Preparation and Characterization of Cellulose Nano-Whiskers Extracted from Microcrystalline Cellulose by Acid Hydrolysis

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산 가수분해를 이용하여 microcrystalline cellulose로부터 추출 된 cellulose nano-whisker의 특성분석

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ABSTRACT : Cellulose nanowhiskers (CNW) gamered increasing interest for their remarkable reinforcement of polymer composites. In this work, we were to produce cellulose whiskers from commercially available microcrystalline cellulose (MCC) by acid hydrolysis with sulfuric and hydrochloric acids. Electron microscopy found that each acid produced sililar cellulose crystals of diameters ranging from 20 to 30 nm and lengths ranging from 200 to 300 nm. Moreover, all samples showed remarkable flow birefringence through crossed polarization filters. Conductometric titration of CNW suspensions revealed that the sulfuric acid treated sample had a surface charge of between 140.00 mmol/kg and 197.78 mmol/kg due to sulfate groups, while that of the hydrochloric acid treated sample was undetectable. Thermogravimetric analysis showed that the thermal decomposition temperature and apparent activation energy (evaluated by Broido's method at different stages of thermal decomposition.) of H1-CNW - prepared by hydrolysis with hydrochloric acid - was higher than those of S1-CNW and S2-CNW - prepared by hydrolyzing MCC with sulfuric acid.

요 약 : 본 연구에서는 친환경적인 특징을 가지면서도 우수한 기계적 특성을 가지고 있어 고분자 복합재료의 보강제로 주목 받고 있는 Cellulose nanowhisker (CNW) 를 염산 혹은 황산을 사용한 산가수분해 방법을 이용하여 Micro-crystalline cellulose (MCC) 로 부터 추출하였다. 염산 혹은 황산을 사용하여 추출된 CNW는 직경이 20 에서 30 nm 정도였고, 길이가 200 에서 300 nm 로써, 형상학적 측면에서 유사한 특성을 가지는 것을 확인하였다. 또한 전해질 용액의 전기전도도를 이용한 적정 (conductometric titration) 결과 황산을 이용하여 제조되어진 CNW의 경우, 셀룰로오스 표면의 sulfate group 에 의해 나타나는 표면전하 값이 각각 140, 197.78 mmol/kg 으로 나타났으며, 염산을 이용하여 제조되어진 CNW 의 경우 셀룰로오스 표면에 약한 전하 값을 가져 표면전하 값을 구할 수 없었다. 황산을 이용하여 추출된 CNW의 열중량 분석 결과 염산을 이용하여 추출된 CNW와 비교하여 열분해 온도가 급격히 감소하는 것을 확인할 수 있었으며, Broido's method를 이용하여 정의 되어진 열분해 거동에 대한 활성화 에너지 역시 상대적으로 낮음을 확인할 수 있었다.

Keywords : cellulose, thermal property, thermogravimetric analysis, acid hydrolysis

Ⅰ. Introduction

Cellulose is the world's most abundant biopolymer and is present in virtually all plants where its main function is reinforcement. Cellulose is a linear chain of 10,000 to 15,000 linked glucose monomers. Many cellulose chains arrange to form microfibrils comprising disordered, amorphous regions and highly ordered, crystalline regions. Microfibrils have di-

ameters of 3 - 20 nm and lengths that can reach several micro-meters, depending on the source of the cellulose (cotton,[1] wood,[1,2] or bacteria[3,4]). Cellulose nanowhiskers (CNWs) are obtained by acid hydrolysis of microcrystalline cellulose (MCC), in which the chemically more reactive amorphous regions are dissolved. The remaining, nano-sized crystalline cellulose is of rod or whisker form (length: 100 - 300 nm, diameter: 3 - 5 nm, for cellulose from wood). Its reinforcing properties are remarkable. The Young's modulus along native cellulose's chain axis has been calculated as 167.5 GPa[5] and ex-

