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Carboxymethylcellulose derivatives with low hydrophilic properties

Summary — New kinds of cellulose derivatives have been obtained by modification of sodium and lithium carboxymethylcellulose (NaCMC and LiCMC, respectively) with commercial octadecylisocyanate (OctI) and hexamethylene-diisocyanate (HDI). The CMC samples were obtained from sugar cane bagasse pulps using sodium hydroxide and anthraquinone mixture. The structural changes of modified samples were observed using infrared spectroscopy (IR), solid state ^{13}C NMR and thermal analysis (TGA). The samples surfaces were visualized using scanning electron microscopy (SEM) method. The presence of characteristic urethane group absorption bands in the region of 1650—1720 cm^{-1} in IR spectra and at 159 ppm in ^{13}C NMR spectra indicates the formation of the product.

Key words: cellulose derivative, NaCMC, LiCMC, modification.

The world's tendencies in scientific and technological progress in the area of new materials show the importance of utilizing the industrial and agricultural residues as raw materials. The utilization of these residues let minimize the problem connected with their accumulation and the use of traditional materials, as reported by many authors [1—3].

Sugar cane bagasse is a cellulose rich material and probably the most promising non-woody raw material. Brazil is one of the largest producers of sugar cane for alcohol and sugar industries. Bagasse remains after the separation of the sugar cane juice, which is used for the production of alcohol and sugar. It is reported [4] that even if a part of this bagasse is burned for the production of energy a great amount still remains.

It is possible to obtain the cellulose from this bagasse *via* pulping processes as reported by Fengel *et al.* [5] and Sjöström [6]. Cellulose obtained from bagasse can be modified in chemical reactions with the hydroxyl groups producing a wide variety of cellulose derivatives. Carboxymethylcellulose (CMC) is an important cellulose derivative used in pharmaceutical, food and perfumery industries [7—9], and can also be used as a substrate in further reactions [10, 11] as well as in its modification with isocyanates. Trejo O'Reilly *et al.* [12] investigated the reactions of the cellulose modification using different modifying agents, including anhydride or isocyanate reactive groups. The objective of their research was to provide a non-polar character of the fibers surface and to produce a new kind of material that can be used as a reinforcing agent in polymeric matrixes. Other reactions of modification are described for hydroxyethylcellulose (HEC) [13, 14] and starch [15] using different polyether based isocyanates as modifying agents. In that case the main objective was to obtain new solid polymer electrolytes with good conductivity, film-forming, mechanical and adhesion properties resulted from the association of polysaccharide and polyether chain.

To synthesize a new type of cellulose derivative, samples of CMC obtained from sugar cane bagasse were modified with hexamethylene-diisocyanate (HDI) and octadecylisocyanate (OctI) in a heterogeneous reaction medium. The main objective of this research was to obtain new kind of cellulose derivatives that can be used as new hydrophobic (*i.e.* less hydrophilic) materials. In this study the mono and diisocyanate were used to produce either modified CMC chains (monoisocyanate) or networks (diisocyanate). The procedures as well as the characterization of the products obtained by reaction of modification of CMC with HDI and OctI are discussed in this paper. The preparation and characterization of LiCMC were also described.

EXPERIMENTAL

Cellulose pulp production

The fiber fraction of bagasse was pre-hydrolyzed (20:1 v/m) for 30 min at 160°C and 90 psi. The pulping reaction was performed with "licor"/bagasse ratio of 13:1 (v/m) at 160°C and 70 psi for 1 h. The "licor" was the mixture of sodium hydroxide and anthraquinone (active alkali 16% and 0.15% of anthraquinone). After

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pulping, the fiber fraction was bleached with sodium chlorite ($NaClO_2$) in acetic acid. The degree of polymerization (*DP* = 233) was determined by viscosity measurements. Copper ethylene diamine — $[Cu(NH_2CH_2CH_2NH_2)_2]OH_2$ — was used as a solvent and *DP* was calculated from $DP^{0.905} = 0.75\eta$ [16].

