Etherification of Starch by 9-(2-chloroethyl)-carbazole

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Abstract Keywords Introduction Experimental Results and Discusion Literature

ABSTRACT

The etherification of the most commonly used biopolymer i.e. starch in the Williamson reaction with 9-(2-chloroethyl)-carbazole is described. The potato starch was used as the polymeric substrate. The properties of etherate by means of degree of substitution, UV-VIS spectra, IR and the changes in molecular mass are described.

KEYWORDS

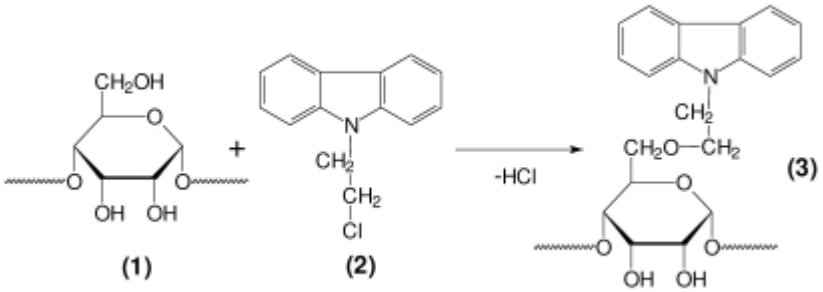
starch, carbazole, etherification.

INTRODUCTION

Starch as a one of the most common and easy to recover biopolymer become in the scope of many research [1]. Its application ranges from typical agricultural ones through food industry and nowadays far beyond its classical perception in modern non-food application. However the raw biopolymer (very often called as "native starch") does not have to much industrial significance, the modification of starch become one of the important industrial and scientific factors [2]. Because of its chemical structure starch could be modified on different ways mostly by reaction at primary or secondary hydroxyl groups. Modification could be group in three groups: oxidation (by means of converting -OH groups into -C=O and -COOH), esterification (with both organic and inorganic acids) and etherification (on different routes depending on the substrate) [3].
From the other hand carbazole based polymers and its derivative find a wide spectra of modern application employing its photo- and electroluminescence properties [4]. Such group of materials could be the vinyl derivative e.g. N-vinylcarbazole (one of the most common carbazole's polymeric materials) or more complicated systems like acrylic derivatives containing carbazole pendant group [5]. The unique properties of carbazole based polymeric material could be also improved by the incorporation into carbazole's aromatic rings some side groups as halogens, formyl group, diazogroup etc. [6].
At this way it seems to be an interesting idea to link the unique properties of carbazole based compounds with biodegradability, water solubility and many others starch properties. It forced us to conduct the described study also as the continuation of some earlier work on carbazole modification [7].

EXPERIMENTAL

The 9-(2-chloroethyl)-carbazole was obtained by the well known method of N-alkylation of carbazole by 1,2-dichloroethane using tetrabutylammonium bromide as the PTC catalyst [6]. After the purifaction of the product by crystallisation from ethanol the 9-(2-chloroethyl)-carbazole was analysed to proved its composition and purity by standard analysis (FTIR, HNMR, GCMS).
The modification of starch was conducted as follows (Scheme 1):

