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Preparation, characterization and sorption properties of crosslinked starch-based exchangers

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Abstract

Starch-based polymers were prepared by a crosslinking reaction of starch-enriched flour using epichlorohydrin as a crosslinking agent in the presence of NH_4OH. Yield, mobility and structural properties of crosslinked starch materials with various compositions were investigated by elemental analysis, electrophoretic mobility and NMR spectroscopy. In particular cross-polarization magic angle spinning (CPMAS) and magic angle spinning (MAS) techniques were used, as well as relaxation time measurements. The homogeneity and the molecular mobility of these polymers were analyzed in terms of cross-relaxation time between protons and carbons (T_{CH}), ^{1}H spin–lattice relaxation in the rotating frame ($T^1_{1\rho}$H) and ^{1}H longitudinal spin–lattice relaxation time (T^1_1H). A correlation was found between the structure, mobility and degree of crosslinking of these sorbents. This correlation was discussed. Finally, these crosslinked starch-based materials, containing tertiary amine groups have been used for the recovery of various dyes from aqueous solutions. Sorption studies are presented, focusing on the polymer and dye structures. The results showed that these polymers exhibited interesting sorption properties and that the sorption mechanism was correlated to the structure of the polymer.

Keywords: Starch; Epichlorohydrin; Modification; Networks; Ion exchanger; Solid state NMR; Relaxation time; Adsorption; Dyes

1. Introduction

Adsorption onto sorbent materials is one of the most popular methods for the removal of pollutants from wastewater. Recently, numerous attempts have been made in finding inexpensive and effective adsorbents containing agricultural residues or natural polymers. Studies showed that many materials, such as peat, sawdust, chitosan, biomass, cyclodextrin, bark, wood, etc., could be used as adsorbents (Babel & Kurniawan, 2003; Bailey, Olin, Bricka, & Adrian, 1999). Amongst these numerous adsorbents, starch and its derivatives represent a cheap and environmentally safe source of material for the preparation of low-cost adsorbents that may be useful for the removal of pollutants from water. This biopolymer represents an interesting alternative as an adsorbent because of its particular characteristics (abundant, renewable and biodegradable raw resource) and properties such as its chemically stability and high reactivity, resulting from the presence of chemically reactive hydroxyl groups in polymer chains. However, it is known that the hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based materials. Chemical derivatization has been proposed as a way to solve this problem and to produce water resistant materials.

Crosslinking starch with epichlorohydrin (EPI) is the most common method used in polysaccharide chemistry (Kuniak & Marchessault, 1972) and in the literature, there have been numerous studies on this reaction (Boutboul, Giampaoli, Feigenbaum, & Ducruet, 2001; Delval, Vebrel, Morcellet, Janus, & Crini, 2000; Dumoulin, Alex, Szabo, Cartilier, & Mateescu, 1998; Seidel et al., 2001;

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Kim & Lim, 1999; Rong & Yuan, 2002; Wesslen & Wesslen, 2002). In our group, experiments are being conducted to evaluate the use of chemically modified polysaccharides as sorbents in waste water treatment. In two previous publications (Delval et al., 2000; Delval, Crini, Janus, Vebrel, & Morcellet, 2001), we tried to chemically modify a starch-enriched flour using EPI as a crosslinking agent. The results showed that these polymers exhibited interesting sorption capacities toward substituted benzene derivatives. Pursuing our interest in such materials, we recently attempted the synthesis of weakly basic ion exchangers by crosslinking a starch-enriched flour with EPI in presence of NH_4OH (Delval et al., 2002, 2003). It is known that reacting EPI with NH_4OH is a convenient and inexpensive way of introducing weakly basic anion-exchange groups into polymer substrates (Simkovic, Laszlo, & Thompson, 1996; Vorchheimer, 1998). In this way, several water-insoluble polyamines having predominantly tertiary amine groups are produced with a view to applications in the recovery of various anionic and non-ionic dyes from aqueous solutions. These polymers have already been characterized using IR techniques (Delval et al., 2002).

In the present paper, experimental conditions were optimized and the yield, mobility, and structural properties of crosslinked starch materials with various compositions were investigated by Brunauer, Emmett and Teller (BET) method, elemental analysis and electrophoretic mobility. Additional information was given by ^{13}C NMR spectroscopy techniques such as cross-polarization magic angle spinning with dipolar decoupling and magic angle spinning (DD–CPMAS). The homogeneity and molecular mobility of these weakly basic ion exchangers have also been analyzed in terms of relaxation parameters such as ^1H spin–lattice relaxation in the rotating frame ($T^1_{1\rho}H$), cross-relaxation time between protons and carbons (T_{CH}) and ^1H longitudinal spin–lattice relaxation time (T^1_1H). The aim of this study was (i) to prepare a weakly basic ion exchanger to optimize the yield of water-insoluble polymer and nitrogen content; (ii) to characterize these polymers by NMR techniques; and (iii) to define the role of the crosslinking reaction. We also described the adsorption properties using the batch method. The results, in terms of sorption capacity, are presented and discussed.

