

Rapid Homogeneous Esterification of Cellulose Extracted from *Posidonia* Induced by Microwave Irradiation

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ABSTRACT: In this article, we report on the synthesis of cellulose esters by the reaction of cellulose and some cyclic anhydrides, such as succinic, maleic, and phthalic anhydrides. For this, an esterification method was finalized. Indeed, cellulose extracted from *Posidonia* biomass was first solubilized in the solvent system lithium chloride (LiCl)/*N,N*-dimethylacetamide and then esterified by cyclic anhydride in the presence of catalysts such as *N,N*-dimethyl-4-aminopyridine, tripropylamine, tributylamine, and calcium carbonate. This method was fast and reproducible with the LiCl system as a solvent and with an efficient activation by controlled microwave power. In this way, the reaction time was reduced from several hours to just a few minutes. The reaction products were character-

ized by IR and solid-state cross-polarization/magic angle spinning ^{13}C -NMR spectroscopy. The degree of substitution (DS) and the grafted ester group content of the different products were obtained by alkali saponification followed by titration of the excess alkali. Two activation methods were compared, and the results show that the application of classical heating gave less successful results than those obtained by microwave activation. Indeed, with microwave activation, a higher DS (2.25) was obtained after 10 min. However, with classical heating, a value of DS equal to 1.2 was obtained after 12 h. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3372–3381, 2011

Key words: esterification; graft copolymers; waste

INTRODUCTION

Posidonia biomass consists of approximately 30% cellulose;¹ this makes it possible to use this waste as an unconventional source of cellulosic materials.

Cellulose is the most abundant of all naturally occurring substances and is widely used as a raw material in numerous industrial applications.^{2,3} Chemical modification of the heterogeneous or homogeneous phases of cellulose is one method for producing value-added products. Interest in the derivatization of cellulose under homogeneous solution conditions has arisen because the physicochemical properties of the obtained products are better controlled than those of products prepared under heterogeneous solution conditions.^{4,6} However, because of its high crystallinity, cellulose is insoluble in water and most traditional organic solvents, which is a major obstacle for cellulose homogeneous modification.

The solvent system lithium chloride (LiCl)/*N,N*-dimethylacetamide (DMAc) shows enormous potential for the analysis of cellulose. It has proven to be the most suitable for the preparation of a wide variety of cellulose derivatives.^{7–18} Its usefulness in anal-

ysis and chemical modification is due to the facts that the solvent is colorless and dissolution succeeds without or at least with negligible degradation, even in the case of high-molecular-weight polysaccharide. We chose the LiCl/DMAc system to study the performance of this esterification method and to prepare different ester cellulose samples. It has been demonstrated by NMR studies that this system is a true solvent for cellulose; that is, the polysaccharide is neither degraded nor transformed into a derivative. In this manner, cellulosic hydroxyl groups are readily accessible, and diffusion and crystallinity limitations are avoided.

Recently, there has been increased interest in microwave heating as an alternative to conventional heating technology to facilitate difficult reactions; microwave heating has been proven to be faster and more efficient.^{19–29} Considerable efforts have been devoted to investigate microwave-assisted reactions in the synthesis and modification of natural polymers. A number of different polysaccharide derivatives, such as cellulose ester,^{22,24,29} starch ester,^{19,26} and *o*-alkyl chitosan,³⁰ have been synthesized with microwaves. To scale up this process, microwave heating was chosen in this study because it gives fast, uniform heating and an enhanced reaction rate.

In this study, we aimed to improve the preparation method by increasing the reaction efficiency and decreasing the reaction time. The rapid reaction

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of cellulose extracted from *Posidonia* with cyclic anhydrides, such as maleic, succinic, and phthalic anhydrides, in LiCl/DMAc was achieved under microwave irradiation. The effects of various reaction times, catalysts, microwave powers, anhydrides, and *N,N*-dimethyl-4-aminopyridine (DMAP) amounts on the degree of substitution (DS) were studied. The percentage ester group content (%G) of the modified cellulose was determined by saponification. Fourier transform infrared (FTIR) and solid-state cross-polarization/magic angle spinning (CP-MAS) ^{13}C -NMR spectroscopy were performed to investigate the reaction.

EXPERIMENTAL

Materials

In this study, the cellulose that we used was isolated from waste *Posidonia oceanica* (collected from the Tunisian coasts) and then characterized as described in our previous article.³¹ All other chemicals used were analytical grade and were purchased from Sigma-Aldrich (Missouri, Saint-Louis).

Measurements

FTIR spectroscopy was performed with a Bio-Rad spectrometer (Brandenburg, Germany). Samples of each modification were ground to pass a 100-mesh screen, oven-dried at 105°C for 4 h, mixed with KBr at a sample-KBr ratio of 1:200 mg and pressed *in vacuo* to form pellets. The absorbance was measured over a range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} in the transmission mode. The baseline was corrected, and the spectra were normalized to the band nearest 1160 cm^{-1} .

The solid-state CP-MAS ^{13}C -NMR spectra were recorded on a Bruker DRX-400 spectrometer (New Brunswick, NJ) at a frequency of 100 MHz with 5 mm of Magic Angle Spinning Broadband (MAS BBO) probe. The acquisition time was 0.063 s. The delay time was 4 s, the special width was 32,051 Hz, and the pulse time was 5 μs .

Dissolution of cellulose

The method used was described by Tosh et al.¹⁶ after modification to perform cellulose solubilization. Indeed, a mixture of cellulose (8 g, 49.3 mmol, on the basis of glucose units) and DMAc (300 mL) was heated up to 130°C for 30 min in a round-bottom flask equipped with a short path condenser. Then, the reaction mixture was cooled to 100°C. After that, LiCl (6.5 g, 153 mmol) was added, and the mixture was heated to 100°C for 5 min. Finally, the reaction mixture was cooled to room temperature and stirred

overnight for dissolution. The cellulose solution prepared previously was diluted to 1% by further addition of the solvent.

