

Investigation of Interaction of Chitosan with Solid Organic Acids and Anhydrides under Conditions of Shear Deformation

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ABSTRACT: Chitosan interaction with stearic, oxalic, malonic, and succinic acids and with phthalic, succinic, and maleic anhydrides under shear deformation was investigated. It was shown that under these conditions the production of corresponding chitosan derivatives takes place. On the basis of elemental analysis, potentiometric titration, and IR spectroscopy data, the possible mechanisms of the reaction are discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 616–622, 2000

Key words: chitosan; solid organic acids; solid organic anhydrides; shear deformation

INTRODUCTION

The study of polymer analogous reactions of chitosan–polysaccharide, formed from parts of glucosamine and the production of its new derivatives has continued to attract the attention of numerous investigators in different countries. This interest is explained by the unique properties of this polymer (nature, origin, biocompatibility, low toxicity, wide spreading in nature) and by the great abilities of its chemical modification, salt and complex formation, etc.

Traditionally, chitosan modification is realized under heterogeneous conditions with preliminary activation of the polymer by grinding or swelling in organic liquids or in water–acid solutions.^{1,2} The reaction proceeding in the solid phase under joint action of high pressure and shear deforma-

tion has some advantages because it allows one to considerably decrease the process duration and reagents' consumption and, in such a way, improve the economical and ecological parameters of the process.³ A comparative investigation of chitosan obtained by traditional suspension and solid-phase methods was done in ref. 4. In the present work, the possibility of chitosan interaction with solid fat stearic acid, solid carboxylic diacids, and solid anhydrides of carboxylic diacids in the absence of liquid under the joint action of high pressure and shear deformations was studied.

EXPERIMENTAL

As the object of our research, chitosan from the shells of crabs with a degree of deacetylation of 0.85, a viscosity of 350 cl, an ash content of 0.16%, a content of insoluble admixtures of 0.15, and a moisture content of 10% and also organic acids,

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including stearic acid (mp 70°C), oxalic acid (mp 185.5°C), malonic acid (mp 135.6°C), and anhydrides, including phthalic anhydride (mp 131.6°C), succinic anhydride (mp 119.3–119.6°C), and maleic anhydride (mp 54°C), of chemically pure grade were used without additional purification.

Sample Treatment Under Pressure

Treatment of the samples was carried out in a two-screw extruder with controlled heating, where the principle of joint action of high pressure (0.2–5.0 MPa) and shear deformation was realized. The dry components were charged into the extruder and the mixture of the reaction product and the unreacted reagents was obtained at the output of the extruder.

Determination of Degree of Substitution (DS)

The synthesized products were purified from the excess reagents by extraction with ethyl alcohol in a Soxhlet apparatus and then characterized according to the DS, where the DS is amount of acid molecules connected with monomer units of the chitosan macromolecule. According to the elemental analysis data obtained on a Carlo Erba 11-08 analyzer, the DS was calculated from the C/N gram-atomic ratio. The type of bonds (ionic or covalent) between the elementary units of chitosan and the substituents was determined by potentiometric titration of suspensions of the products in hydrochloric acid with a sodium hydroxide solution using a Radiometer RTS-822 titrator. The DS by the ionic mechanism was calculated on the basis of the titration results, because only the substituents linked by ionic bonds can be determined by potentiometric titration.

IR Spectroscopy

IR spectra were taken on a Specord-80 spectrophotometer ("Carl Zeiss"), pressing the samples as tablets with KBr; concentration of the investigated substances was 0.3%.

Optical Density (D)⁵

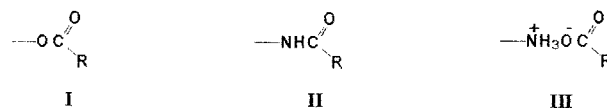
Optical density (D) was calculated according to $D = -\lg I/I_0$, where D is the optical density; I_0 , the intensity of the free followed ray; and I , the intensity of the ray throw sample.

Solubility of Products

The product solubility was investigated by preparing 1% solutions in 0.1M HCl, 2% acetic acid, distilled water, and 0.1M NaOH.

