

Fatty Esters of Cellulose from Olive Pomace and Barley Bran: Improved Mechanical Properties by Metathesis Crosslinking

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ABSTRACT: Agricultural wastes such as olive pomace and barley bran have been transformed in plastic by esterification with fatty acid chlorides after acidic or alkaline delignification. These esterifications were carried out in homogeneous solution DMA/LiCl by classical heating or microwave activation. The plastics obtained were characterized by IR and NMR spectra, and tested for their mechanical

properties and potentiality of biodegradation. The mechanical properties were improved by olefin metathesis of undecylenic ester from olive cellulose. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 751–755, 2006

Key words: fatty acid ester; cellulose; crosslinking; olefin metathesis; plastic films

INTRODUCTION

More than 270 Mt of gas and petroleum are consumed each year by the polymer industry and, because of their poor biodegradability, these oil-based plastics constitute a growing environmental nuisance. On the other hand, oil and gas natural resources will be exhausted within a century or less.

Biomass valorization has gained an increasing interest during the last years because of the actually huge amounts lost, little valorized or simply considered as a waste. Cellulose material constitutes the most important part of this biomass and could be a good candidate for the replacement of fossil hydrocarbons as a starting material in the field of polymer industry, since it is renewable and may lead to biodegradable plastics.

This work is a contribution to the study of biomass valorization especially in the field of agricultural wastes such as olive pomace and barley bran.

Olive wastes resulting from olive manufacturing wastes are very abundant in Mediterranean areas. Olive pressing yields¹ an aqueous phase (50%), an oily

phase (30%), and a solid residue called pomace (20%) which is generally used as cattle feeds or combustible material. Barley bran is mainly used as a complement in the feed for farm cattle.

The aim of this work is to valorize these resources by producing plastic materials with mechanical properties that meet fairly well the standards required for industrial applications. The methodology consists in esterifying the cellulosic part of the vegetal waste by fatty acid derivatives, and on the other hand, cellulose undecenoate was crosslinked by using the olefin metathesis reaction.

MATERIALS AND METHODS

Materials

Olive pomace is supplied by a Tunisian olive oil production plant at Ksar Hellal in the Monastir area. The solid residues are dried in an oven at 50°C for 5 days. Barley bran from the same region of Tunisia is used without further treatment. Acyl chloride and DMAP from ACROS > 97% pure are used as received. Dioxane, DMA, methanol, chloroform, and petroleum ether from ACROS (Noisy LeGrand, France) or Fisher Scientific (Elancourt, France) are products for synthesis. LiCl (99%) from Merck Eurolab (Strasbourg, France) was stored under vacuum.

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TABLE I
Results of Esterifications of Olive and Barely Bran Cellulose

Cellulose origin	Delignification mode	Heating		Microwave	
		Massic yield (%)	DS	Massic yield (%)	DS
Olive pomace	Acidic 1M HCl, 1 h 30 min	12	2.23	88	2.20
	Acidic 1.5M HCl, 3 h 30 min	298	2.96	320	2.90
	Alkaline	56	2.5	142	2.6
Barley bran	Acidic 1M HCl, 1 h 30 min	283	2.27	290	2.95
	Alkaline	267	2.7	281	2.8

Methods

Fat extraction

Olive pomace was extracted in a Soxhlet apparatus with petroleum ether then by methanol for 24 h. We obtain 6% oil, 79% solid residue, and 15% others.

Delignification

Acidic: 25 g of pomace are suspended in 400 mL of a mixture containing 90% of dioxane and 10% of 1.5M HCl.² After 3.5 h under reflux, the residue is washed thoroughly with 90/10 dioxane/water and dried. Fine powder (11.5 g, 46%) is obtained.

Barley bran, when subjected to the same treatment, gives 9 g (36%) of a pulp-like material.

Alkaline: 25 g of pomace or barley bran are immersed in 200 mL of 2M NaOH aqueous solution and stirred at 80°C for 5 h. The residue is filtered and washed with 20% AcOH solution, then with water until neutral pH. The solid is dried in an oven at 50°C until constant mass; yield: 10.5 g (42%), barley bran: 8.5 g (34%).

Cellulose dissolution

Bran or olive cellulose are dissolved in the DMA/LiCl system as previously described.^{3,4} Briefly, after two solvent exchanges (methanol then DMA)^{5,6} cellulose is stirred for 24 h in a 8% LiCl/DMA (w/v) solution to obtain a clear solution.

Cellulose acylation

Two methods were used: classical heating or microwave activation. One gram of cellulosic residue was dissolved in 50 mL of LiCl/DMA with 8 equiv of acyl chloride and 0.5 equiv of DMAP. This mixture was either heated at 70°C for 12 h or activated in a domestic microwave oven for 5 min.^{7,8} The cellulose ester is then obtained by solubilization in CHCl₃ and precipitation by MeOH.

