Polymer Bulletin 49, 265–272 (2002)

Polymer Bulletin

Synthesis of starch benzoate in aqueous media

Željko Stojanović, Katarina Jeremić (✉) and Slobodan Jovanović

Department of Physical Chemistry and Electrochemistry, Faculty of Technology and Metallurgy, Karnegijeva 4/IV, 11000 Beograd, Yugoslavia

kjeremic@elab.tmf.bg.ac.yu +381/11/3370 387

Received: 18 March 2002/Revised version: 18 October 2002/ Accepted: 28 October 2002

Summary

The results of investigating starch benzoate (SB) synthesis in aqueous media are presented in this study. Starch esterification with benzoyl chloride was performed in two steps, the first step being the alkalization of starch and the second step esterification. The influence of the concentration of reactants, reaction medium composition, temperature and time of synthesis on the degree of substitution (DS), degree of swelling in water and thermal stability of the synthesized starch benzoate was investigated. The optimal conditions for the synthesis of starch benzoate with degree of substitution from 0.23 to 1.76 were determined. It was shown that starch benzoate with a DS of 1.76 practically did not swell in water. However, starch benzoate is less thermally stable than native starch probably due to a change in the supermolecular order induced by the esterification reaction.

Introduction

Starch, as a polyalcohol, readily forms esters with organic and inorganic reagents. The number of hydroxyl groups of starch glucose units involved in esterification is affected by the reagent, reaction conditions and the degree of branching in the amylopectin component.

Starch esters are interesting because the properties of starch can be modified and its application widened by introducing different side groups in the starch molecule. They have been investigated since the beginning of the last century, but interest in them has been renewed in the last two decades as they are biodegradable and obtainable from renewable raw materials [1].

Starch itself has only limited applications as a thermoplastic polymer. One of its main disadvantages is its high hydrophilicity. The introduction of hydrophobic groups by the esterification of starch significantly decreases hydrophilicity . The esterification of starch with benzoyl chloride produces starch benzoate the hydrophobicity of which depends on the degree of substutuion. Starch benzoate was synthesized mainly in two ways. In the first type of esterification, starch was treated with azeotropic pyridine-water mixture at elevated temperature and subsequently benzoyl chloride was added [2]. In the second type of esterification starch benzoate was synthesized mainly in suspension by the reaction of benzoyl chloride with starch but the reaction medium was different [3, 4, 5]. In some cases only an aqueous solution of NaOH was used [3]. In reference [4] a starch suspension in aqueous NaOH was heated in pyridine and chloroform was added to the reaction medium. In reference [5] a suspension of starch in 50 % iso-propyl alcohol or aqueous solution of Na_2SO_4 was used.

In this study, the possibility of applying the same procedure developed for the synthesis of carboxymethyl starch to the synthesis of starch benzoate was investigated. In this procedure a mixture of water and ethanol was used as the reaction *medium, and sodium hydroxide* as a base [6]. Starch esterification with benzoyl chloride was performed in two steps, just as the etherification. The alkalization of starch is the first step and it is the same as for etherification [7,8]:

$$\text{St-OH} + \text{NaOH} = \text{St-O-Na}^+ + H_2O \qquad (1)$$

In the second step, esterification occurs:

$$\text{St-O-Na}^+ + C_6H_5COCl = \text{St-O-CO-}\ C_6H_5 + NaCl \qquad (2)$$

Starch benzoate is obtained in granular form. It was easily to separated it from the reaction medium. The other advantage of this type of starch esterification compared to procedures where pyridine was used, is that much more environmental friendly solvents are used -ethanol and water. Ethanol can also be easily recycled.

The goal of this study was to optimise the reaction conditions by investigating the influence of the reaction medium composition, concentration of reactants, temperature and time of synthesis on the degree of substitution (DS), degree of swelling in water and thermal stability of the synthesized starch benzoate.

