Novel Cation-Exchange Composites Resulting from Polymerization/Cross-Linking of Acrylic Acid/N-Methylolacrylamide Mixtures with Cellulose

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SYNOPSIS

Novel cation-exchange composites were prepared by polymerizing/cross-linking of mixtures of acrylic acid (AA) and N-methylolacrylamide (NMA) in the presence of cellulose pulp using ammonium persulfate in conjunction with a sodium thiosulfate, sodium metabisulfite, or glucose initiating redox system. The $(NH_4)_2S_2O_8/Na_2S_2O_3 \cdot 5H_2O$ redox system proved to be efficient for aqueous polymerization/cross-linking reactions and/or interactions of cellulose with highly concentrated mixtures of NMA and AA, used as commercially available, at very low polymerization temperature (30°C) and for a very short duration of polymerization (90 s) using a liquor-to-cellulose ratio of 6.25 L/kg. Various parameters that affect the synthesis of these composites, such as reaction temperature, concentration of redox system components, and drying temperature as well as AA and NMA concentrations, were reported. Four kinds of cation-exchange composites of different nitrogen and carboxyl contents were synthesized and characterized by investigating their potentiometric titrations, water solubilities, and swellabilities as well as their durabilities. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Recent work from this division has dealt with the synthesis, characterization, and application of new ion-exchange resins,[1-5] as well as new cation-exchange composites based on cellulose,[6] starch,[7,8] and poly(vinyl alcohol).[9] This stimulates the present study, which aims to (a) prepare new cation-exchange composites based on cellulose/N-methylolacrylamide/acrylic acid polymerization cross-linking reactions and (b) characterize these composites by investigating their potentiometric titrations, water solubilities, and swellabilities as well as their durabilities.

EXPERIMENTAL

Materials

Cellulose sheets, rayon-grade pulp, were ground before use. The average degree of polymerization was

found to be 500.[10] The particle-size distribution (using US Sieve Series and Taylor Equipment, ASTM-E-11-61) showed that 61% of the pulp had an average size in the range of 0.105–0.0731 mm and 39% in the range of 0.0731–0.053 mm.

Acrylic acid (AA), containing 200 ppm hydroquinone monomethyl ether, and N-methylolacrylamide (NMA), as an aqueous solution of 40% solid content, supplied by Hoechst, were used as received.

Ammonium persulfate, $(NH_4)_2S_2O_8$, was used as an oxidant; reductants included sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, sodium metabisulfite, $Na_2S_2O_5$, and glucose, $C_6H_{12}O_6$. All were laboratory-grade chemicals.

Preparation Method

All cation-exchange composites were prepared in polypropylene beakers under atmospheric oxygen using a minimum liquor-to-cellulose ratio of 6.25 L/kg. The general preparation procedure, as an example, was carried out as follows: Certain amounts of a reductant and oxidant solutions were added to a polypropylene beaker containing a thermostated

AA/NMA mixture and stirred gently. The cellulose pulp was added quickly afterward with vigrous mixing. The contents of the beaker were then allowed to react in a thermostatic water bath. Details of the reaction conditions are given in the text. An exothermic reaction took place with the evolution of the water vapor, followed by complete solidification of the reactants in a very short time. Fifty milliliters of an aqueous solution of hydroquinone (500 ppm) were then added to the precooled disintegrated product and kept at 5°C for 24 h, followed by filtration through a sintered glass crucible and washed with 50 mL of distilled water. The filtrate was then taken to assess its unsaturation (double bond) content, and the obtained product (crude composite) was dried at a specific temperature for a certain period of time.

Purification of the Crude Composite

The crude composite was ground, vigorously stirred in boiling water for 5 min to remove any soluble part, filtered onto a sintered glass crucible, thoroughly washed on the crucible with boiling water, followed by ethanol, then dried at ambient conditions for 24 h and then over P_2O_5 for at least 48 h before analysis.

