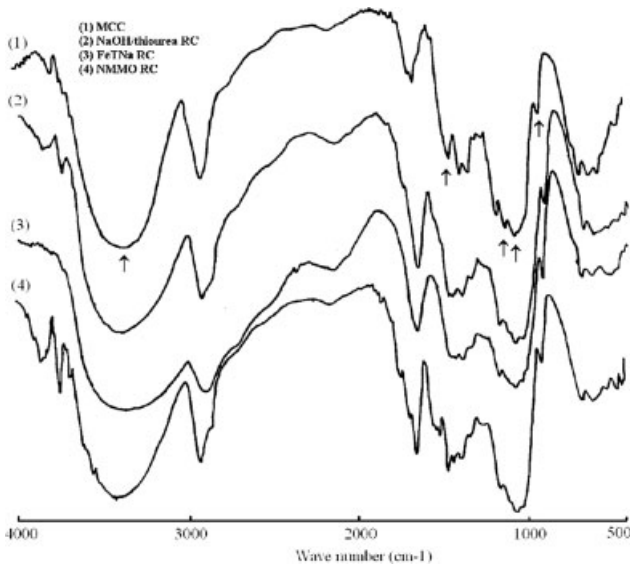

Figure 3 FTIR spectra of regenerated cellulose (RC) samples.

FTIR of regenerated cellulose

FTIR spectroscopy can also be used to determine the degree of crystallinity and crystalline modification of pure cellulose. The intensity of certain bands in IR spectra has been found to be sensitive to variations in cellulose crystallinity or crystalline form. Such variation may be determined using the ratio of the intensity of a band that is affected by cellulose crystallinity to that of a band that is comparatively insensitive to crystallinity changes. The ratio of the absorbance of the peaks at 1429 cm^{-1} to those at 894 cm^{-1} (A_{1429}/A_{894}) and A_{1372}/A_{2900} have been used to measure the relative cellulose crystallinity.[35] Figure 3 shows the IR spectra of MCC and regenerated cellulose samples obtained using the different solvent systems. The relative cellulose crystallinity calculated from these spectra is shown in Table II; the results are in accordance with that obtained from the XRD. FTIR spectra showed that the absorption band at about 1430 cm^{-1}, which is assigned to the CH_2 bending, became very week in all regenerated cellulose samples when compared with that of microcrystalline cellulose indicating breaking of the intramolecular hydrogen bond involving O6 in glucose units. The band at 1110 cm^{-1} in the spectra of MCC is medium but appeared as a weak shoulder in the regenerated cellulose samples due to broadening of the 1060 cm^{-1} band. In addition, the band at about 895 cm^{-1}, which belongs to β-anomers or β-linked glucose polymers, became more intense in the regenerated sample due to the more amorphous character. The O—H stretching band of the hydroxyl groups at about 3350 cm^{-1} was shifted to higher wave number and slightly broadened as a result of regeneration confirming weaker intra- and intermolecular hydrogen bonding, i.e., lower crystallinity.

Effect of regeneration on thermal stability of regenerated cellulose

Thermal stability of cellulose is an important property that may limit its use in applications where cellulose is subjected to heat. Cellulose is a polymer of moderate thermal stability. The thermal degradation of cellulose is known to be due to a pyrolytic fragmentation that leads to aromatized entities and finally to a highly crosslinked carbon skeleton.[33]

The effect of regeneration using the different dissolution systems was studied using TGA. Table III shows the TGA data derived from the TG and differential TG (DTG) curves (Fig. 4). The kinetics of thermal degradation of cellulose was studied using the Freidman equation[36] as follows:

$$\ln d\alpha/dt = \ln Z + n \ln (1 - \alpha) + E/RT$$

where α is the fractional weight loss and R is the gas constant. The value of ln $d\alpha/dt$ can easily be obtained from the DTG curve. The value of ln $(1-\alpha)$ can be obtained from the TG curve. The values of ln $d\alpha/dt$ were plotted against $1/t$, and then E can be determined from the slope of the plot. The plot of ln $(1-\alpha)$ versus $1/T$ will give the order of the reaction (n) from the maximum slope of the line. Finally, the Ln Z (the frequency factor) can readily be calculated through the equation at a certain temperature.