RESULTS AND DISCUSSION

The interaction of polybase chitosan with dicarboxylic acids and with anhydrides of dicarboxylic acids leads to formation of products of a complex structure, where the fragments of acids and anhydrides may bond to hydroxyl groups and to amino groups of polymer by ether (I), amide (II), and salt (III) bonds:



For establishment of the possibility to bond anhydrides to chitosan hydroxyl groups with the formation of ether bonds under the condition of shear deformation, an additional investigation of phthalic anhydride interaction with cellulose having only hydroxyl functional groups was carried out. The investigation of the obtained products by IR spectroscopy showed the presence in the spectrum of weak characteristic bands, which are attributed to the absorption of the benzene ring at 1600 cm^{-1} , carbonyl groups at 1780 and 1420 cm^{-1} , and aromatic ethers at 1250 cm^{-1} . The elemental analysis data showed a high amount of C compared with the initial cellulose in the samples synthesized at 100°C . Thus, the obtained results allowed one to conclude the possibility of the proceeding of the *O*-acetylation reaction, but the DS is not higher than 0.1 (Table I). Unlike the cellulose, the IR spectra of the products of chitosan modification by phthalic anhydride show intensive absorption bands of the benzene ring (1600 cm^{-1}) (Fig. 1) and, in the case of modification by maleic and succinic anhydrides, also the absorption bands of the CH group at 2950 and 1640 cm^{-1} .

We studied the effect of pressure and shear deformation on the solid blends of chitosan with the first members of the homologous series of dicarboxylic acids (oxalic, malonic, and succinic) and with anhydrides of dicarboxylic acids (phthalic, succinic, maleic) in the range 25 – 100°C .

Table I Characteristics of the Products Obtained by Solid-phase Reaction Between Polysaccharides and Dicarboxylic Acid Anhydrides

Sample No.	Reagent	Reagent: Polysaccharide (mol/base-mol)	Temperature (°C)	C : N	N _{am} : N _{tot}	DS			Solubility in 0.1M HCl (%)
						Total	Ionic	Covalent	
1	Phthalic anhydride	0.50	100	—	—	0.06	—	0.06	—
2	Phthalic anhydride	1	50	—	—	~ 0	—	~ 0	—
3	Phthalic anhydride	1	100	—	—	0.1	—	0.1	—
4	Phthalic anhydride	0.50	50	6.29	0.90	~ 0	~ 0	~ 0	99
5	Phthalic anhydride	0.50	100	7.96	0.89	0.21	0.07	0.14	59
6	Phthalic anhydride	1	25	8.05	0.89	0.22	0.17	0.05	96
7	Phthalic anhydride	1	50	8.86	0.90	0.32	0.30	0.02	98
8	Phthalic anhydride	1	100	9.95	0.53	0.45	0.22	0.23	35
9	Succinic anhydride	0.25	25	6.69	—	0.10	0.10	~ 0	83
10	Succinic anhydride	0.25	50	6.93	0.89	0.16	0.08	0.08	81
11	Succinic anhydride	0.50	100	8.19	0.59	0.47	0.27	0.20	40
12	Maleic anhydride	0.25	25	7.33	0.90	0.25	0.07	0.18	58
13	Maleic anhydride	0.25	50	7.33	0.88	0.25	0.09	0.16	—

Samples 1–3 are the cellulose derivatives, and samples 4–13 are the chitosan derivatives.

In this temperature range, the starting compounds usually do not enter the reaction and do not undergo any changes. Table I lists the parameters of the reaction of chitosan with anhydrides of dicarboxylic acids and Table II lists the parameters of some products of the reaction of chitosan with dicarboxylic acids under these conditions. The data in Tables I and II indicate that under a significant excess of the reagents the addition proceeds by a mixed (but mainly ionic) mechanism. Thus, in the product of the reaction between chitosan and malonic acid at 100°C (Table II), the total DS, determined using the data of elementary analysis, is 0.46. The results of potentiometric titration give the DS by ionic bonds as 0.33 and, hence, the DS by covalent bonds is $0.46 - 0.33 = 0.13$; in other words, 33 molecules are linked by ionic bonds and 13 by covalent bonds. The balance with respect to the titrated amino groups of chitosan shows the presence of two crosslinkages through amide bonds.

The partial loss of solubility of the samples in acidic aqueous media apparently suggests the occurrence of intermolecular crosslinkages. It is obvious that a considerable decrease in the solubility of the products obtained by the reaction of succinic acid with chitosan as compared with oxalic and malonic acids is associated with the fact that the chain of succinic acid is longer and, as a result, the probability of both intermolecular and intramolecular crosslinking is high.