Esterification without a catalyst

The cellulose ester derivatives containing free carboxylic groups were prepared by the reaction of extracted cellulose with cyclic anhydrides, such as phthalic, succinic, and maleic anhydrides, in the LiCl/DMAc systems by microwave activation. The procedure was as follows: a desired amount of esterifying agent [6 : 1 molar ratio of etherifying agent to anhydroglucose units (AGUs) in cellulose] was added to 50 mL of a 1% w/v cellulose solution. This mixture was irradiated at room temperature without further stirring in a 500-mL ultrasonic bath (Newpower, Guangzhou, China) until complete dissolution was achieved (ca. 5 min). After that, the resulting solution was subjected to activation in a microwave oven for various time periods (in minutes) at different power outputs (160 and 350 W). Upon completion of the reaction, the resulting reaction mixture was cooled, and the soluble ester product was isolated by precipitation with acetone. The excess anhydrides and byproducts were removed by Soxhlet extraction with acetone for 16 h. Finally, the modified cellulose was dried overnight at 65°C.

Esterification with an organic catalyst

The organic catalysts (DMAP, tripropylamine, and tributylamine) and cyclic anhydrides (succinic, maleic, and phthalic anhydrides) were added to the cellulose solution, and this mixture was irradiated at room temperature for 5 min without further stirring in a 500 mL ultrasonic bath. After that, the resulting solution was subjected to activation in a microwave oven for various time periods (min) at different power outputs (90, 160, and 350 W). In a typical experiment, to 50 mL of a 1% w/v (0.5 g, 3.1 mmol) cellulose solution, a 1 : 1–3 : 1 molar ratio of organic catalyst to AGU and cyclic anhydride (1 : 1–12 : 1 molar ratio of anhydride to AGU) were added. The final temperature was between 120 and 155°C. The reaction product was precipitated in acetone and collected by vacuum filtration. The solid was subjected to Soxhlet extraction with acetone to remove the free anhydride, and finally, the modified cellulose was dried again.

Esterification with an inorganic catalyst

Succinic anhydride (1.86 g) and calcium carbonate (CaCO_3 ; 0.3 g, 1 : 1 molar ratio of CaCO_3 to AGU in cellulose) were added to 50 mL of the 1% w/v cellulose solution. After irradiation in an ultrasonic bath

for 5 min, the reaction mixture was activated with microwaves to obtain the cellulose ester. After the required time, the reaction vessel was then cooled to room temperature. CaCO_3 was isolated from the reaction mixture by filtration. The reaction product was precipitated in acetone and purified by Soxhlet extraction with acetone. The process of phthalic and maleic anhydride treatment was similar to that for succinic anhydride.

Determination of the average ester group content (%G) and DS

To estimate the average %G of the modified cellulose, 0.5 g of finely ground sample was weighed and placed in an Erlenmeyer flask, and 5 mL of an NaOH alcoholic solution (0.25M) was added. The contents were warmed to 80°C with stirring and held at this temperature for 17 h. The sodium hydroxide solution saponified the modified cellulose, and excess alkali remaining in the medium was titrated with 0.1M HCl with a phenolphthalein indicator. Sometimes, the product underwent a minor degradation because of the treatment with a caustic in an alcoholic system. Therefore, it was necessary to treat the native cellulose in the same manner to obtain the blank value. The %G value of the sample was calculated with the following formula:³²

$$\%G = \frac{(V_b - V_e) \times [\text{HCl}] \times M}{m} \times 100 \quad (1)$$

$$\text{DS} = \frac{M_{\text{AGU}} \times \%G}{100M - \%G \times M}$$

where V_b and V_e are the volumes of HCl solution necessary to neutralize the remaining NaOH of the untreated cellulose and modified cellulose, respectively (L); [HCl] is the molarity of the hydrochloric acid solution (mol/L); m is the mass of the sample (g); M is the molar mass of grafted groups (g/mol); and M_{AGU} is the glucose unit molecular weight (g/mol).

RESULTS AND DISCUSSION

Effects of the process parameters on the esterification of cellulose

Microwave heating of a polar solvent differs from conventional heating. Generally speaking, the reaction is accelerated under microwave conditions, mainly because of the speed with which a mixture can be heated and the high temperatures easily obtained. DMAc is a good solvent for reactions in microwaves because it absorbs microwave radiation very well and heats up rapidly.

Microwave activation represented a suitable and effective method for the chemical modification of cel-

lulose in the LiCl/DMAc system, particularly the esterification with cyclic anhydrides, such as succinic, maleic, and phthalic anhydrides (Fig. 1). The system acted as a solvent for both the starting cellulose and the final products. By varying the process parameters, we were able to prepare esters with a wide range of DS values up to 2.25. The parameters were the reaction time, microwave power, nature of the catalyst, and amounts of anhydride and catalyst (Table I).

First, tributylamine (TBA) and tripropylamine (TPA) were used as organic catalysts because they had sufficiently high boiling points to not evaporate during microwave irradiation. DMAP, which is a less harmful byproduct of pyridine, was used as catalyst. Furthermore, DMAP was a much more effective catalyst because of the mesomeric donor effect of the amine function, which strikingly, increased the nitrogen basicity of the pyridine ring. CaCO_3 was chosen as an inorganic base.

The protocol used with these various catalysts consisted of holding in suspension (for CaCO_3) dissolving (for the organic catalyst) the catalyst, adding the cyclic anhydrides (maleic, succinic or phthalic), and then, using microwaves for heating. Before the activation, the solution of cellulose containing the catalyst was homogeneous in the case of amines and heterogeneous in the case of CaCO_3 . The results of this experimental series are represented in Table I.