Starch benzoate is used for hard, clear coatings or as an adhesive for paper, glass, steel, glass fibers, etc [3,9,10]. The renewed interest in starch benzoate comes from the need to find a hydrophobic and relatively cheap modified biopolymer, which might be used for blending with more expansive biodegradable thermoplastic polymers.

Experimental part

The following types of starch, all obtained from "Jabuka" Starch Industry, Serbia, were used for the synthesis of starch benzoate: native corn starch (NS)(25 % amylase, 12 % H_2O), oxidized starch (OS) (starch oxidized by hypochlorite solution, the content of carboxyl groups between 0.40 – 0.60 vol.%), and starch enriched by amylopectin (WX) (99 % amylopectin).

All the other chemicals used in this investigation (NaOH, benzoyl chloride and ethanol) were produced either by Zorka (Šabac, Serbia) or Aldrich. Water, ethanol or their mixture were used as the reaction medium.

Starch esterification was carried out in two steps in a standard glass reactor (250 cm^3) with a stirrer and reflux condenser. In the first step, the alkalization was performed by dispersing NS (10 g)(as received) in a reaction medium (120 cm^3), adding 27 cm^3 11.5 M NaOH (0.31 mol) aqueous solution at 25 ^0C and stirring for 20 min. In the second step, the esterification of alkalized starch was performed by adding 18 cm^3 (0.155 mol) of benzoyl chloride (BC) dropwise to the reaction mixture which was thermostated at the designated temperature. The reaction mixture was stirred for a designated time. The reaction was ended by filtering the precipitated SB, which was then washed with water and ethanol and dried under vacuum at 40 ^0C. When the soluble fraction of starch benzoate was obtained during the synthesis, it was precipitated by ethanol, filtered and further treated in the same way as the insoluble fraction.

The degree of substitution of dried starch benzoate was determined by UV spectrophotometry following the procedure of Weaver and Otey with slight modification [11]. Starch benzoate (0.4 g) was hydrolyzed by 0.05 M NaOH in a mixture of water/methanol (2:1) (30 cm^3) for 1 hour while stirring at elevated temperature. The solution was then diluted to the concentration of 0.04 g/dm^3. The amount of sodium benzoate present in the solution was determined by measuring UV absorbance at the wavelength of 220 – 230 nm and using a calibration diagram. Sodium benzoate was used as the standard compound for the calibration curve determination.

The degree of swelling of the SB samples was determined gravimetrically. For these measurements the samples were in the form of discs 25 mm of diameter and 2.0 mm thickness. These samples were prepared using a special mold, which was filled with 1.2 g of SB, kept at 160 ^0C for 30 min and then a pressure of 2 MPa was applied for 2 min.

The thermal stability of NS and SB was investigated by non-isothermal thermogravimetric analysis (TG) using a Perkin Elmer TGS-2 instrument. All the measurements were conducted in nitrogen the flow rate of which was 25 cm^3/min, the sample mass was about 3 mg and the heating rate was 10 ^0C/min.

Results and discussion

Influence of the reaction medium

In order to determine the optimal conditions for the esterification of starch with benzoyl chloride in alkaline medium, the esterification was performed in pure water, ethanol or mixtures of water and ethanol with 15, 30, 50 and 75 vol % of ethanol at 4 ^0C. Native starch was used for these experiments and the fraction of reactants in the reaction mixture was the same in all of them. The influence of the type of reaction medium and content of ethanol on the DS of the obtained starch benzoate is shown in Fig. 1 together with the calculated reaction efficiency. The highest DS was obtained when the esterification was performed in pure water. When the fraction of ethanol in the mixture with water was increased to 50 vol % , the DS decreased from 0.82 to 0.09. Further increase of the ethanol fraction did not significantly change the values of the DS. The reaction efficiency was influenced in the same way.