perimental analysis found the elastic modulus of tunicin whiskers to be 143 GPa.[6] CNWs are defined as fibrous, high-purity, single crystals of nanometer dimensions. CNWs could reinforce polymer-based molded components in a similar way to fiberglass in car bumpers. Many industries, such as automotive, railway, aircraft, irrigation systems, furniture, sports and leisure, could use and benefit from CNW reinforced components.[7-11] CNWs have several advantages when compared with inorganic fillers. Their organic origins make them renewable, relatively low in cost, and supportive of an agricultural-based economy. They are, also capable of improving the storage shear modulus in thermoplastics above the T_g (glass transition temperature) (fibers bond well with polymers providing strong, rigid reinforcement), comparatively easy to process, generally lighter in weight than other comparable fillers, and relatively reactive (possibly allowing chemical functionality). The potential market for CNWs is substantial.[12]

Despite these attractive properties, a drawback of using cellulose is that the crystallites have to be isolated. Acid hydrolysis of cellulose is a well-known process used to remove amorphous regions and isolate cellulose whiskers. The nomenclature of cellulosic colloidal particles is varied: whiskers, monocrystals, nanocrystals, and cellulose crystallites are all used herein.[13-15] The acid hydrolysis of native cellulose used to obtain stable CNW suspensions introduced negative groups to the outer surface of the cellulose which would decrease its thermal stability by dehydration reactions. The thermal stability of cellulose whiskers is important, considering its hoped for application as reinforcing filler in polymer composites, especially for thermoplastics, as processing temperatures often exceeds 200 ℃.[16]

The aims of this paper are twofold: to isolate cellulose whiskers from commercially available MCC by acid hydrolysis with sulfuric acid or hydrochloric acid and to investigate their thermal decomposition by establishing their activation energies through a thermogravimetric analysis by Broido's method at different stages of their thermal decomposition.

Ⅱ. Experimental

1. Materials

The MCC was purchased from JRS (Germany). The MCC product (Vivapur® 102) consisted of highly purified agglomerates of celluloses with outer mean diameter of 90 to 160 μm and a bulk density ranging from 0.28 to 0.33 g/cm³ was used as starting material for the preparation of the CNWs in this study. Hydrochloric and sulfuric acids were purchased from Junsei Chemical Co., Ltd.

2. Preparation of cellulose nanowhisker suspension

Stable colloidal dispersions of CNW were prepared according to a previously described method.[17] To extract the CNWs, the agglomerated MCC was first mixed with deionized water and stirred for 5 min at room temperature. The resulting suspension was then stirred in an ice bath while concentrated hydrochloric acid or sulfuric acid was added drop-wise until the desired acid concentration was reached (see Table 1 for details). This MCC / acid mixture was subsequently stirred and refluxed. Reaction were terminated by 5-fold dilution. The suspensions were then washed with deionized water using repeated centrifuge steps at 12,000 rpm for 10 min. The supernatant was removed and replaced by fresh deionized water and mixed. The centrifuge steps were stopped before the supernatant became turbid. The resulting suspensions were placed in cellulose dialysis membranes (purchased from Sigma-Aldrich) having a molecular weight cut off of 12,000 - 13,000 and dialyzed against deionized water for several days until the water pH remained constant. Finally, the samples were then sonicated for 30 min at 50 % output control (Model No. GEX-750, Ultrasonic Processor) while cooling in an ice bath to avoid overheating.

