

Characteristics of water-soluble fiber manufactured from carboxymethylcellulose synthesis

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Abstract—Carboxymethylcellulose (CMC), which is water-soluble fiber at room temperature, was manufactured from cellulose in this study. Experimental parameters included reaction temperature, time, concentration of NaOH, and monochloroacetic acid. In mercerization and etherification, the solubility and DS increased when NaOH (or MCA) concentration increased, and maximum solubility and DS were achieved when NaOH or MCA was 30%. The effect of MCA concentrations was larger than that of the NaOH concentration on DS. Tensile strength of the CMC fiber was affected and decreased by an increase in reaction time, reagent concentration and reaction temperature increase. Tensile strength also decreased by NaOH and MCA. However, low decrease of tensile strength was observed in near neutral region.

Key words: Carboxymethylcellulose (CMC), Cellulose, Viscose Rayon, Water-Soluble Fiber, Mercerization, Etherification

INTRODUCTION

Renewable raw materials (wood, cereals, fats and oils) are gaining significant importance because of the constant global demand for energy and raw materials as alternatives to fossil fuel [1,2]. Cellulose is the most abundant renewable resource on the earth. The cellulose formed by photosynthesis was about 10^9 - 10^{12} tonnes per year and 5% of the total timbers felled were converted into cellulose by sulphite or sulphate pulping. Of this quantity approximately 5 million tonnes are processed into purified cellulose. As pure cellulose is not soluble in either cold or hot water due to intramolecular hydrogen bonding between the hydroxy groups in position 3 and the ring oxygen atoms of the neighboring glucose units and intermolecular hydrogen bonds between the 6-hydroxy groups and the oxygen bonds of the glycosidic linkages, 35% of the purified cellulose is converted to the reaction products cellulose esters (25%) and cellulose ethers (10%) [3]. These cellulose derivatives may be water soluble and can be used in many technical applications [4-7]. However, it is possible to achieve different properties of cellulose ethers such as water retention capacity, pseudo-plasticity, film formation, complexation and surface activity by varying their structure [8,9] and thus making them applicable to a wide range of applications [10-14]. Moreover, cellulose ethers are physiologically harmless and tolerated by the skin and mucous membranes [15]. Therefore, these are being used in pharmaceutical, cosmetic and food products [16-18].

One of the important features of cellulose is that it can be converted into derivatives by rather simple chemical modification. It is well known that the solubility of cellulose derivatives strongly depends not only on the degree of substitution (DS) but also on the distribution of the substituents in the glucose units and along the cellulose chain. Kötzt et al. [19] studied the characterization of these unconventionally synthesized CMC samples with regard to their macromolecular and electrochemical data and showed some special colloidal features which can open up new fields of application

for this special type of CMC. Kim et al. [20] studied the reaction condition for preparation of a highly substituted CMC directly from the cotton-knit-waste. To increase the DS of the synthesized CMC, various reaction conditions were tested and the synthesized CMC was tested with X-ray diffraction, IR, and viscosity meter. In their report, viscosity of CMC from cotton-knit-waste was higher than that of the commercial product derived from wood pulp. Racz and Borsa [21] investigated the swelling of cellulosic fibers having different carboxyl contents over a wide range achieved by varying the parameters during carboxymethylation, and demonstrated that the concentration of sodium hydroxide was the dominant factor among the investigated reaction parameters.

This prompted us to manufacture water-soluble CMC fiber at room temperature from the viscose rayon of non-woven fiber type. However, synthetic fiber causes many environmental problems, and natural fiber is difficult to reuse and to decompose. Thus soluble fiber was developed to solve this problem. First, carboxymethylcellulose (CMC) was prepared from viscose rayon which is a regenerated cellulose fiber. Second, water solubility of CMC was tested at room temperature. Third, effect of experimental parameters on DS was tested. And finally, its tensile strength was measured.

