

New Cation Exchange Composite Based Upon Cellulose/Melamine Formaldehyde/Citric Acid Reaction Products

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SYNOPSIS

A new cation exchange composite was synthesized through the reaction of cellulose with both melamine formaldehyde precondensate and citric acid. Factors affecting the reaction such as reactants' molar ratios, liquor ratio, time, and temperature were reported. Reaction conditions were selected to prepare a cation exchange composite having a carboxyl content of 120 meq/100 g and a nitrogen percent of 22.1. Potentiometric titration of this exchanger showed that it behaves like a tribasic acid, and the strengths, pK_a , of each stage of ionization are 5, 6.7, and 9.7, respectively. Water solubility as well as durability to use of the prepared exchanger were evaluated. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Extensive studies are being done in this division concerning the synthesis and characterization of ion exchange cellulose. ¹⁻⁴ The present work is a continuation of these studies with the objective of synthesis and characterization of a new cation exchange composite as a product of the reaction of cellulose with both melamine formaldehyde precondensate and citric acid.

EXPERIMENTAL

Materials

Cellulose sheets, rayon grade pulp, supplied by Misr Co. for Rayon and Synthetic Silk (Kafr-El-Dawar, Egypt), were ground before use. The average degree of polymerization was determined ⁵ and found to be 500.

Melamine formaldehyde (MF) precondensate in the form of highly methylated trimethylol melamine (an aqueous solution of MF content of 1.9 mol/L), supplied by a commercial source, was used.

Citric acid (CA) used was an analytical grade chemical.

Reaction

Unless otherwise stated, the reaction was carried out as follows. MF precondensate was introduced into a 100-mL stoppered glass bottle containing the thermostated CA-cellulose aqueous mixture. The bottle was stoppered and kept in a thermostated water bath under continuous shaking. After the desired reaction time, the hard gel formed was ground and stirred vigorously in boiling water (50 mL/1 g cellulose initially used) for 5 min, and then filtered through a perforated glass funnel using a filter paper. It was observed that the obtained cake consisted of two layers: a fibrous upper layer and a fine-powdered lower layer attached to the filter paper. The lower layer was neglected, whereas the fibrous upper layer was subjected to another four stirring-filtration operations, with the neglect of the powder layer each time. Disappearance of formation of the lower layer was observed after the third stirring-filtration operation. Finally, the fibrous layer was washed with alcohol, filtered, dried at 55°C for 24 h, and then dried over P₂O₅ for 24 h before analysis.

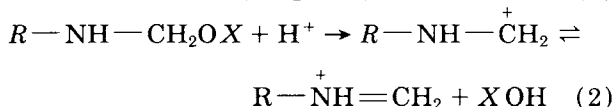
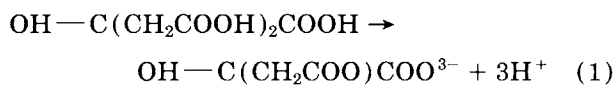
Analysis and Test Methods

Nitrogen content was determined according to the Kjeldahl method. Carboxyl content was determined by a method described elsewhere. ⁶ Water solubility of the exchanger was evaluated according to Kunin ⁷ by estimating the percent loss in its weight after 10,

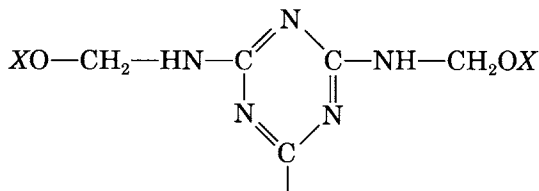
20, and 50 cycles of water extraction in a soxhlet. Durability of the exchanger to use was determined¹ by measuring its capacity (carboxyl content) after 5, 10, 15, and 25 cycles of use at 50°C, each cycle consisting of four steps, viz., exhaustion, washing, regeneration, and rewashing.