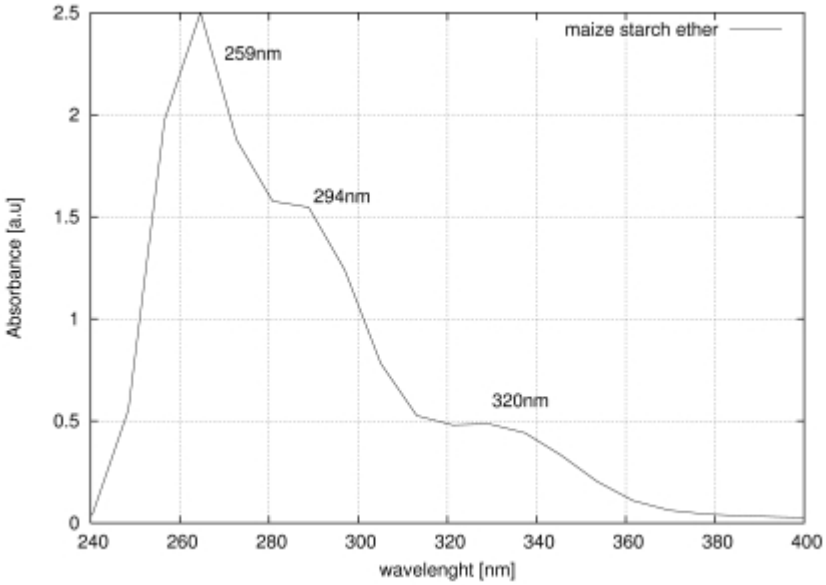


Scheme 1: Etherification of starch by 9-(2-chloroethyl)-carbazole

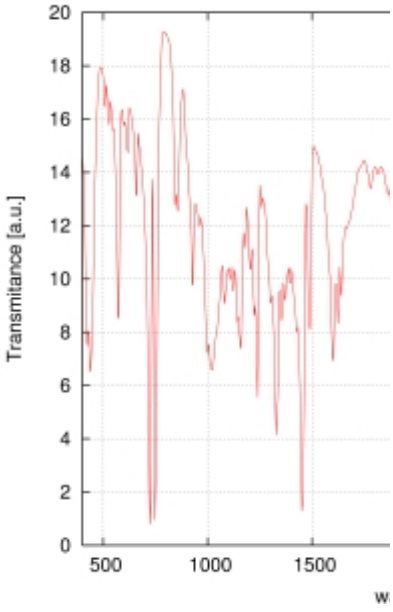
2,5g of potato starch (**1**) was dissolved in DMSO at 60^{o}C. After the process was finished the finely grounded NaOH was added. The mixture was vigorously stirred for 1 hour and the the 9-(2-chloroethyl)-carbazole (**2**) was added as the DMSO solution. The temperature of the process was set up to 70^{o}C and the mechanical stirring continue by 16 hour. After the reaction the mixture was poured into the acetone and centrifugated. The obtained solid was washed with water and neutralize by 10% HCl solution. The precipitated starch was than centrifugated, dried and analysed. The degree of substitution was estimated using UV method at 320nm. The IR spectra was done using JascoFT/IR 4000 Spectrofotometer as the KBr pellets. The molecular mass was estimated using gel permeation chromatography (the system of two columns was used: 380mmx16mm and 460mmx16mm both filled with S-200 and S-500 Sephadex gels). As the eluent the 0,003mol/L Na_2CO_3 was used with the flow rate 0,128mL/min. The analysis was done at 20^{o}C using RI detection. Collected fraction allowed determining the sum of carbohydrates in the sample by means of anthron method [8]. Molecular mass of amylose and amylopectine polymers were determined by means of potassium-iodide complex analysis of collected fractions [9].

RESULTS AND DISCUSION

As a result of our investigation we have obtained a new material called as starch ether which after the preliminary analysis looks very promising. The UV spectra presented at Scheme 2 shows the strong absorption at wavelenghts characteristic for carbazole molecules. The observed band can not be seem at the spectra of pure starch at all. According to the UV spectra the degree of substitution was estimated at the level of 2,9% what shows quite good yield of substitution.
Scheme 3 shows the IR spectra of obtained material. At the spectra a characteristic for both starch and carbazole moieties bands are observed. In the case of starch we can see the bands of: glicosidic bound (at 1156cm^{-1}), stretching vibration of -OH (3350cm^{-1}) and -C-O (at 1015cm^{-1}) and others. For carbazole it is worth to pointed out the presence of aromatic rings (1430-1620cm^{-1}) and the absorption by C-N bound (at 1330cm^{-1}). But most carbazole peaks are muffled by the carbohydrate bands because of the dramatic difference in the amount of both components. The detailed analysis of this spectra can force us to the point that the 9-(-2-chloroethyl)-carbozole was incorporated into the starch structure however it seem be necessary to make some other investigation on this matter.