MATERIALS AND METHODS

1. Materials

Viscose rayon of non-woven fiber type (MW=12,000-14,000, DP=300, degree of crystallinity=30-40%, fiber dimensions=25 cm×25 cm, fineness (d)=1.5, elongation=20-25%) was supplied by TEXTECH Co., Ltd. Sodium hydroxide, monochloroacetic acid, hydrochloric acid and ethyl alcohol were purchased from Duksan Pure Chemical Co., Ltd.

2. Carboxymethylation

The mechanism of carboxymethylation of cellulose is shown in Fig. 1 and the experimental procedure is shown in Fig. 2. 2 g of viscous rayon (sample) was made to react with the mixture solution of ethanol and aqueous sodium hydroxide in a constant temperature bath. After mercerization was completed, sample was reacted with monochloroacetic acid for etherification in constant temperature

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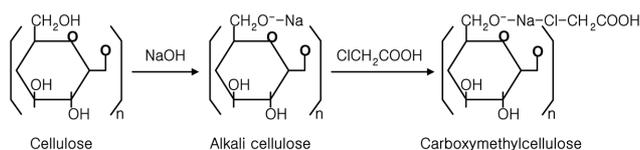


Fig. 1. Mechanism of carboxymethylcellulose process.

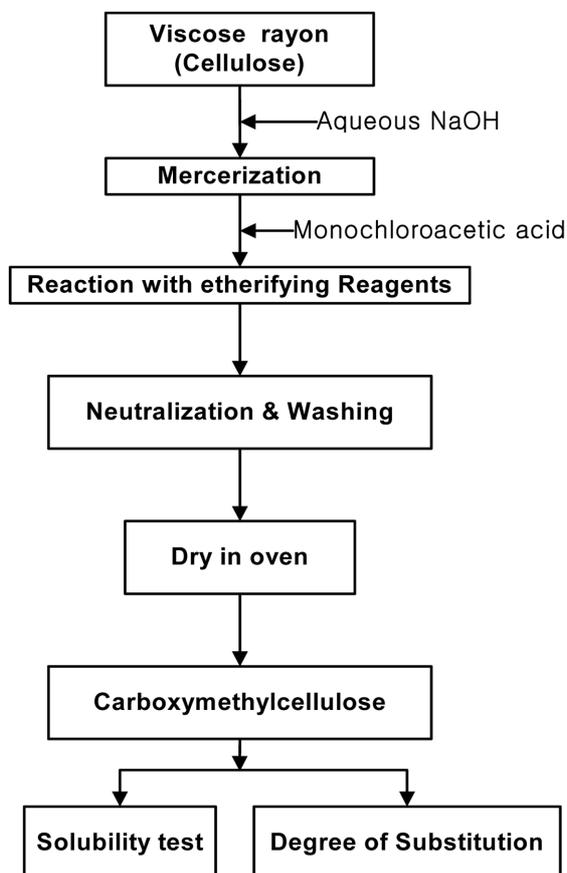


Fig. 2. Process of experiment.

bath. It was then neutralized and washed with a mixture of ethanol and hydrochloric acid. Final product was dried in an oven at 70 °C for 15-30 min.

3. Solubility Test

Weighed final products (5 cm × 5 cm) was dispersed into 100 ml of water for 30 min at room temperature with agitation at 60 rpm. The solubility of products was defined by Eq. (1):

$$\text{Solubility (\%)} = \frac{M-R}{M} \times 100 \quad (1)$$

where M was the amount of undissolved sample (g), and R was the amount of manufactured CMC sample (g).

Three parameters (concentration of reagent, time period and reaction temperature) were varied while dipping, washing, and drying conditions were held constant. The concentration of sodium hydroxide solution was varied from 5 to 50%. The ratio of sodium hydroxide in region of its maximum solubility and monochloroacetic acid was between about 0.3-2. Reaction time was varied from 5 to 90 min for mercerization and for etherification.

