

HYDROPHOBATION OF POLYSACCHARIDES WITH SUNFLOWER OIL AND ITS DERIVATIVES.

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ABSTRACT

Sunflower oil and its derivatives (triglycerides, fatty acids and fatty acid methyl esters) were used to achieve the fatty acylation of common polysaccharides: cellulose and starch. The obtained products (fatty esters of polysaccharides) presented a water affinity completely different from the non-modified biopolymers. The yield of reaction was studied as a function of reaction conditions. The lipophilic character thus conferred to cellulose and starch is essential for their application in the field of biodegradable agro-materials.

INTRODUCTION

In the last years, an increasing interest has been developing on the non-food applications of renewable resources. In particular, vegetal oils constitute a source of fatty molecules that can be used as valuable reagents for chemical modifications. Among these reactions, the grafting of aliphatic fatty chains onto vegetal substrates is an important step that finds important outcomes in the field of materials and more precisely, in the field of agro-materials.

Inexpensive substrates such as cellulose and amylose are abundant on Earth and technologically attractive. The natural materials containing them (e.g., wood, cotton, and starch) are appreciated for various common applications such as wood-plastic composites. However, their high content in free hydroxyl groups confers them a strong hydrophilic character. Direct utilization of natural cellulose and starch in such applications is thus limited. The modification of their hydrophilic-hydrophobic affinity by chemical modification with fatty compounds is necessary for their use in those applications and interesting for less conventional applications, e.g., water-repellent textiles, weather-resistant wood, selective lipophilic fibers, etc. It is the global object of this research work to use the fatty molecules directly or indirectly derived from sunflower oil for the grafting of aliphatic chains by acylation reactions onto lignocellulosic or starchy substrates.

Conventional fatty acylation reaction used to employ expensive reagents such as fatty-acid chlorides or anhydrides either in the presence of toxic organic solvents [Malm *et al.*, 1951] or through environmental-friendly processes [Thiebaud *et al.*, 1995; Kwatra *et al.*, 1993]. Present tendencies are to promote the use of less expensive and simpler products closer to the original vegetal oil. In this connection, fatty acids [Vaca-Garcia *et al.*, 1998] and fatty acid methyl esters [Latetin *et al.*, 1968; Rooney, 1976] have been used in acylation reactions. However, the extremely low reactivity of these products towards cellulose and amylose, forced them to use co-reagent and toxic solvent. More recently, a solvent-free acylation of

cellulose was accomplished with fatty acids and acetic anhydride as co-reagent [Vaca-Garcia and Borredon, 1999].

In the present work, we open the scope of fatty acylation reactions with some results obtained by the direct reaction of cellulose and starch with three kind of fatty compounds: fatty acids, fatty acid methyl esters and triglycerides directly obtained from sunflower oil.

EXPERIMENTAL PROCEDURES

Materials. Alpha-cellulose (4% pentosans) and amylose were purchased from Sigma France. Sunflower oil was obtained from Sidobre-Sinova (France). Other reagents and chemicals were of reagent purity and purchased from usual providers. They were used without further purification or treatment.

Acylation reactions. A homogeneous emulsion with controlled quantities of fatty reagent (sunflower oil, fatty acid or fatty acid methyl ester), polysaccharide (cellulose or amylose), water or ethanol, salt of fatty acid (used as emulsifier and catalyst) was obtained by vigorous stirring in a homogeniser working at 2000 rpm. After removal of water at 130°C for 30 min, the reaction was conducted at 190-195°C for 2-6 hr.

Products characterisation. The efficacy of the reaction was controlled measuring the Degree of Substitution (D.S.) by the saponification method. The hydrophobic character was verified measuring the contact angle of the product.