Analysis and Test Methods

The unsaturation content was determined as described elsewhere,[11] from which the percent total conversion (% TC) was calculated as follows:

$$\% \ TC = 100(X - Y)/X$$

where X and Y are the unsaturation contents before polymerization and in the filtrate, respectively.

The % yield of the purified composite was calculated as follows:

$$\% \ \text{yield} = 100L/N$$

where L and N are the dry weight of the purified composite and the total weight of the starting materials (cellulose, AA, and NMA), respectively.

The nitrogen content was evaluated by the Kjeldahl method. The carboxyl content was assessed as described elsewhere.[12] Potentiometric titration was performed according to Benerito et al.[13] Water solubility and swellability were conducted as described by Kunin.[14] Durability was determined[1] by evaluating the nitrogen and carboxyl contents of the purified composites after 5,

10, and 20 cycles at 30°C; each cycle consists of four alternating steps, viz., exhaustion (in $0.1N$ N_aOH), thoroughly washing with distilled water on a sintered glass funnel, regeneration (in $0.1N$ HCl), and rewashing. Exhaustion and regeneration were carried out by shaking for 5 h using a liquor-to-composite ratio of 500 L/kg.

RESULTS AND DISCUSSION

The present work forms a part of a research program aiming to establish conditions and to gain more information about the preparation, characterization, and application of new ion-exchange composites based on natural or synthetic carriers.[6-9] This work presents the results of studying such factors affecting the synthesis of new cation-exchange composites based on polymerization/cross-linking of highly concentrated aqueous solutions of NMA and AA along with cellulose pulp using $(NH_4)_2S_2O_8$ as an acid-free radical catalyst in the absence or presence of $Na_2S_2O_3 \cdot 5H_2O$, $Na_2S_2O_5$, or $C_6H_{12}O_6$ as a reductant and then to characterize the produced cation-exchange composites.

Redox Components

Table I shows the effect of using $Na_2S_2O_3 \cdot 5H_2O$, $Na_2S_2O_5$, or $C_6H_{12}O_6$ as a reductant (0.025 mol/L) along with $(NH_4)_2S_2O_8$ (0.1 mol/L) for polymerizing of highly concentrated aqueous mixtures of NMA (1.06 mol/L) and AA (9.72 mol/L) with cellulose pulp at 50°C using a liquor-to-cellulose ratio (LR) of 6.25 L/kg, on the duration and extent of polymerization, expressed as solidification time and % TC, respectively, as well as on the % yield and nitrogen and carboxyl contents of the purified composites. A perusal of the results indicates that (a) the presence of the used reductants independently along with the oxidant, i.e., in a redox system, is accompanied by a significant shortening in the duration of polymerization as well as a remarkable increment in the % yield and carboxyl content of the purified composites, irrespective of the reductant used; (b) the highest % N is obtained in the absence of reductants, which can be attributed to higher extent of acrylamidomethylation[15]; and (c) incorporation of any of the used reductants along with $(NH_4)_2S_2O_8$ has no effect on the extent of polymerization.

Differences in the ability of the used initiating systems to promote polymerization/cross-linking reactions and/or interactions among cellulose pulp,

Table I   Effect of Reductant Type on the Solidification Time, % *TC*, and the Properties of the Purified Composite

Reductant (0.025 mol/L)	Solidification Time (s)	% *TC*	Purified Composite		
			% Yield	% N	Carboxyl Content (meq/100 g)
None	900	99.1	44.7	1.95	680
$Na_2S_2O_3 \cdot 5H_2O$	30	99.5	54.6	1.75	793
$Na_2S_2O_5$	300	99.5	50.0	1.82	750
$C_6H_{12}O_6$	180	99.5	52.0	1.79	765

[AA], 9.72 mol/L; [NMA], 1.06 mol/L; [$(NH_4)_2S_2O_8$], 0.1 mol/L; LR, 6.25 L/kg; reaction temp, 50°C; drying at 90°C for 1.5 h.