TABLE III
Effect of Regeneration System on Thermal Stability of Regenerated Cellulose

	First-stage onset degradation temperature (°C)	First-stage maximum weight loss temperature* (°C)	Second-stage onset degradation temperature (°C)	Second-stage maximum weight loss temperature* (°C)	Ash formation temperature (°C)	Activation energy (kJ/mol)	Order	Ln Z (at onset degradation temp.)
FeTNa	264	351	365	536	590	109	1.8	25.0
NaOH/thiourea	267	348	365	530	700	111	1.7	25.9
NMMO	259	321	365	554	594	83	1.7	18.3
MCC	275	328	–	–	547	282	0.97	59.4

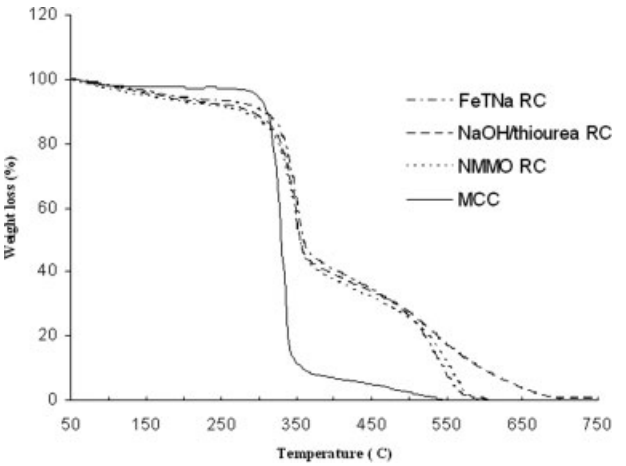

Figure 4 TGA and DTGA curves of regenerated cellulose (RC) samples.

Figure 5 shows Friedman plots for the determination of kinetic parameters of the thermal degradation of regenerated cellulose (RC) samples.

As shown from the results, MCC showed the highest onset degradation temperature when compared with all the regenerated cellulose samples. This is in accordance with the crystallinity results mentioned earlier. MCC showed two major degradation stages, the first one (from $\sim$ 290 to 360°C) ended with loss of about 90% of cellulose weight. On the other hand, although of lower onset degradation temperature of different regenerated cellulose samples, they showed much slower rate of degradation as it is clear from the steepness of the TG curves. In addition, the first-stage maximum weight loss temperature of regenerated cellulose samples was much higher than MCC except for NMMO RC, which showed slightly lower maximum weight loss temperature. At about 360°C, the regenerated cellulose samples lost 54–55% of their weight. The onset degradation temperature of regenerated cellulose samples were in the following order: NaOH/thiourea RC > FeTNa RC > NMMO RC. This is also in accordance with the crystallinity results mentioned earlier. In addition, complete degradation of all regenerated cellulose samples (marked as ash formation temperature in Table III) took place at higher temperature than MCC. NaOH/thiourea RC had the lowest rate of degradation and complete degradation ends at exceptionally high temperature (700°C).

The activation energy calculated for the first degradation stage of the different regenerated cellulose samples (Table III) showed the following order: MCC > NaOH/thiourea RC > FeTNa RC > NMMO RC, i.e., the same order of crystallinity of samples. A significant decrease of the activation energy took place as a result of regeneration. The order of the thermal degradation reaction seems to be in general a first order one and the frequency factor, Ln Z, had the same order of activation energy of the regenerated cellulose samples.

Effect of regeneration on chemical reactivity of regenerated cellulose

The effect of regeneration of cellulose using the NaOH/thiourea, FeTNa, and NMMO systems on the reactivity of regenerated cellulose toward chemical modification was studied to investigate the feasibility of regeneration, as a pretreatment, to increase the reactivity of cellulose. It has been recently reported that NMMO-regenerated cellulose was three times more reactive than that of untreated cellulose in hydrolysis reactions.[16]

In this work, three reaction systems were chosen: acetylation using glacial acetic acid/sulfuric acid (nonaqueous medium), carboxymethylation using monochloroacetic acid/isopropanol/NaOH/water system (alcoholic/aqueous medium), and cyanoethylation using acrylonitrile/NaOH/water (aqueous medium). FTIR spectra of modified regenerated cellulose samples (Fig. 6) showed the characteristic peaks of the prepared derivatives, i.e., C=O band of the carbonyl group at 1730 cm^{-1} in case of acetylation, C=O band of the carboxylate group at 1630 cm^{-1} in case of carboxymethylation, and CN band of the nitrile group at 2250 cm^{-1} in case of cyanoethylation. Table IV shows the effect of regeneration on the reactivity of the regenerated cellulose samples. In case of acetylation (nonaqueous medium), MCC showed higher reactivity than all regenerated samples. This may be due to that MCC used was a fine powder of micrometer size while the regenerated celluloses used were small flakes and no swelling is expected due to the absence of water or alkaline medium. NMMO RC showed higher reactivity toward acetylation than both NaOH/thiourea RC and FeTNa RC. This is in accordance of crystallinity of the NMMO-regenerated cellulose. In case of etherification using cyanoethylation and carboxymethylation, all the regenerated cellulose samples showed slightly higher reactivity than MCC. This is in accordance with the results of crystallinity, which showed that all regenerated cellulose samples had lower crystallinity than MCC. However, the reactivity was not always in accordance with the order crystallinity of regenerated cellulose samples. In both reactions, sodium hydroxide is used and swelling of cellulose will occur regardless the morphology of cellulose.