When the esterification was carried out in pure water, two fractions of starch benzoate with different DS were obtained. The average DS value is presented in Fig.1, and the values of the DS of both fractions, together with their masses, are given in Table 1 . One of the fractions was soluble and the other insoluble in water. When the reaction medium was pure ethanol or a mixture of water and ethanol, only one, insoluble, fraction of starch benzoate was obtained. Consequently, all further experiments were carried out in a mixture of water and 15 vol % ethanol. One fraction was obtained and the DS of SB was still relatively high.

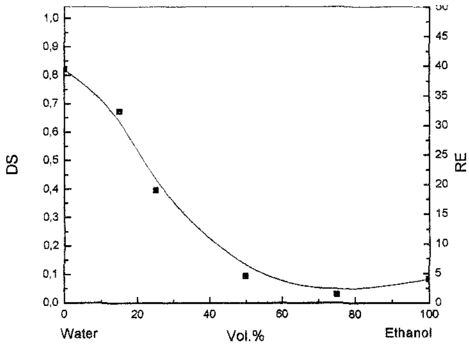

Fig. 1. The dependence of the DS and RE of the SB samples on the reaction medium composition (10 g NS, 18 cm^3 BC (0.155 mol), 27 cm^3 11.5 M NaOH (0.31 mol), 120 cm^3 reaction medium, t = 4 ^{0}C and τ =3.5 h)

Influence of the reaction temperature

The influence of the temperature of the second esterification step on the DS and RE of starch benzoate, was investigated by esterifying NS in pure water, ethanol or in water with 15 vol % of ethanol at several temperatures in the interval from 4 to 85 ^{0}C. The value of DS and RE of the obtained SB samples are shown as a function of temperature in Fig.2. The results show that the starch benzoate with the largest DS was obtained when the esterification was conducted in pure water at 4 ^{0}C and in a water/ethanol mixture at 30 ^{0}C. Unfortunately, in both cases two fractions with different DS were obtained (Table 1), so all further experiments were performed in a water /ethanol (15 vol %) mixture at 4 ^{0}C. It is interesting to note that at 65 ^{0}C (the gelatinization temperature of starch) SB with almost the same DS value was obtained in all three solvents.

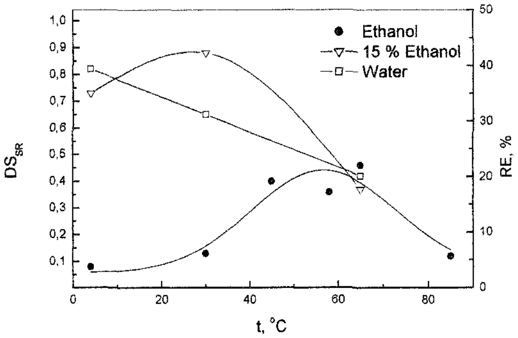

Fig. 2. The dependence of the DS and RE of the SB samples on the reaction temperature (10 g NS, 18 cm^3 BC (0.155 mol), 27 cm^3 11.5 M NaOH (0.31 mol), 120 cm^3 reaction medium,τ =3.5 h)

Table 1. Influence of temperature on DS of SB samples (10 g native starch, 18 cm^3 BC (0.155 mol), 27 cm^3 11.5 M NaOH (0.31 mol), 120 cm^3 reaction medium, τ = 3.5 h)

t, °C	Reaction medium									
	15 vol.% ethanol					water				
	DS(is)[a]	m(is)[b]	DS(s)[c]	m(s)[d]	<DS>[e]	DS(is)	m(is)	DS(s)	m(s)	<DS>
4	0.73	15	-	-	0.73	1.43	8.14	0.14	7.14	0.82
30	1.22	11.3	0.26	6.2	0.88	0.96	7.5	0.18	5	0.65
65	0.74	3	0.27	10.6	0.37	0.90	4.82	0.25	7.1	0.42

a) DS of insoluble fraction; b) mass of insoluble fraction; c) DS of soluble fraction; d) mass of soluble fraction and e) average value of DS