2. Experimental

2.1. Materials

Starch-enriched flour was kindly provided by Sauvin, S.A. (Patornay, France). This product was an industrial agro alimentary garbage. The dyes were purchased from various suppliers and used as received.

2.2. Polymer synthesis

The crosslinked starch-based sorbents were prepared in one step via the crosslinking of starch-enriched flour with EPI in presence of NH_4OH. The synthetic procedure has already been described in detail elsewhere (Delval et al., 2002). The procedure introduced by Simkovic (Simkovic, 1996; Simkovic et al., 1996) was used with some minor modifications, namely an increase in the amount of EPI added, in order to obtain mechanically stable polymers. A typical crosslinking reaction was carried out as follows (polymer 4 in Table 1): in a thermostated reactor vessel, NaOH (20 ml, 50% w/w) was heated to 50 °C after which 5 g of starch-enriched flour was suspended. The mixture was stirred vigorously with a mechanical stirrer for 2 h. The desired amount of EPI and NH_4OH were slowly added dropwise. The viscosity of the solution increased so strongly and rapidly that it could not be stirred and after a few minutes a solid polymer was obtained. Acetone was then added and heating was continued for 30 min. After cooling, the polymer was purified using the soxhlet procedure as described previously (Delval et al., 2000) and finally granulated to particle sizes of 1–2 mm in diameter. A series of polymers was prepared with different molar ratios of EPI and NH_4OH as described in Table 1. The reaction can be schematically described as presented in the Fig. 1. The polymer structure contains a mixture of glucose units joined by a three coordinated nitrogen atom. It was possible to obtain a large range of materials with different crosslinking degrees with different amounts of EPI and NH_4OH.

2.3. Characterization

Elemental analyses of the polymers were carried out on a spectrometer EA 1108W (Thermo Finnigan) using the classical technique based on the Dumas-Pregl method

Table 1
Experimental conditions of the synthesis and characteristics of the polymers used during this study

Polymer	EPI (ml)	NH_{3aq} (ml)	Yield[a]	% N[b]	S[c]	ξ[d]
Polymer 1	35	0	240	0	60	–
Polymer 2	35	23	220	4.98	174	–
Polymer 3	35	35	340	7.2	220	–
Polymer 4	10	13.5	170	8.3	280	+9.4
Polymer 5	20	27	380	8.7	272	+15.6
Polymer 6	35	47	564	9.1	330	+19.5
Polymer 7	50	67.5	710	9.3	325	+24.4
Polymer 8	60	80	713	9.34	336	–
Polymer 9	70	94.5	714	9.5	330	+26.1
Polymer 10	35	70	581	9.33	321	–

[a] Calculated on basis of flour, in %.
[b] Nitrogen content from elemental analysis.
[c] Specific surface area obtained by the BET method, in m^2/g.
[d] Zeta potential, in mV.