By analyzing the evolution of %G according to the catalyst, we observed that the values obtained in the presence of CaCO_3 were slightly higher than those obtained without a catalyst. The cellulose esters synthesized in the presence of carbonates had a %G value lower than those obtained in the presence of organic bases; this was attributed to the heterogeneity of the reaction media. Indeed, cellulose solution/anhydride/organic catalyst was homogeneous during the reaction. For experiments conducted in the presence of CaCO_3 , they were heterogeneous. If three organic bases were compared, high values of DS and %G were obtained in the case of DMAP. This result can be probably explained by the fact that the doublet of the nitrogen in the case of DMAP was more nucleophilic and less hindered than in the case of the two other organic catalysts.

The microwave irradiation was studied with a well-defined medium: 0.5 g of cellulose in 50 mL of the LiCl/DMAc system, a 1 : 1 molar ratio of DMAP to AGU, and a 6 : 1 molar ratio of cyclic anhydride to AGU. Different power outputs were used to irradiate this mixture. The values of DS and TE for each grafted sample are illustrated in Table I (samples 6–8, 15–17, and 25–27).

Obviously, the increase in microwave power from 90 to 160 W resulted in an increase in the reaction temperature and, thus, an increase in the DS values of the products from 1.21 to 2.18 for maleic

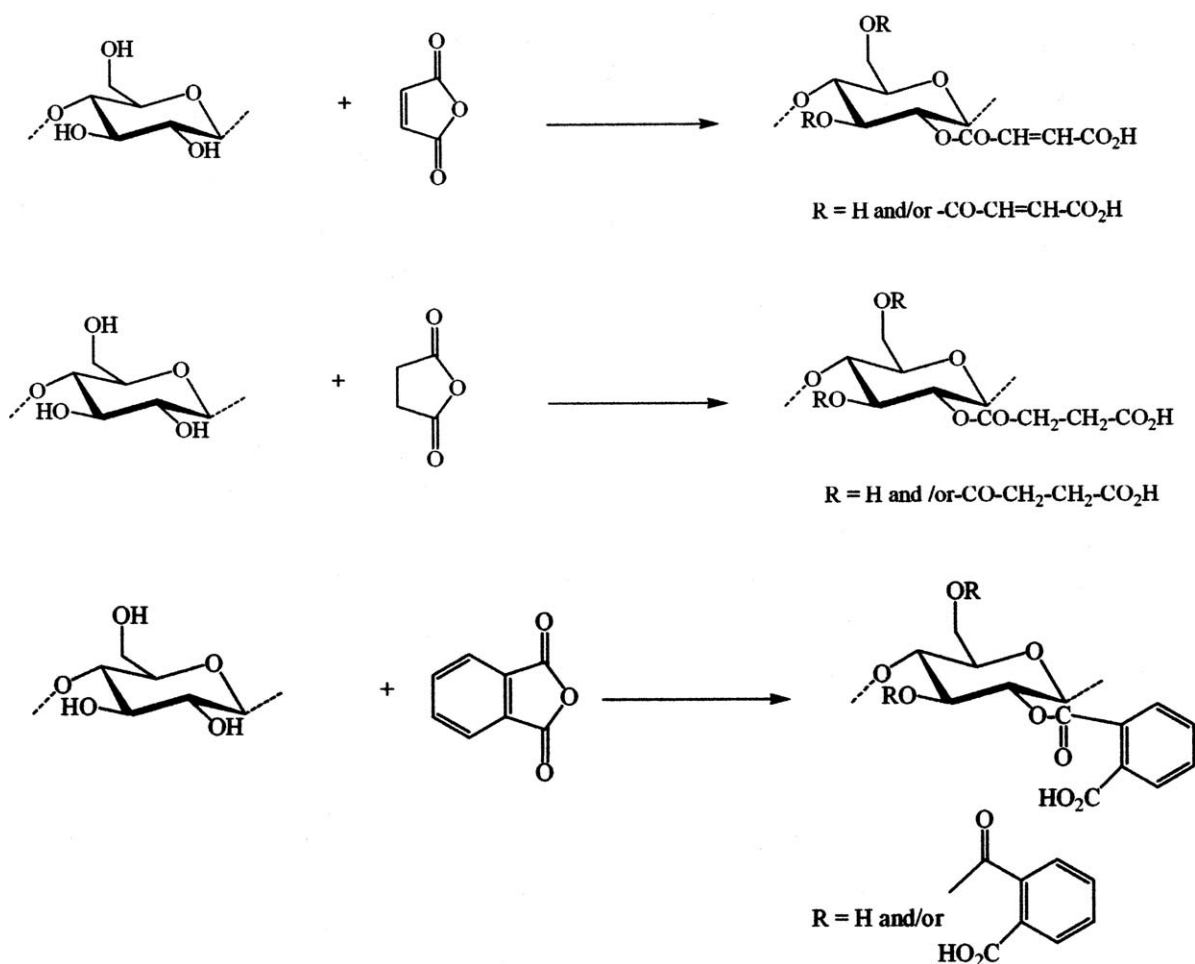


Figure 1 Schematic representation of the esterification of the hydroxyl groups of the extracted cellulose with the cyclic anhydrides.

anhydride, from 0.57 to 0.85 for succinic anhydride, and from 0.6 to 1.06 for phthalic anhydride. The reason for this enhancement was presumably the favorable effect of the temperature on the maleation, phthalation, and succinylation reactions. A higher temperature would enhance the mobility of the reacting molecules and the diffusion of the catalyst and esterifying agents into the cellulosic molecules. In contrast, a further increase in the reaction temperature from 140°C (160 W) to 155°C (350 W) resulted in a slight decrease in DS from 2.18 to 2.22, 0.85 to 0.81, and 1.06 to 1.04 for the maleic, succinic, and phthalic anhydrides, respectively. This phenomenon revealed that a much higher power (higher temperature), such as 350 W, resulted in the hydrolysis of the formed ester; this, consequently, reduced DS. Therefore, a microwave power of 160 W (reaction temperature = 140°C) was considered optimal for the other samples.