4. Determination of DS (Degree of Substitution)

Green's [22] method was adapted in the determination of DS. 2 g sample was dried for 1 hr at 100 °C in a weighing bottle and weighed by difference in a 500 ml Erlenmeyer flask. Then 15 ml of 70% methanol was added and the mixture was allowed to stand for a few minutes, and finally 200 ml of water and 50 ml of 0.5 N sodium hydroxide were added. The mixture was shaken for 3-5 hr until the sample was dissolved. The solution was then back-titrated with 0.4 N hydrochloric acid using phenolphthalein as an indicator. The DS was calculated by

$$\text{DS} = \frac{162 \times f \times (10.0 - C \times N)}{1000 \times S - (58 \times f \times (10.0 - C \times N))} \quad (2)$$

where S was oven-dry weight of CMC sample (g), C was the volume of standard HCl solution (ml), N was the normality of HCl solution, and f was the correction factor of standard HCl solution.

5. Determination of Tensile Strength

Tensile strength was measured by constant rate of traverse and grab method was used to measure the tensile strength (KS K 0520) (Fig. 3). Grab method is usually applied to estimate tensile strength in textile. This is a convenient method if many samples are to be tested. Test sample (treated or untreated viscous rayon) was prepared in MD (machine direction) length of 10 cm and CD (cross direction) length of 15 cm. The tensile rate was 200 mm/min, and average value was calculated after measuring ten times for each test sample.

6. FT-IR Analysis of Manufactured CMC Fiber

The sample was shattered and mixed with KBr to make KBr pellets. In order to analyze the sample, FT-IR spectrum was then recorded using FT-IR (BRUKER, TENSOR 27).

RESULTS AND DISCUSSION

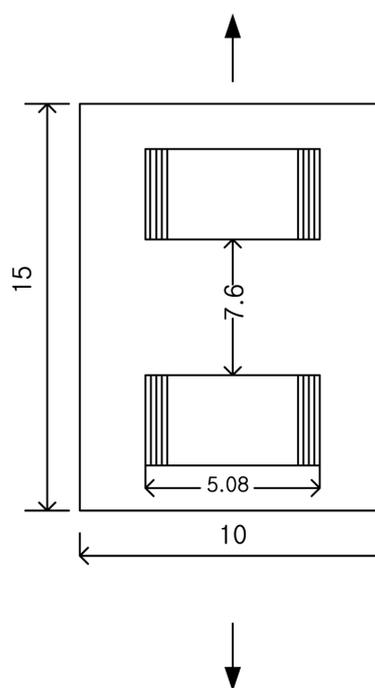


Fig. 3. Form of test sample according to experimental method.

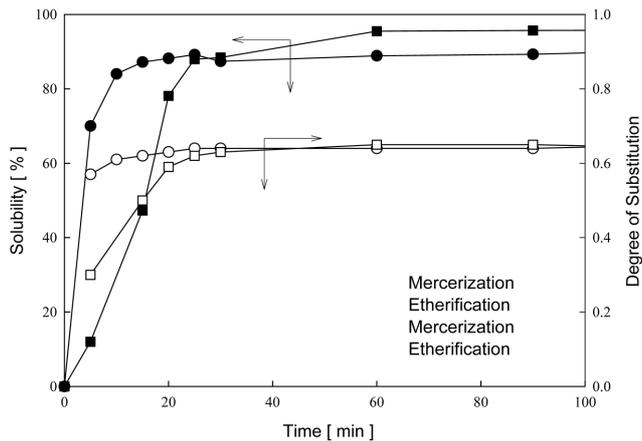


Fig. 4. The effect of reaction time of mercerization and etherification on solubility and degree of substitution.

1. Effect of Reaction Time on Mercerization

The effect of reaction time on mercerization was shown in Fig. 4. The reaction temperature and concentration of NaOH were kept constant at 45 °C and 40% (w/v), respectively, during this experiment. As the reaction time increased, product was well-dissolved in water, and the difference in the solubility was very small after 30 min. Degree of substitution (DS) varied from 0.62-0.65 and did not show much difference depending on the reaction time. The optimal reaction time was 30 min, and DS was 0.65.

