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Studies upon the synthesis of cellulose stearate under microwave heating

Ginka Antova*, Palmira Vasvasova, Magdalen Zlatanov

Department of Chemical Technology, University of Plovdiv 'Paisii Hilendarski', 24, Tsar Assen Str., 4000 Plovdiv, Bulgaria

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Abstract

The possibility of obtaining cellulose stearate by transesterification of methylstearate with low-molecular microcrystalline cellulose under microwave heating was studied. The influence of different parameters such as the molar ratio of the initial substances, quantity of catalyst, duration of reactions and power of the microwave heating upon the degree of esterification were established. The suitable conditions for carrying out transesterification under microwave heating are: molar ratio (cellulose:methylstearate) = 1:3, catalyst quantity 0.25×10^{-2} mol *p*-toluene sulphonic acid per mol cellulose, 600 W-power of the microwave heating and the reaction time—10 min. The resultant cellulose stearate containing 65% combined stearic acid and 0.95 degree of substitution of hydroxyl groups.

The influence of the reaction time, the temperature and the quantity of methylstearate upon the degree of destruction of cellulose under microwave heating was studied. The destruction of microcrystalline cellulose under these conditions is described by an equation of the second order.

Keywords: Cellulose stearate; Microwave heating; Microcrystalline cellulose; Transesterification; Destruction of cellulose

1. Introduction

Cellulose is one of the most widespread natural polymers and of all the possible chemical modifications of natural products, the reactions based on cellulose rank among the most important. With a view to the changing its hydrophilic and thermoplastic properties, the production of lipocellulose is one of the most interesting aspects of its chemical modification.

Esterification of cellulose with higher fatty acids has long been a research objective. Of all the methods available, the only effective ones turned out to be esterification with fatty acid chlorides and transesterification with methyl esters of fatty acids. The only disadvantages of these methods are the cost of the chemicals and the difficulties in scaling up to an industrial process (Hiatt & Rebel, 1971). There are recent reports of the successful utilization of microwave heating in esterification processes. It has been shown that through esterification of carboxylic acids and transesterification of methyl and ethyl esters with different (light and heavy) alcohols in the absence of solvents, esters with high yields (90–97%) are obtained for a short period of time (up to 10 min) under simplified process conditions (Loupy, 1994; Loupy et al., 1993). Similar studies on obtaining cellulose esters from the higher fatty acids have not been carried out so far. Cellulose laurate is synthesized only under microwave heating but again in the presence of acid chloride (Gourson et al., 1999). Having in mind all these facts, our studies have been aimed at applying microwave heating to obtaining cellulose esters through transesterification of methyl ester of one of the most widespread saturated fatty acids in nature-stearic acid.

The aim of this research is to study the influence of the conditions under which the reaction takes place (temperature, reaction time, molar proportion of the initial substances and quantity of the catalyst) on the degree of esterification of the products obtained.

2. Materials and methods

The starting materials in all reactions are as follows:

Microcrystalline cellulose with average degree of polymerisation—200.

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* Corresponding author.
E-mail address: ginant@pu.acad.bg (G. Antova).

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Stearic acid (octadecanoic acid) $CH_3(CH_2)_{16}COOH$ ($M = 284.47$) containing 92–94% pure stearic acid. *Methylstearate*—obtained through esterification of stearic acid with absolute methanol and sulphuric acid as catalyst. The obtained methylstearate contains 0.4% free stearic acid.

Catalyst (*p-toluene sulphonic acid*) was added as 0.5 or 0.05 M solution in absolute methanol.

Synthesis of cellulose stearates through transesterification under microwave heating. The methyl ester was heated up to 30 °C and the catalyst was added, the mixture became homogeneous and the cellulose sample was added only then was the microwave heating applied. The samples were put into the microwave oven LG 'Gold Star' at room temperature and were processed at 600 W for different periods of time. The initial temperature of all samples was equal, then it was quickly increased and its value varied in the end products depending on the duration of the reaction. The obtained product was cooled and then purified by soxhlet extraction with diethyl ether for 6 h and vacuum dried at 55 °C for 24 h.

