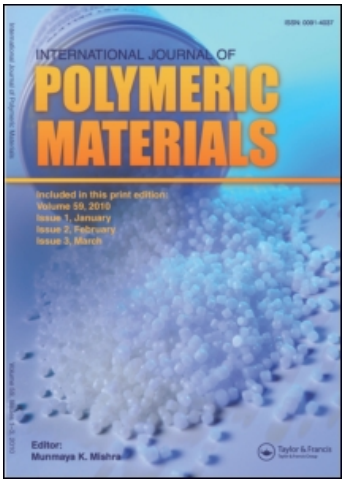

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Carboxymethylation of Cotton Linter in an Alcoholic Reaction Medium

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The effect of isopropanol, isobutanol and butanol on the carboxymethylation of cotton linter was investigated. The reaction was conducted for two hours at 55° by using different concentrations of sodium hydroxide and monochloroacetic acid. The amounts of introduced carboxymethyl groups, rheological properties and infrared spectra of the products were evaluated. It was found that, unlike butanol, isopropanol in the reaction medium results in lower yield and lower degree of substitution, but higher viscosity.

Keywords: Carboxymethylation; Cotton linter; Alcohols; Rheology; IR spectra

INTRODUCTION

Since carboxymethyl cellulose (CMC) was first prepared by Jansen, it was suggested as a substitute for some products such as gelatin, glue, gum *etc.* [1]. CMC and its salt are readily soluble or dispersible in water or alkaline solutions to form highly viscous solutions utilized for their thickening, suspending and stabilizing properties to aid in the suspension of pigments and other finely divided solids in liquid media, and to stabilize emulsions of various type [2]. CMC is one of the derivatives with widespread industrial applications including its use in textile industry, paper industry, detergents, pharmaceutical, lubricants, food industry, ceramics, cosmetics, oil drilling fluid, emulsion

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paints, *etc.* High viscosity CMC is practically useful as a thickening or suspending agent [3].

The quality and solution properties of the produced CMC depend on both the degree of substitution (DS) and degree of uniformity in the substituent distribution within the anhydroglucose units. It was found that CMC samples synthesized under homogeneous reaction conditions using LiCl and DMAc as a cellulose solvent contain a significantly higher amount of both 2,3,6-tri-O-carboxymethylated and unsubstituted units in the polymer chain than those obtained from a slurry of cellulose in isopropanol and water at comparable DS values [4].

Carboxymethylation medium plays an important role in the reaction. Organic solvents are usually applied for the preparation of CMC with higher DS [5], but the use of aqueous solvent is reported to give higher substitution than when water or solvent is used alone [6].

The aim of this work was to investigate the effect of isopropanol, isobutanol and butanol on the carboxymethylation of cotton linter to get a product with improved rheological properties.

EXPERIMENTAL

Purified cotton linter from Abo Zaable Chemicals Company (Abo Zaable, Egypt) was used for CMC preparations. NaOH, MCA (monochloroacetic acid) and alcohols were laboratory grade chemicals.

Carboxymethylation

It was carried out by stirring the cotton linter in the solvent, in liquor ratio 18 : 1, for 15 minutes, then the desired amount of NaOH was added dropwise within 30 minutes from a 30% aqueous NaOH solution, and stirring was continued for one hour. MCA dissolved in the solvent in 1 : 1 ratio was added dropwise to the reaction medium within 30 minutes and the reaction continued for two hours at 55° with stirring. Then the reaction mixture was neutralized with 10% acetic acid, poured into an excess of 70% methanol, filtered by using a G2 sintered funnel and washed with methanol. The produced CMC was dried in a vacuum oven at 55° for 8 hours. Carboxymethylation was

carried out by using isopropanol, isobutanol and butanol as a reaction medium and by using various concentrations of NaOH and MCA as shown in Table I. The yield was determined and the DS was estimated [7].

Rheological Properties

The rheological properties of CMC, 4% solution, were measured on a Haake rotary viscometer at 30°. Apparent viscosity was calculated from the following equation, $I = T/D$ where, I apparent viscosity in poise, T shear stress (dyn/cm^2) and D rate of shear (sec^{-1}).