Table I clearly shows that DMAP was indispensable for catalyzing the cellulose esterification. Indeed, the %G values obtained in the presence of the catalyst were widely higher than those obtained without

a catalyst under the same experimental conditions. We deduced from Table I (samples 11, 12, 21, 22, 31, and 32) that in all cases, there were no significant differences in DS when two concentrations of DMAP were used.

In conclusion, the amount of DMAP had no significant effect on the characteristics of the reactions (DS, %G), but its absence caused an important decrease in DS.

Figure 2 shows the time courses of cellulose esterification with the succinic, maleic, and phthalic anhydrides. Under the reaction conditions (1 equiv of DMAP, 6 equiv of cyclic anhydrides), the DS values of the product increased with increasing reaction time and reached 2.24, 1.44, and 1.5 within only 10 min for the maleic, phthalic, and succinic anhydrides, respectively. This increasing trend of DS with reaction time could have been due to the increasing rate and collision time of the esterifying agents with cellulosic molecules. However, a further increase in the reaction time from 10 to 12 min had a detrimental effect on cellulose esterification, and the DS values decreased from 2.24 to 1.95, 1.44 to

TABLE I
Influence of the Operating Conditions on DS

Anhydride	Sample number	Catalyst	Conditions	Anhydride concentration ^a	Catalyst concentration ^b	DS	%G
Maleic	1	TBA	160 W, 5 min	6 : 1	1 : 1	0.39	19.2
	2	TPA	160 W, 5 min	6 : 1	1 : 1	0.41	20
	3	CaCO ₃	350 W, 15 min	6 : 1	1 : 1	0.16	8.9
	4	CaCO ₃	160 W, 5 min	6 : 1	1 : 1	0	0
	5	CaCO ₃	160 W, 10 min	6 : 1	1 : 1	0.12	7.3
	6	DMAP	160 W, 5 min	6 : 1	1 : 1	2.18	57.1
	7	DMAP	90 W, 5 min	6 : 1	1 : 1	1.21	42.5
	8	DMAP	350 W, 5 min	6 : 1	1 : 1	2.22	58.2
	9	—	350 W, 15 min	6 : 1	—	0.09	5.2
	10	—	160 W, 10 min	6 : 1	—	0.11	6.2
	11	DMAP	160 W, 10 min	6 : 1	1 : 1	2.24	57.7
	12	DMAP	160 W, 10 min	6 : 1	3 : 1	2.16	56.8
Succinic	13	TBA	160 W, 5 min	6 : 1	1 : 1	0.67	29.2
	14	TPA	160 W, 5 min	6 : 1	1 : 1	0.66	28.9
	15	DMAP	160 W, 5 min	6 : 1	1 : 1	0.85	34.4
	16	DMAP	90, 5 min	6 : 1	1 : 1	0.75	31.6
	17	DMAP	350, 5 min	6 : 1	1 : 1	0.81	35.7
	18	CaCO ₃	350 W, 15 min	6 : 1	1 : 1	0.15	8.9
	19	—	350 W, 15 min	6 : 1	—	0.04	6.4
	20	—	160 W, 10 min	6 : 1	—	0.14	7.9
	21	DMAP	160, 10 min	6 : 1	1 : 1	1.5	48
	22	DMAP	160, 10 min	6 : 1	3 : 1	1.59	49.5
Phthalic	23	TBA	160 W, 10 min	6 : 1	1 : 1	0.99	47.4
	24	TPA	160 W, 10 min	6 : 1	1 : 1	0.97	46.6
	25	DMAP	160 W, 5 min	6 : 1	1 : 1	1.06	49.1
	26	DMAP	90, 5 min	6 : 1	1 : 1	0.6	35.4
	27	DMAP	350, 5 min	6 : 1	1 : 1	1.04	48.7
	28	CaCO ₃	350 W, 15 min	6 : 1	1 : 1	0.13	23.1
	29	—	350 W, 15 min	6 : 1	—	0.12	19.8
	30	—	160 W, 10 min	6 : 1	—	0.22	16.7
	31	DMAP	160 W, 10 min	6 : 1	1 : 1	1.44	56.8
	32	DMAP	160 W, 10 min	6 : 1	3 : 1	1.5	57.8

^a Ratio of the cyclic anhydrides to AGU in cellulose (mol/mol).

^b Ratio of the catalyst to AGU in cellulose (mol/mol).

0.88, and 1.5 to 0.96 for the maleic, phthalic, and succinic anhydrides, respectively. These data indicate that a more stretched time period, such as 10–12 min, resulted in cellulose degradation and hydrolysis of the formed esters, which therefore, reduced the reaction yield (%G) and (DS). For this reason, we chose to irradiate the reaction medium for 10 min at 160 W.

The data in Figure 3 indicate that the concentration of cyclic anhydride also had an important effect on the reaction efficiency. An increase in the molar ratio of anhydride units to AGUs in cellulose from 3 : 1 to 6 : 1 led to increases in the DS values from 0.5 to 2.25, 0.74 to 1.45, and 0.36 to 1.51 for the maleic, phthalic, and succinic anhydrides, respectively. This increase in the reaction efficiency with the reacting molar ratio was interpreted by the greater availability of anhydride molecules in the proximity of these cellulose molecules at a higher concentration of the esterifying agents.³³ When the anhydride/AGU ratio became equal to or greater than 6, the DS values then reached constant values of about 2.24,

1.44, and 1.5 for the maleic, phthalic, and succinic anhydrides, respectively. Similar results were reported in the esterification of starch with succinic anhydride and classical heating.³³

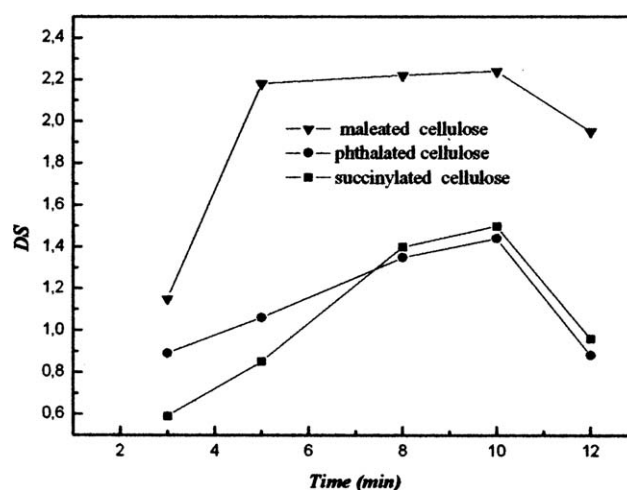


Figure 2 Effect of the reaction time on DS.