2. Effect of Concentration of NaOH on Mercerization

Sodium hydroxide swells the fiber when applied to cellulose. In the mercerization reaction, sodium hydroxide dissolved the hemicelluloses and formed a light brown liquid. This process was used in the viscose rayon manufactured from cellulose pulp. Fig. 5 showed the effect of NaOH concentration on solubility and DS at 45 °C after 30 min of reaction time. Solubility and DS increased when NaOH concentration increased up to 40%. However, solubility and DS decreased with further increase in NaOH concentration. It was thought that the NaOH does not completely dissolve in pure water, and recrystallization occurred when mixed with ethanol. Thus, sample was not completely in contact with NaOH, and the mercerization

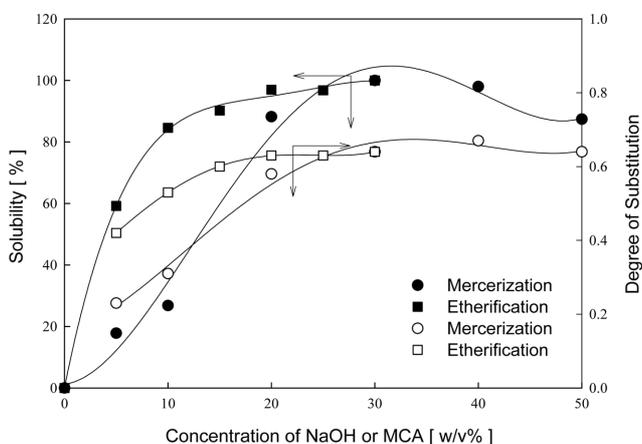


Fig. 5. The effect of NaOH or MCA concentration in mercerization or etherification.

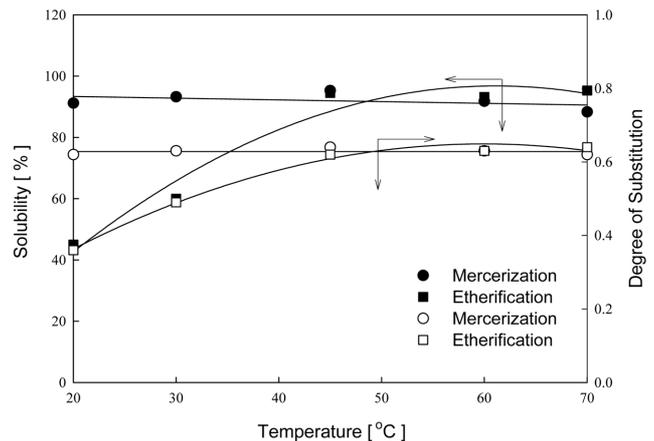


Fig. 6. The effect of reaction temperature in mercerization and etherification.

reaction occurred in only NaOH wetted region. This caused the lower value of solubility and DS.

3. Effect of Reaction Temperature on Mercerization

Temperature range of mercerization was varied from room temperature to 70 °C and is shown in Fig. 6. The reaction time and concentration of NaOH were kept constant at 30 min and 40% w/v, respectively, during this experiment. Optimum temperature of general mercerization is known at 0-5 °C; however, mercerization temperature for manufactured water-soluble fiber was found to be 45-50 °C. At this temperature, fiber dissolved well in the water. But change in solubility was very small. Also, DS did not show any differences according to the reaction temperature variation. Thus, it was concluded that the temperature is not a critical factor in the mercerization reaction.