Influence of the reaction time

Five experiments of esterifying native starch were performed under standard conditions but with different reaction times. The DS and RE of the obtained starch benzoate are presented in Fig. 3 as a function of reaction time. The results indicate that the highest degree of substitution (DS = 0.73) was obtained already after 90 min. For longer reaction times the DS starts to decrease achieving a value of 0.56 in 5 hours. This slight decrease of the DS values could probably be explained by the onset of starch benzoate hydrolysis occurring simultaneously with the esterification of NS:

$$\text{St-CO-C}_6\text{H}_5 + \text{NaOH} = \text{St-OH} + \text{C}_6\text{H}_5\text{COOH} \qquad (3)$$

Therefore, the esterification time in the further experiments was reduced to 90 minutes.

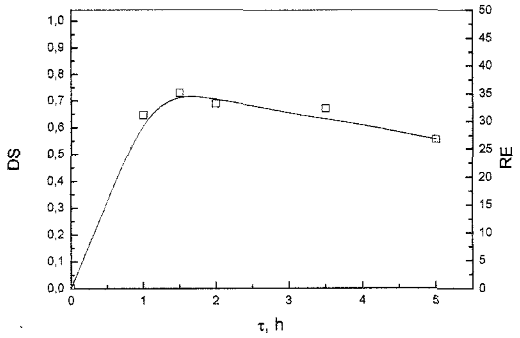

Fig. 3. The dependence of the DS and RE of the SB samples on the reaction time (10 g NS, 18 cm^3 BC (0.155 mol), 27 cm^3 11.5 M NaOH (0.31 mol), 120 cm^3 15 vol % ethanol, t = 4 ^{0}C)

Influence of NaOH

The -OH groups from starch can react with benzoyl chloride (eq.2) only if they are activated, i.e. transformed into $-O^- Na^+$ (eq.1). Keeping this in mind, the esterification of the native starch was performed with different values of the molar ratio of NaOH and anhydroglucose units (AGU), n(NaOH)/n(AGU). The influence of n(NaOH)/n(AGU) on the DS and RE is presented in Fig. 4. As may be seen, by increasing the molar ratio n(NaOH)/n(AGU) from 2 to 4, the DS increases from 0.88 to 1.10, whereas further increase of the molar ratio causes the DS to decrease. Increase of the amount of NaOH in the reaction mixture certainly increases the number of activated hydroxyl groups ($-O^- Na^+$), however it also increases the rate of reaction defined by eq. 3, as well as the hydrolysis of benzoyl chloride, which all leads to a decrease of the DS of the obtained starch benzoate.

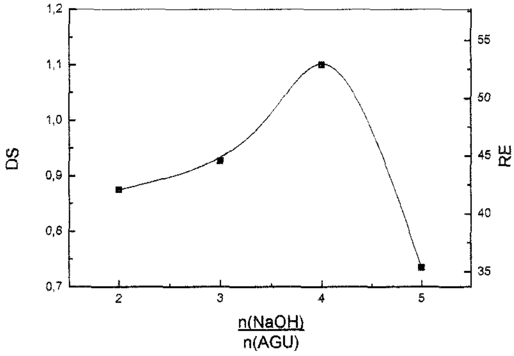

Fig. 4. The dependence of the DS and RE of the SB samples on the n(NaOH/n(AGU) ratio (10 g NS, 18 cm^3 BC (0.155 mol), 120 cm^3 15 vol % ethanol, t = 4 ^{0}C, τ = 1.5 h)

Influence of benzoyl chloride

The molar ratio of benzoyl chloride and AGU, n(BC)/n(AGU), in the reaction mixture also influences the DS and RE. The esterification of native starch was conducted under standard conditions but changing the values of this ratio from 1 to 4. The obtained results are shown in Fig. 5.