CONCLUSIONS

Supermolecular, supramolecular structure, and thermal stability of regenerated cellulose depend on the solvent systems used in dissolution even if the

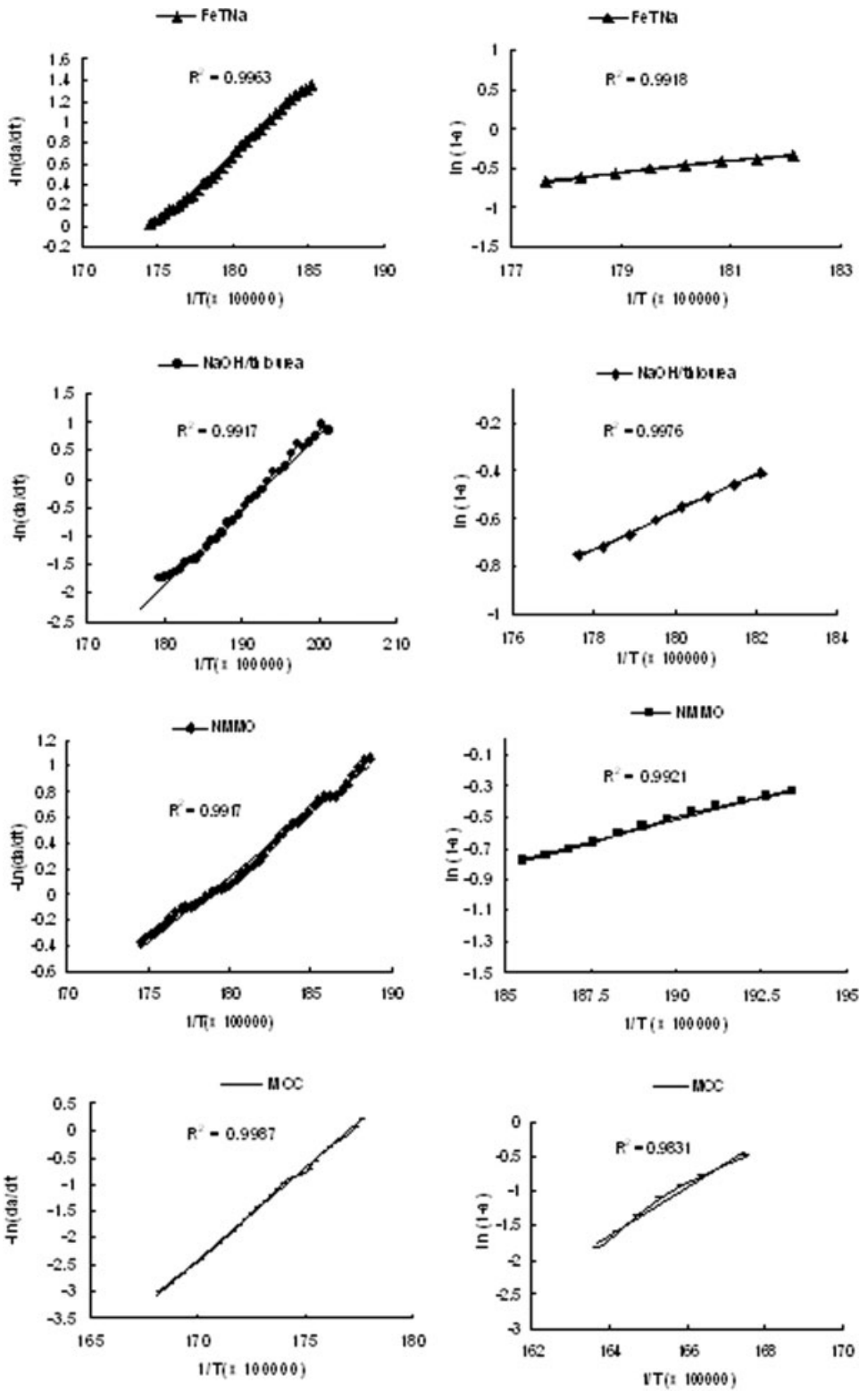

Figure 5 Friedman plots for the determination of kinetic parameters of the thermal degradation of regenerated cellulose (RC) samples. Values on curves are the correlation coefficients of the trend lines.

solvents cause the same change in the crystalline form. Temperature seems to play a major role in cellulose degradation during dissolution. The use of NaOH/thiourea dissolution system produced regenerated cellulose having higher DP than that of FeNaT and NMMO systems. The use of NMMO dissolution system produced regenerated cellulose having lower crystallinity than that of FeNaT and

NaOH/thiourea systems. Under the conditions used in this work, reactivity of regenerated cellulose toward chemical modification depends mainly on the reaction system used and not on the order of crystallinity of the regenerated cellulose samples.