3. Characterizations

The cellulose particles' surface charge was determined using the method described by Katz et al.[18] and is based on changes

Table 1. Acid Hydrolysis Conditions for Each Sample

Sample	Acid conc.	MCC conc.	Temperature	Time	Sonication time
	(%, w/w)	(g/100ml)	(℃)	(min)	(min)
MCC	-	-	-	-	-
S1-CNW	H_2SO_4, 55.00	10.00	50	120	30
S2-CNW	H_2SO_4, 65.00	10.00	50	120	30
H1-CNW	HCl, 15.50	5.00	80	230	30

in conductance of the suspension, which in turn is related to the concentration of the most highly conducting ions, i.e. hydrogen and hydroxyl. Approximately 0.5 g of the freeze-dried cellulose was mixed with 45 ml of deionized water and 5 ml of 0.01 M NaCl before measurement. 0.5 ml NaOH (0.1 M) was then added to the suspension every 5 min while stirring continuously. The conductivity was recorded by a conductometer (METTLER TOLEDO, MC 226). The conductivity decreased until excess acid was neutralized. Further additions of alkali reacted with the acid groups bound to the cellulose and did not change the conductivity. Excess alkali again raised the conductivity.

As the CNWs are rigid rod-like particles, they have a strong tendency to align along a vector director, resulting in a macroscopic birefringence that can be directly observed through crossed polarization filters.[19] In this study, flow birefringence was investigated using two crossed polarization filters. All samples were diluted to a concentration of 0.1 g/100 ml before examination.

Field-emission scanning electron microscopy (FE-SEM) was performed to investigate the morphology of the MCC and CNWs with a HITACHI S4800 instrument operated at 15 kV. The samples were prepared by spray coating on glass and overnight drying at 80 ℃.

As mentioned above, CNWs as reinforcing filler in polymer composites has attracted wide interest because of their renewable nature and mechanical properties.[6,20-24] The thermal stability of CNWs is important for these applications, especially for thermoplastics, because the processing temperature often exceeds 200 ℃.[16] The thermal stabilities of CNWs prepared by hydrochloric acid and sulfuric acid hydrolysis were therefore analyzed by a TGA Q500 (TA instruments) from room temperature to 600 ℃ at a heating rate of 10 ℃/min under a nitrogen atmosphere.

Ⅲ. Results and discussion

1. Surface charge of CNWs and morphology

The conductometric titration curve of the CNW suspensions is shown in Figure 1. Those of the sulfuric acid prepared suspensions showed three regions. In the first, the conductivity decreases with increasing neutralization. This is due to the disappearance of free H^+ ions by the neutralization of strong acid groups on the cellulose whiskers. The second, horizontal region corresponds to the neutralization of weak acid groups, such as carboxylic acid. The third shows the conductivity increasing due to excess free OH^- ions. By contrast, those of the cellulose whiskers prepared with hydrochloric acid rose continuously from the onset. This indicates that no acid groups were present after hydrolysis by hydrochloric acid.[2] The con-
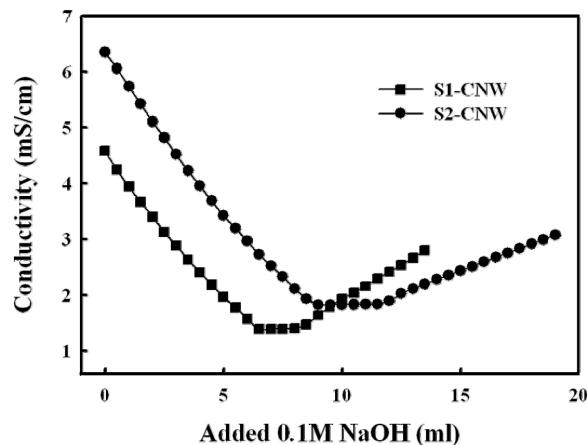

Figure 1. Conductometric titration curves of the S1-CNW and S2-CNW prepared by hydrolyzing MCC with sulfuric acid.