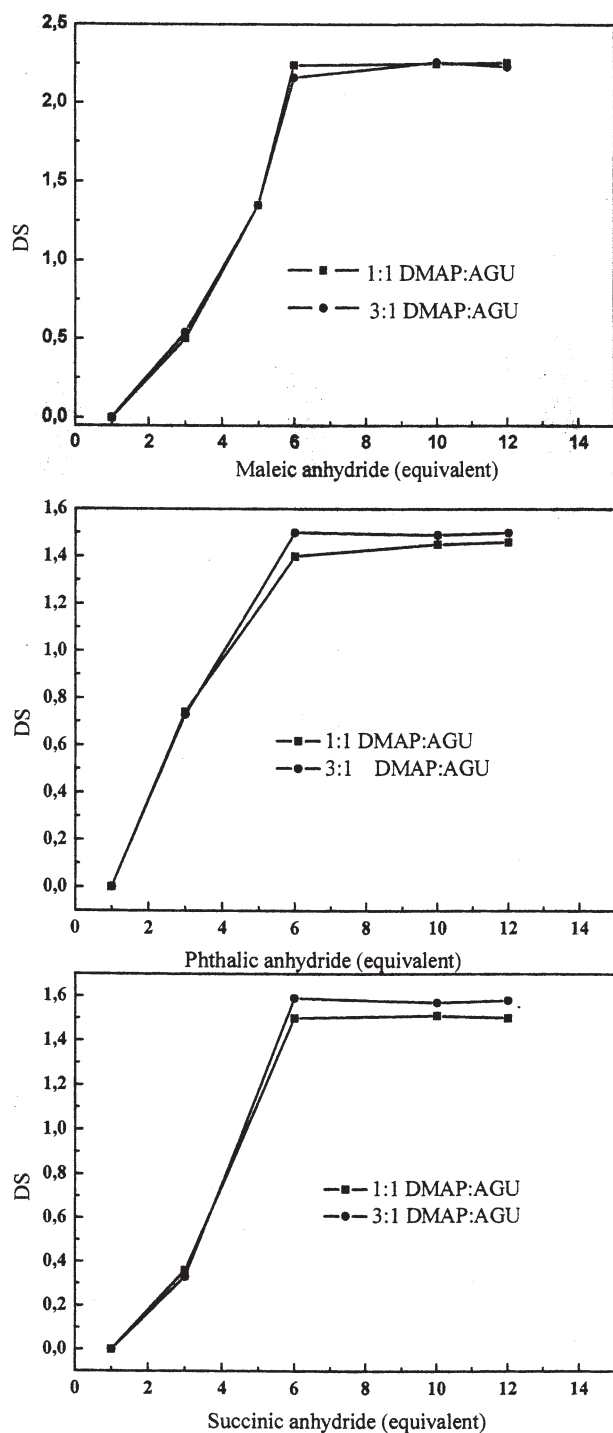


Figure 3 Effect of the cyclic anhydrides on DS.

On the other hand, manipulations with a molar ratio of anhydride to AGU of 1 : 1 in cellulose were realized. However, no product was isolated, although the reaction took place well. If the reaction did not take place, the cellulose would have precipitated by the addition of acetone. The obtained product during this reaction with a very low DS was soluble in the LiCl/DMAc/acetone mixture and did not yield to solid material.

Microwave heating gave higher DS values as compared to conventional heating (Fig. 4). Cellulose, cyclic anhydride (6 equiv), and DMAP (1 equiv) were made to react for 12 h at 130°C. The maleated, succinylated, and phthalated celluloses were obtained with DS values equal to 1.12, 0.53, and 0.74, respectively (the DS values obtained from microwave heating for 10 min were 2.24, 1.5, and 1.44, respectively). Thus, conventional heating gave esters with about half the DS value of those obtained by microwave-assisted reaction.

According to the literature, if there is an increase in the polarity of the medium or charge separation in the reaction transition state, a faster reaction is observed under microwave irradiation because the transition state is stabilized, which decreases the activation energy.^{34,35} It is expected that one will consider a reaction mechanism that proposes a charge separation in the reaction transition state, similar to that presented in Figure 5.¹⁶

Characterization of the cellulose esters

FTIR spectra characterization

Transmission FTIR analysis was used to verify the progress of the esterification reaction. As an example, Figures 6–8 compare the FTIR transmission spectrum of unmodified cellulose with those of the celluloses modified with phthalic anhydride (Fig. 6), succinic anhydride (Fig. 7), and maleic (Fig. 8) anhydrides. The spectrum of the unmodified cellulose confirmed perfectly that reported in the literature.