Infrared Spectra

IR spectra were registered on a fully automatic ATI Mattson–Genesis Series FTIR Spectra-Photometer. The wave length accuracy as determined by the instrument was better than $\pm$ cm^{-1}, while the percent transmittance T% accuracy is $\pm$ 1%. The KBr disc technique was applied and the spectrum of the above samples were obtained.

RESULTS AND DISCUSSION

The results of carboxymethylation under different conditions of chemical concentrations and by using different solvents as a reaction medium are listed in Table I.

TABLE I Conditions and results of carboxymethylation

Sample No.	*MCA %*	*NaOH %*	*Solvent*	*Yield %*	*DS*
1	60	40	Isopropanol	105	0.10
2	90	60	Isopropanol	126	0.26
3	120	80	Isopropanol	167	0.34
4	150	100	Isopropanol	166	0.50
5	60	40	Isobutanol	131	0.21
6	90	60	Isobutanol	134	0.36
7	120	80	Isobutanol	150	0.60
8	150	100	Isobutanol	169	0.75
9	60	40	Butanol	127	0.44
10	90	60	Butanol	130	0.52
11	120	80	Butanol	163	0.61
12	150	100	Butanol	160	0.58

By increasing caustic soda concentrations, the accessibility of cellulose to react with higher concentrations of the carboxymethylating agent, MCA, is improved by the formation of inter crystalline swollen alkali cellulose, thus, the yield and DS are increased. Butanol in the reaction medium gave, in general, superior yield and DS results than isobutanol, while isopropanol gave inferior results.

Figures 1, 2 and 3 plot the rheological properties for the CMC solution at a concentration of 4% in distilled water. It is obvious that all samples examined exhibited a non-Newtonian behavior because the relation between the rate of shear and shearing stress is not linear. It is also seen that the up and down flow curves are not coincident, indicating thixotropic characteristics of all samples under investigation.

As viscosimetry represents a suitable and simple method to evaluate the products, the viscosity values were calculated from the rheograms and Table II shows apparent viscosity values at different rates of shear.

The results from Table II show that apparent viscosity decreases as the rate of shear increases for all samples. Decrement in apparent

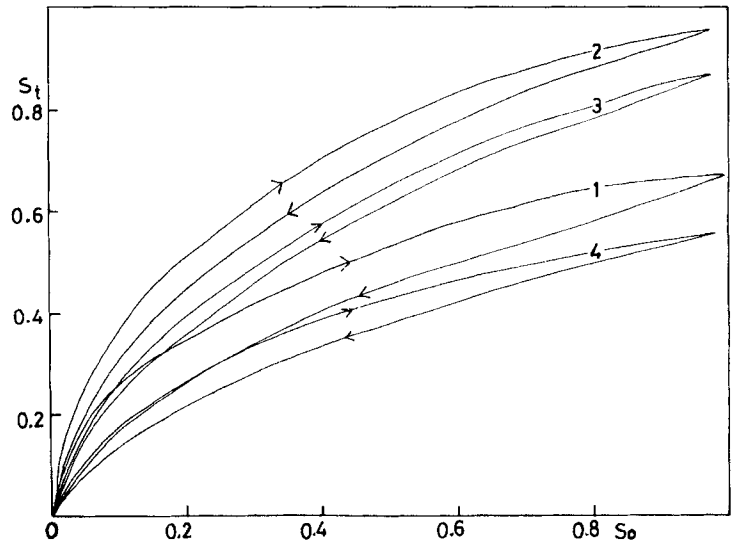

FIGURE 1 Rheograms of CMC samples prepared in isopropanol reaction medium using different concentrations of NaOH and MCA. (1) 40 and 60, (2) 60 and 90, (3) 80 and 120, (4) 100 and 150% respectively.