Table 2. The Amount of Acidic Groups on Hydrolyzed Cellulose with Different Treatments

Sample	S1-CNW	S2-CNW	H1-CNW
Sulfate groups (mmol/kg)	140.00	197.78	-

ductometric titration curves allow precise determination of the amount of strong acid on the cellulose whiskers (Table 2). S2-CNW showed a higher concentration of strong acid, sulfate groups of 197.78 mmol/kg compared with S1-CNW. This is notably higher than what has been reported by Araki et al., 84 and 140 mmol/kg.[2,25] Although the H1-CNW hydrochloric acid treated suspension contained only a small amount of weak acid groups, such as carboxylic acid, it could form a stable colloid at the very low ionic strength attained by dialysis. Thus, the use of sulfuric acid for cellulose whisker preparation leads to more stable whisker suspensions than those prepared using hydrochloric acid.[2] However, the stability of the hydrochloric acid treated suspension is expected to be improved by additional chemical or physical methods such as functionalization and sonication.

Cellulose whiskers were prepared by acid hydrolysis of MCC and analyzed by FE-SEM, as shown in Figure 2. The expected high density of hydroxyl groups on the cellulose strongly interact and cause particle agglomeration. Thus, individual cellulose whiskers became visible in FE-SEM micrographs when the suspension was spray coated onto glass at 80 ℃ hot-plate. The FE-SEM images of the prepared cellulose whiskers show isolated whiskers in the nanometer scale having lengths ranging from 200 to 300 nm and widths ranging from 20 to 30 nm. Moreover, low stirring led to birefringent domains in suspensions prepared with either acid when observed with polarized light between crossed polarization filters
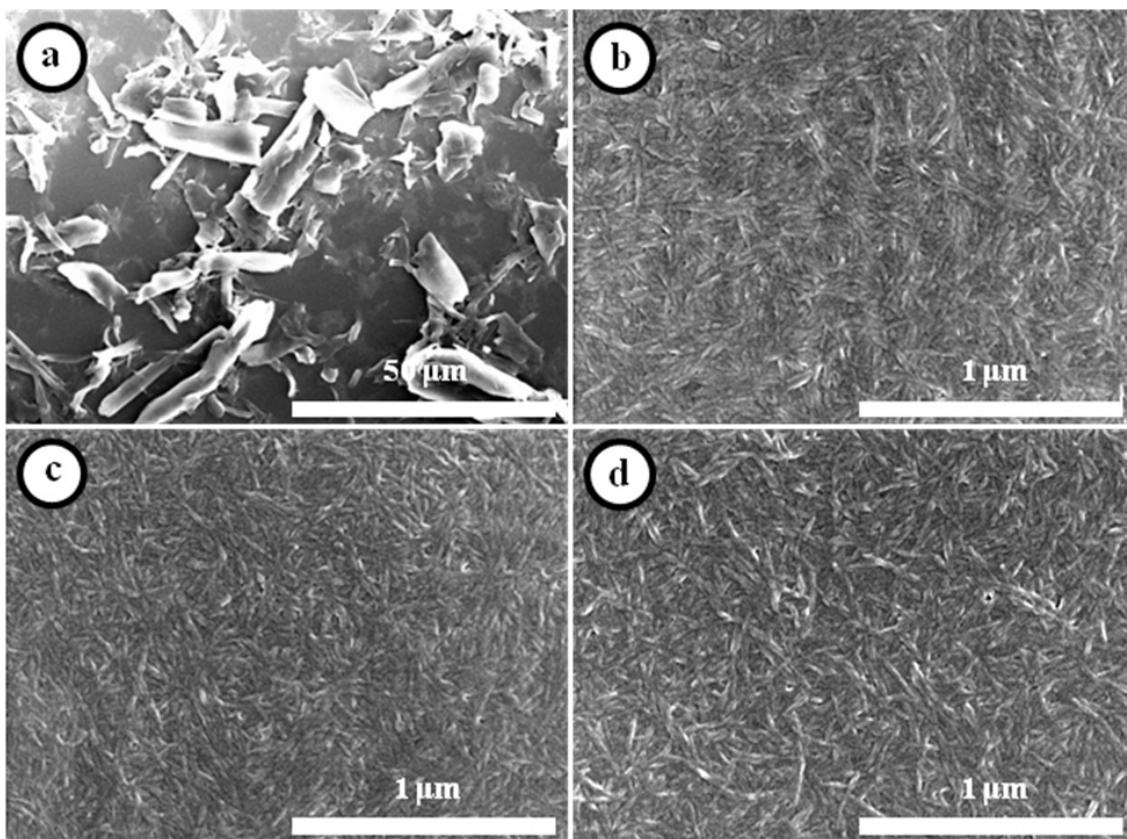
Figure 2. FE-SEM images of (a) commercial available MCC and cellulose nanowhisker samples ((b) S1-CNW, (c) S2-CNW and (d) H1-CNW) with different treatments.