In order to determine the influence of the catalyst quantity, the duration of the process and the quantity of methylstearate on the degree of substitution of the hydroxyl groups in the final product, studies are carried out with different quantities of the catalyst ($0-0.5 \times 10^{-2}$ mol *p*-toluene sulfonic acid per mol cellulose) at different duration of the process (3,5,7 and 10 min), at molar ratios (cellulose structural unit : methylstearate) of 1:3, 1:6 and 1:9. The microwave power was always 600 W.

Analysis of cellulose stearate. The degree of substitution (DS) represents the average number of esterificated hydroxyl groups in one cellulose structural unit. The degree of substitution of hydroxyl groups of the products obtained was determined on the basis of the quantity of the combined stearic acid. The quantity of the combined stearic acid ($X\%$) was determined by means of alkaline hydrolysis with an alcoholic solution of potassium hydroxide (KOH 0.5N) and the amount left was titrated with hydrochloric acid (HCl—0.5N) (Obolenskaya, Shtegolev, Akim, & Akim, 1965). The degree of substitution (DS) was calculated from the following formula:

$$DS = \frac{162X}{M_x 100 - (A - 17) \times X}$$

where

$X\%$, quantity of the combined stearic acid
M_x, molar mass of the stearic acid
A, molar mass of the ester group of the stearic acid
17, molar mass of the hydroxyl group
162, molar mass of the one cellulose structural unit.

The degree of polymerisation (DP) of the cellulose esters were determined by gel permeation chromatography (GPC) calibrated as described elsewhere (Sealey, Frazier, Samaranayake, & Glasser (2000).

3. Results and discussion

The degree of substitution of the hydroxyl groups increases up to 0.25×10^{-2} mol catalyst per mol cellulose (as shown in Fig. 1), at higher levels it starts to decrease. Further studies were carried out with the optimum catalyst level (0.25×10^{-2} mol).

The degree of substitution of hydroxyl groups in the products increases with an increase in the reaction time as shown in Fig. 1. At 0.1×10^{-2} and 0.25×10^{-2} mol catalyst quantity per mol cellulose the process runs at a higher rate and the cellulose stearates obtained have a higher degree of substitution.

These studies show that through transesterification of microcrystalline cellulose with methylstearate at a molar ratio 1:3 in the presence of the optimum acid catalyst level, the highest degree of substitution is reached after a reaction time of 10 min. Under these conditions the cellulose stearate obtained contains 65% combined stearic acid and the degree of substitution of the hydroxyl groups is 0.95.

We carried out transesterification of microcrystalline cellulose at different molar ratio (cellulose:methylstearate) 1:3, 1:6 and 1:9, quantity of the *p*-toluene-sulphonic acid 0.25×10^{-2} mol per mol cellulose for different reaction times (3–10 min) in order to determine the influence of the quantity of methylstearate on the process. The results for the quantity of combined stearic acid in the obtained cellulose stearates and the degree of substitution are presented in Table 1.