NaCMC synthesis

5 g of air-dried cellulose pulp were dispersed in a solution of 132 cm^3 of isopropanol and 9 cm^3 of water. All syntheses were performed with stirring. After 20 min at room temperature, aqueous NaOH (13.64 g of solid NaOH; 40% m/v) was dropwise added for 30 min. Then the solution of 12 g of monochloroacetic acid in 15 cm^3 of isopropanol was dropwise added for 30 min. The temperature was raised to 55°C and the reaction left for 3.5 h. The reaction product was first filtered, then suspended in 250 cm^3 of aqueous methanol (80%, v/v) and neutralized with acetic acid. After filtration, the product was twice washed with aqueous methanol (80%, v/v) and twice with pure methanol. The NaCMC with degree of substitution *DS* = 1 was dried in vacuum at 55°C [17]. The weight increase, determined by conductometric titration, was 54% for this sample.

LiCMC synthesis

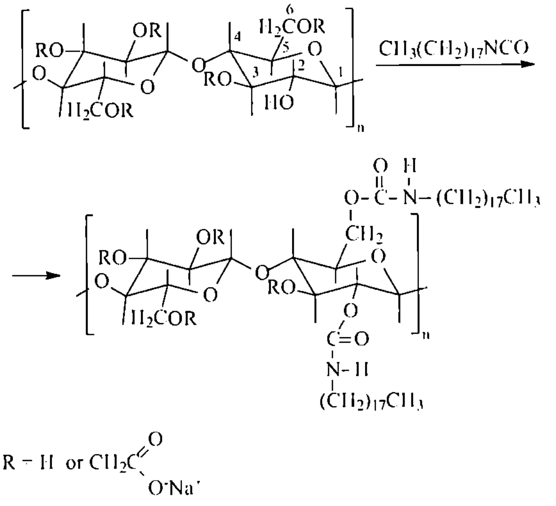
1 g of air-dried cellulose pulp dispersed in 30 cm^3 of isopropanol and 10 cm^3 of water was stirred vigorously while 2 g of LiOH powder were added for 10 min. at room temperature. The stirring was continued for 3.5 h and a solution of 3 g of monochloroacetic acid in 4 cm^3 of isopropanol was dropwise added. The mixture was placed in an oil bath at 55°C for 4 h with stirring. The product was filtered, then suspended in 25 cm^3 of aqueous methanol (80%, v/v) and neutralized with acetic acid. The LiCMC with *DS* = 1.13 was twice washed with aqueous methanol (80%, v/v), and twice with pure methanol and dried at 40°C [13]. The weight increase for this sample was 72%.

Table 1. Conditions and reagents used in the reactions of LiCMC and NaCMC modification

	Substances and quantities			
CMC	1 g LiCMC	0.5 g LiCMC	1 g NaCMC	0.26 g NaCMC
Isocyanate	4.5 g HDI (98%)	5.4 g OctI (98%)	4.5 g HDI (98%)	1.9 g OctI (98%)
Solvent	dichloromethane (99.5%)	DMAc/LiCl (distilled 100%)	dichloromethane (99.5%)	dichloromethane (99.5%)
Washing Substance	hexane (99%) (reflux)	ethanol (99.5%) (reflux)	hexane (99%) (reflux)	hexane (99%) (reflux)
Reaction time, hours	16	16	16	1/2