(Figure 3). This colloidal behavior has previously been observed elsewhere and originates from the repulsion between the negative charges on the rod-like cellulose crystals' surfaces.[17] In this study, all samples showed remarkable flow bi-refringence through crossed polarization filters, which is supportive of the existence of cellulose whiskers.[25,26]

2. Thermal gravimetric analysis

2.1 Thermal decomposition pattern and char residue

The TG curves of MCC and CNW are shown in Figure 4. Below 150 ℃, a weight loss (5 - 7 wt%) was observed for all samples due to evaporation of the physically adsorbed
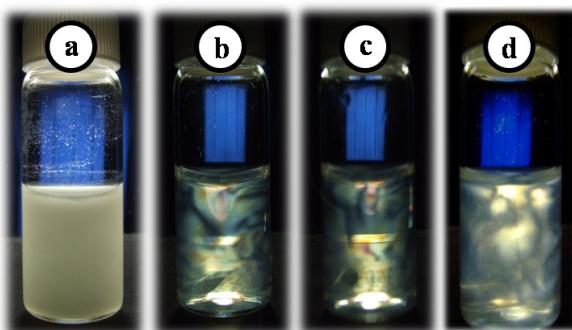

Figure 3. Flow birefringence of (a) MCC, (b) S1-CNW, (c) S2-CNW and (d) H1-CNW suspensions seen between two crossed polarizing films. (All samples were diluted to a concentration of 0.1 g/100ml before examination.)
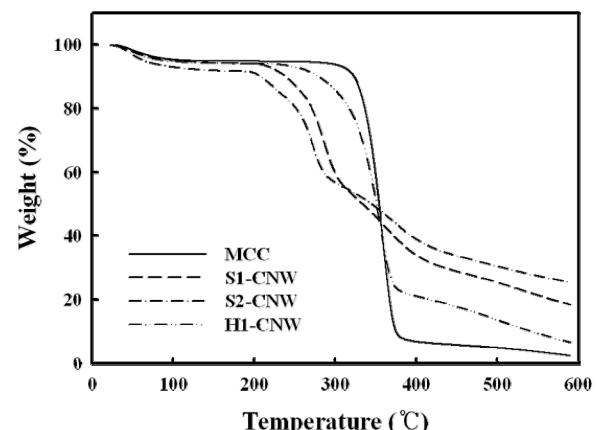

Figure 4. TGA curves of commercial available MCC and cellulose nanowhisker samples with different treatments.

Table 3. The Water Content and Char at 590℃ of MCC and CNW Samples Obtained from TGA Curves

Sample	Water content[a]	Char at 590℃
	(%)	(%)
MCC	4.86	2.35
S1-CNW	5.14	18.35
S2-CNW	7.31	25.37
H1-CNW	5.42	6.54