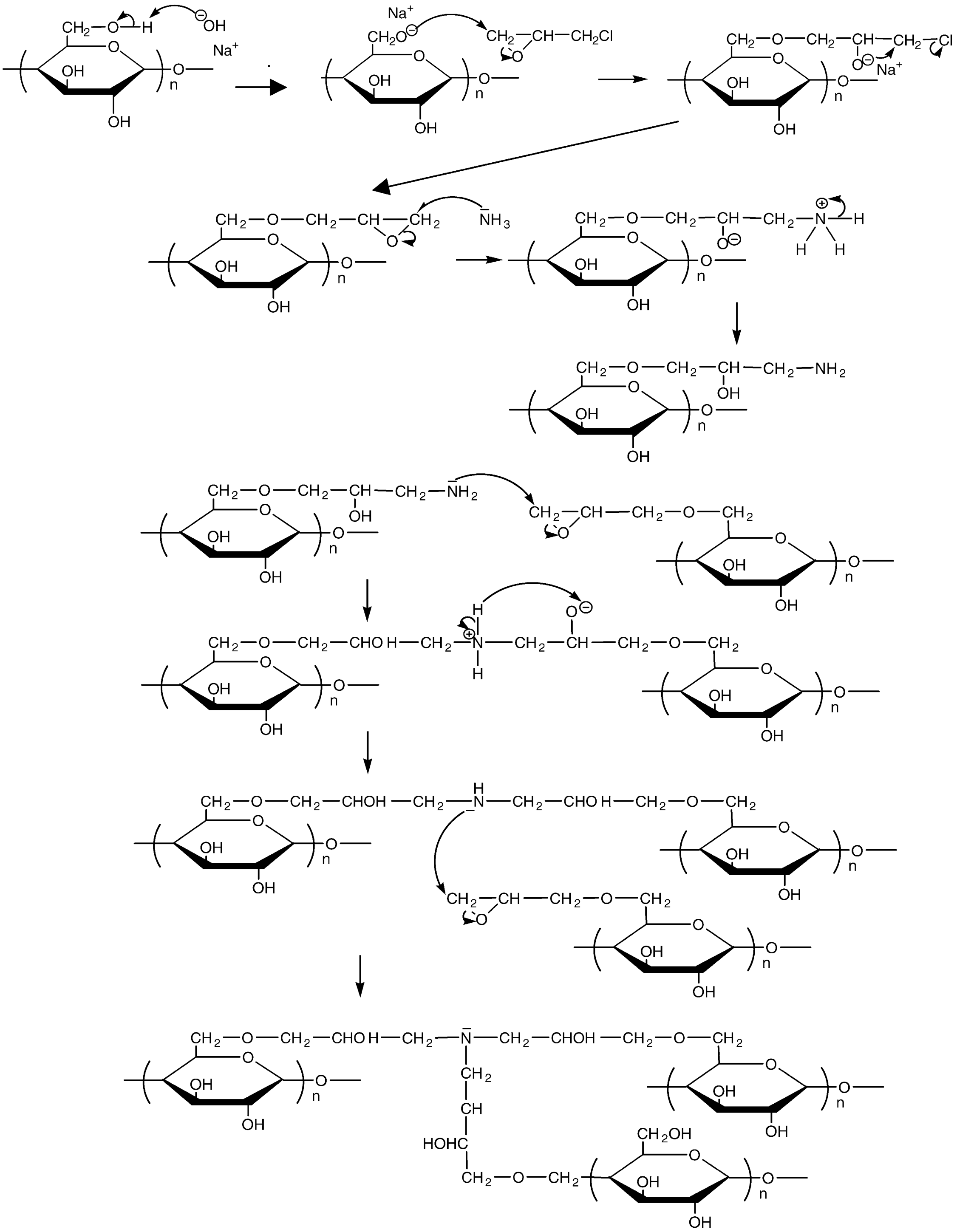

Fig. 1. Reaction scheme of the starch-enriched flour with EPI and NH_4OH in a basic media.

(Patterson, 1973). In this way, we can estimate the level of nitrogen incorporation in the different weakly basic ion exchangers synthesized. Before measurement, a sample of solid polymer was ground to a powder and dried at 100 °C for 24 h, then analyzed to measure the carbon and nitrogen content. The specific surface of the polymers was measured using the BET method described by Brunauer, Emmett, and Teller (1938).

Solid state ^{13}C NMR data were collected at a ^{13}C frequency of 75.46 MHz on a Bruker ASX-300 spectrometer operating at 297 K using a 7 mm WB CPMAS probe head. The samples were finely powdered, packed into a zircon rotor, and sealed with Kel-F caps. The rotor held 220–240 mg of each sample. The spectra were referenced to external Me_4Si via the low-field resonance of adamantane at 38.6 ppm. A magic-angle spinning rate of 4 kHz was used.

The 90° pulse width was 3.7 μs with a recycle time of 6 s. A contact time of 1.2 ms was used for all samples. Spectra were obtained with 1024 data points in the time domain, 512 scans being performed for each experiment. A polynomial baseline correction was manually corrected where necessary after Fourier transform and phasing. A series of experiments was performed as a function of the contact time using the Eq. (1) (Geppi et al., 1997; Ngono-Ravache, Foray, & Bardet, 2000):

$$y = \frac{I}{\left(1 - \frac{T_{CH}}{T_{1\rho}}\right)}\left[\exp\left(-\frac{x}{T_{1\rho}}\right) - \exp\left(\frac{x}{T_{CH}}\right)\right] \quad (1)$$

where y is the signal intensity, x is the variable contact time (τ_{CP}) and I is the maximum intensity of the signal.

The signal intensity was reported against the contact time; from these data, T_{CH} and $T_{1\rho}(^1H)$ were obtained. ^1H spin–lattice relaxation time is determined through ^{13}C observation by means of a ^1H inversion-recovery experiment followed by cross-polarization (Bovey, 1988; Koenig, 1992).

The zeta potential was calculated from measured electrophoretic mobilities, using the Smoluchowski's equation. The electrophoretic mobility data were collected with a Rank Brothers Mark II apparatus equipped with a parallelipidic microelectrophoresis cell. The zeta potential is determined by placing fine particles in an electric field and measuring their mobility using a suitable microscopic technique. The Eq. (2) shows a direct relation between zeta potential (ζ) and electrophoretic mobility (EM) at 25 °C.

$$\zeta = \frac{4\pi\mu}{\varepsilon}\mathrm{EM} \quad (2)$$

where EM is electrophoretic mobility at actual temperature, μ is the solution viscosity, ε is dielectric constant, and ζ zeta potential.