Reaction of modification

LiCMC and NaCMC were modified with monoisocyanates (OctI, see eqn. 1) and diisocyanates (HDI). To avoid the residual humidity of the CMC samples, they were dried in vacuum at 60°C for 12 hours before the modification. For this synthesis two solvents were used: dichloromethane, due to its low boiling temperature and DMAc/LiCl, similarly to the procedure described by Williamson and McCormick [18] for the synthesis of cellulose derivatives. In this case the purpose was to dissolve the CMC but without success. All the reactions were realized in a dry glove box. LiCMC and NaCMC were suspended in the solvent, as indicated in Table 1, with magnetic stirring for 10 min at room temperature. Then the solution of isocyanate in the same solvent and 5 drops of dibutyltin dilaurate as a catalyst were added at room temperature. The stirring was continued at different reaction times (Table 1). The mixture was then poured into either hexane or alcohol [18, 19] and left with magnetic stirring for 24 h. The product in white powder form was separated by centrifugation and dried at 50°C, then washed under reflux for 14 h in carbon tetrachloride [13, 20] and vacuum dried at 60°C. The weight increase for the NaCMC with HDI was 100% and 248% with OctI. For the sample of LiCMC/HDI the weight increase was 95% and for LiCMC/OctI it was 412%.



(1)

Measurements

The FT-IR spectra were recorded in a BOMEM apparatus model MB-102 using KBr pellets in the proportion of 100:1 (KBr/sample). The product was dried for 12 h under vacuum at 60°C.

The TGA curves were obtained using SHIMADZU TGA-50 equipment in a nitrogen dynamic atmosphere (flow rate 20 cm^3/min) with heating rate 10°C/min, and temperature ranging from room temperature to 800°C.

The solid state ^{13}C NMR spectra were recorded using a VARIAN UNITY 400 spectrometer operating at 100.58 MHz. The spectra were obtained by cross polarization method with magic angle spinning (CP/MAS) with spectral bands of 50—70 kHz for CP and decoupling, contact time for cross polarization 2 ms and repetition time 3 s. The pulse of 1 H was 4 µs, and the spectra were obtained with 2048 points. Hexamethylbenzene was taken as an external reference at 132.3 ppm from tetramethylsilane. For each spectrum, 3000 transients were collected. The samples were analyzed in a zircon rotor 5 mm of diameter and spinning rate about 10 kHz. For dephased decoupling the repetition time was 3 s and the contact time was 3 ms with a delay of 3 µs, in the decoupling, during acquisition [21, 22].

The surfaces of the modified CMC samples were visualized by scanning electron microscopy (SEM) using the digital apparatus model LEO-440. The samples were deposited on adhesive carbon tape and covered with gold.

RESULTS AND DISCUSSION

The synthesis of these new types of cellulose bagasse derivatives based on the condensation reaction between the hydroxyl and isocyanate groups, resulting in new urethane groups. This reaction that yields a high molecular weight product can also occur with the carboxyl groups of the acid CMC forms, which is not the subject of this study. The formation of urethane groups that show a characteristic absorption band in the infrared region can be identified by IR spectroscopy. Figure 1 shows the infrared spectra of NaCMC and LiCMC and the products of their modification with HDI and OctI. As it can be seen, the spectra of CMC samples show very similar results where the peaks in the region of 3400—3450 cm^{-1} can be attributed to the main O-H stretching. Other bands in the region of 2880—2900 cm^{-1} can be attributed to the C-H stretching, to ether at 1150— 1085 cm^{-1} and to the carboxyl group at 1650—1550 cm^{-1}. The IR spectra of modified products show the additional very well defined bands; one in the region of 1650—1720 cm^{-1} is characteristic for the urethane group and the other one, sharp at 3500—3200 cm^{-1}, is characteristic for the N-H group. As it can be seen also in this figure there are no significant differences between the samples obtained using dichloromethane and DMAc/LiCl. However it seems that in the case of LiCMC/OctI obtained in the presence of DMAc/LiCl and washed with ethanol, the N-H band is a little more intensive than for NaCMC/OctI sample obtained in the presence of dichloromethane. This fact can be attributed to the eventual reaction of alcohol with remaining isocyanate, which results in small molecules containing urethane groups. If these molecules were not removed during the extraction, process they could contribute to the obtained high weight increase of the samples. Also these molecules can not be identified by IR spectra as they show the same absorption bands as the formed products. The indication of remaining isocyanate after the synthesis can be proved in the case of NaCMC modified with HDI where a small band at 2268 cm^{-1} is observed. This band can be attributed to the stretching of non-reacted NCO groups.

