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Short Communication

Rapid homogeneous esterification of cellulose induced by microwave irradiation

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Abstract

The aim of this work is the esterification of cellulose with long chain acyl chloride in homogeneous media induced by microwave irradiation. The system used was cellulose/lauroyl chloride/*N*,*N*-dimethylacetamide/LiCl and *N*,*N*-dimethylaminopyridine as a catalyst. The use of microwave resulted in a dramatic drop in reaction time: 1 min irradiation was sufficient, compared with 30 min to 2 days, when conventional heating is used. We studied the degrees of substitution (DS), weight increase and molar yields in function of lauroyl chloride and *N*,*N*-dimethyl-4-aminopyridine amounts. We also determined mechanical and thermal properties of a sample with DS = 2.4 and the biodegradability for samples with DS ranging from 0.7 to 2.6. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biodegradation; Cellulose; Esterification; Microwave

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1. Introduction

Currently, 270 million tons of petroleum and gas are globally used every year for the manufacture of plastics. The impact of these activities on the environment is considerable for two reasons: firstly, petroleum is not a renewable product and, secondly, certain plastics are not recycled. It is known that cellulose is one of the most abundant renewable biopolymer and that its fatty acid esters constitute potentially biodegradable plastics (Glasser, Mc Cartney, & Samaranayake, 1994; Heinze & Glasser, 1998). These polymers are convenient for packaging, which represents approximately 40% of the conventional use of plastics. In this way, fatty acid cellulose esters could be a good solution to alleviate both of these environmental problems.

Acylation of cellulose with short-chain carboxylic acids is well known (Marson & El Seoud, 1999; Sealey, Frazier, Samaranayake, & Glasser, 2000), but esterification with fatty acids is more recent, because it is more difficult to set up. The first attempts at heterogeneous acylation have been carried out by classical activation (Chauvelon et al., 1999; Gourson et al., 1999a; Wang & Tao, 1995) or, more rapidly, by microwave irradiation (Gourson et al., 1999b). Then, fatty acid esters of cellulose were synthesized in an homogeneous medium like LiCl/*N*,*N*-dimethylacetamide (LiCl/DMAc), but this resulted in long reaction times: 30 min (Heinze & Glasser, 1998) to 1 or 2 days (Samaranayake & Glasser, 1993; Sealey, Samaranayake, Todd, & Glasser, 1996). In these experiments, pyridine was used as a catalyst and no systematic study of the effect of degree of substitution (DS) on the properties was performed.

This work deals with a large range of DS, since this parameter is very important for studying biodegradability. We also considerably reduced the reaction time by using microwave activation.

2. Experimental

2.1. Materials

Microcrystalline cellulose (Aldrich ≈ 20 μ), lauroyl chloride (Acros 98%) and *N*,*N*-dimethyl-4-aminopyridine (DMAP) (Acros 99%) were used without further purification. Solvents were purified and stored using conventional methods. LiCl (Merk Eurolab 99%) was stored under vacuum.

2.2. Methods

2.2.1. Solubilization of cellulose

Cellulose was washed with bidistilled water for 1 h at 4 °C. After filtration, a solvent exchange was made: firstly with methanol (3 × 30 min) and then with DMAc

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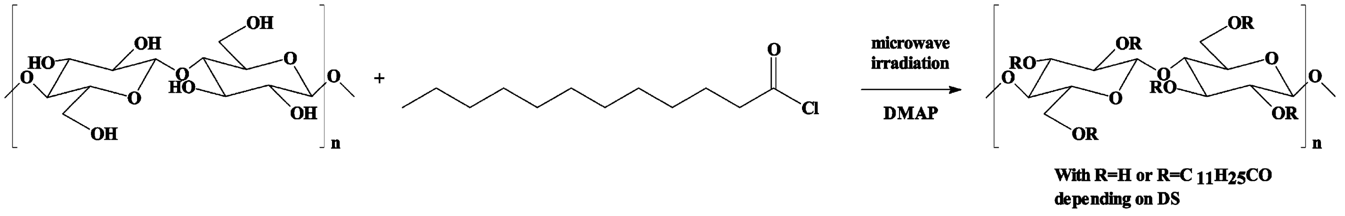

Scheme 1. Acylation reaction.