NMA, and AA could be interpreted in terms of differences in accelerating oxidant decomposition, in initiating polymerization, in shortening the induction period, as well as in propagating and terminating the growing polymer chains.[16]

Reaction Temperature

The reaction was carried out at different temperatures (25, 30, and 50°C) using the $(NH_4)_2S_2O_8/Na_2S_2O_3 \cdot 5H_2O$ redox system and keeping the concentrations of all other reactants constant (Table II). As is evident, the solidification time decreases significantly by raising the reaction temperature within the range examined. The swellability of the cellulose structure, mobility and diffusivity of the monomers, and rate of decomposition of the redox system to generate free radicals are most likely enhanced by increasing the reaction temperature, thereby shortening the induction period and, subsequently, the duration of the reaction.

Table II also shows that raising the reaction temperature up to 50°C, for the given set of reaction conditions, keeps the % *TC*, % yield, and nitrogen and carboxyl contents practically unchanged. This

could be associated with the highly exothermic nature of the polymerization reaction, which seems to cancel the effect of the starting reaction temperature on the aforementioned parameters.

Concentration of Redox System Components

Table III shows the effect of the concentration of the redox system components [$(NH_4)_2S_2O_8/Na_2S_2O_3 \cdot 5H_2O$] on the % *TC*, solidification time, % yield, and nitrogen and carboxyl contents, when the reaction was carried out at 30°C using a $(NH_4)_2S_2O_8$-to-$Na_2S_2O_3 \cdot 5H_2O$ molar ratio of 4 and keeping the concentrations of all other reactants constant.

It is clear (Table III) that increasing the concentration of the redox system, in the range studied, is accompanied by (a) a sharp decrease in the solidification time, which could be ascribed to the accompanying increase in the number of free radical species and (b) a marginal increase in the % *TC*. The latter attains very high values even at the lowest redox system concentration, which could be explained in terms of two factors: (a) the use of highly concentrated solutions of the monomers and (b) the

Table II   Effect of Reaction Temperature on the Solidification Time, % *TC*, and the Properties of the Purified Composite

Temperature (°C)	Solidification Time (s)	% *TC*	Purified Composite		
			% Yield	% N	Carboxyl Content (meq/100 g)
25	120	98.1	54.2	1.77	788
30	90	99.2	54.4	1.76	790
50	30	99.5	54.6	1.75	793

[AA], 9.72 mol/L; [NMA], 1.06 mol/L; [$(NH_4)_2S_2O_8$], 0.1 mol/L; [$Na_2S_2O_3 \cdot 5H_2O$], 0.025 mol/L; LR, 6.25 L/kg; drying at 90°C for 1.5 h.

Table III   Effect of the Concentration of Redox System on the Solidification Time, % *TC*, and the Properties of the Purified Composite

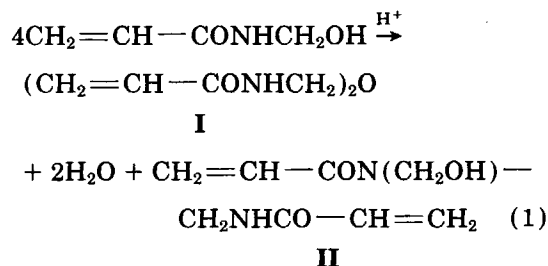| Concentration (mol/L)		Solidification Time (s)	% *TC*	Purified Composite		
$(NH_4)_2S_2O_8$	$Na_2S_2O_3 \cdot 5H_2O$			% Yield	% N	Carboxyl Content (meq/100 g)
0.025	0.00625	360	98.0	33.3	1.95	528
0.050	0.01250	180	98.5	46.1	1.80	710
0.075	0.01875	140	98.9	51.2	1.78	760
0.100	0.02500	90	99.2	54.4	1.76	790
0.125	0.03125	45	99.4	54.8	1.75	795

[AA], 9.72 mol/L; [NMA], 1.06 mol/L; LR, 6.25 L/kg; reaction temperature, 30°C; drying at 90°C for 1.5 h.