4. Effect of Reaction Time on Etherification

The effect of reaction time of etherification on solubility and DS at 45 °C and in 30% w/v of MCA is shown in Fig. 4. Solubility increased up to 1 hr of the etherification reaction time, and remained constant thereafter, as shown in Fig. 8. Similarly, DS increased sharply

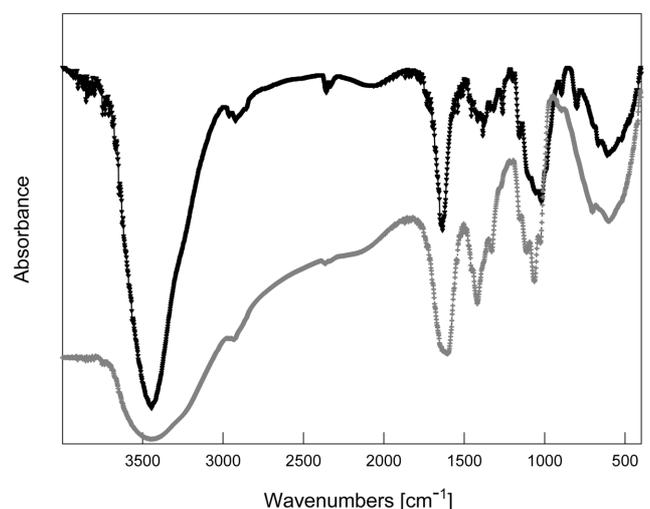


Fig. 7. FT-IR spectrum of original viscous rayon (----) and manufactured water-soluble fiber (CMC) (----).