3. Results and discussion

3.1. Synthesis of polymers

Table 1 shows the influence of EPI and NH_4OH on the yield and nitrogen content. The results showed an increase with the increase of NH_4OH introduced during the synthesis for a given volume of EPI. This can be explained by a more intensive crosslinking reaction. Furthermore, the yield and the nitrogen content reach a plateau for polymer 10. As described by Simkovic et al. (1996), a poly(hydroxyproplyamine)-based material could be produced by reacting only EPI with NH_4OH in a basic media. The nitrogen content was estimated to 10.72%. We can consider that polymers 6 and 10, with 9.1 and 9.33%, respectively, have a high nitrogen content and crosslinked structure. In conclusion, it seems unnecessary to introduce a large amount of NH_4OH to obtain crosslinked starch-based exchangers having important amount of tertiary amine groups. Thus, the EPI/NH_4OH ratio (53% in terms of molar ratio) of polymer 6 is chosen for the following study.

Maintaining fixed experimental conditions as well as a constant EPI/NH_4OH ratio, the yield and the nitrogen content increased as the quantity of EPI introduced during the synthesis was increased. However, for polymers 7, 8 and 9 yield and nitrogen content seem to reach a plateau; this confirmed that it was not necessary to introduce large quantity of crosslinking agent to obtain the best results. However, all these polymers showed higher values for yield and nitrogen content than polymer 1 (synthesized without NH_4OH); this confirmed the reactivity and the efficient nitrogen incorporation of the starch enriched flour.

Table 1 also showed the zeta potential for different polymers. As expected, polymer 1, without tertiary amine groups, was not charged. On the other hand, the polymers prepared in the presence of NH_4OH had a partial positive charge. The zeta potential was proportional to the nitrogen content (Fig. 2) confirming the presence of charged tertiary amine groups. We could conclude that the nitrogen content of these polymers could be controlled by the synthetic conditions and that a charged polymer could be prepared by increasing the amount of the crosslinking agent introduced during the synthesis.

3.2. Specific surface

One of the most important parameters, with respect to wastewater treatment and especially to the evaluation of the sorption capacities of these polymers, is the specific surface area of these sorbents. The results, evaluated by the BET method, are reported in the Table 1. Firstly, we observed that the specific surface values increased for polymers 1–5, and then reached a plateau at about 330 m^2/g for polymers 6–10. Secondly, we noted an important increase of the specific surface area for polymers 2–10 in comparison with the value of the polymer 1 synthesized without NH_4OH. Thirdly, the values for polymers 4–10 were high (between 280 and 336 m^2/g). This is important because the sorption

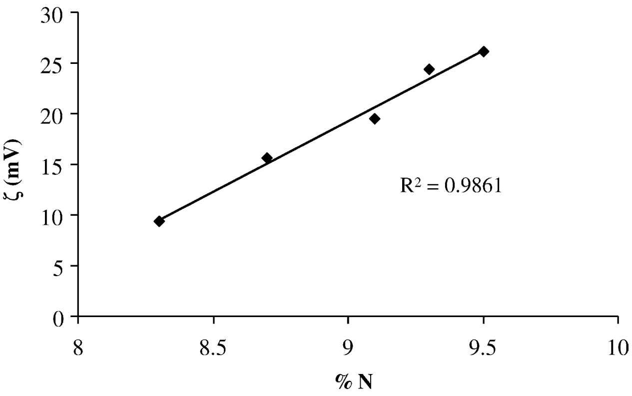

Fig. 2. Correlation between the nitrogen content and the zeta potential of the weakly basic ion starch-based exchangers.