cross-linking effect of the methylol groups of NMA. The first factor results in entanglement of the growing chains with each other, whereas the second results in binding a lot of these chains in a fixed cross-linked structure; i.e., the movements of the growing polymer chains are highly restricted and the probability of termination by collision of two chain ends is extremely reduced, which permits polymerization to proceed nearly to completion with high % *TC*. The marginal increase in the % *TC* on increasing the redox system concentration could be associated with the increase in the number of cellulose macro-radicals and/or activated monomers as a result of the accompanying increase in the number of free radical species.
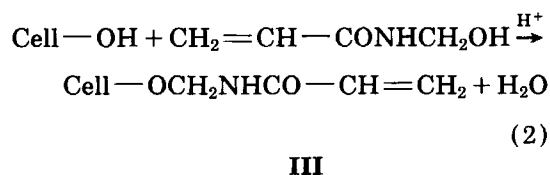
Table III reveals that the % yield and the carboxyl and nitrogen contents of the purified composites depend on the redox system concentration, in such a manner that increasing the concentration of the latter is accompanied by increasing both the % yield and carboxyl content as well as by decreasing the nitrogen content. In addition to the decomposition of the redox system to generate free radical species, it is possible to classify the other main reactions into (a) acrylamidomethylation of cellulose, (b) graft copolymerization of AA and NMA onto cellulose, (c) copolymerization of AA and NMA monomers, (d) homopolymerization of AA and NMA monomers, and (e) cross-linking reactions between the methylol groups of any produced polymer and or copolymer with the nearest labile hydrogen as well as between the methylol groups themselves. It seems that increasing the redox system concentration favors reactions (b), (c), and (e) rather than reactions (a) and (d), which gives rise to increased % yield and carboxyl content as well as lowering the nitrogen content.

With the above in mind, the following scheme is suggested for explaining polymerization–cross-linking reactions and/or interactions of NMA and AA with cellulose in the presence of the $(NH_4)_2S_2O_8/Na_2S_2O_3 \cdot 5H_2O$ redox system to form cellulose–NMA–AA cation-exchange composites:

1. Decomposition of the redox system[17] giving rise to SO_4^-, $HO^\cdot$, and $S_2O_3^-$ radical species. Riggs and Rodriguez,[18] however, showed that $S_2O_3^-$ radicals are unreactive in initiating of polymerization and that initiation can be achieved by SO_4^- and $HO^\cdot$ radical species.

2. Self-condensation of NMA[19,20]:

$$4CH_2\!=\!CH\!-\!CONHCH_2OH \xrightarrow{H^+}$$

$$(CH_2\!=\!CH\!-\!CONHCH_2)_2O$$

$$\mathbf{I}$$

$$+\ 2H_2O + CH_2\!=\!CH\!-\!CON(CH_2OH)\!-\!$$

$$CH_2NHCO\!-\!CH\!=\!CH_2 \quad (1)$$

$$\mathbf{II}$$

3. Acrylamidomethylation of cellulose[15]:

$$Cell\!-\!OH + CH_2\!=\!CH\!-\!CONHCH_2OH \xrightarrow{H^+}$$

$$Cell\!-\!OCH_2NHCO\!-\!CH\!=\!CH_2 + H_2O$$

$$(2)$$

$$\mathbf{III}$$

4. Polymerization reactions:

$$\mathbf{III} + R^\cdot \rightarrow Cell\!-\!OCH_2NHCO$$

$$-\dot{C}H\!-\!CH_2R \xrightarrow{+nM} \text{grafted cellulose} \quad (3)$$

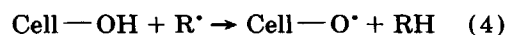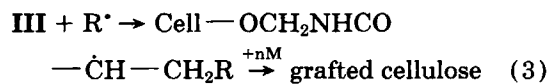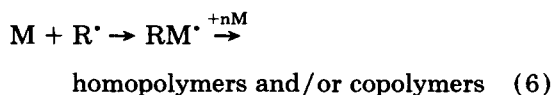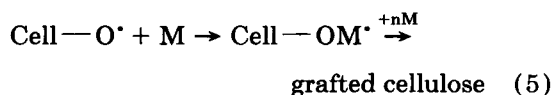$$Cell\!-\!OH + R^\cdot \rightarrow Cell\!-\!O^\cdot + RH \quad (4)$$