Scheme 2: UV spectra of the modified starch

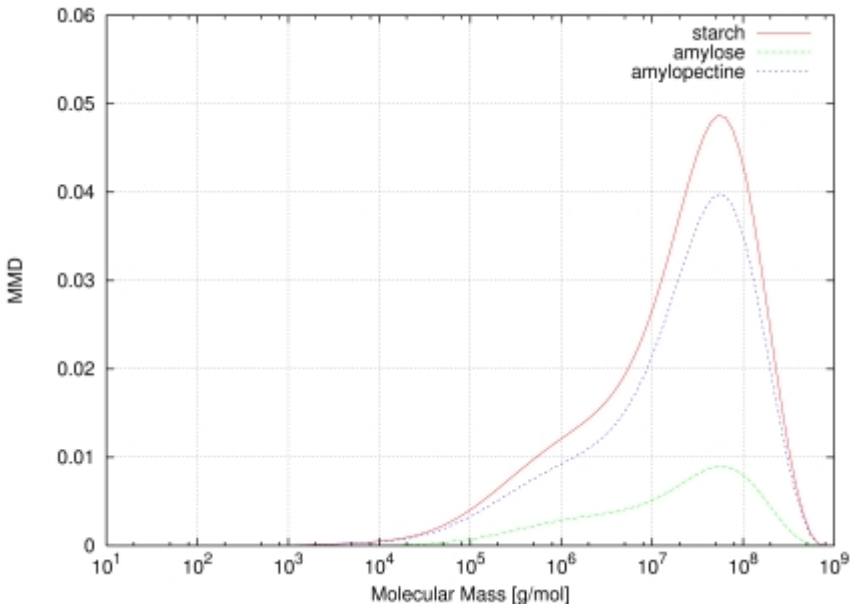


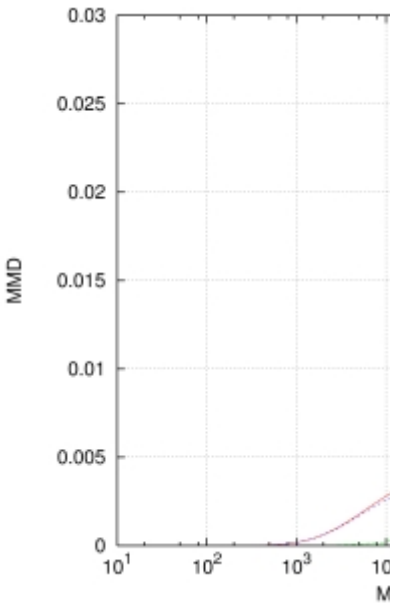
Scheme 3: IR spect

Going into the investigation of molecular mass it is worth to mention that as in almost all chemical modification of carbohydrates the decrease of the molecular mass of starch was observed. The phenomenon occurs in both Mn and Mw value of strach and its basic components i.e. amylose and amylopectine (Table 1). The modification guides also to the lowering of the polydispercity what can be observed at Molecular Mass Distributions (Scheme 4 and 5). The changes in the molecular mass are higher for amylopectine rather than amylose. The changes in the length of the carbohydrate chains seems to be quite moderate and should not influence on properties of the modified material.

Table 1. Molecular Mass of a starting material and starch ether.

	Native starch			Starch ether		
	Starch	**Amylose**	**Amylopectine**	**Starch**	**Amylose**	**Amylopectine**
Mn [g/mol]	$2{,}1\times10^{6}$	$2{,}8\times10^{5}$	$1{,}5\times10^{5}$	$1{,}6\times10^{4}$	$1{,}3\times10^{5}$	$5{,}2\times10^{4}$
Mw [g/mol]	$5{,}9\times10^{7}$	$1{,}2\times10^{6}$	$6{,}0\times10^{7}$	$6{,}4\times10^{6}$	$4{,}1\times10^{5}$	$4{,}3\times10^{6}$





Scheme 4: Molecular Mass distribution of native potato starch.

Scheme 5: Molecular Mas

As a conclusion we can state that presented preliminary study on etherification of starch by 9-(2-chloroethyl)-carbazole guides to the new material which probably might possess both carbazole (according to its electro and photo luminescence) and starch (i.e. water solubility, biodegradability etc.) properties. The research could be also improved by replacing the simple carbazole by its derivatives.

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