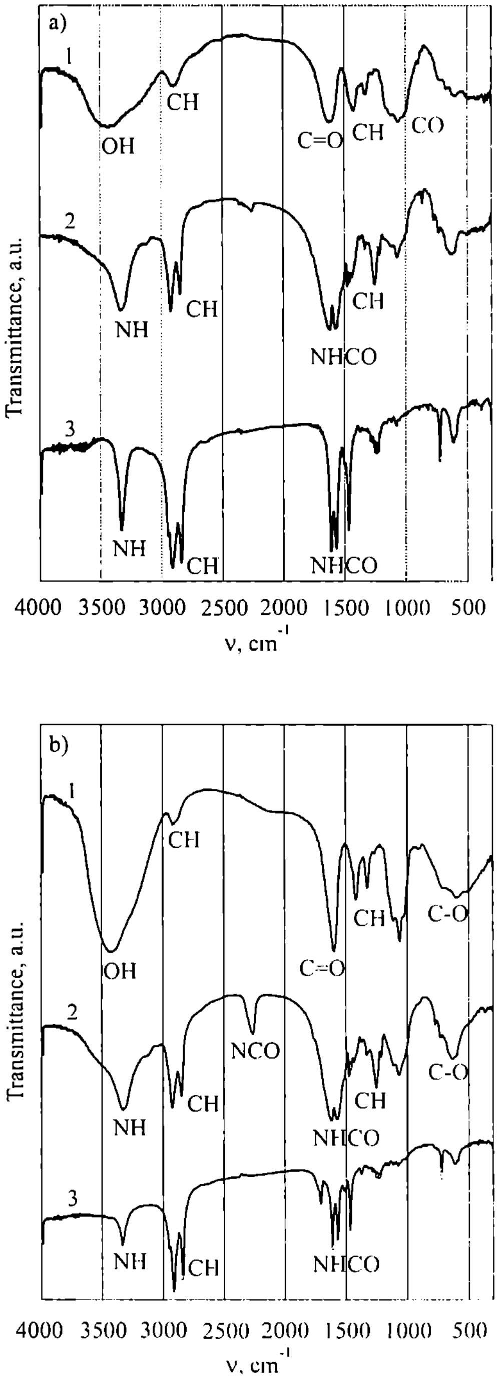


Fig. 1. Infrared spectroscopy of LiCMC (a) and NaCMC (b) and their modified products; LiCMC or NaCMC: pure — curves 1, with HDI — curves 2, with OctI — curves 3

Samples modified with OctI also show much sharper IR absorption bands probably due to the long isocyanate carbonyl chain. All these results compared with the published ones [17, 23, 24] indicate that modified CMC was obtained.

For better characterizing of CMC and its modification products, ^{13}C NMR measurements of the samples have been done. The results obtained for CMC (Figures 2a and 2b) show peaks at 105, 84—89 and 66—63 ppm, which correspond to C1, C4 and C6 of anhydroglucose units, respectively. Peaks between 80—70 ppm belong to C2, 3 and 5 of anhydroglucose. The characteristic peaks for CMC that appear at 175—180 cm^{-1} can be attributed to the COO$^-$ group and the ones that appear in the region of 85 ppm — to the carbon of CH$_2$ group [25, 26]. The CMC modified products show peaks at 42 ppm probably from the carbon of CH$_2$-NHCO group and very small peaks at 159 ppm from urethane group (C=O). These results suggest the formation of the modified products as reported by Williamson and McCormick [18] for cellulose derivatives synthesized with isocyanate in homogenous solution of DMAc/LiCl, and