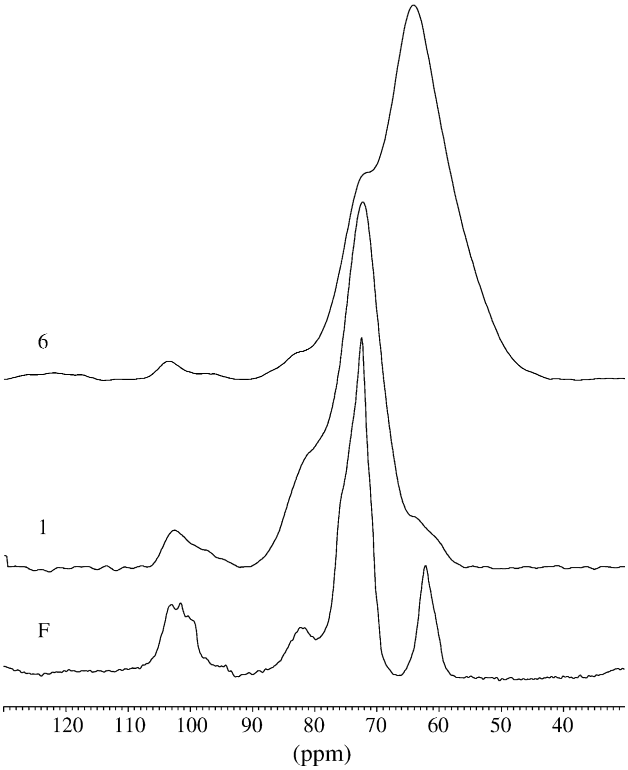

Fig. 3. ^{13}C DD–CPMAS spectra of (F) starch-enriched flour, (1) polymer 1 and (6) polymer 6.

properties of these materials are due to a physical adsorption which is related to their structural characteristics.

3.3. Solid state NMR studies

Solid state NMR methods such as ^{13}C DD–CPMAS and ^{13}C DD–MAS techniques have been widely applied in high-resolution NMR studies of materials (Bovey, 1988; Schmidt-Rohr & Spiess, 1994; Sozzani, 1993). These useful techniques allow the identification, analysis and characterization of different kinds of solids and also give various information on their molecular mobility (Bovey, 1998; Koenig, 1992; Tonelli, 1998). Generally speaking, the use of the carbon–proton dipolar interaction in a ^{13}C DD–CPMAS experiment is a very efficient tool for the analysis of rigid structures, as it is even able to distinguish the mobile components in solid polymers. The ^{13}C DD–MAS method shows signals arising principally from the mobile component. MAS spectra are performed with different $D1$ (i.e. the time between scans). This time, which is correlated with the relaxation time T_1, provides an idea of the polymer rigidity. By definition, T_1 is the time it takes for the magnetization of a nuclear spin to return to its equilibrium value along the direction of the static magnetic field from which it has been perturbed by the radiofrequency pulse. If T_1 is a small value, relaxation is fast, whereas if T_1 is a large value, relaxation is slow. In this way, using a short $D1$ value, it is possible to obtain information for highly mobile components of materials.

Because of the high proton density usually present in organic materials, proton spin–lattice relaxation times are generally strongly influenced by the spin diffusion process. Comparison of the values determined for the various phases of a heterophasic system gives an indication of the morphology (Geppi et al., 1997). Fig. 3 shows the ^{13}C DD–CPMAS spectra of the flour and polymers 1 and 6 taken at the appropriate contact times. This result was confirmed with the T_{CH} and $T^1_{1\rho}$H parameters (Table 2), which corresponded to the polarization of proton spins that could be transferred to a dilute spin system with a rate $1/T_{\mathrm{CH}}$ and to the polarization of proton spins that could be dissipated to the lattice by relaxation under the spin-locked conditional rate $1/T_{1\rho}$, respectively. The T_{CH} values were constant (between 45 and 60 μs), and so the different CPMAS spectra could be compared. Since T_{CH} is sensitive to motions with long correlation times, it represents a useful tool for investigating the rigidity of a system. Table 2 also provides the values of the ^{1}H spin–lattice relaxation in the rotating frame for the flour and different polymers ($T_{1\rho}$). A big difference between the flour and the polymers, revealing the addition of a strong amorphous component into the polymers, was found. On the other hand, the $T^1_{1\rho}$H values of the different carbon atoms for the polymers were similar. They indicated the homogeneity of the phase, and so the materials were considered homogeneous; this confirmed that the different DD–CPMAS spectra could be compared. $T^1_{1\rho}$H depends on motions in the mid-kHz range and is not very sensitive to motion of singular molecular groups. We observed a broadening of the peaks in the range 60–85 ppm for polymer 1 (Fig. 3), which was synthesized with a small amount of EPI without NH_4OH. This broadening could be due to the mobility change of

Table 2
T_{CH} (μs) and $T^1_{1\rho}$H (ms) values for the flour and different polymers

	C-1		C-4		C-2,3,5		C-6	
	T_{CH}	$T^1_{1\rho}$H	T_{CH}	$T^1_{1\rho}$H	T_{CH}	$T^1_{1\rho}$H	T_{CH}	$T^1_{1\rho}$H
Flour	56	6	46	5.4	59	6.9	59	7.4
Polymer 4	58	3	51	2.7	54	2.8	49	2.6
Polymer 5	52	3.7	31	3.5	49	3.5	41	3.4
Polymer 6	52	3	41	3	50	3	43	3
Polymer 7	51	3.8	38	3.7	49	3.7	46	3.6
Polymer 9	44	4.1	42	3.9	42	3.9	42	4