Table IV Effect of Drying Temperature and Time on the Properties of the Purified Composite

Drying Temp/ Time	% Yield	% N	Carboxyl Content (meq/100 g)	Color
30°C/24 h	54.4	1.76	789	White
80°C/1.5 h	54.3	1.77	791	White
90°C/1.5 h	54.4	1.76	790	White
120°C/1.5 h	54.5	1.75	788	Yellow

Conditions of preparation of the composite are the same as those of the fourth row (downward) of Table III.
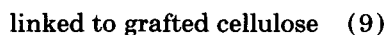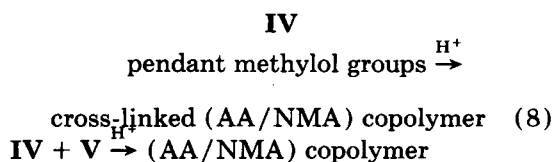
$$\text{Cell} - \text{O}^{\cdot} + \text{M} \rightarrow \text{Cell} - \text{OM}^{\cdot} \xrightarrow{+nM}$$

grafted cellulose (5)

$$\text{M} + \text{R}^{\cdot} \rightarrow \text{RM}^{\cdot} \xrightarrow{+nM}$$

homopolymers and/or copolymers (6)

5. Crosslinking reactions[19,20]:

Grafted cellulose containing

IV

pendant methylol groups $\xrightarrow{\text{H}^+}$

cross-linked grafted cellulose (7)
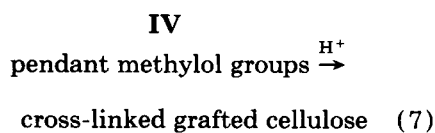
(AA/NMA) copolymer containing

IV

pendant methylol groups $\xrightarrow{\text{H}^+}$

cross-linked (AA/NMA) copolymer (8)

IV + V $\xrightarrow{\text{H}^+}$ (AA/NMA) copolymer

linked to grafted cellulose (9)

where $\text{R}^{\cdot}$ = free radical, e.g., $\text{HO}^{\cdot}$ or $\text{SO}_4^{\cdot}$, and M = AA, NMA, **I**, or **II** individually or in admixtures.

It is noted that any polymer containing pendant methylol groups can be linked to unreacted cellulose through the hydroxyl groups of the latter and that poly(NMA) can undergo similar cross-linking reactions.

Accordingly, the resultant of all these reactions is expected to be a mixture of homopolymers, copolymers, as well as grafted, acrylamidomethylated, and unreacted cellulose. The components of this mixture are cross-linked to different extents and most likely are entangled with each other. This mixture (crude composite) is expected to lose most, if not all, of its soluble components during the purification step, and the remaining components form the so-called purified cellulose/NMA/AA cation-exchange composite.

Drying Temperature

A crude composite was prepared using reaction conditions similar to those of the fourth row (downward) of Table III, and the step of impregnation in hydroquinone solution was eliminated. This composite was divided into 4 parts; each was dried at specific temperature and time, then purified, and its properties investigated. The results are shown in Table IV, where it can be seen that increasing drying temperature from 30°C for 24 h up to 80, 90, or 120°C for 1.5 h has no effect on the % yield and nitrogen and carboxyl contents of the purified composites. This indicates that the heat of polymerization is enough to accomplish cross-linking reactions; thereby, the drying temperature has no effect on these reactions. The yellow color obtained at 120°C for 1.5 h could be attributed to partial oxidation of

Table V Effect of Using AA, NMA, or AA/NMA Mixture on the Solidification Time, % TC, and the Properties of the Purified Composite

Concentration (mol/L)			Solidification Time (s)	% TC	Purified Composite		
AA	NMA	Total			% Yield	% N	Carboxyl Content (meq/100 g)
3.696	0.000	3.696	18,000[a]	12.5	40.0	0.0	50
0.000	3.696	3.696	20	99.9	99.0	10.3	0
1.848	1.848	3.696	40	99.1	81.2	5.63	247

$(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.1 mol/L; $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 0.025 mol/L; LR, 6.25 L/kg; reaction temperature, 30°C; drying at 90°C for 1.5 h.
[a] It did not solidify.