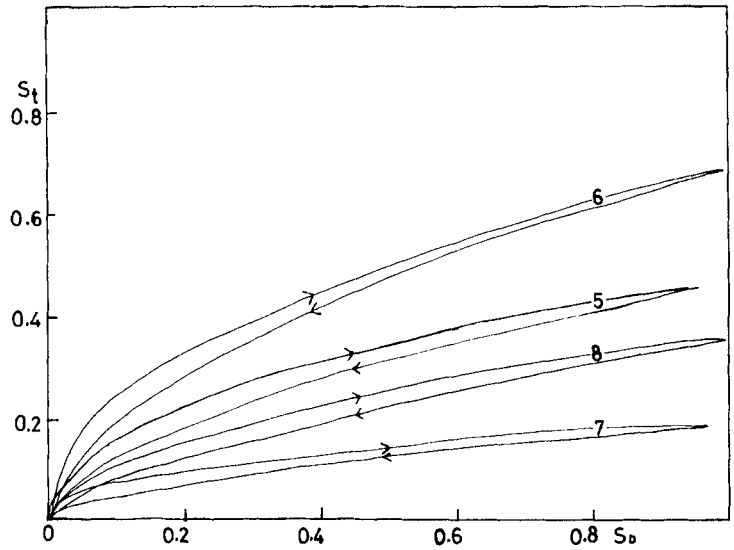

FIGURE 2 Rheograms of CMC samples prepared in isobutanol reaction medium using different concentrations of NaOH and MCA. (5) 40 and 60, (6) 60 and 90, (7) 80 and 120, (8) 100 and 150% respectively.

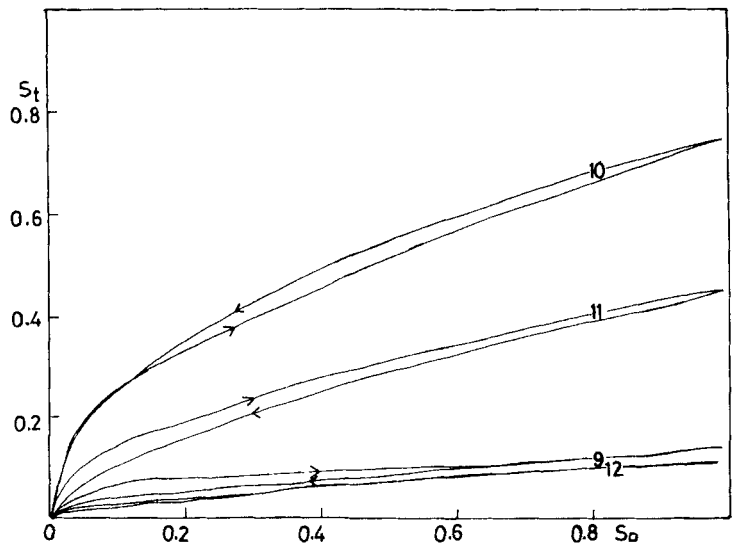

FIGURE 3 Rheograms of CMC samples prepared in butanol reaction medium using different concentrations of NaOH and MCA. (9) 40 and 60, (10) 60 and 90, (11) 80 and 120, (12) 100 and 150% respectively.

TABLE II Apparent viscosity, in m.pas/s, at different rates of shear (sec^{-1}) for different CMC samples

Share rate / *Sample No.*	129	258	387	516	645	774	903	1032	1161
1	1213	817	658	554	485	431	392	361	334
2	1689	1190	952	809	711	638	580	531	484
3	1237	910	759	663	597	544	502	466	435
4	793	600	501	435	389	352	323	300	280
5	747	523	428	364	321	289	266	246	229
6	1167	537	618	524	463	420	387	363	342
7	341	219	174	148	131	118	107	100	94
8	499	359	296	259	232	212	199	187	176
9	303	168	131	106	91	78	73	70	68
10	1199	817	658	568	505	459	421	393	369
11	691	467	373	327	291	264	247	233	220
12	177	93	78	72	68	64	60	58	57

Sample numbers are the same as in Table I.

viscosity by increasing the rate of shear is a direct consequence of the non-Newtonian behavior of the samples examined, as already indicated [8]. It is further observed from the table that viscosity is influenced by the reaction medium and reaction conditions.

Isopropanol, which results in lower yield and DS, gave samples with higher viscosity, unlike butanol, which results in inferior viscosity properties, while isobutanol is in between the both. It is also observed that, regardless of solvent used, higher viscosity values were obtained by carboxymethylation with 90% MCA and 60% NaOH under the reaction conditions applied, while lower viscosity values are obtained by using the higher chemical charge 150% MCA and 100% NaOH. This is due to the fact that, at higher chemical charges depolymerization could occur and viscosity values are mainly influenced by the differences in the sample degree of polymerization [9].