RESULTS AND DISCUSSIONS

CA dissociates in the reaction medium to produce hydrogen ions, which can protonate the *N*-methoxymethyl (or *N*-methylol) groups of MF precondensate, giving rise to carbonium-immonium ion⁸ according to the following reactions:

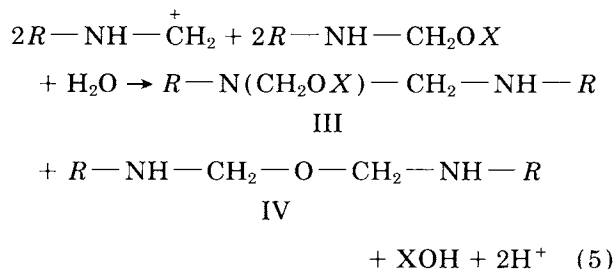
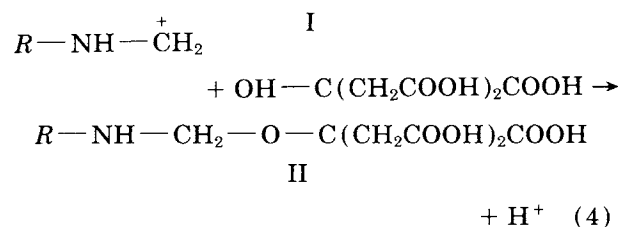
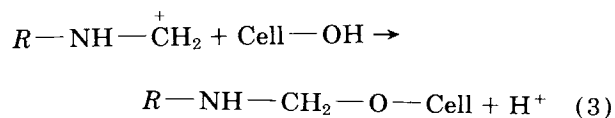


where *R* is



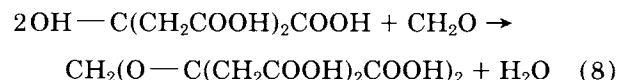
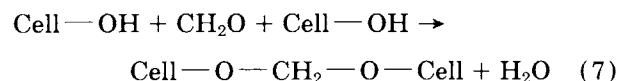
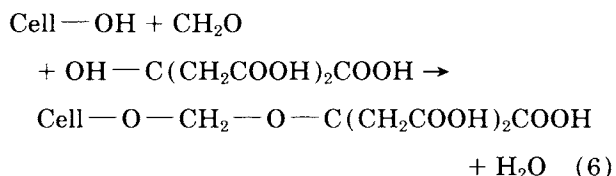
and *X* is either CH₃ or H.

This ion can attack (1) cellulose hydroxyls,⁹ (2) CA hydroxyls,^{10,11} and (3) NH and *N*-methoxymethyl, as well as *N*-methylol groups of MF precondensate. This can result in linking an MF molecule onto cellulose (compound I) or CA (compound II), as well as the production of MF dimers (compounds III and IV), as can be illustrated by the following reactions:



Each compound from I-IV can be further protonated and can hence react with itself, other compounds, and/or undergo a series of reactions similar to those from 3-5 to produce a new set of active compounds (which contain the active *N*-methoxy or *N*-methylol groups) that are able to enter in reactions in a similar manner, and so on. The final product of these reactions is mixed polymers and copolymers, which may contain (1) cellulose-MF-CA copolymer, (2) cellulose-MF copolymer, (3) MF-polymer, and (4) MF-CA reaction adducts. The latter probably consists of a set of polymers of varying degrees of polymerization and different degrees of fixation of CA onto MF.

In addition to the aforementioned reactions, there are other types of reactions that may occur to a minor extent due to the presence of free formaldehyde in MF precondensate solution. These reactions can be illustrated as follows:



Under the stirring-filtration operations described in the experimental section, it is expected to get rid of (1) water-soluble products and (2) high quantities of MF polymer, as well as MF-CA reaction adducts that are loosely attached to cellulose fibers. However, a substantial amount of these polymer and reaction adducts is expected to be strongly attached to the cellulosic phase through all or some of the following routes: (1) deposition in the fiber crevices and lumen, (2) adhering mechanically or

physically to the fiber surface, and (3) cohering the fibers to each other. Therefore, it is expected that the obtained product, after stirring–filtration, is a mixture of all or some of the following: (1) cellulose–MF–CA copolymer, (2) cellulose–MF copolymer, (3) cellulose–formaldehyde–CA reaction product, and (4) that substantial amount of the aforementioned polymer and reaction adducts that is strongly attached to the cellulosic phase. This obtained mixture will be called cellulose–MF–CA cation exchange composite.

Citric Acid-to-Melamine Formaldehyde Molar Ratio

Figure 1 shows the effect of CA-to-MF molar ratio on the carboxyl and nitrogen contents of the composite. Reaction was carried out at 75°C for 2 h at α -anhydroglucose unit-to-MF molar ratio of 1. Liquor-to-cellulose ratio (LR) was 20.