(3 × 30 min) (Sjöholm, Gustafsson, Eriksson, Brown, & Colmsjö, 2000). A solution of 8% (w/v) LiCl in DMAc was prepared by stirring for 1 h at 60 °C. Then cellulose was added and stirred at the same temperature overnight.

2.2.2. Acylation of cellulose

DMAP and lauroyl chloride were added to the cellulose solution, and this mixture was subjected to activation in a microwave oven (Merk Eurolab Synthewave 402) for 1 min at 300 W output (Scheme 1). In a typical experiment, 1 g of cellulose was dissolved in 50 ml DMAc/LiCl. Then, 2.4–14 equiv. lauroyl chloride and 0.05–0.5 equiv. DMAP were added. The final temperature was between 140 and 165 °C. The reaction product was precipitated in water and purified by a repeated solubilization precipitation process using the chloroform/methanol system.

2.2.3. Casting

The plastic was solubilized in 30 ml chloroform and then the solvent was evaporated under normal atmosphere.

2.2.4. Determination of the degree of substitution

The DS was determined by a volumetric method (Gourson et al., 1999a) or by ^{1}H NMR method in $CDCl_3$ by using a Bruker DRX-400 spectrometer (operating at 400.13 MHz).

2.2.5. Mechanical properties

Uniaxial tensile tests were performed on 12 identical samples with a constant strain rate of 2.78 s^{-1}.

2.2.6. Thermal analysis

Thermogravimetric analysis was performed using a Setaram B85 microbalance (precision ±10 μg). The heating rate was set at 5 °C/min until a limit of 300 °C was reached.

2.2.7. Biodegradability

For each value of DS, a sample of plastic film of known weight was transferred to a flask containing 10 ml of phosphate buffer. The medium was inoculated with *Chromobacterium violaceum*, a Gram negative strain isolated in a previous work (Gourson et al., 1999a).

The flasks were incubated at room temperature on a rotary shaker (150 rpm) for 6 months. After centrifugation and desiccation, the residual solid was weighed and the loss of weight converted into a biodegradation ratio.

3. Results and discussion

3.1. Optimization of the microwave irradiation

The microwave irradiation was optimized by using a well-defined medium: 1 g of cellulose in 50 ml of LiCl/DMAc system (8% (w/v)), 18 ml (13 equiv.) lauroyl chloride and 0.9 g DMAP. Different reaction times (t) and power outputs (P) were used to irradiate this mixture. For each value of these two parameters, no change in DS was observed. All DS measured were about 2.7. The weight increase (WI) was determined for each experiment (Table 1). A maximum was reached for an irradiation power of 300 W for 60 s. Increasing reaction time beyond 1 min resulted in a temperature increase and cellulose degradation as attested by a drop in WI (Table 1). For these reasons, we chose to irradiate the reaction medium for 60 s at 300 W in the following study.

3.2. Effects of the lauroyl chloride and DMAP quantities

We added to the cellulose solution 2.4–14 mol lauroyl chloride per glucose unit and 0.05–0.5 equiv. of DMAP with respect to lauroyl chloride. The mixture was irradiated as described in Section 3.1. The corresponding yields and DS are shown in Table 2.

DMAP did not have any influence on the DS, but the yield was dependent on DMAP especially for the lowest lauroyl

Table 1
Optimization of microwave irradiation

t^a (s)	P^b (W)	WI^c (%)
60	120	0
60	180	124
60	240	124
60	300	149
70	300	125
90	300	132
120	300	92

[a] Irradiation time.
[b] Irradiation power.
[c] WI of cellulose (standard error = 15).