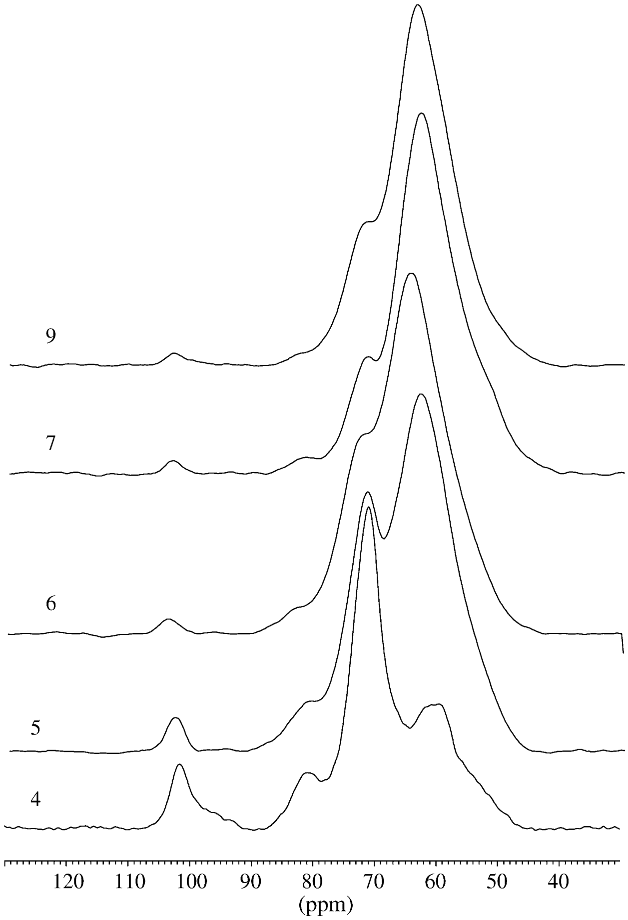

Fig. 4. ^{13}C DD–CPMAS spectra of several polymers.

the material. The crosslinking strongly modified the flour structure. The C-1 signal (100–105 ppm) was still visible but showed a large loss of resolution; this could be explained by an increase in the disorder introduced by the crosslinking. The DD–CPMAS spectra of polymer 6 showed an important broadening in the range 50–85 ppm, confirming the presence of the tertiary amine group signals (Simkovic et al., 1996).

Fig. 4 shows the ^{13}C DD–CPMAS spectra of the polymers 4–7 and 9 taken at the appropriate contact times. The C-1 signal (100–105 ppm) decreased when the amount of EPI and NH_4OH were increased. This could be explained by a reduction of the glucose quantity but also by an increase in the disorder introduced by the crosslinking. We also observed a broadening in the range 50–80 ppm with the increase of crosslinking agent; this broadening could be due to the lower homogeneity and/or to the lower mobility of the material induced by the more extensive reaction.

Fig. 5 compares the ^{13}C DD–CPMAS spectra and ^{13}C DD-MAS spectra with $D1$ values of 4 and 20 s for polymers 4, 7 and 9. For the polymer 4, the ^{13}C DD–MAS spectra with $D1=4$ s showed an intense signal at 62.5 ppm. It is attributable to the hydroxymethyl groups of the EPI terminal residue (Crini 1998, 2000). In fact, for these short experimental delays, more intense signals were obtained because of the high mobility of this group.

With respect to the C-1 peak for all the polymers two groups could be formed: one with polymer 4 for which all the resonances were defined, and another with polymers 7 and 9, for which there was an important loss of resolution. For polymer 4, the C-1 resonance was pronounced in the ^{13}C DD–CPMAS spectrum (4a), was reduced for the ^{13}C DD–MAS spectrum with $D1=4$ s (4b), and almost reached the CPMAS intensity with $D1=20$ s (4c). This could be explained by a higher contribution to the total signal intensity of the most mobile carbons with a low value of $D1$. For $D1=20$ s, a more rigid structure could be observed, and so a spectrum close to the one obtained with ^{13}C DD–CPMAS was observed. For polymer 7, the more