Table VI   Effect of Concentrations of AA and NMA on the Solidification Time, % *TC*, and the Properties of the Purified Composite

Concentration (mol/L)			Solidification Time (s)	% *TC*	Purified Composite			
AA	NMA	Total			% Yield	% N	Carboxyl Content (meq/100 g)	Designation
7.78	1.58	9.36	55	99.8	61.5	2.88	690	A
8.75	1.32	10.07	80	99.5	59.0	2.24	757	B
9.72	1.06	10.78	90	99.2	54.4	1.76	790	C
11.67	0.53	12.20	190	99.0	46.8	0.92	830	D

[(NH$_4$)$_2$S$_2$O$_8$], 0.1 mol/L; [Na$_2$S$_2$O$_3 \cdot$5H$_2$O], 0.025 mol/L; LR, 6.25 L/kg; reaction temp, 30°C; drying at 90°C for 1.5 h.

some of the composite components at such elevated temperature.

The Role of *N*-Methylolacrylamide

To investigate the role of NMA in forming the composites, AA, NMA, and their mixture (of equal molar ratio) were polymerized with cellulose, as shown in Table V. The concentration of AA, NMA, or their mixture was kept constant at 3.696 mol/L, which is the maximum allowable concentration of NMA after adjusting for the redox system solutions. It is evident (Table V) that no solidification was observed in case of AA alone and that the % *TC* was

12.5 even after 5 h. Using NMA alone or in mixture with AA, however, results in forming the composite in a very short time with approximately complete conversion. This shows clearly that (a) NMA is much more reactive than is AA and (b) mixing of NMA with AA enhances the reactivity of the latter, possibly by copolymerizing with it and/or by acting as a radical transfer agent. Obviously, it is necessary to mix NMA with AA to promote both the % yield and the extent of AA fixation (carboxyl content) onto the composite.

Acrylic Acid and *N*-Methylolacrylamide Concentrations

To study the effect of changing the concentration of AA and NMA and in the same time to use them as supplied with no dilution except that from the addition of the redox system solutions, four mixtures of AA and NMA were polymerized with cellulose, as shown in Table VI. It is obvious that increasing
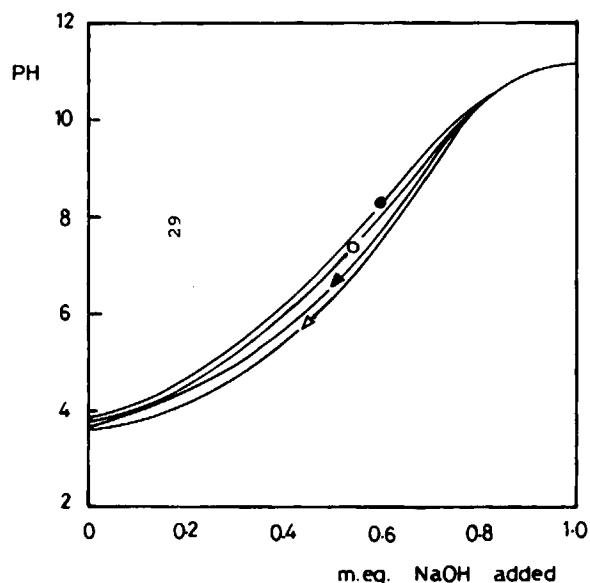

Figure 1   Potentiometric titration of cellulose/NMA/AA cation-exchange composites vs. standardized 0.1*N* NaOH at 30°C in 0.5*M* NaCl: (●) A; (○) B; (▲) C; (△) D. For explanation of A, B, C, and D, see Table VI.