The infrared spectra of the raw and carboxymethylated cotton linter are shown in Figures 4–7. From these figures, the infrared crystallinity index was determined, by the method of Nelson and O'Connor [10]. The $2900\,cm^{-1}$ band has been chosen as an internal standard to determine the relative absorbance of certain IR bands following the base line correction method [11], and also relative optical density were calculated [12] and used for comparison. Table III summaries the results of crystallinity index and relative absorbance (RA) and relative optical density (OD) for the common bands.

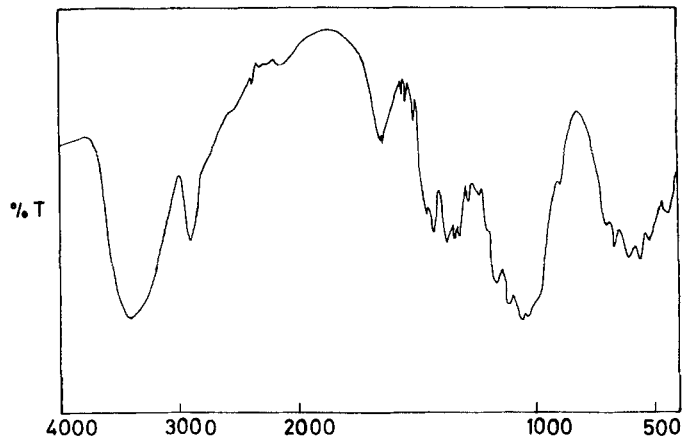

FIGURE 4 Infrared spectra of untreated cotton linter.

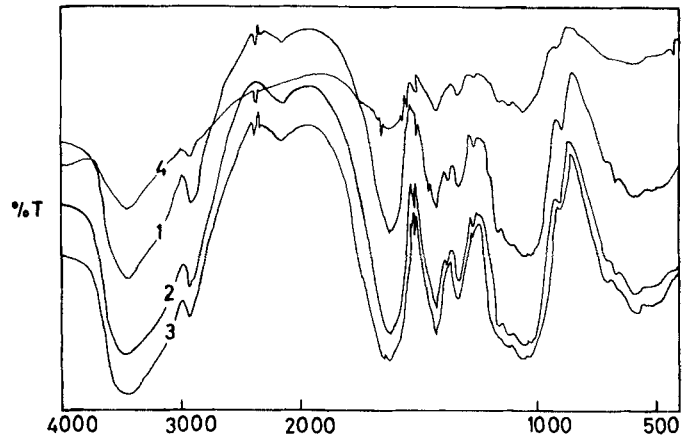

FIGURE 5 IR spectra of CMC samples prepared in isopropanol reaction medium using different concentrations of NaOH and MCA. (1) 40 and 60, (2) 60 and 90, (3) 80 and 120, (4) 100 and 150% respectively.

From Table III, it is obvious that the crystallinity index for cotton linter is much higher than that of the carboxymethylated sample. It is also noticed, for different carboxymethylation series, that the crystallinity index first decreased and then increased by increasing the DS.

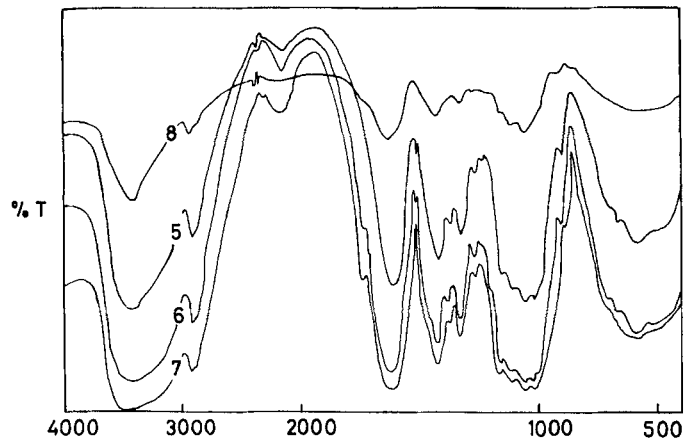

FIGURE 6 IR spectra of CMC samples prepared in isobutanol reaction medium using different concentrations of NaOH and MCA. (5) 40 and 60, (6) 60 and 90, (7) 80 and 120, (8) 100 and 150% respectively.