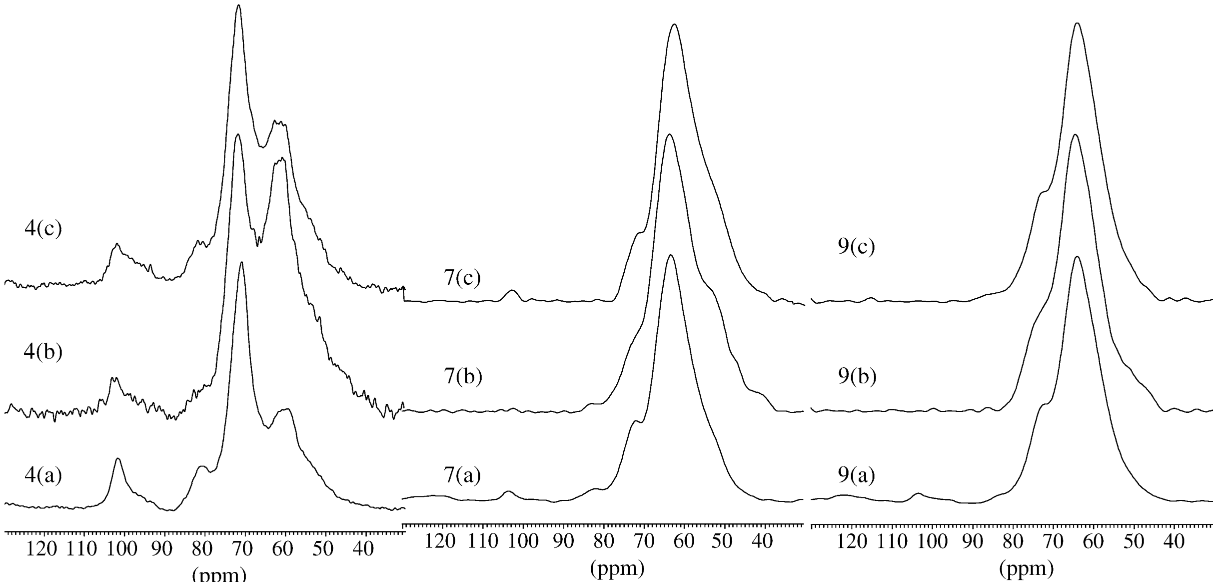

Fig. 5. Influence of the crosslinking degree on (a) ^{13}C DD–CPMAS, (b) ^{13}C DD–MAS with $D1=4$ s and (c) ^{13}C DD–MAS with $D1=20$ s spectra of polymers 4, 7 and 9.

Table 3
T_1^1H (s) values for the industrial flour before and after mixed in an aqueous sodium hydroxide solution without a crosslinking agent and for different polymers

	C-1	C-4	C-2,3,5	C-6
Industrial flour	0.93	1	0.93	0.94
Treated flour (with NaOH)	0.24	0.26	0.26	0.23
Polymer 4	0.9	0.9	0.9	0.9
Polymer 5	1.6	1.6	1.6	1.6
Polymer 6	2	2	2	2
Polymer 7	2.1	2	2	2.1
Polymer 9	2.7	2.7	2.1	2.1

rigid structure induces a loss of the signal in the ^{13}C DD–MAS spectrum with a $D1$ of 4 s (7b). The CPMAS intensity is partially recovered for the ^{13}C DD–MAS spectrum with a $D1=20$ s (7c). For polymer 9, the C-1 signal was not present for $D1=4$ s or $D1=20$ s. This result could be explained by an increase in the rigidity of the material involving a loss of the signal for all the MAS experiments. For the larger amounts of EPI used during the synthesis, the crosslinking step was more important, inducing more rigid and amorphous materials.

This was also confirmed by the T_1^1H values reported in the Table 3 for the flour investigated before and after being mixed in an aqueous sodium hydroxide solution without crosslinking agent, and different polymers. T_1^1H was an efficient parameter for translating the rigidity of the materials. We observed a decrease when the flour was mixed in basic media; this indicated a loss of the crystalline structure and thus a more mobile system. The increase between the treated flour and polymer 4 and especially polymers 7 and 9 confirmed the increase in the rigidity with the amount of the crosslinking agent during the synthesis.

In this study, we observed an increase in the rigidity with the amount of the crosslinking agent added during the synthesis. We could control the structures of the different polymers which were directly related to the amount of EPI and NH_4OH. A correlation is expected between the degree of crosslinking, the structure and the mobility of these crosslinked starch derivatives and their sorption properties for dyes compounds.

3.4. Sorption properties

Among industrial wastewaters, dye wastewater from paper, textile and dyestuff industries is one of the most difficult to treat. This is because dyes usually have complex aromatic molecular structures, which make them more stable and more difficult to be degraded. Therefore, it would be advantageous to develop technologies to eliminate them. Amongst the numerous technique of dye removal, adsorption is a procedure of choice for the removal of pollutants from wastewater.

In this study, we propose the use of crosslinked starch-based materials containing tertiary amine groups for the recovery of various dyes from aqueous solutions. Dyes are classified as follows (Fu & Viraraghavan, 2001; Mishra & Tripathy, 1993): anionic (direct, acid, mordant and reactive dyes), cationic (basic dyes) and nonionic (disperse dyes).