Crosslinking of the polymer by olefin metathesis

Cellulose undecenoate was prepared by the same method as previously described by using undecenoyl

chloride and cellulose from olive pomace. This ester (2.5 g) is dissolved in 200 mL CH₂Cl₂, and this solution is degassed by argon bubbling for 2 h.⁹ Grubbs catalyst I (75 mg) dissolved in CH₂Cl₂ is introduced stepwise with a syringe. After 3 h of reaction, the sample is subjected to casting.

Casting

Esters were dissolved in 30–50 mL chloroform and put in petri dishes (10–20 cm diameter). The contents were left to evaporate in a quiet atmosphere.

Mechanical properties

Mechanical tests on esters of olive and barley bran cellulose were performed at the Mechanical Engineering Laboratory of Monastir (Tunisia). The 5 KN LLOYD apparatus 638 ASTM type IV worked at a constant velocity of 50 mm min⁻¹ at room temperature. The sample dimensions were 8 × 2 cm² and the thickness 0.15 ± 0.03 mm.

Determination of the degree of substitution

The degree of substitution (DS) of plastic films was determined by ¹H NMR integration of aliphatic chain protons and cellulosic sugar protons^{10,11} and calculated according to the formula:

$$DS = \frac{10I_{CH_3}}{3I_g + I_{CH_3}}$$

Where I_{CH_3} is the CH₃ terminal group integration and I_g glucosidic protons integration.

RESULTS AND DISCUSSION

Lauric esters of olive and barley bran

Cellulose from olive and bran obtained after acidic or alkaline treatment was acylated by lauroyl chloride either by classical heating for 12 h or microwave activation for 5 min. Massic yields and the degrees of substitution are summarized in Table I.

TABLE II
Results of Olive Cellulose Esterification

Acyl chlorides	Massic yield (%)	DS
Stearoyl	302	2.84
Palmitoyl	298	2.90
Myristoyl	286	2.95

When crude olive pomace is delignified by using 1M HCl in dioxane for 1.5 h, the ester yield is low and DS rather good (2.23). The use of 1.5M HCl and 3-h reaction time greatly increased the massic yield (300%) and the DS (2.9). In each case, the microwave mode of activation gives better results. For this substrate, an alkaline delignification leads to moderate yields in cellulosic ester.

On the contrary, barley substrates subjected to either acidic or alkaline delignification give similar yields and DS. Microwave activation also leads to better yields than classical heating. These higher yields could be explained by the microwave stabilization of a transition state that is more polar than ground state reactants.¹²

Other cellulosic saturated esters

Long chain fatty acid esters of cellulose have been less studied, although they have interesting proper-

ties.¹³⁻¹⁶ We proceeded to microwave activated acylation of cellulose obtained from olive pomace by acidic treatment with myristoyl, palmitoyl, and stearoyl chlorides.

The reaction conditions are the same as for lauroyl chloride and we observe that the results are similar in terms of massic yields and DS (Table II)

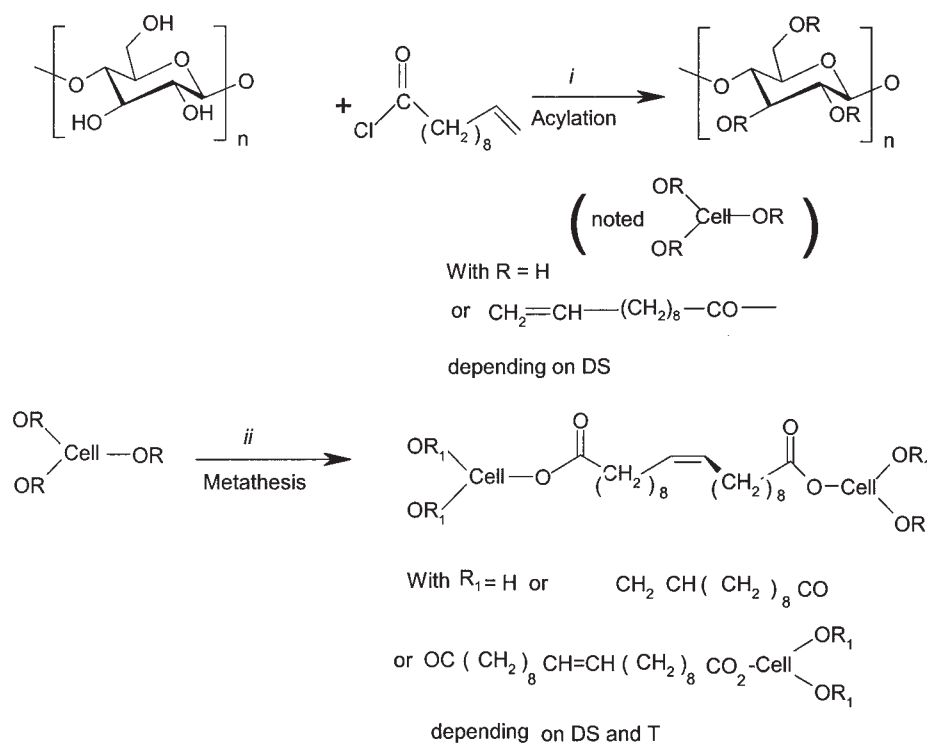
Crosslinking by olefin metathesis

With the aim of improving the mechanical properties of cellulosic esters obtained from olive pomace, we decided to realize a crosslinking of the cellulosic chains.