FTIR spectra of the phthalated cellulose

Figure 6 shows the FTIR spectra of the unmodified cellulose (spectrum 1) and those of the phthalated cellulose samples with DS values equal to 0.22 and 1.04 (spectra 2 and 3, respectively). The absorbencies

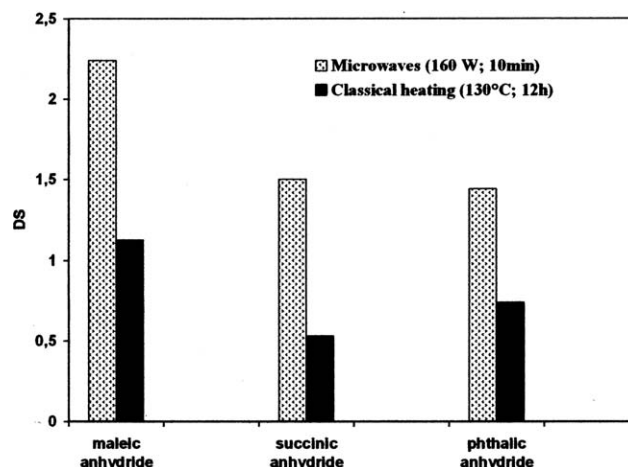


Figure 4 Comparison of the two methods of activation.

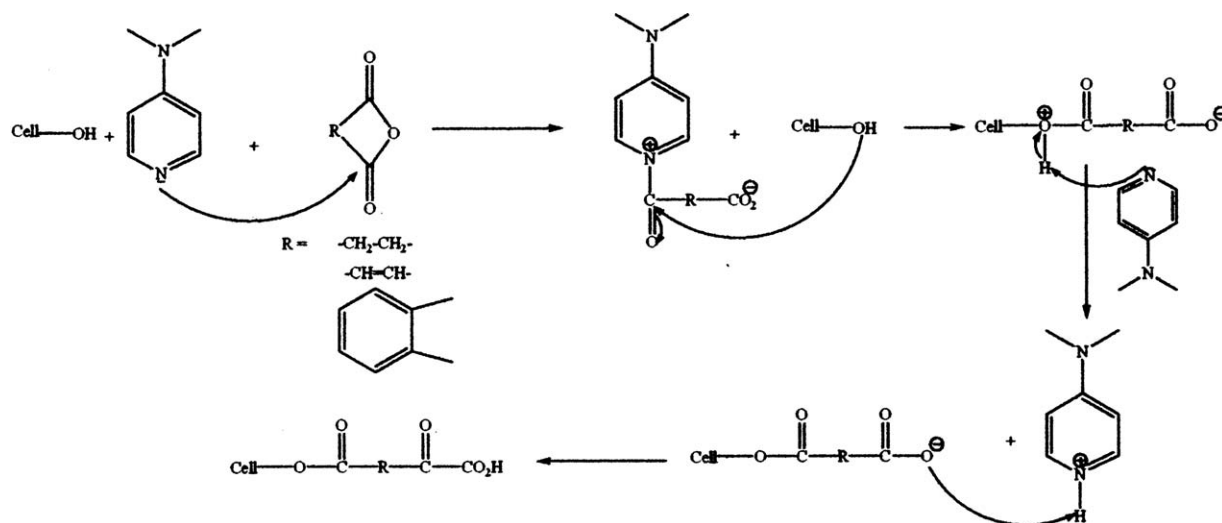


Figure 5 Proposed mechanism for the esterification of the extracted cellulose by a cyclic anhydride in the presence of DMAP as a catalyst under microwave activation.

at 3440, 2923, 1635, 1380, 1150, and 1032 cm^{-1} shown in spectrum 1 were associated with native cellulose. Indeed, the absorption of 3440 cm^{-1} was due to the stretching of OH groups, and the one at 2923 cm^{-1} was due to C-H stretching. The band at 1635 cm^{-1} corresponded to the bending mode of the absorbed water. Each spectrum gave a peak at 1380 cm^{-1} , which was attributed to O-H bending. The absorption band at 1150 cm^{-1} was related to C-O antisymmetric bridge stretching. The C-O-C pyranose ring skeletal vibration occurred in the region 1032 cm^{-1} .

More importantly, spectra 2 and 3 gave evidence of phthalation. The band at 1721 cm^{-1} was indicative of absorption by carbonyl groups in carboxyl and esters. In general, the absorption by carbonyl

bonds in esters gives bands at 1740 cm^{-1} , and that in carboxylic acids shows a band at 1700 cm^{-1} .³⁶ The two bands strongly overlapped, and this, therefore, resulted in a band centered at 1721 cm^{-1} . Interestingly, a strongly increasing intensity of the bands in the range 1250–1300 cm^{-1} was observed in the spectrum of the modified cellulose. The bands at 1263 and 1121 cm^{-1} were related to C-O symmetric and antisymmetric stretching, respectively, in ester. These observations revealed that an ester and a carboxylic acid were formed during the reaction. In addition, the intensity of the absorption bands at 1603 cm^{-1} for aromatic ring vibrations and at 746 cm^{-1} for out-of-plane C-H bending of the disubstituted benzene was observed after phthalic anhydride treatment (spectra 2 and 3). This indicates that

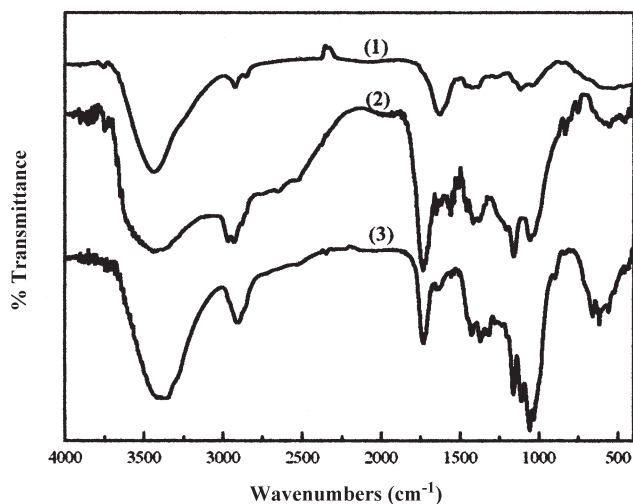


Figure 6 FTIR spectra of the (1) unmodified cellulose, (2) phthalated cellulose with DS = 0.22, and (3) phthalated cellulose with DS = 1.04.