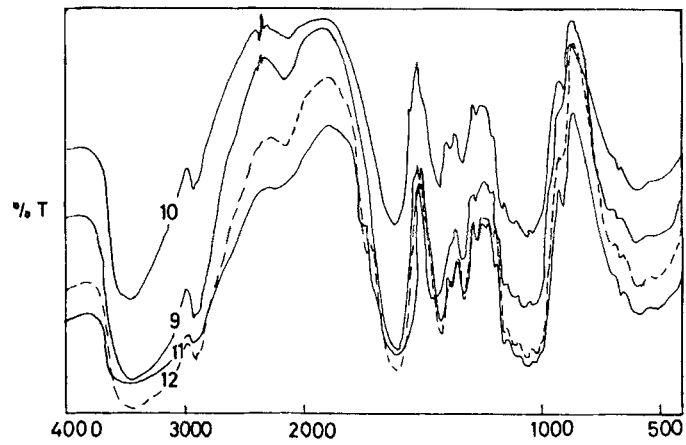

FIGURE 7 IR spectra of CMC samples prepared in butanol reaction medium using different concentrations of NaOH and MCA. (9) 40 and 60, (10) 60 and 90, (11) 80 and 120, (12) 100 and 150% respectively.

On carboxymethylation the O—H stretching band at 3420 cm^{-1} in cotton linter is shifted to 3450 cm^{-1} due to disruption of intermolecular hydrogen bonds in cellulose by alkaline treatments [13]. The RA and OD increased by increasing the DS in different samples.

TABLE III Relative absorbance and relative optical density of IR bands

	RA and OD relative to that at 2900 cm^{-1}											
	Cryst.	3450		1620		1420		1320		1050		595	
	index	*RA*	*OD*	*RA*	*OD*	*RA*	*OD*	*RA*	*OD*	*RA*	*OD*	*RA*	*OD*
C.L.	3.43	2.5	2.3	0.9	0.6	0.9	0.8	0.6	0.6	2.2	2.2	1.6	1.4
1	2.00	3.2	3.5	2.8	2.4	1.1	1.0	0.8	0.7	2.7	2.5	1.6	1.4
2	1.82	3.6	3.7	2.8	3.1	1.3	1.3	0.8	0.9	2.7	2.6	1.9	1.8
3	2.55	3.9	4.1	3.2	3.7	1.3	1.6	0.9	1.0	2.8	3.0	1.9	2.3
4	2.66	4.4	4.3	3.8	3.7	1.6	1.8	0.9	1.1	3.2	3.4	2.3	2.4
5	2.00	3.4	3.4	3.7	3.5	1.3	1.1	0.7	0.7	2.8	2.7	2.1	1.6
6	1.56	3.5	3.7	4.0	3.5	1.3	1.4	0.9	0.7	2.8	2.8	2.2	1.7
7	1.56	4.0	4.0	4.9	3.7	1.6	1.5	0.9	0.9	3.3	3.3	2.6	1.9
8	2.67	5.0	5.2	5.2	4.0	2.0	1.7	1.1	1.0	3.5	3.5	3.4	2.1
9	2.32	3.5	3.9	3.5	3.1	1.6	1.5	0.9	0.8	3.2	3.1	2.3	1.9
10	2.00	3.6	4.1	4.2	3.4	1.7	1.6	1.1	0.9	3.7	3.2	2.4	2.0
11	2.10	3.8	4.1	5.2	3.8	2.5	1.7	1.3	1.0	4.4	3.3	4.0	2.0
12	2.42	4.5	5.0	5.6	3.8	3.2	1.7	2.1	1.0	5.0	3.5	5.3	2.1

Sample numbers are the same as in Table I, C.L. cotton linter, RA relative absorbance, OD relative optical density.

The 2900 cm^{-1} bands is attributed to C—H stretching frequency in methyl and methylene groups are used in this study as standard band for comparison.