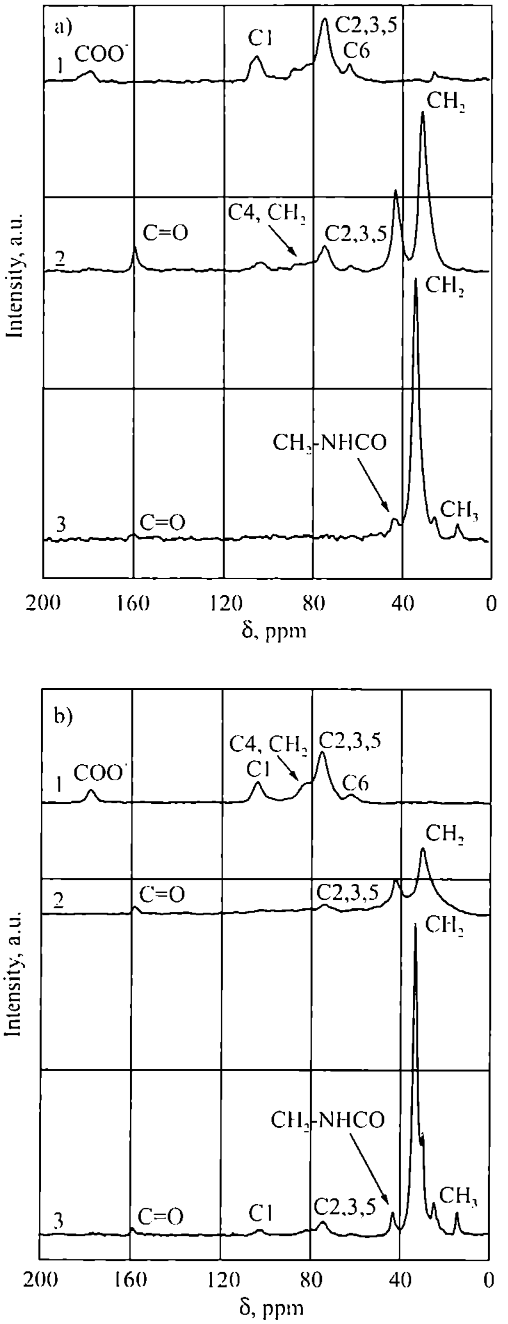


Fig. 2. Solid state ^{13}C NMR spectra of LiCMC (a) and NaCMC (b) and their modified products; LiCMC or NaCMC: pure — curves 1, with HDI — curves 2, with OctI — curves 3