The discovery of new catalysts with low sensitivity to organic functions by Grubbs and coworkers¹⁷ has brought the olefin metathesis as a very useful reaction. So, we chose to undergo the reticulation of cellulosic plastics by the means of metathesis on an acyl ester bearing an ethylenic function on the terminal group of the chain.

Olive pomace cellulose was first acylated by ω undecylenic acid chloride in the same conditions as previously described. The yields and properties are similar to those observed for lauric ester.

This ester dissolved in CH_2Cl_2 is then subjected to metathesis reaction by stepwise addition of the Grubbs I catalyst solution (Scheme 1). The viscosity of



Scheme 1 Reaction sequences for cellulose crosslinking. (i) DMAP in LiCl/DMAc, microwave irradiation. (ii) Grubbs's catalyst I $[\text{RuCl}_2(\text{PCy}_3)_2=\text{CH-Ph}]/\text{CH}_2\text{Cl}_2$ under argon.

the solution markedly increases and a casting is realized after 3 h of reaction (yield: 97%).

Characterization of the plastic films

Plastic films were analyzed by FTIR (Table III). For the ethylenic esters in addition to the usual bands corresponding to the ester aliphatic chain, we observed the signals corresponding to the double bond at 3070, 908, and 723 cm^{-1} .

^1H NMR spectra were realized to check the purity and to determine the DS. It should be noticed that olefine metathesis reaction applied to the cellulosic undecylenic ester is not stereoselective, since the E/Z ratio is variable from one experiment to another, as previously reported.⁹

Determination of the crosslinking ratio

A sample of crosslinked plastic is saponified by alcoholic sodium hydroxide and the long chain acids recovered after acidification. This mixture of mono and diacids are separated by preparative TLC. After weighing the two acids, the crosslinking ratio is calculated according to the following formula.

$$T = \frac{n_d}{2n_d + n_a} \times 100$$

Where n_d is the mole number of diacid and n_a the mole number of monoacid.

We found a crosslinking ratio of 74% for the undecylenic ester subjected to the Grubbs reaction.

Mechanical properties

To improve the mechanical characteristics of the new plastics obtained from olive pomace and bran, we have introduced two modifications in their composition: first, in increasing the length of the fatty ester and the second by crosslinking the cellulosic chains.

From the force–displacement graphs, we determined the average of the principal mechanical characteristics of these materials namely the tensile failure

TABLE IV
Mechanical Properties of Various Esters of Olive and Bran Cellulose

Cellulose origin	Acyl group	σ_T Tensile failure stress (MPa)	ϵ_T Failure strain (%)	Young modulus (MPa)
Olive	Lauric	11.04	17	45
	Myristic	13.37	62	53
	Palmitic	14.47	36	82
	Stearic	20.37	144	60
	Undecylenic	12.37	26	45
Barley bran	Crosslinked	12.66	200	102
	Lauric	7.71	76	58

stress, the failure strain, and the Young modulus (Table IV).

A special attention has been given to rigor and reliability of the experimental results of simple traction. Indeed, the repetitiveness of the tests has made possible to make a first selection of the tests to be kept, and mainly to select the most significant graph in terms of speed and values. It should be noticed that the increasing of the chain length of the ester improves both tensile failure stress and Young modulus. Crosslinking of undecylenic ester greatly improves the failure strain and the Young modulus.

These materials present great similarities with commercial polyethylene films in terms of tensile failure stress especially those made from olive pomace cellulose.

Biodegradation

Preliminary biodegradation tests were realized on lauric ester of olive pomace cellulose in the presence of *Streptomyces samsonii*. The samples were kept in contact with bacteria for 5 months. It was noticed a 12% mass loss after this period of time.

CONCLUSIONS

In this work, we describe an efficient method for producing plastics from agricultural wastes that are poorly valorized. By using microwave irradiation, the reaction time is diminished, and consequently the energy consumed for the reaction is greatly reduced. The mechanical properties of the plastics obtained are improved by a new reaction applied to polymers: the cross metathesis of olefins. Thus, the plastics match the properties of the polyethylene currently used and produced from fossil resources.

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TABLE III
Band Assignments of Cellulosic Esters (Plastic Films)

Wave numbers (cm^{-1})	Band assignments
2848.7–2923.7	CH
1748	C=O (ester)
1467.3	CH ₃
1417.3	CH ₂
1378.4	CH
1150.2	C—O—C (bridge)

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