RESULTS AND DISCUSSION

1. Transesterification reactions with sunflower oil and fatty acid methyl esters

1.1 Amylose fatty esters

The reaction between amylose and methyl laurate with potassium laurate as catalyst was investigated. The effect of the main parameters: reaction time (X1, hr) and catalyst concentration (X2, meq/eq glucose), were evaluated by a central composite experimental design. The amount of ethanol used for the emulsification is fixed at 2.5 meq/eq glucose. The studied responses were the degree of substitution (DS) and the recuperation yield of the amylose laurate. The maximum DS (0.61) was obtained with 18 meq potassium laurate/eq glucose and 4.5 hr of reaction giving a recuperation yield of 52%.

The above optimised conditions were then used to investigate the performance of other catalysts. The results are shown in the following table:

Catalyst	DS	Recuperation yield (%)
Sodium acetate	0.58	57
Sodium laurate	0.56	59
Potassium laurate	0.61	52
Sodium stearate	0.23	62

Reaction of amylose with methyl laurate with different catalysts (18 meq/eq glucose)

It was observed that catalyst bearing long aliphatic chains (C₁₈) reduces the grafting efficiency of the aliphatic chain suggesting a steric hindrance. Conversely, when comparing

two catalysts having the same aliphatic chain, the type of cation showed no significant influence. The highest DS was obtained when using potassium laurate. This catalyst was therefore applied to test sunflower oil and other fatty reagents with amylose under the same optimized conditions, as shown in the table below:

Reagent	Ester content (meq/kg)	Recuperation yield (%)
Palmkernel oil	2389	51
Sunflower oil	2086	43
Linseed oil	86	100
Methyl laurate	2260	52

Reaction of amylose with fatty reagents with potassium laurate catalyst (18 meq/eq glucose)

Sunflower and palmkernel oils, which are rich in saturated fatty acids, resulted in an ester content comparable to that obtained with methyl laurate. Linseed oil showed little reactivity towards amylose. With these preliminary results we are unable to explain the effect of insaturations. Except for this derivative, all the amylose esters presented a neat hydrophobic character.

1.2 Cellulose fatty esters

Contrarily to amylose, cellulose is a high crystalline biopolymer. Acylation reactions with fatty reagents carried out without solvent lead to extremely low yields. In previous research work, we have used the solvent exchange technique as a pretreatment for cellulose to increase its reactivity. This technique includes soaking of cellulose with water, washing with ethanol and finally, washing with the fatty reagent [Vaca-Garcia and Borredon, 1999]. In the present work, we propose emulsification as a novel cellulose pretreatment to improve the penetration of the fatty reagent into the cellulose fibres and to increase its reactivity. We have compared both pretreatments by using the following reaction conditions: sodium laurate as catalyst (0.01 eq /eq OH), methyl laurate as reagent (4.4 eq/eq OH) and water for emulsification (3 eq/eq OH). Solvent-exchanged cellulose was reacted with methyl laurate and sodium acetate as catalyst at 195°C for 6 hrs.

Pretreatment	DS	Recuperation yield (%)	Degree of polymerisation *
None (control)	0.03	86	380
Solvent exchange	0.12	85	490
Emulsification	0.12	85	450

(*) Cellulose has an initial DP of 980.

Reaction of cellulose with methyl laurate and sodium laurate as catalyst with different pretreatments

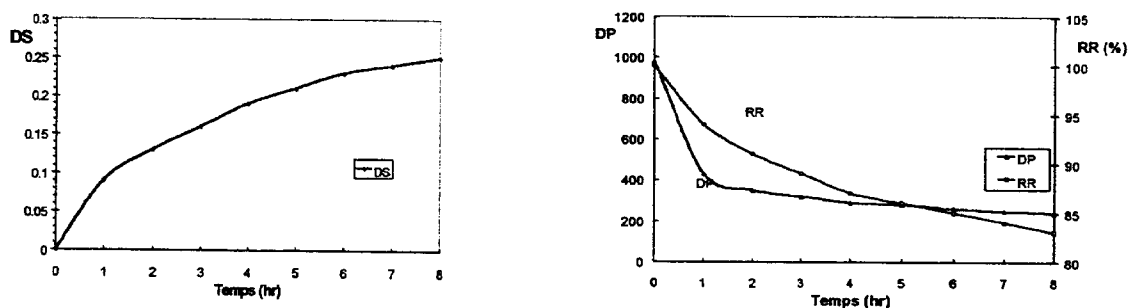
Emulsification lead to the same results than solvent exchange. However, the former is more convenient as it is easier to achieve.