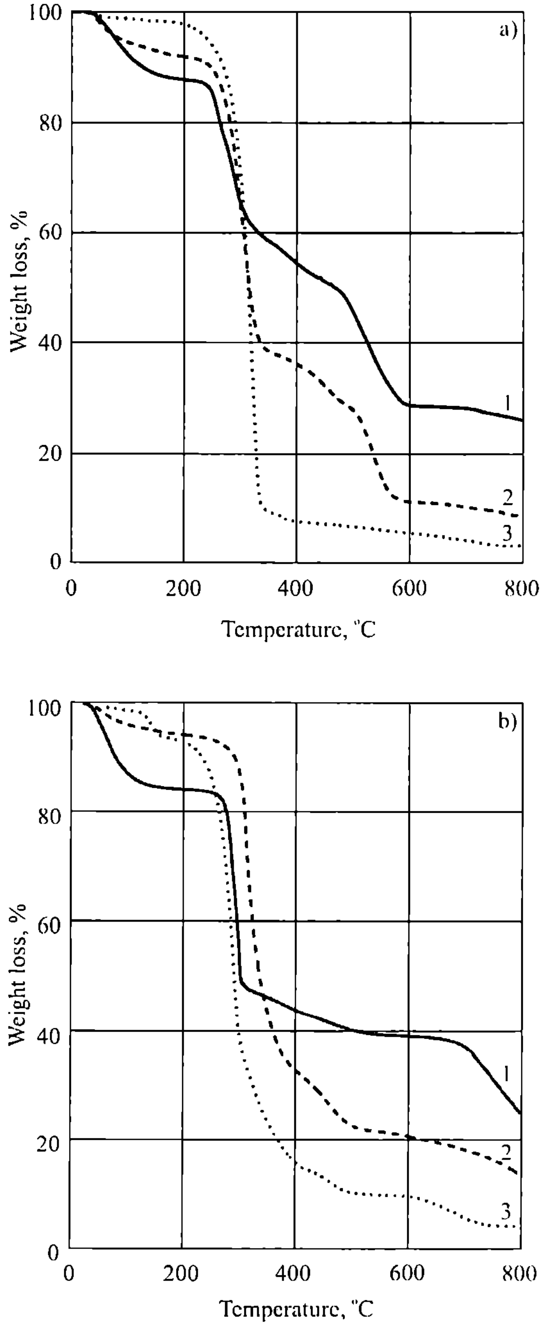


Fig. 3. TGA measurements of LiCMC (a) and NaCMC (b) and their modified products; LiCMC or NaCMC: pure — curves 1, with HDI — curves 2, with OctI — curves 3

Désilets *et al.* [27] in their ^{13}C NMR urethane group study.

The samples of CMC and its derivatives were also subjected to thermogravimetric analyses (TGA) presented in Figures 3a and 3b. The CMC TGA results show an initial weight loss of *ca.* 15% at temperature lower than 120°C probably due to the water loss. Samples of HDI modified CMC show weight loss at the same temperature, but for these polymers the weight loss is *ca.* 5%. The decrease in the weight loss after reaction of modification can be an indicator that when the hexamethylene chain is associated with the polysaccharide, a higher hydrophobic character is achieved. The sample of OctI/LiCMC does not show weight loss in the indicated temperature and the sample of OctI/NaCMC shows weight loss of *ca.* 5% at about 150°C, similarly to the HDI/CMC samples. This less hydrophilic character of the modified samples was also observed when they fluctuated on water surface. It can be concluded that when HDI and OctI hydrocarbon is added to the cellulose derivative the hydrophilic character almost disappears. Other remarkable changes are observed above 200°C, when the degradation process starts. The LiCMC and NaCMC samples show a two-stage degradation process, which was already observed by Kaloustian *et al.* [28] for cellulose and some of its other types derivatives. For the samples of modified CMC single-stage (CMC/ OctI) and two-stage (CMC/HDI) degradation processes were observed. These results are very similar to those concerning various cellulose derivatives described by Kaloustian *et al.* [28], where the samples like HPC, HEC, hydroxypropylmethylcellulose and others showed either single or two-stage degradation processes. Kaloustian *et al.* [28] also observed that in most cases this process occurred at temperature lower or similar to that for pure cellulose samples. In the present study the degradation process temperature of bagasse cellulose was *ca.* 330°C (onset temperature) and for all modified samples it was also lower as for cellulose and almost the same as for both LiCMC and NaCMC samples that showed the onset temperature about 300°C. At 800°C the presence of residues can be observed, which is probably due to the formation of Li carbonate (for LiCMC) and Na carbonate (for NaCMC). It can be also noted, that at this temperature the residues of the CMC samples are greater than the ones of the modified products. For both CMC samples (Li and Na) the remaining mass is about 25%; for the HDI modified CMC it is about 10% and for OctI modified CMC — about 5%. These differences can be explained by the increase of organic parts in the samples when either HDI or OctI are introduced into the CMC chains. As a consequence there is a decrease of metal ion (Li and Na) contents in the modified products resulting in a decrease in the residue amount. The differential scanning calorimetry (DSC) measurements (not presented here) of both modified CMC samples showed the small change of the base line centered at *ca.* 30°C. This change can be attributed to the glass transition temperature (T_g).