The absorption band at 1620 cm^{-1} is attributed to the vibration of adsorbed water molecules in the non crystalline regions in cellulose [14]. It may be also assigned to the caboxylate anion COO^-. The RA and OD of this band is about 3–4 times higher in carboxymethylated samples than in cotton linter. Also, the RA and OD of the 1620 cm^{-1} band is obviously increased by proceeding the carboxymethylation reaction, for all series.

The band at 1420 cm^{-1} is attributed to CH_2 bending and also to the O—H bending in the COOH group. The RA and OD of this band is higher for the carboxymethylated sample and increases for samples with a higher DS.

The band at 1320 cm^{-1} is assigned to the O—H bending and C—O stretching in COOH and also for CH_2 wagging. The RA and OD of this band are slightly higher than that of cotton linter and slightly increased through carboxymethylation.

The 1050 cm^{-1} band is attributed to skeletal vibration involving stretching of C—O and C—C bonds attached to the glucose rings

[15], and also to C—O stretching in alcohols. The RA and OD of this band is higher for carboxymethylated samples and increased by increasing the DS.

The band at 595 cm^{-1} is assigned to the O—H out-of-plane bending. The RA and OD of this band are also higher for carboxymethylated samples and increase through carboxymethylation.

CONCLUSION

The accessibility of cotton linters towards carboxymethylation is improved by increasing the NaOH and MCA concentrations. Using butanol in the reaction medium gave superior yield and DS than in the case of isobutanol, while isopropanol gave inferior results.

From the rheological properties it is obvious that all carboxymethylated samples exhibited a non-Newtonian and thixotropic behavior. Apparent viscosity decreases as the rate of shear increases for all samples. Isopropanol in the reaction medium gave samples with higher viscosity in comparison with butanol, while isobutanol is in between. Higher viscosity values, for all solvents used, were obtained by carboxymethylation with 90% MCA and 60% NaOH.

Infrared spectra of raw and carboxymethylated cotton linter confirm that the crystallinity index decreased through carboxymethylation while the absorbance and optical density, relative to the band at 2900 cm^{-1}, for different bands at 3450, 1620, 1420, 1320, 1050 and 595 cm^{-1} were higher for the carboxymethylated samples and increased by increasing the carboxymethylation degree.

References

[1] Jansen, E. (1918). *German Patent*, **332**, 203.
[2] Hollabaugh, C. B., Burt, L. H. and Walsh, A. P. (1945). *Industrial and Engineering Chemistry*, **37**, 943.
[3] Schriewer, B. and Mross, W. (1981). *Angew. Macromol. Chem.*, **98**, 279.
[4] Heinze, T., Erler, U., Nehls, I. and Klemm, D. (1994). *Angew. Makromol. Chem.*, **215**, 93.
[5] Xiquan, L. and Tingzhu, Q. (1990). *Acta Polymerica*, **41**, 220.
[6] Majid, S. A., Jahan, I. A. and Rahman, A. (1990). *Bangladesh J. Sci. Ind. Res.*, **XXV**, 1.
[7] Achwal, W. B., Nabar, G. M. and Pudmanabhan, C. V. (1958). *J. Sci. Ind. Research*, **17B**, 497.

[8] Hebeish, A., El-Kashouti, M. A., Abdel-Thalouth, L., Haggag, K. and El-Halwagi, A. (1994). *Cellulose Chem. Technol.*, **28**, 409.
[9] Heinze, T., Heinze, U. and Klemm, D. (1994). *Angew. Makromol. Chem.*, **220**, 123.
[10] Nelson, M. L. and O'Connor, R. T. (1964). *J. Appl. Polym. Sci.*, **8**, 1311.
[11] Sarkanen, K. V., Chang, H. H. and Allan, G. G. (1967). *Tappi J.*, **50**(12), 583.
[12] Nagieb, Z. A., El-Hamouly, W. S. and Hassan, H. N. H. (1986). *Nordic Pulp and Paper Res. J.*, **2**, 46.
[13] Reddy, S. S. (1992). *Cellulose Chem. Technol.*, **26**, 559.
[14] Tsuboi, M. (1957). *J. Polym. Sci.*, **25**, 159.
[15] Poy, A. K., Sen, S. K., Bag, S. C. and Pandey, S. N. (1991). *J. Appl. Polym. Sci.*, **42**, 2943.