[a] Weight loss at 110℃

water. In contrast, only minor weight loses were observed for acid hydrolyzed MCC (S1-CNW, S2-CNW and H1-CNW) below 300 ℃. Moreover, the thermal decomposition of S1-CNW and S2-CNW (the sulfuric acid prepared specimens) demonstrated two, well separated, pyrolysis processes. One process occurred between 200 and 280 ℃ and the other between 300 and 400 ℃. In the lower temperature range (200 - 280 ℃), the dehydration reaction firstly took place at cellulose chain units directly containing sulfate groups. The subsequent degradation (from 300 - 400 ℃) occurred at those cellulose chains not in direct contact with the catalyst or those in the cellulose crystal interior.[27] Thermal decomposition of S2-CNW was noticeably lower than that of S1-CNW above 300 ℃, and the amounts of char residue at 590 ℃, obtained from the TG curves (listed in Table 3), were much greater in samples with acid sulfate groups (S1-CNW, S2-CNW) than those of MCC and H1-CNW. Sulfuric acid is known as a dehydration catalyst and so facilitated the char residue formation.[28-30] The results from the higher temperature decomposition (300 - 400 ℃) of those cellulose chains not in direct contact with the catalyst and those in the crystal interior with the slow charring process

of the solid residue, and this result was in good agreement with the conductometric titration results (see the Table 3). In addition, it is noticeable that the thermal decomposition temperature of H1-CNW was higher than those of S1-CNW and S2-CNW. This may be attributable to the hydrochloric acid treated suspension (H1-CNW) containing fewer weak acid groups, as reported previously.[2]

2.2 Pyrolysis kinetics

In this study, Broido's method[31] was applied for TGA data to evaluate the energy of activation (E_a) for the thermal decomposition reaction. According to the Horowitz-Metzger method,[32] an auxiliary variable temperature is given by: $\theta = T - T_m$ (where T_m is the temperature of the maximum degradation rate) and it is given by:

$$\ln[\ln[1/(1-\alpha)]] = \frac{E_a}{RT_m}\theta$$

where α represents the degraded weight fraction, $\alpha = (W_0 - W_t) / (W_0 - W_f)$ (where W_0 is the initial weight of the sample, W_f the final weight of the sample W_t the weight remaining at a given temperature), R is the ideal gas constant (8.31 kJ/mol) and E_a is the activation energy. Using as mentioned assumptions Broido derived that:

$$\ln[\ln[1/(1-\alpha)]] = \frac{E_a}{RT} + const.$$

Consequently, plotting (as shown in Figure 5) $\ln[\ln[1/(1-\alpha)]]$ vs. $1000/T$ gives a straight line of gradient equal to the activation energy (E_a), shown in Table 4.
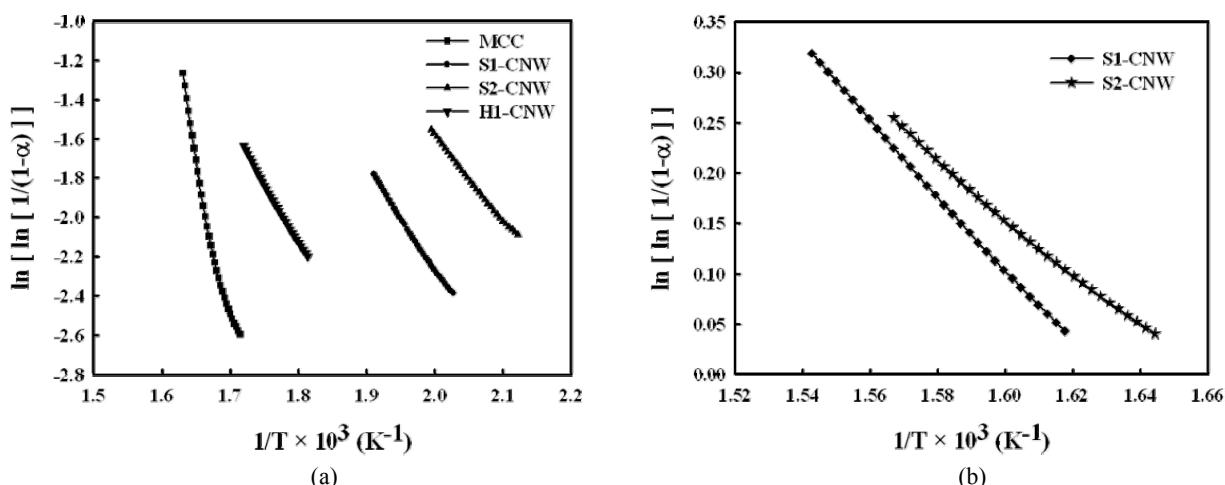