It is clear (Fig. 1) that the composite has a substantial nitrogen content at zero CA-to-MF molar ratio. The catalytic activity may be due to the generation of formic acid through the oxidation of free formaldehyde present in MF precondensate solution.⁹ Introducing CA into reaction medium and increasing its molar ratio (based upon MF) up to 1.5 is accompanied by a noticeable increase in both of the carboxyl and nitrogen contents of the composite. This may be a direct reflection of the increase in the hydrogen ion concentration and the accompanied enhancement in the carbonium–immonium ion

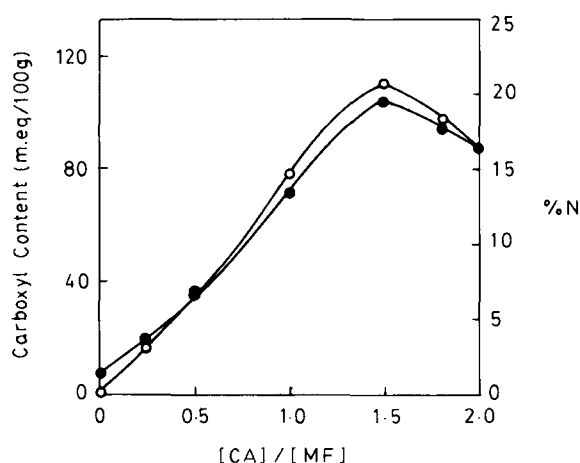


Figure 1 Effect of CA-to-MF molar ratio on the carboxyl and nitrogen contents of the composite. Temperature, 75°C; time, 2 h; (MF)/(α -anhydroglucose unit), 1; LR, 20; (○), carboxyl content; (●), nitrogen content.

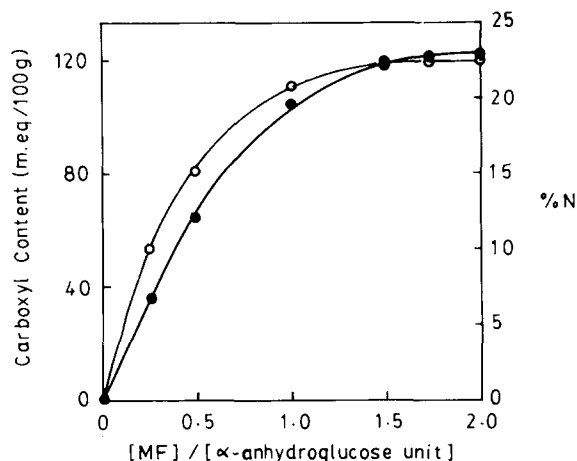


Figure 2 Effect of MF-to- α -anhydroglucose unit molar ratio on the carboxyl and nitrogen contents of the composite. Temperature, 75°C; time, 2 h; (CA)/(MF), 1.5; LR, 20; (○), carboxyl content; (●), nitrogen content.

concentration that lead to higher fixation of CA and MF in the composite. It is also clear that the carboxyl and nitrogen contents decrease upon further increase in CA-to-MF molar ratio beyond 1.5. This adverse effect suggests that beyond this ratio the process preferably proceeds toward the formation of low-molecular-weight, water-soluble MF–CA adducts that can be easily drained off on the washing operation of the composite.

Melamine Formaldehyde-to- α -Anhydroglucose Unit Molar Ratio

The effect of MF-to- α -anhydroglucose unit molar ratio on the carboxyl and nitrogen contents of the composite is shown in Figure 2. Reaction was carried out at 75°C for 2 h at an LR of 20 and CA-to-MF molar ratio of 1.5.

Figure 2 shows that both the carboxyl and nitrogen contents increase significantly on increasing MF-to- α -anhydroglucose unit molar ratio from 0 to 1.5. This can be attributed to the increase in both CA and MF concentrations in the reaction medium. The slight increase in both the carboxyl and nitrogen contents beyond a ratio of 1.5 could be due to the depletion of cellulose hydroxyls and/or the formation of low-molecular-weight, water-soluble MF–CA adducts beyond this ratio.