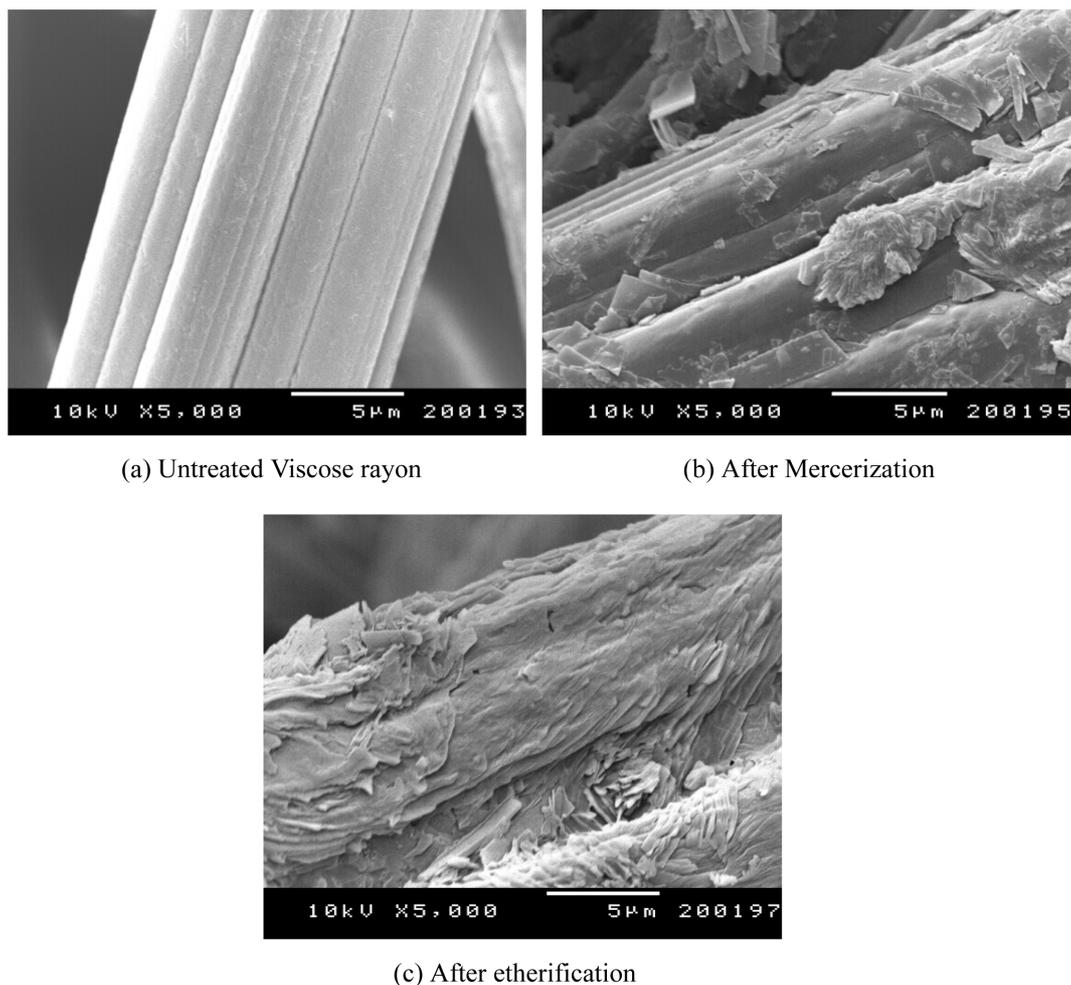


Fig. 8. The SEM images of viscose rayon fiber after mercerization and etherification (10 KV×5,000).

at the beginning up to 0.65, and remained constant since then. The highest DS was 0.65 at the reaction time of 0.5-1 hr. Solubility slightly increased when powder cellulose was used, and a similar pattern with mercerization was observed. DS ranged from 0.52 to 0.77, and the highest DS was observed at 1.5 hr. DS indicates the extent of reaction or conversion. Though important industrially, manufactured CMC covers a DS range of 0.5 to 1.0. It was also reported that a decisive change in material properties of water soluble CMC can be obtained by chemical modification of a rather small fraction of the total number of hydroxyl groups [22].

5. Effect of Concentration of Monochloroacetic Acid on Etherification

Monochloroacetic acid (MCA) was dissolved in ethanol, and CMC was manufactured with different concentrations of MCA (Fig. 5). The reaction temperature and time were kept constant at 45 °C and 30 min, respectively, during this experiment. The ratio of NaOH to MCA was fixed at 3 : 4. As the concentration of MCA increased, solubility and DS increased. Viscose rayon of non-woven fiber type was completely dissolved at 30% MCA. On this occasion, the value of DS ranged from 0.6 to 0.7.

6. Effect of Reaction Temperature on Etherification

The effect of temperature on etherification was studied (Fig. 6). The reaction time and concentration of MCA were kept constant at

30 min and 30% w/v, respectively, during this experiment. Etherification was carried out from 20 °C (room temperature) to 70 °C. Solubility increased with increase in temperature up to 50 °C, and then it remained constant. This may be a very important finding for ethanol use. Previously, etherification was carried out at 70 °C and a large quantity of ethanol was lost during the etherification due to the volatile nature of ethanol. However, etherification is just as good at 50 °C as shown in this experiment. Therefore, loss of ethanol may be reduced greatly.

7. Tensile Strength

In this study, CMC was manufactured from non-woven fabrics, and manufactured fabrics should show similar tensile strength with existing fabrics. Tensile strength of the non-woven fabrics CMC was measured. The unit of the tensile strength was expressed as N (KS K 0520). In general, most fabrics showed different tensile strengths according to weight.

In this study, viscose rayon of the machine direction (MD) length of 10 cm and cross direction (CD) length of 15 cm was used. Ratio of tensile strength of the MD and CD was about 7 : 3. Weight of the viscose rayon was about 3.5 g. The solubility and the degree of substitution of non-woven CMC fabrics were affected by reaction time, reagent concentration and reaction temperature, except for the effect of temperature on solubility during mercerization and etherifi-

cation where it was independent of temperature. The tensile strength was significantly affected by these parameters. The effects of reaction time, NaOH concentration, the amount of NaOH and reaction temperature during mercerization and etherification on the tensile strength are shown in Table 1-4. As the solubility of test sample increased, tensile strength decreased. Tensile strength decreased as reaction time increased in Table 1. It is thought that tensile strength

Table 1. Effect of reaction time of mercerization and etherification process on tensile strength and solubility of fiber