The sorption capacity was investigated using acid blue 25 (AB25), acid green 25 (AG25), acid orange 8 (AO8), acid red 1 (AR1), reactive blue 19 (RB19), mordant blue 79 (MB79), disperse blue 1 (DB1), disperse blue 3 (DB3), disperse red 19 (DR19), basic blue 9 (BB9) and basic blue 3 (BB3) as model guest solutes. Adsorption experiments of the polymers were determined by the batch method. This method has already been described in detail (Crini, 2003; Delval et al., 2003). The polymer was mixed with an aqueous solution of the dye at a known concentration in a tightly closed flask and at pH = 6.5. The solution was then shaken at room temperature. Preliminary kinetic experiments had shown that 60 min contact time was sufficient for an equilibrium to be reached. After centrifugation, the residual concentration of the dye was determined by spectrophotometry and the sorption capacity was calculated. The results are reported as percentage uptake (R in %) which represents the ratio between the amount of adsorbed dye and the initial amount of dye.

The comparison of the sorption capacity of several dyes on polymer 1 and 6, without and with tertiary amine groups, respectively, is reported in Table 4. The two polymers display good sorption properties since the quantity of dye adsorbed is significant. However, performance is dependent on the type of material used. If we compare the values obtained, we observe an important increase in the sorption for polymer 6, which contains amine groups. These results can be explained not only by the presence of amine groups, but also by physical adsorption due to the polymer network introduced by EPI. Polymer 6 has a high surface area, which could explain its good sorption ability. It is also characterized by its high nitrogen content, principally in the form of amine groups that is responsible for dye ion binding through anion exchange mechanisms. Amine sites are the main

Table 4
Comparison between sorption capacity (R in %) of 11 dyes on four polymers in water using the batch method (dye concentration = 5.10^{-4} M; contact time 60 min; pH = 6.5)

Dye	Polymer 1	Polymer 4	Polymer 6	Polymer 9
AB25	66	98.5	98.4	100
RB19	80.5	80.5	96.8	95.1
AG25	78	86	92	100
AR1	7.2	10	91.6	95.1
DB1	58	87	79	65
DR19	34	81	74	63
DB3	67.3	66.4	66.3	69.2
AO8	17	22	51	46
MB79	23	29	38	44
BB9	12	5	2	0
BB3	3	2.1	0	0

reactive groups for dyes though hydroxyl groups may also contribute to adsorption by hydrogen bonding interactions. The difference in the chemical structure between these 11 dyes can also explain the obtained values. Both acid and reactive dyes display the best interactions with starch-based materials. This confirms that the interactions between anionic dyes and protonated tertiary amines (shown by the zeta potential of the polymers) play a major role in the sorption mechanism. The chromophores in the anionic dyes are anthraquinone types. It also seems that the presence of these anthraquinone groups favors the sorption whereas the cationic dyes (BB9 and BB3) containing thiazine chromophores do not interact with polymers 1 and 6.

In order to confirm these conclusions, we also studied the sorption abilities of other polymers. Table 4 also shows the comparison of the sorption capacity of several dyes on polymers 4, 6 and 9. Polymers 6 and 9 possess the same surface area but differ in their amine content. As expected, the overall trend is an increase in the sorption capacity with increasing amounts of amine groups, corresponding to an increase in interactions between amine groups and anionic dyes. This confirms that the values are mainly correlated to the amount of amine groups. No sorption was observed for BB9 and BB3 which are basic dyes containing cationic functions that are not efficient for the dye-starch-based materials interaction. However, for DR19 and DB1, the sorption decreases when the nitrogen content is higher; this could be explained by the fact that the crosslinking agent created a network between the polymer chains, which induced a steric effect. As described in the NMR section, we concluded that polymer 9 has a more rigid and crosslinked structure than polymers 4 and 6. This could indicate steric restrictions for the sorption for a more extensive crosslinking reaction. So, it was not necessary to have a high level of crosslinking to obtain the best sorption results.

4. Conclusions

Crosslinked starch-based materials containing amine groups were prepared by crosslinking a starch-enriched flour with EPI in the presence of NH_4OH. The results showed that the nitrogen content of the polymers could be controlled by the synthetic conditions. The NMR results confirmed that a more important crosslinked step inducing a rigid structure could be expected when the amount of EPI used during the synthesis was more important. We showed that the experimental conditions used control the structure of the polymers. These polymers have then been used as adsorbents for the removal of dyes from aqueous solution. The starch-based materials possess good sorption properties for acid, reactive and disperse dyes, but are ineffective against basic dyes. Physical adsorption in the polymer structure and chemisorption of the dye via ion exchange are all involved in the sorption process. Dye sorption results were found to be a function of the degree of crosslinking.

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