Liquor Ratio

Figure 3 shows the effect of LR on the carboxyl and nitrogen contents of the composite when the reac-

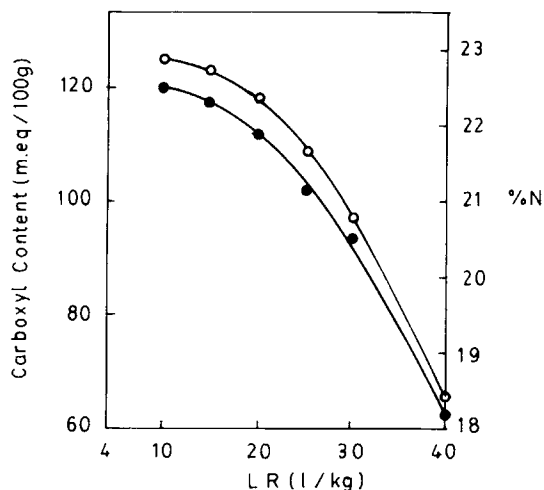


Figure 3 Effect of LR on the carboxyl and nitrogen contents of the composite. Temperature, 75°C; time, 2 h; (α -anhydroglucose unit)/(MF)/(CA), 1/1.5/2.25; (O), carboxyl content; (●), nitrogen content.

tion was carried out at 75°C for 2 h at α -anhydroglucose unit-to-MF-to-CA molar proportion of 1/1.5/2.25. It is obvious that increasing the LR is accompanied by a decrease in both the carboxyl and nitrogen contents of the composite, which may be associated with the decrease in the concentration of the reactants upon increasing the LR.

Reaction Time

Figure 4 shows the effect of reaction time on the carboxyl and nitrogen contents of the composite.

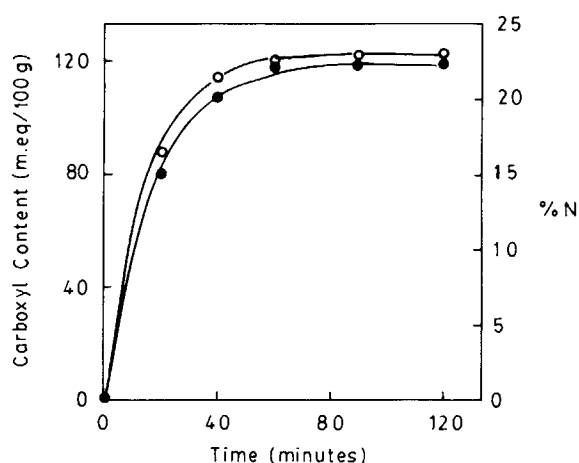


Figure 4 Effect of time on the carboxyl and nitrogen contents of the composite. Temperature, 75°C; (α -anhydroglucose unit)/(MF)/(CA), 1/1.5/2.25; LR, 15; (O), carboxyl content; (●), nitrogen content.

Reaction was carried out at 75°C, LR of 15, and α -anhydroglucose unit-to-MF-to-CA molar proportion of 1/1.5/2.25.

It is evident (Fig. 4) that both of the carboxyl and nitrogen contents increase initially at very fast rates, decrease with time, and then level off after 60 min. Leveling off could be associated with (1) depletion in MF, CA, and cellulose hydroxyls as the reaction proceeds; (2) MF-CA reaction adducts and/or MF homopolymerization seem to prevail over both cellulose-MF-CA and cellulose-MF reaction products during the latter stages of the reaction; and (3) the polymers attached to or deposited on the fiber surface during the initial stages of the reaction limit the diffusion of MF and CA into the fiber structure.

Reaction Temperature

Figure 5 shows the effect of reaction temperature on the carboxyl and nitrogen contents of the composite when the reaction was continued for 60 min at an LR of 15 and α -anhydroglucose unit-to-MF-to-CA molar proportion of 1/1.5/2.25.

It is seen (Fig. 5) that both the carboxyl and nitrogen contents increase by increasing reaction temperature from 0 to 75°C; further increase in reaction temperature is accompanied by a decrease in the carboxyl content with a slight increase in the nitrogen content. The increase in the carboxyl and nitrogen contents up to 75°C may be due to (1) increasing the diffusion of CA and MF molecules