As it has been previously demonstrated the CMC modification processes promoted structural changes of the CMC samples. For better characterization of the products formed the surfaces of modified LiCMC and NaCMC were visualized using SEM (micrographs are shown in Figs. 4—6). A significant difference can be clearly noted in the surface image, between the CMC samples (Figure 4) and modified with HDI and OctI. LiCMC and NaCMC modified with HDI seem to have the fibrillar structure (Figures 5a and 5b), contrarily to the samples modified with OctI (Figures 6a and 6b), which have compact plaque structure similar to the pure LiCMC. This plaque arrangement can be due to the waxy film derived from the olefinic substituent formed during the sample drying process performed above its T_g. These surface changes of the modified CMC samples are another indication of the reaction of modification occurrence and this different arrangement can be also associated to the length and functionality of the hydrocarbon chain introduced into the cellulose derivative. As it was

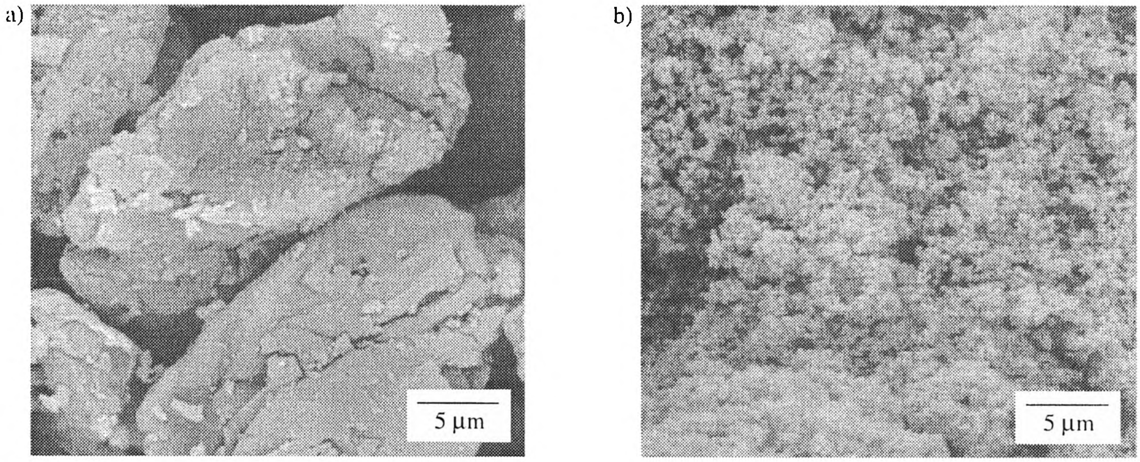


Fig. 4. SEM micrographs of LiCMC (a) and NaCMC (b)