Reaction time (min)	Mercerization			Etherification		
	Tensile strength (N)		Solubility (%)	Tensile strength (N)		Solubility (%)
	MD	CD		MD	CD	
5	64.68	13.72	70.0	69.58	20.58	12
10	63.70	13.72	84.0	69.58	19.60	30
15	62.72	12.74	87.2	68.60	19.60	47.3
20	62.72	12.74	88.2	68.60	20.58	78.1
25	61.74	12.74	89.2	66.64	19.60	88
30	64.68	12.74	87.4	64.68	17.64	88.4
60	53.90	12.74	88.9	58.80	17.64	95.5
90	53.90	12.74	89.3	40.18	10.78	95.7
120	54.88	12.74	90.4	47.04	12.74	95.8
150	39.20	9.80	91.1	43.12	10.78	95.8
180	40.18	10.78	93.9			
210	35.28	7.84	92.1			
240	31.36	6.86	92.4			

Table 2. Effect of NaOH concentration (in mercerization) and MCA concentration (in etherification) on tensile strength and solubility of fiber

NaOH (%)	Mercerization			MCA (%)	Etherification		
	Tensile strength (N)		Solubility (%)		Tensile strength (N)		Solubility (%)
	MD	CD			MD	CD	
5	42.14	11.76	17	5	53.90	17.64	59.2
10	61.74	13.72	40	10	57.82	18.62	84.6
20	54.88	13.72	88	15	58.80	15.68	90.2
30	56.84	12.74	100	20	59.78	12.74	97.0
40	43.12	10.78	99	25	57.82	12.74	96.8
50	22.54	10.78	87.4	30	56.84	12.74	100

Table 3. Effect of NaOH : MCA solution ratio on tensile strength and solubility of fiber

NaOH : MCA (ml)	Tensile strength (N)		Solubility (%)
	MD	CD	
6 : 2	32.34	11.76	60
6 : 4	35.28	14.70	82.1
6 : 6	51.94	21.56	88.7
6 : 8	40.18	10.78	92.8
6 : 10	28.42	9.80	93.5
6 : 12	26.46	12.74	94.4

Table 4. Effect of reaction temperature of mercerization and etherification process on tensile strength and solubility of fiber

Temp. (°C)	Mercerization			Temp. (°C)	Etherification		
	Tensile strength (N)		Solubility (%)		Tensile strength (N)		Solubility (%)
	MD	CD			MD	CD	
25	49.98	12.74	91.2	25	65.66	16.66	45
30	49.00	12.74	93.2	30	65.66	12.74	60
45	40.18	10.78	95.3	45	63.70	12.74	94.5
60	19.60	2.94	91.8	60	51.94	10.78	93.2
70	14.70	0.98	88.3	70	40.18	10.78	95.3

was maintained at constant value for some time in comparison with mercerization reaction time. Thus, fabrics were damaged by acid and base. However, a comparison between NaOH and MCA concentration showed that the effect of NaOH concentration was higher than that of the MCA concentration. But decline of tensile strength was more affected by acid concentration than by base concentration.

Thus, decline of tensile strength may be controlled by the neutralization of acid and base. Effect of reaction temperature of the mercerization and etherification on tensile strength is shown in Table 4. In both cases, a lower tensile strength was observed when higher reaction temperature was used.

8. FT-IR and Morphological Analysis

FT-IR (BRUKER, TENSOR 27) analysis of manufactured CMC fiber was done in order to find hydrophilic group compounds. Fig. 7 shows the conclusion of FT-IR spectrum analysis in the CMC sample. Hydroxyl group's peak is greatly found at $3,500\text{ cm}^{-1}$ in FT-IR analysis. It may be the main functional group when sample is dissolved in water. Also, carbonyl group is found $1,700\text{ cm}^{-1}$ in FT-IR analysis. SEM pictures of viscous rayon, mercerized (alkali cellulose) and etherified fiber (CMC) are shown in Fig. 8. This clearly shows the surface of alkali cellulose and carboxymethylcellulose.