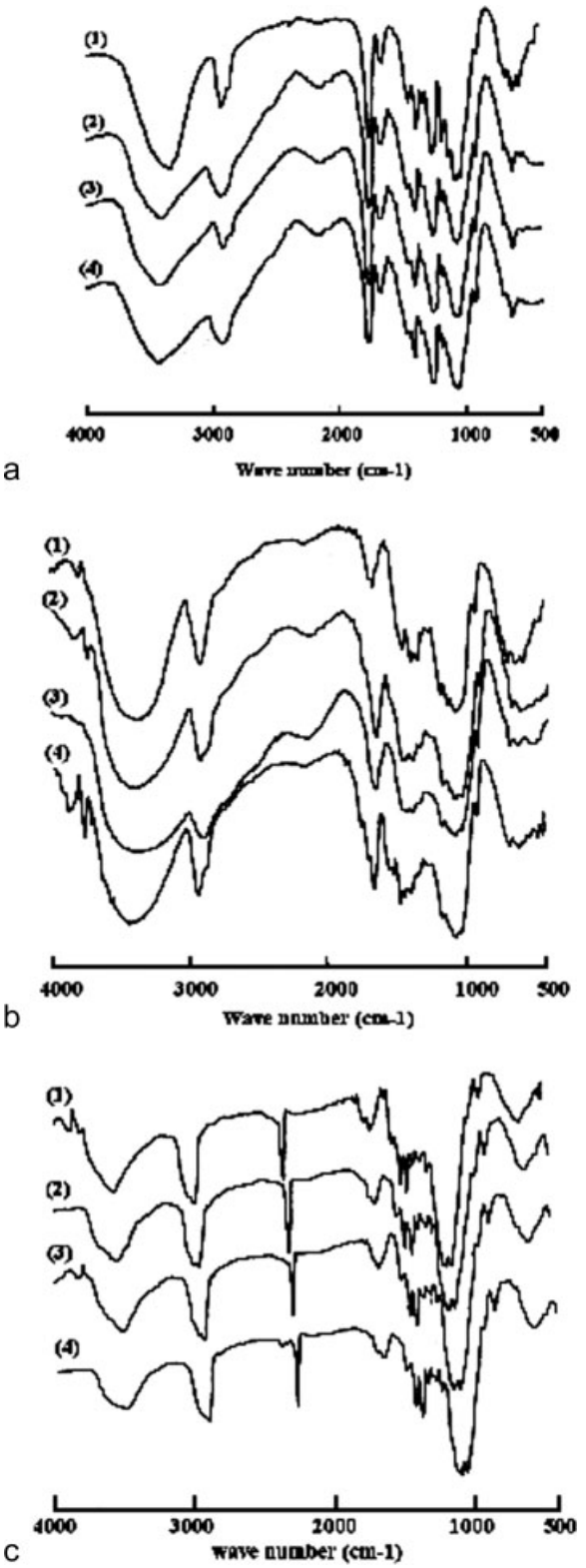

Figure 6 FTIR spectra of (a) cyanoethylated regenerated cellulose (RC), (b) carboxymethylated regenerated cellulose (RC), and (c) acetylated regenerated cellulose (RC).

TABLE IV
Effect of Regeneration System on Reactivity of Regenerated Cellulose Toward Cyanoethylation, Carboxymethylation, and Acetylation

	Degree of substitution of cyanoethyl cellulose	Degree of substitution of carboxymethyl cellulose	Acetyl content of cellulose acetate
FeTNa	2.57	0.44	5.82
NaOH/thiourea	2.67	0.56	5.14
NMMO	2.58	0.48	7.62
MCC	2.46	0.32	12.0