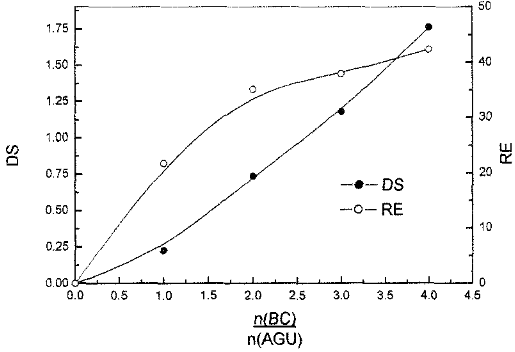

Fig. 5. The dependence of the DS and RE of the SB samples on the n(BC)/n(AGU) ratio (10 g NS, 27 cm^3 11.5 M NaOH (0.31 mol), 120 cm^3 15 vol % ethanol, t = 4 ^{0}C, τ = 1.5 h)

The DS increases almost linearly with increase of the molar ratio n(BC)/n(AGU) in the reaction mixture, whereas the reaction efficiency increases only up to n(BC)/n(AGU) = 2 and then stays practically constant. Thus, there was no point of performing the esterification of starch with benzoyl chloride under the mentioned experimental conditions for n(BC)/n(AGU) larger than 2.

Influence of starch type

Three types of starch were used for the synthesis of starch benzoate: native starch, NS, starch enriched with amylopectin, WX, and an oxidized starch, OS. The esterification was conducted under standard conditions. The obtained values of the DS and RE are presented in Table 2. The results from Table 2 show that the starch type significantly influences the esterification. Two fractions of starch benzoate are obtained as products of the esterification (one soluble and the other insoluble in water) only in the case of starch enriched with amylopectin. The esterification of native starch gave two fractions of starch benzoate only when the reaction medium was either pure water or a mixture of water and ethanol at a reaction temperature of 30 ^{0}C.

Table 2. Influence of starch type on the DS and RE of SB samples (10 g NS, 18 cm^3 BC (0.155 mol), 27 cm^3 11.5 M NaOH (0.31 mol), 120 cm^3 15 vol % ethanol, t = 4 ^0C, τ = 1.5 h)

	NS	WX		OS
Starch type	insoluble fraction	soluble fraction	insoluble fraction	insoluble fraction
m, g	15	13.9	5.9	15.1
DS	0.73	1.41	0.11	1.15
<DS>	0.73	1.02		1.15
RE	35.1	49.0		55.3

No acceptable explanation for the different behavior of the WX starch can yet be offered. The other interesting result shown in Table 2 is that the esterification of oxidized stach yields the starch benzoate with a higher DS than starch benzoate obtained from NS under the same experimental conditions. This is probably due to the fact that oxidized starch swells better in the reaction medium and is more available to the reactants. Better swelling is a consequence of the partly destroyed supermolecular structure of starch during the reaction of oxidation.

Swelling behavior

Starch macromolecules are very hydrophilic due to the large amount of hydroxyl groups. They bind 8 to 14 mass % of water depending on the relative air humidity under normal conditions of temperature and pressure. One of the reasons of starch modification with benzoic acid was to reduce the hydrophilicity of starch. The influence of the DS of starch benzoate on its affinity towards water was investigated by determining the degree of swelling of SB samples with different DS in water. The obtained results are presented in Fig.6 as the degree of swelling vs. the time of swelling at room temperature. It may be seen that the increase of the DS from 0.23 to 0.73 results in a decrease of the degree of swelling from 85 to 15 mass % for a swelling time of 150 min. The SB sample with a DS of 1.73 has a degree of swelling less than 1 mass % and behaves as a standard hydrophobic synthetic polymer.