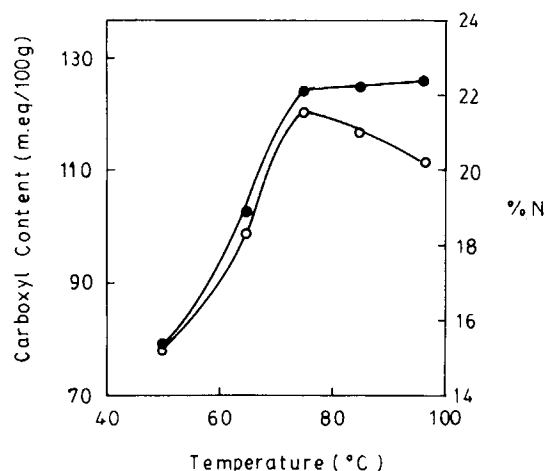


Figure 5 Effect of temperature on the carboxyl and nitrogen contents of the composite. Time, 60 min; (α -anhydroglucose unit)/(MF)/(CA), 1/1.5/2.25; LR, 15; (O), carboxyl content; (●), nitrogen content.

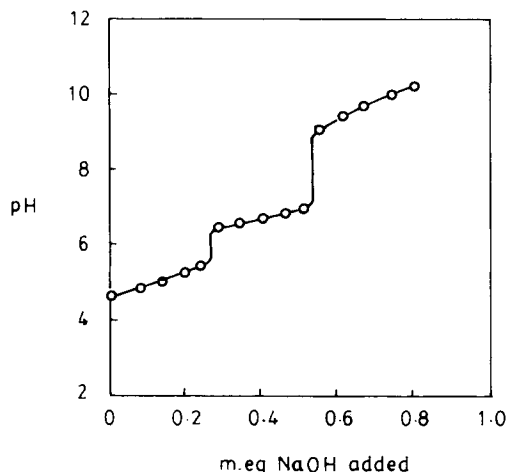


Figure 6 Potentiometric titration of 0.8 meq cellulose-MF-CA cation exchange composite vs. standardized 0.1N NaOH at 25°C in 1M NaCl.

into the cellulosic structure, (2) increasing the accessibility of cellulose hydroxyls as a result of increasing cellulose swelling, and (3) addition of adequate energy to the system to exceed the activation energy barrier of the process. The decrease in the carboxyl content and the accompanied slight increase in the nitrogen content beyond 75°C may be associated with (1) prevalence of MF-CA reaction adducts over cellulose-MF-CA reaction products at elevated temperature and (2) the sluggish continuation of cellulose-MF reaction beyond 75°C.

Characterization of the Cation Exchange Composite

Cellulose was reacted with MF and CA at 75°C for 60 min using α -anhydroglucose unit-to-MF-to-CA molar proportion of 1/1.5/2.25 and an LR of 15. Chemical analysis showed that the carboxyl and nitrogen contents of the prepared composite were 120 meq/100 g and 22.1%, respectively. This exchanger

Table I Water Solubility of Cellulose-MF-CA Cation Exchange Composite

	No. of Cycles		
	10	20	50
Loss in weight (%)	0.43	0.43	0.43

Capacity 120 meq/100 g.

Table II Durability of Cellulose-MF-CA Cation Exchange Composite

	No. of Cycles				
	0	5	10	15	25
Capacity (meq/100 g)	120	110	105	105	105

was characterized by investigating its potentiometric titration, water solubility, and durability to use.

Potentiometric Titration

Potentiometric titration of the prepared cation exchange composite is shown in Figure 6, where it can be seen that the obtained curve is consistent with that of a tribasic acid. Close investigation, however, shows that the carboxyl groups of the composite can be classified, like those of CA, into three sets of equal quantities and different strengths. The strength, pK_a , of each set equals the pH at half neutralization of each of the three corresponding portions of the obtained curve of Figure 6. Therefore, the strength of the first, second, or third set of the carboxyl groups of the exchanger is 5, 6.7, or 9.7, respectively.

Water Solubility

Table I shows the water solubility of the prepared cation exchange composite, where it can be seen that a very slight loss in weight is observed during the first 10 cycles, beyond which the exchanger weight remains unchanged.

Durability to Use

Table II shows the durability of the prepared cation exchange composite to use. It is clear that the exchanger loses 12.5% of its capacity during the first 10 cycles, which may be due to the inclusion of some acid and/or alkali hydrolyzable components in the composite. These components probably consist of (1) the product of linking CA onto cellulose via their reaction with formaldehyde (reaction 7) and (2) some linear polymers of CA-modified MF. After the exclusion of these components during the first 10 cycles, it is most probable that the remained composite exclusively consists of a mixture of three-dimensional polymers and copolymers, which are acid- and alkali-fast, as is evident by the constant capacity manifested in the next cycles.

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