References

1. Schurz, J. Prog Polym Sci 1999, 24, 481.
2. Ikuya, M.; Yoshio, M.; Toshihiko, M.; Kunihiko, O. Polym J 1995, 27, 1113.
3. Klemm, D.; Philipp, B.; Heinze, U.; Wagenknecht, W. Functionalization of Cellulose; Wiley-VCH: Weinheim, 1998; Vol. 2.
4. Myasoedova V. V. Physical Chemistry of Non-Aqueous Solutions of Cellulose and its Derivatives; Wiley: Chichester, 2000; pp 3–36.
5. Cuculo, J. A.; Smith, C. B.; Sangwatanaroj, U.; Stejskal, E. O.; Sankar, S. S. J Polym Sci Part A: Polym Chem 1994, 32, 229.
6. Cuculo, J. A.; Smith, C. B.; Sangwatanaroj, U.; Stejskal, E. O.; Sankar, S. S. J Polym Sci Part A: Polym Chem 1994, 32, 241.
7. Kazuyuki, H.; John, A. C.; Samuel, M. H. J Polym Sci Part A: Polym Chem 2002, 40, 601.
8. Makiko, H.; Takehiro, K.; Yoshihiko, S.; Masatoshi, S. Polym J 1998, 30, 43.
9. Makiko, H.; Yoshihiko, S.; Masatoshi, S. Polym J 1998, 30, 49.
10. Chen, L. F. U.S. Pat. 5,290,349 1994.
11. McCormick, C. L.; Callais, P. A.; Hutchinson, B. H. Macromolecules 1985, 18, 2394.
12. Matsumoto, K.; Tatsumi, D.; Tamai, N.; Takaki, T. Cellulose 2001, 8, 275.
13. Chanzy, H.; Dubeand, M.; Marchessault, R. H. J Polym Sci Polym Lett Ed 1979, 17, 219.
14. Lenz, J.; Schurz, J.; Wrentschur, E. Acta Polym 1992, 43, 307.
15. Bochek, A. M.; Petropavlovsky, G. A.; Kallistov, O. V. Cellul Chem Technol 1993, 27, 137.
16. Fink, H. P.; Weigel, P.; Bohn, A. J Macromol Sci Phys 1999, B38, 603.
17. Zhao, H.; Kwak, J. H.; Wang, Y.; Franz, J. A.; White, J. M.; Holladay, J. E. Carbohydr Polym 2007, 67, 97.
18. Kenji, K.; Kunihiko, O.; Keisuke, K. Polym J 1992, 24, 21.
19. Guang, Y.; Hitomi, M.; Chihiro, Y.; Kunihiko, O. Polym J 2007, 39, 34.
20. Isogal, A.; Atalla, R. H. Cellulose 1998, 5, 309.
21. Zhang, L.; Ruan, D.; Gao, S. J Polym Sci Part B: Polym Phys 2002, 40, 1521.
22. Chen, X.; Burger, C.; Fang, D.; Ruan, D.; Zhang, L.; Hsiao, B. S; Chu, B. Polymer 2006, 47, 2839.
23. Fischer, S.; Leipner, H.; Thümmler, K.; Brendler, E.; Peters, J. Cellulose 2003, 10, 227.
24. Potthast, A.; Rosenau, T.; Kosma, P.; Chen, C. L.; Gratzl, J. S. Holzforschung 2000, 54, 101.
25. Potthast, A.; Rosenau, T.; Adorjan, I.; Hofinger, A.; Sixta, H.; Firgo, H.; Kosma, P. Cellulose 2002, 9, 283.

26. Röder, T.; Morgenstern, B. Polymer 1999, 40, 4143.
27. Nehls, I.; Wagenknecht, W.; Philipp, B. Cellul Chem Technol 1995, 29, 243.
28. Browning, B. L. Methods of Wood Chemistry; Interscience: New York, 1967; Vol. 2.
29. Sidiras, D. K.; Koullas, D. P.; Vgenopoulos, A. G.; Koukios, E. G. Cellul Chem Technol 1990, 24, 309.
30. Pavlov, P.; Makazchieva, V.; Simeonov, N.; Dimov, K. Cellul Chem Technol 1983, 17, 575.
31. Biganska, O.; Navard, P.; Bédué, O. Polymer 2002, 43, 6139.
32. Fink, H. P.; Weigel, H. J.; Ganster, J. Prog Polym Sci 2001, 26, 1473.
33. Klemm, D.; Philipp, B.; Heinze, U.; Wagenknecht, W. Fundamentals and Analytical Methods; Wiley-VCH: Weinheim, 1998; Vol. 1.
34. Zhang, L.; Ruan, D.; Zhou, J. Ind Eng Chem Res 2001, 40, 5923.
35. Nelson, M. L.; O'Connor, R. T. J Appl Polym Sci 1964, 8, 1325.
36. Jimenez, A.; Berengner, V.; Lopez, J.; Sanchez, A. J Appl Polym Sci 1993, 50, 1565.