Table VII   Water Solubility of Cellulose/NMA/ AA Cation-exchange Composites

No. Cycles	Composite							
	A		B		C		D	
	Form							
	H	Na	H	Na	H	Na	H	Na
	Loss in Weight (%)							
10	0	0.10	0	0.15	0	0.19	0	0.30
20	0	0.14	0	0.20	0	0.26	0	0.50
50	0	0.14	0	0.20	0	0.26	0	0.50

For explanation of A, B, C, and D, see Table VI.

Table VIII   Water Swellability of Cellulose/ NMA/AA Cation-exchange Composites

	Composite						
	A		B		C		D
	Form						
	H	Na	H	Na	H	Na	H	Na
Increase in volume (%)	105	200	165	300	310	420	410	660

For explanation of A, B, C, and D, see Table VI.

NMA concentration in the mixture is accompanied by a significant decrement in the solidification time, a remarkable increment in both the % yield and the nitrogen content as well as a noticeable decrease in the carboxyl content.

Characterization of the Cation-exchange Composites

Those composites designated as A, B, C, and D as shown in Table VI were selected for characterization by investigating their potentiometric titrations, water solubilities, and swellabilities as well as their durabilities. Presented below are the results of this characterization.

Potentiometric Titration

Figure 1 shows the potentiometric titrations of the selected composites according to Benerito et al.[13]

The obtained curves indicate that these composites are weak base cation exchangers, a result that is consistent with a previous report.[8] The strength, pK_a, of each composite equal to the pH value at half-capacity of the corresponding titration curve. These values were found to be 6.1, 5.9, 5.7, and 5.3 for composites A, B, C, and D, respectively. This finding is in accordance with previous reports[1,8,21] that revealed that the pK_a value of a carboxyl cation exchanger decreases on increasing its capacity.

Water Solubility

Table VII shows the water solubilites of the composites in both the hydrogen and sodium forms, as described by Kunin.[14] It is clear that (a) the hydrogen forms are insoluble, (b) the sodium forms are slightly soluble, and (c) the observed solubility slightly increases on increasing the carboxyl content or decreasing the % N. Similar situations were observed in previous reports[1,21] and the present solubility could be similarly associated with (a) the solubility of some of the modified hemicelluloses and/ or (b) the presence of some poly(AA) entangled in the composite structure, which could be dissolved when transformed to its sodium form.

Water Swellability

Table VIII shows the water swellabilities of the composites in their hydrogen and sodium forms according to Kunin.[14] Evidently, the swellabilities of the hydrogen forms are lower than those of the sodium forms, which reflects the higher hydrophilic character of the latter than that of the former. It is also clear that the swellability increase follows the order A < B < C < D, which is the same order as

Table IX   Durability of Cellulose/NMA/AA Cation-exchange Composites

	Composite							
	A		B		C		D	
	Property							
No. Cycles	% N	C.C.[a]	% N	C.C.[a]	% N	C.C.[a]	% N	C.C.[a]
0	2.88	690	2.24	757	1.76	790	0.92	830
5	2.80	683	2.19	741	1.70	768	0.84	805
10	2.77	680	2.15	737	1.68	760	0.82	798
20	2.77	680	2.15	737	1.68	760	0.82	798

For explanation of A, B, C, and D, see Table VI.
[a] Carboxyl content (meq/100 g).

that of the increasing of the carboxyl content (capacity) and decreasing of the nitrogen content (degree of cross-linking).

Durability

Table IX shows the measured nitrogen and carboxyl contents of the composites after 5, 10, and 20 cycles of use as described elsewhere.[1] Obviously, there are some drops in both the nitrogen and carboxyl contents of the composites after the first 10 cycles, and these drops decrease in the direction from D to A. This may be due to the solubility of some of the modified hemicelluloses and/or the entangled homopolymer under the action of the alkali/acid treatment used in the test. However, no drops in nitrogen and carboxyl contents were observed after that, which implies the durabilities of these composites after the first 10 cycles. Accordingly, it is recommended that these composites should not be used before adequate successive treatments with aqueous solutions of $0.1N$ NaOH and HCl.

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