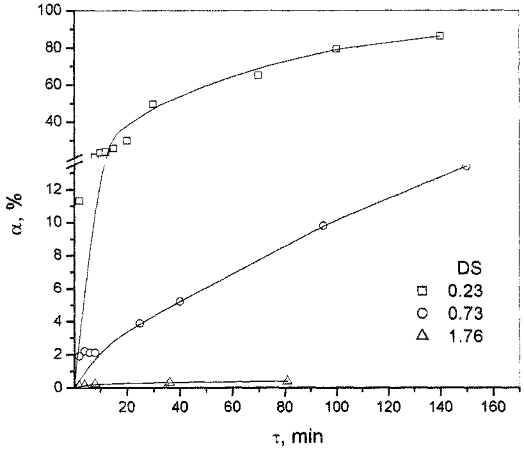

Fig. 6. The degree of swelling in water vs. time for starch benzoate samples with different DS at room temperature

Thermal analysis

Typical non-oxidative non-isothermal TG curves obtained for native starch and starch benzoate with DS = 0.67 are shown in Fig.7. It is obvious that the two starches behave differently with increasing temperature. Due to its hydrophilic nature native starch looses absorbed moisture between 50 and 100 ^{0}C and the onset of thermal degradation of the polymer occurs at about 320 ^{0}C. The starch benzoate sample does not show any mass loss below 100 ^{0}C indicating volatile substances such as water and alcohol, were not present in this sample. The onset of thermal degradation of starch benzoate occurs at about 190 ^{0}C and the maximum rate of mass loss is at 360 ^{0}C. These results show that starch benzoate is less thermally stable than native starch, which could be ascribed to a change in the supermolecular order induced by the esterification of native starch.

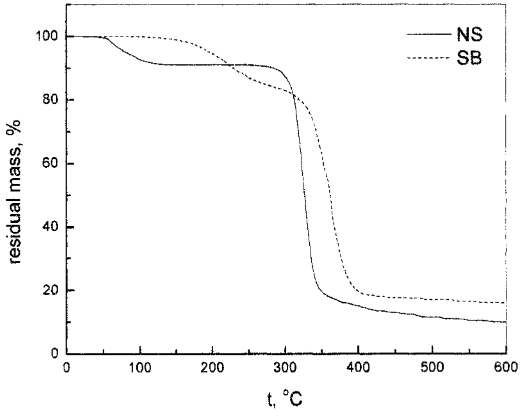

Fig. 7. Characteristic non-isothermal TG curves of native starch and starch benzoate (DS = 0.67) in nitrogen, heating rate 10 deg/min, gas flow rate 25 cm^3/min

Acknowledgements. This work was financially supported by the Ministry of Science, Technolgies and Development of Serbia (research project number: 1948).

References

1. Eierdanz H (ed) (1996) Perspektiven nachwachsender Rohstoffe in der Chemie, VCH, Weinheim
2. Mullen JWII, Pascu E (1942) Ind.Eng.Chem. 34:1209
3. Galinke J. Kowald B. Sibert K. Stimberg H.J. (1972) Ger. Patent 2,039,812; Chem.Abstr. 76:155921u
4. Lipparini L, Garutti MA (1967) Quad. Merceol. 5:35; Chem.Abstr. 67:65675b
5. Galinke J. Kowald B. Sibert K. Stimberg H.J (1972) Ger. Patent 2,039,812; Chem.Abstr. 76:155921v
6. Stojanović Ž, Jeremić K, Jovanović S (2000) Starch/Stärke 52:413
7. Khalil MI, Hashem A, Hebeish A (1990) Starch/Stärke 42:60
8. Tijsen CJ, Scherpenkate HJ, Stamhuis EJ, Beenackers AACM (1999) Chem.Engng.Sci. 54:2765
9. Yazawa S (1977) Jpn.Kokai Tokkyo Koho 77 123,477; Chem.Abstr. 88(1978):122897k
10. Berkhout F, Nieuwenhuis HJW (1972) Ger.Patent 2,134,686; Chem.Abstr. 76:129166g
11. Weaver MO, Otey FH (1982) Starch/Stärke 34:26