Table 2
Yields and DS (each result is the average of three experiments)

DMAP equivalents	Lauroyl chloride equivalents	2.4	2.9	5	8.1	10.2	14
0.05	Yield[a]	< 5	< 5	47	62	50	74
	DS[b]	–	–	1.9	1.9	2.1	2.2
0.1	Yield	< 5	< 5	44	67	62	69
	DS	–	–	1.8	1.8	2.3	2.5
0.3	Yield	< 5	< 5	67	70	75	80
	DS	–	–	1.9	2.2	2.2	2.2
0.5	Yield	22	36	76	72	67	72
	DS	0.7	1.0	1.7	2.1	2.5	2.6

[a] In % (standard error = 5).

[b] Standard error = 0.2.

chloride concentrations. Either DS or yield was greatly influenced by lauroyl chloride amounts. Indeed, with this method, it was possible to synthesize cellulose esters with a large range of DS: from 0.7 to 2.6 (Fig. 1). In terms of WI, we can see in Fig. 2 that it rose dramatically from −60 up to 120% (cellulose with a very low DS was soluble in MeOH/$CHCl_3$ and did not lead to solid material), when the lauroyl chloride equivalents varied from 2.4 to 5. Beyond 5 equiv., WI still rose up to 169% for 14 mol of lauroyl chloride per glucose unit.

3.3. Mechanical properties

The plastic tested had a DS of 2.4. The tensile failure stress σ_R (10.6 MPa) was close to commercial products, such as packaging materials. Nevertheless, failure strain level ϵ_R (36%) was lower than those of commercial materials ($\approx$ 1100%); which means that these plastics are less ductile and more brittle. The elastic modulus (or Young modulus) E (85 MPa) is much lower than those of packaging products ($\approx$ 300 MPa). This means that the material studied is more deformable.

3.4. Thermal analysis

A thermogravimetric analysis was performed on 12 mg of a cellulose ester exhibiting DS = 2.4. The thermal decomposition temperature of this sample was 185 °C. The loss of weight was 65%. Comparable results have been obtained by Sealey et al. (1996).

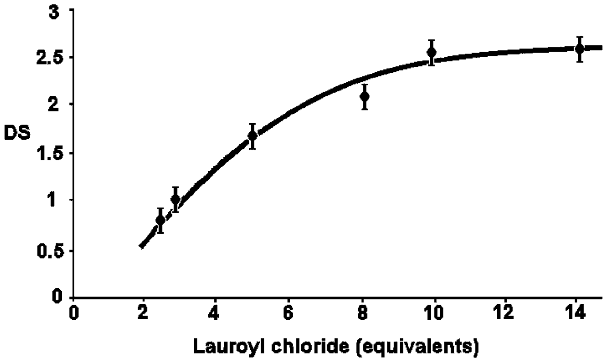

Fig. 1. DS variation in function of lauroyl chloride quantity (as mole per glucose unit) in presence of 0.5 DMAP equivalent.

3.5. Biodegradation studies

The weight loss measured as described in Section 2.2.6 revealed a modest biodegradation of the plastic films for a DS > 1. A loss of 15% in weight was observed for DS = 0.7. No weight loss was measured in a control flask containing only sterile water and an identical amount of material.

This index of biodegradation is somewhat higher than those reported by Glasser et al. (1994). According to these authors, the biodegradability of lauric esters of cellulose with a DS = 0.3 was 5%. The difference with our results is undoubtedly the fact that we used a microorganism and Glasser a purified cellulolytic enzyme instead. This microorganism actually produced different enzymes working in synergy to degrade the plastic films.

It is noteworthy that a significant modification in mechanical properties of the residual solid was observed, the material increasing in brittleness.

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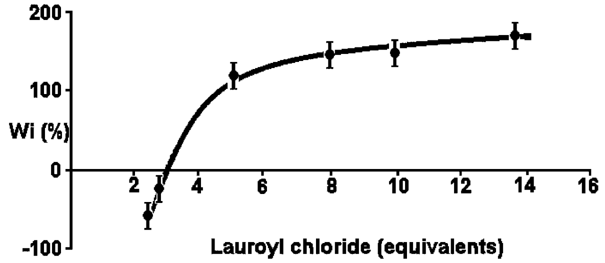

Fig. 2. WI variation in function of lauroyl chloride quantity (as mole per glucose unit) in presence of 0.5 DMAP equivalent.

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