CONCLUSIONS

Water-soluble fiber was manufactured from cellulose material through mercerization and etherification. The solubility, degree of substitution, and tensile strength were measured for the manufactured carboxymethylcellulose with varying conditions of reaction temperature, time, and concentrations. More than 80% of CMC was dissolved in water at room temperature, and DS ranged from 0.6 to 0.7. Both NaOH and MCA concentrations were found to be the most important factor in CMC manufacture. In mercerization, solubility and DS increased when NaOH concentration increased up to 40%. Maximum solubility and DS were achieved when 30% MCA was added in etherification process. Both NaOH and MCA concentration greatly affected the solubility, and the effect of MCA concentration was larger than that of the NaOH concentration for DS. Optimal reaction temperature falls in from $45\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$ in mercerization and etherification. In mercerization and etherification processes, 1 hr is the optimal reaction time. Tensile strength of the CMC fiber was affected and decreased by all the conditions including reaction time, reagent concentration and reaction temperature increase. Tensile strength also decreased by NaOH and MCA. However, low

decrease of tensile strength was observed in the near neutral region.

REFERENCES

1. A. E. Humphery, In *Cellulose as a chemical and energy resource*, Wilkman, C. R. ed., Wiley, New York (1975).
2. S. Kim and Y. Eom, *Korean J. Chem. Eng.*, **23**, 409 (2006).
3. H. Krässig, J. Schurz, R. G. Steadman, K. Schliefer and W. Albrecht, *Cellulose*, In Ullmann's Encyclopedia of Industrial Chemistry, Gerhartz, W., ed., Vol. A, 5th Ed., Wiley-VCH, Weinheim (1992).
4. K. D. Oh and C. Kim, *Korean J. Chem. Eng.*, **4**, 105 (1987).
5. C. Y. Park, Y. W. Ryu and C. Kim, *Korean J. Chem. Eng.*, **18**, 475 (2001).
6. H. H. Yoon, *Korean J. Chem. Eng.*, **15**, 631 (1998).
7. L. Y. Zheng and Y. L. Xiao, *Korean J. Chem. Eng.*, **21**, 201 (2004).
8. R. L. Whistler and J. N. BeMiller, *Industrial gums-polysaccharides and their derivatives*, 2nd Ed., Academic Press, New York (1973).
9. J. F. Kennedy, G. O. Phillips, D. J. Wedlock and P. A. Williams, *Cellulose and its derivatives-chemistry, biochemistry and applications*, Ellis Horwood, Chichester (1985).
10. W. Burchard, *Polysaccharide*, Springer, Berlin (1995).
11. R. D. Gilbert, *Cellulosic polymers*, Carl Hanser, München (1994).
12. Y. L. Melzer, *Water soluble polymers, development since 1978*, Noyes Data Corp, New Jersey (1994).
13. W.-M. Kulicke, O. Arendt and M. Berger, *Colloid Polym. Sci.*, **276**, 1019 (1998).
14. E. E. Treiber, In: *Cellulose chemistry and its applications*, T. P. Nevell and S. H. Zeronian (eds.), Ellis Horwood, Chichester, UK, pp. 445-495 (1985).
15. S. H. Shelanski and A. M. Clark, *Food Res.*, **13**, 29 (1948).
16. W. Kern, *Pharm. Ind.*, **21**, 45 (1959).
17. Y. Pomeranz, *Functional properties of food components*, 2nd Ed., Academic Press, San Diego (1991).
18. H.-D. Belitz and W. Grosch, *Lehrbuch der lebensmittelchemie*, 4th Ed., Springer, Berlin (1992).
19. J. Kötzt, I. Bogen, T. Heinze, S. Lange and W.-M. Kulicke, *Colloids Surf. A*, **183**, 621 (2001).
20. B. S. Kim, S. P. Mun, K. K. Na, J. M. Rhee and S. C. Cho, *J. Korean Fiber Soc.*, **31**, 96 (1994).
21. I. Racz and J. Borsa, *Cellulose*, **4**, 293 (1997).
22. J. W. Green, *Cellulose ether*, In *Method in Carbohydrate Chemistry*, Whistler, R. L., ed., Academic Press, New York Vol. 3, pp. 322 (1963).