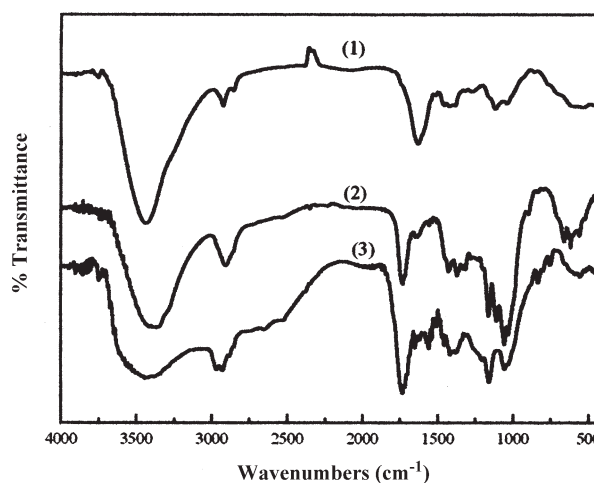


Figure 7 FTIR spectra of the (1) unmodified cellulose, (2) succinylated cellulose with DS = 0.85, and (3) succinylated cellulose with DS = 1.59.

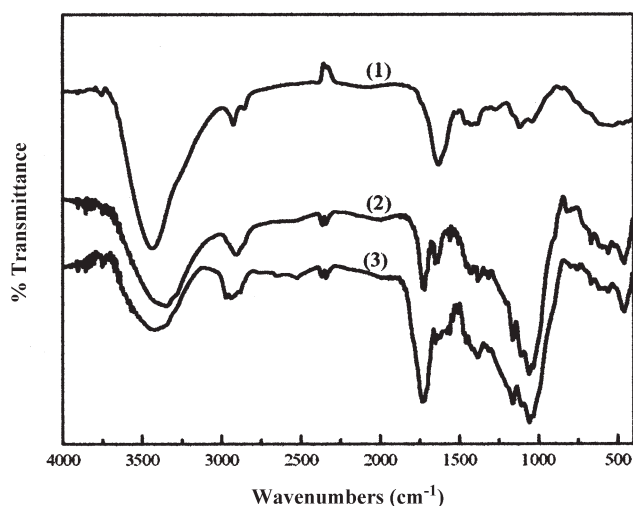


Figure 8 FTIR spectra of the (1) unmodified cellulose, (2) maleated cellulose with DS = 1.21, and (3) maleated cellulose with DS = 2.18.

the phthalyl group was introduced into cellulosic molecules.³⁷ As expected, the absence of the band at 1745 cm^{-1} in spectra 2 and 3 of the phthalated cellulose confirmed that cellulose reacted with dicarboxylic acid anhydride to form a monoester under the stated conditions. As shown in Figure 6, an increase in DS from 0.22 (spectrum 2) to 1.04 (spectrum 3) led to an increase in the intensity of the bands at 1721 cm^{-1} for C=O stretching in ester and carboxyl groups.

FTIR spectra of the succinylated cellulose

Figure 7 shows the FTIR spectra of raw cellulose (spectrum 1) and succinylated cellulose samples with DS values equal to 0.85 and 1.59 (spectra 2 and 3, respectively). In the FTIR spectra of succinylated cellulose, strong absorptions at 1736 and 1162 cm^{-1} were observed; these confirmed the existence of carboxylic esters and provided evidence of succinylation. The former band was indicative of absorption by carbonyl groups in carboxyls and esters, and the latter band was derived from the antisymmetric stretching of ester groups. These results confirmed the formation of an ester and a carboxylic acid, which suggested that the monoester of succinylated cellulose was formed in the LiCl/DMAc system under the given conditions. As expected, the absence of the band at 1850 and 1780 cm^{-1} in the spectra of the succinylated cellulose confirmed that the products were free of the unreacted succinic anhydride. The relative intensity of these bands increased progressively with increasing DS values, as illustrated in Figure 7 (spectra 2 and 3) for succinylated cellulose.

FTIR spectra of the maleated cellulose

The chemical structure of maleated cellulose was changed compared to untreated cellulose, as indicated by the FTIR spectra (Fig. 8). Obviously, the maleated cellulose (spectra 2 and 3) was characterized by the presence of two important ester bands at 1730 and 1162 cm^{-1} . The former band, at 1730 cm^{-1} , was attributed to absorption by carbonyl bond esters. The latter band, at 1162 cm^{-1} , was assigned to the C–O stretching of ester groups. It is very likely that the carbonyl bonds in free carboxylic acids at 1712 cm^{-1} strongly overlapped with the previous one, and the formation of the monoester in the homogeneous esterification by microwave activation was dominant. In addition, the intensity of the absorption bands at 1636 cm^{-1} for C=C bonds was observed after maleic anhydride treatment (spectra 2 and 3); this indicated that the maleyl group was introduced into the cellulosic molecules.³⁸ These bands existed in the FTIR spectra of all of the maleated celluloses that we investigated, and their intensity was found to increase with DS (Fig. 8).