Reaction conditions were then optimized by using a central composite experimental design as in the case of amylose. The studied variables were catalyst, reagent and water concentrations. The maximum DS (0.18) was obtained with an 85% recuperation yield at the following conditions: [sodium laurate] = 1 meq/eq OH; [methyl laurate] = 7.6 eq/eq OH and [H₂O] = 3 eq/eq OH. It was also observed that a low concentration of catalyst is preferable to obtain both high DS and high recuperation yield. Moreover, a high amount of catalyst increases the cellulose degradation. Native cellulose absorbed water immediately, whereas cellulose laurate with a DS of 0.18 presented a contact angle of 95°, demonstrating its hydrophobic character.

2. Esterification reactions of cellulose with fatty acids

The above protocol was used in the study of esterification reaction of cellulose. Emulsification was used as pretreatment of cellulose and optimization was carried out through a central composite experimental design. The studied variables were catalyst, reagent and water concentrations.

The maximum DS (0.23) was obtained with a 85% recuperation yield (RR) at the following conditions: [potassium laurate] = 0,01 eq/eq OH; [octanoic acid] = 10 eq/eq OH and [H₂O] = 3 eq/eq OH. These optimized conditions were then used to study the kinetics of the reaction. The evolution of DS, on the one hand, and of RR and DP (degree of polymerization), of the other hand are represented in the following figures:



Kinetic of cellulose esterification by octanoic acid

The DS increased significantly up to 5 hours and then leveled off. The abrupt decrease of RR and DP demonstrated an important degradation of the polymer since the beginning of the reaction. The biopolymer is probably hydrolyzed and the oligomers with low DP cannot be precipitated at the end of the reaction and remain in the liquid phase. The performance of other catalysts was studied using the above optimised conditions. The results are shown in the following table:

catalyst	DS	RR (%)
C ₁₂ , K ⁺	0.23	85
C ₁₈ , K ⁺	0.20	85
C ₁₈ , Na ⁺	0.14	92
C ₁₂ , Na ⁺	0.17	85
C ₂ , Na ⁺	0.16	88
NaOH	0.19	85
K ₂ CO ₃	0.19	86

Reaction of cellulose with octanoic acid with different catalyst (0.01 eq/eqOH)

Potassium salts were the most efficient catalysts. On the contrary, the chain length of the catalyst showed no significant influence on the grafting efficiency. The highest DS was obtained with potassium laurate. This catalyst was then applied for the reaction of different fatty acids under the same optimized conditions, as shown in the table below:

Fatty acid (C _n)	DS	RR (%)
C ₈	0.23	85
C ₁₀	0.17	82
C ₁₂	0.12	84
C ₁₄	0.11	82
C ₁₆	0.10	83
C ₁₈	0.10	80

Effect of chain length of fatty acids on efficacy of cellulose esterification reaction

Higher fatty acids led to lower DS; when the chain length increases, the diffusion of the fatty acid into cellulose fibers is believed to be more difficult and its reactivity decreases. All of the obtained products were demonstrated to be hydrophobic.

CONCLUSION

Sunflower oil and its derivatives were successfully utilized for the grafting of aliphatic chains on cellulose and amylose. Simple and environment-friendly processes were used for this purpose. No organic solvent was used and all the reagents are obtained from renewable resources. The esters thus obtained were highly hydrophobic and they open new outlets for their use in the non-food applications, especially in the agromaterials field. Future research should be oriented to the optimization of these reactions under the scope of a particular application.

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