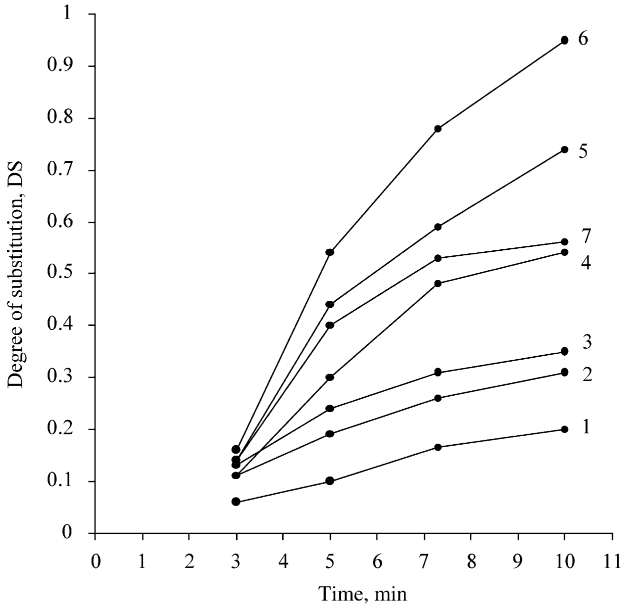

Fig. 1. Variation of the degree of substitution according to the reaction time. (1) Catalyst 0 mol/mol cellulose. (2) Catalyst 0.005×10^{-2} mol/mol cellulose. (3) Catalyst 0.01×10^{-2} mol/mol cellulose. (4) Catalyst 0.05×10^{-2} mol/mol cellulose. (5) Catalyst 0.1×10^{-2} mol/mol cellulose. (6) Catalyst 0.25×10^{-2} mol/mol cellulose. (7) Catalyst 0.5×10^{-2} mol/mol cellulose.

Table 1

Influence of the molar ratio and the reaction time on the quantity of the combined stearic acid (*X%*) and the degree of substitution (DS)

Molar ratio, cellulose:methylstearate	3 min		5 min		7 min		10 min	
	X%	DS	*X%*	DS	*X%*	DS	*X%*	DS
1:3	22.0	0.16	50.3	0.54	59.8	0.78	65.0	0.95
1:6	31.6	0.25	53.5	0.60	62.6	0.86	66.5	0.99
1:9	39.0	0.35	57.6	0.71	65.9	0.96	67.3	1.04

Table 2

Influence of the reaction time, molar ratio and temperature on the average degree of polymerisation (DP) of cellulose and rate constant of the depolymerisation

Molar ratio, cellulose:methylstearate	3 min		5 min		7 min		10 min		Rate constant k, (min^{-1})
	T (°C)	DP	*T* (°C)	DP	*T* (°C)	DP	*T* (°C)	DP	
1:3	68	160	79	135	86	120	88	105	0.006
1:6	75	143	90	115	94	100	101	82	0.008
1:9	83	125	105	95	108	83	110	70	0.009

It is evident that when the molar ratio is increased from 1:3 to 1:9 the quantity of the combined stearic acid in the cellulose product and hence the degree of substitution of the hydroxyl groups for a given reaction time increases.

It was found out that the temperature at the end of the reaction increases with reaction time independent of the molar ratio of the reagents. The dependence of the degree of polymerisation on the quantity of methylstearate and the temperature is shown in Table 2.

It is evident that as the time and temperature increase, the average degree of polymerisation of the cellulose decreases. At a 10 min reaction time, molar ratio—1:9 and temperature—110 °C, the average degree of polymerisation drops from 200 to 70, which is indicative of the significant depolymerisation taking place.

The depolymerisation of cellulose is described by an equation of the second order (Sharplez, 1971):

$$\frac{1}{P_{n\tau}} - \frac{1}{P_0} = k\tau \tag{1}$$

where

$P_{n\tau}$, represents the average degree of polymerisation at the time τ

P_0, the average degree of polymerisation of the original cellulose

k, rate constant

Fig. 2 shows that this equation describes the depolymerisation of microcrystalline cellulose during its processing under microwave conditions well.

The rate constant of the process of destruction of microcrystalline cellulose at different molar ratio is calculated by the slope of the resulting straight lines. The rate constant increases with the quantity of methylstearate.

Although the highest degree of substitution is obtained at molar ratio 1:9 and duration of the process-10 mins ($X\% = 67.3\%$ and $\mathrm{DS} = 1.04$), but the product obtained has lower average degree of polymerisation ($\mathrm{DP} = 70$),