Solid-state CP–MAS ^{13}C -NMR spectra

CP–MAS ^{13}C -NMR spectroscopy is the most effective of the few methods for the characterization of the cellulose and is capable of directly providing detailed information on solid samples.^{37,39} In this article, the maleation, succinylation, and phthalation reactions of cellulose extracted from *Posidonia* were also studied by CP–MAS ^{13}C -NMR spectroscopy. The spectra of native cellulose (spectrum a) and the succinylated (spectrum b, DS = 1.59), phthalated (spectrum c, DS = 1.04), and maleated (spectrum d, DS = 2.18) celluloses are shown in Figure 9. The peaks were assigned according to the literature. The appearance of new resonance peaks in the spectra of the treated cellulose, typical of aliphatic (29–35 ppm), aromatic (131–137 ppm), and carboxylic carbons (172–175 ppm), gave additional evidence of the occurrence of the esterification reaction. In the spectrum in Figure 9(b), the appearance of the 31- and 175-ppm bands of cellulose treated with succinic anhydride arose from the methylene group (CH_2) and carbonyl group ($\text{C}=\text{O}$) of the succinyl group, respectively. The spectrum of cellulose treated with phthalic anhydride is shown in Figure 9(c), and the intensity of the 131.9- and 172.91-ppm (aromatic ring and carbonyl group, respectively) bands were slightly enhanced after treatment. Figure 9 shows the spectrum of maleated cellulose. The appearance of the 137.5- and 172.7-ppm bands of cellulose treated with maleic anhydride [Fig. 9(d)] arose from methylenidene ($\text{HC}=\text{CH}$) and carbonyl ($\text{C}=\text{O}$) groups of the maleyl group, respectively.

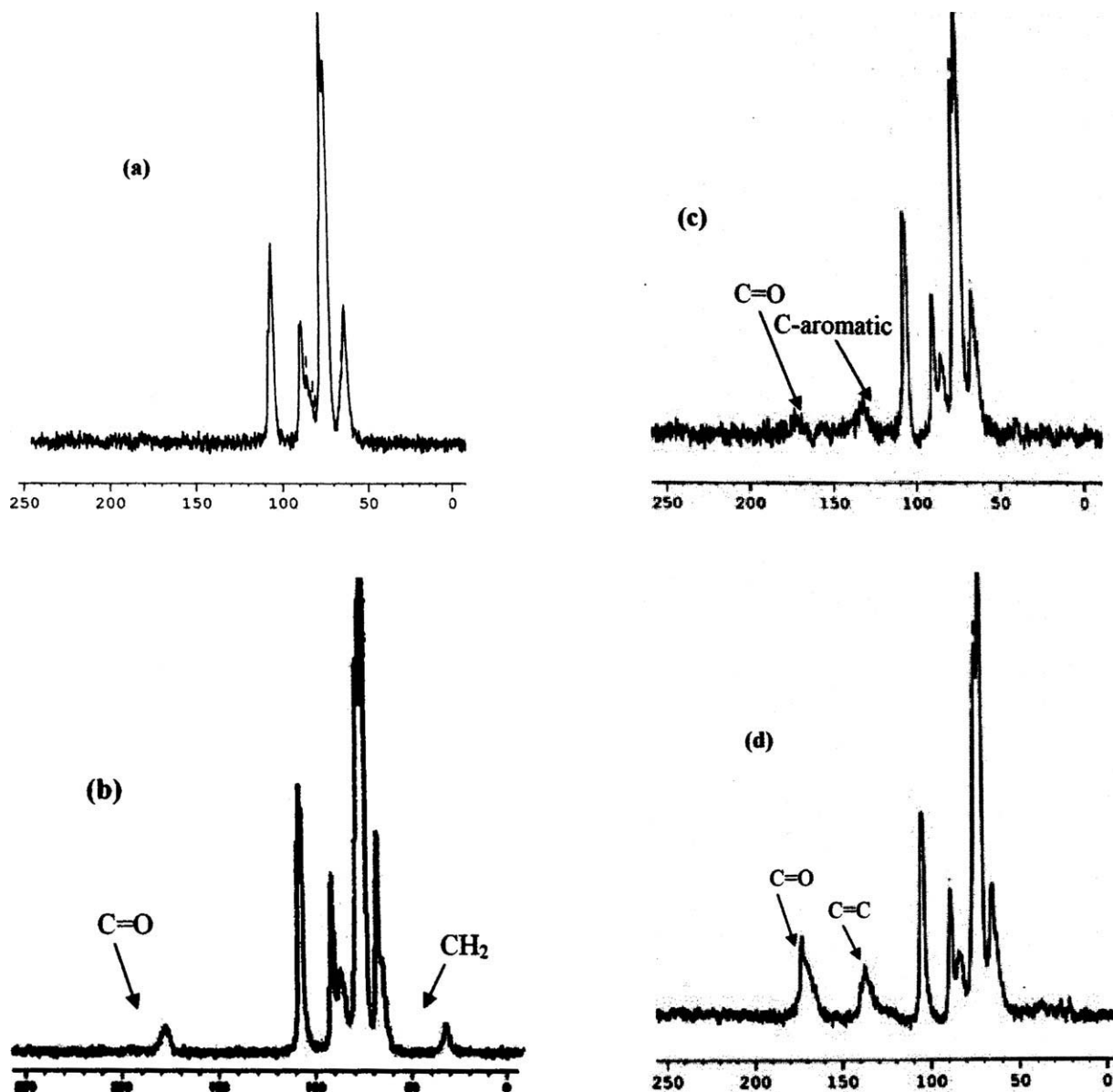


Figure 9 Solid-state CP-MAS ^{13}C -NMR spectra of the (a) unmodified cellulose, (b) succinylated cellulose (DS = 1.59), (c) phthalated cellulose (DS = 1.04), and (d) maleated cellulose (DS = 2.18).

CONCLUSIONS

Maleated, succinylated, and phthalated celluloses were synthesized with a wide range of DS values by the perfection and optimization of a new, rapid, reproducible method with solubilization in LiCl/DMAc solvent and microwave irradiation with controlled power. The reaction time was reduced from several hours to 10 min. DMAP was more active as a catalyst for esterification than the other catalysts used. The DS values of the cellulose derivatives ranged from 0.14 to 2.25 and increased with increasing reaction time from 2 to 10 min, with increasing microwave power from 90 to 350 W, and with increasing molar ratio of anhydride to AGU in cellulose in the range from 1 : 1 to 12 : 1. The catalyst

amount did not influence DS. FTIR and CP-MAS ^{13}C -NMR spectroscopy revealed that the esterification of cellulose extracted from *Posidonia* with cyclic anhydride occurred.

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