(a)

(b)

Figure 5. Plots of $\ln[\ln[1/(1-\alpha)]]$ vs. $10^3 \times T^{-1}$ (K^{-1}) using *Broido's method* for MCC and CNW samples during (a) first process and (b) second process.

Table 4. Activation Energy of MCC and CNW Samples Calculated by *Broido's Method*

Sample	First process			Second process		
	Onset Temp.[a]	Temp. range	E_a	Onset Temp.[a]	Temp. range	E_a
	(℃)	(℃)	(kJ mol^{-1})	(℃)	(℃)	(kJ mol^{-1})
MCC	310.77	310-340	133.61	-	-	-
S1-CNW	221.54	220-250	44.06	345.14	345-375	30.88
S2-CNW	198.60	198-228	35.89	335.65	335-365	23.10
H1-CNW	278.86	278-308	49.97	-	-	-

During the first thermal decomposition, (termed "1st process" in Table 4), $T_{1st\ onset} \sim T_{1st\ onset} + 30$ ℃, the MCC showed the high activation energy of 133.61 kJ/mol between 310 and 340 ℃. On the other hand, S1-CNW and S2-CNW showed lower activation energies of 44.06 and 35.89 kJ/mol, respectively. In addition, H1-CNW had an activation energy higher than S1-CNW and S2-CNW of 49.97 kJ/mol. As mentioned above, this result was occurred due to the dehydration reaction taking place first at cellulose chain units directly containing sulfate groups and/or carboxyl groups, with a great number of free end chains due to their small particle size.[27,33] In the second thermal decomposition range (termed "2nd process" in Table 4), $T_{2nd\ onset} \sim T_{2nd\ onset\ t} + 30$ ℃, S1-CNW's higher activation energy of 30.88 kJ/mol, greater than S2-CNW's arose from the sulfate groups, which are a well known dehydration catalyst so facilitating the char residue formation.[28-30]

Ⅳ. Conclusions

Sulfuric and hydrochloric acids have been used to hydrolyzed microcrystalline cellulose and form cellulose whiskers, whose subsequent isolation from the MCC was confirmed by FE-SEM. They had lengths ranging from 200 to 300 nm and widths ranging from 20 to 30 nm. Also, cellulose whisker presence was supported by the remarkable flow birefringence through crossed polarization filters of the suspensions. S1-CNW and S2-CNW had sulfate groups present to the extents of 140.00 and 197.78 mmol sulfate groups / kg cellulose whisker, respectively.

Comparing with MCC, the decomposition of cellulose whiskers started at lower temperature. This distinction was mainly caused by significant difference of particle size between cellulose whisker and MCC. Furthermore, the amount of charred residue of S1-CNW and S2-CNW at 590 ℃ was greater for samples with more sulfate groups, confirming that the sulfate groups act as flame retardants. In addition, the decomposition temperature of H1-CNW was higher than those of S1-CNW and S2-CNW. This may be attributable to the hydrochloric acid treated suspension (H1-CNW) containing only a small amount of weak acid groups.

Therefore, we can conclude that the use of sulfuric acid for cellulose whiskers preparation leads to more stable whisker suspensions than those prepared using hydrochloric acid. However, the colloidal stability of hydrochloric acid treated suspension is expected to be improved by chemical or physical methods such as functionalization and homogenization. In addition, the use of hydrochloric acid makes more thermally stable whiskers than those prepared using sulfuric acid, potentially leading to their use as reinforcement for polymer composites.

Acknowledgment

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