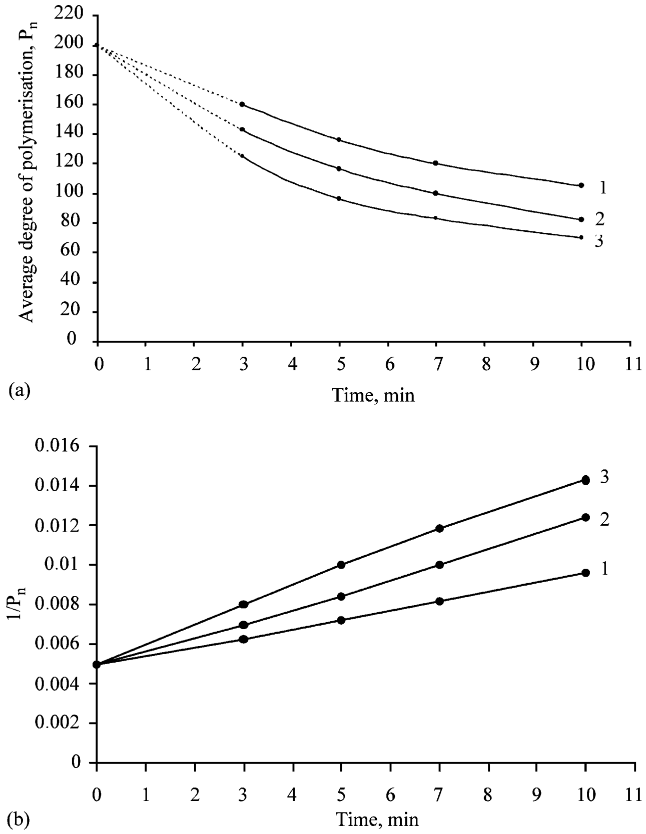

Fig. 2. (a) Variation of the average degree of polymerisation according to the reaction time. (b) Linearized kinetic curves representing the degree of polymerisation. (1) Molar ratio (cellulose structural unit: methylstearate) = 1:3. (2) Molar ratio (cellulose structural unit: methylstearate) = 1:6. (3) Molar ratio (cellulose structural unit: methylstearate) = 1:9.

Table 3
Comparison of the results for the degree of substitution of cellulose stearate obtained through transesterification of cotton, alkaline and microcrystalline cellulose under microwave heating

Types of cellulose	3 min		5 min		7 min		10 min	
	X%	DS	*X*%	DS	*X*%	DS	*X*%	DS
Cotton	26.3	0.20	35.9	0.31	37.5	0.33	31.2	0.25
Alkaline	27.0	0.20	27.7	0.21	31.1	0.25	42.9	0.41
Microcrystalline	22.0	0.16	50.3	0.54	59.8	0.78	65.0	0.95

compared to the cellulose stearate obtained at molar ratio 1 : 3 for the same period of time which has DS = 0.95 and DP = 105. On account of that the most suitable molar ratio for carrying out of the process is determined by the desired properties of the product.

At equivalent proportions of the reagents, catalyst (*p*-toluene sulphonic acid) quantity 0.25×10^{-2} mol per mol cellulose and 10 min reaction time, the resulting product is cellulose stearate which contains 65% combined stearic acid, has 0.95 degree of substitution of hydroxyl groups and partial depolymerisation of the product (DP = 105). On the other hand, under conventional heating conditions for a time of 360 min in the presence of a solvent (dimethylsulphoxide) at 140 °C and 0.0142 g catalyst quantity per 1 g cellulose the obtained cellulose stearate has a degree of substitution of 0.35, 38% combined stearic acid but a higher degree of depolymerisation (Antova, Vasvasova, & Zlatanov, 1998).

The results obtained the transesterification of microcrystalline cellulose at equivalent proportion of the initial reagents, catalyst (*p*-toluene sulphonic acid) quantity 0.25×10^{-2} mol per mol cellulose and reaction time—10 min were compared to the results of transesterification of other types of cellulose—cotton (non-activated) cellulose with DP = 1600 and alkaline (activated) cellulose with DP = 1100-carried out under the same conditions.

The results (as shown in Table 3) demonstrate that cellulose stearates with higher degrees of substitution are obtained in the presence of low-molecular size microcrystalline cellulose.

4. Conclusions

Cellulose stearates are obtained through transesterification of microcrystalline cellulose and methylstearate under microwave heating. The transesterification is carried out for a short period of time (up to 10 min) at relatively low temperatures (~ 90 °C), while at the same time the degree of esterification is three times higher than the one obtained under conventional heating conditions, and a lower degree of destruction of cellulose (below 50%) is achieved. Microwave heating is a promising method for synthesizing high molecular cellulose esters under mild conditions and in the absence of solvents.

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