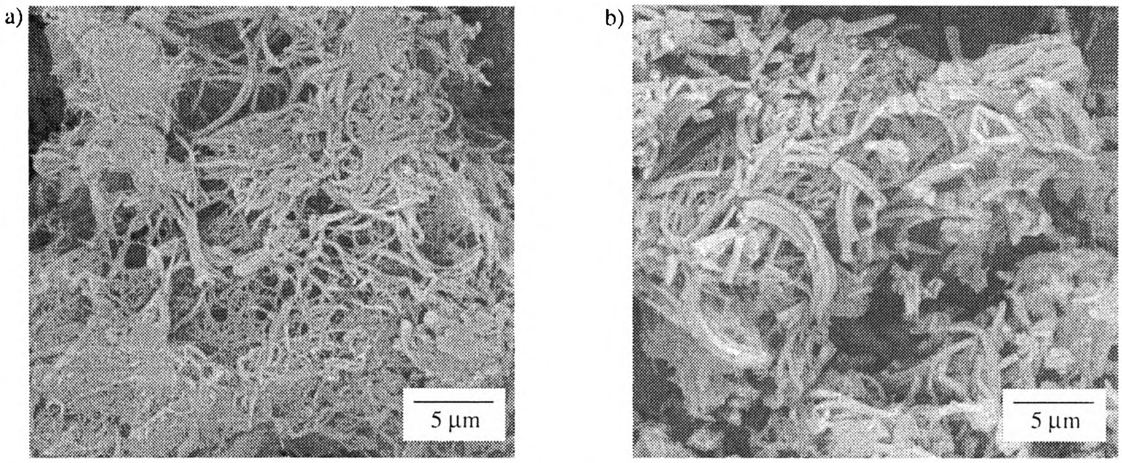


Fig. 5. SEM micrographs of LiCMC (a) and NaCMC (b) modified products with OctI

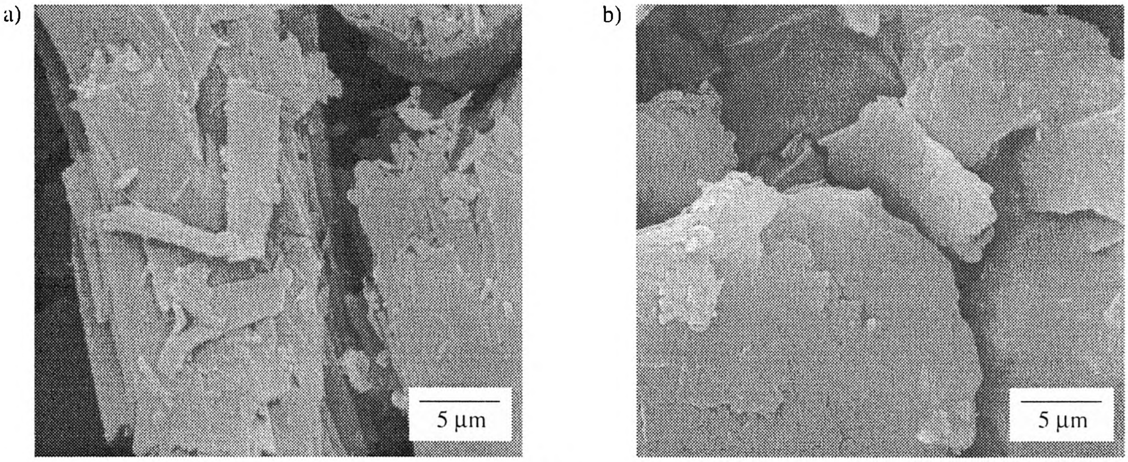


Fig. 6. SEM micrographs of LiCMC (a) and NaCMC (b) modified products with HDI

mentioned in the introduction the bifunctional HDI modifying agent due to the two isocyanate groups at one hexamethylene molecule can lead to the network formation while mono-functional OctI can only lead to the modified product. As both modified samples were insoluble in many organic solvents it is difficult to distinguish the network from the modified polymer obtained. However all the results presented in this paper indicate the occurrence of a condensation reaction between CMC and isocyanate leading to the formation of new CMC derivatives.

CONCLUSIONS

Bagasse-based CMC derivatives were successfully synthesized using hexamethylene diisocyanate and octadecylisocyanate as modifying agents. The characterization by infrared spectroscopy confirmed the formation of characteristic urethane bonds in the product obtained. A detailed ^{13}C NMR study showed characteristic peaks for new CH_2-NHCO and C=O groups present in the samples obtained. The surface changes, caused by the reactions of modification, were observed by the SEM technique evidencing where differences between the samples modified with HDI and OctI could be seen. The HDI micrographs evidenced the fibrillar structure of the samples, contrarily to the OctI modified products that showed a compact plaque look. This can be due to the formation of waxy film during the sample drying above T_g. These differences can be also due to the chain length and functionality of the modifying agent. Thermal analyses indicate a loss of hydrophilic properties with the aggregation of hydrocarbon branches in the cellulose derivative and the residues quantity at 800°C decreases with the increase of the hydrocarbon chain introduced into the CMC chain.

ACKNOWLEDGMENTS

We are grateful to Nilson C. Melo Embrapa — CNPDIA, Alessandro Gandini — EFPG and A. Aprigio S. Curvelo — IQSC for their scientific contributions. We would also like to acknowledge the financial support given by FAPESP.

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Received 26 III 2002.