The total amount of substituents is increased with an excess of a carbonyl-containing reagent and temperature. The most influence that the increase of temperature has is for the formation of covalent bonds; by this, the amide bonds are formed only under a significant excess of reagents, which testifies to the decrease of the ratio N_{am}/N_{tot} (where N_{am} is the nitrogen content in amino groups, and N_{tot} , the total nitrogen content) in products of the interaction of chitosan with phthalic anhydride and succinic anhydride

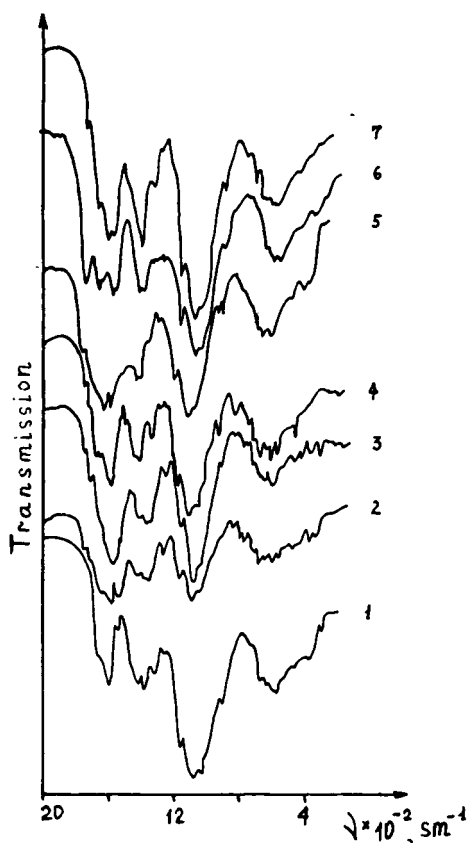


Figure 1 Regions of the IR spectra of (1) chitosan and products of its reactions with (2) oxalic, (3) malonic, and (4) succinic acids at 100°C and with (5) maleic, (6) succinic, and (7) phthalic anhydrides at 50 and 100°C, respectively.

obtained at 100°. The chitosan interaction with maleic anhydride proceeds quantitatively both under room and increasing temperatures. Under

these reaction conditions, the reaction capacity of dicarboxylic acids and anhydrides changes as follows: oxalic acid > malonic acid > succinic acid; maleic anhydride > succinic anhydride > phthalic anhydride.

It is shown that under the conditions studied succinic anhydride has a higher reactivity than that of succinic acid. As can be seen from Table I, the interaction of chitosan with phthalic anhydride takes place only under increasing temperature up to 100°C or under an increasing amount of anhydride in the reaction mixture up to an equimolar ratio, which leads to obtaining a product in which about one-half of the substitutes are joined by amide bonds. It may be supposed that the presence of the benzene ring causes some steric difficulties for the interaction of phthalic anhydride with the chitosan amino groups. Phthalic anhydride has a minimal reactivity among the anhydrides used and the degree of its transformations even under 100°C does not exceed 45%. Succinic anhydride has an immediate position and, as may be expected, it is significantly more reactive than is succinic acid. In the case of succinic acid, the DS of chitosan and the type of the bond formed is dependent on the reagents' ratio and process temperature.

The tables show that the more active reagent is maleic anhydride, which contains, besides the reaction capacity of the anhydride group, also a double bond. The interaction of chitosan with the maleic anhydride group proceeds quantitatively under both room and increased temperatures and products of its interaction have the lowest solu-

Table II Characteristics of the Products Obtained by Solid-phase Reaction Between Chitosan and Dicarboxylic Acids

Sample No.	Reagent	Reagent: Chitosan (mol/base-mol) ^a	Temperature (°C)	C : N	DS			Solubility in 0.1M HCl (%)
					Total	Ionic	Covalent	
14	Stearic acid	1.5	25	10.74	0.16	0.16	—	83
15	Stearic acid	1.5	50	11.29	0.22	0.22	—	68
16	Oxalic acid	1.5	25	7.82	0.42	0.34	0.08	98
17	Oxalic acid	1.5	50	7.85	0.43	0.23	0.20	94
18	Malonic acid	1	50	7.57	0.20	0.20	—	96
19	Malonic acid	1.5	50	8.22	0.40	0.36	0.04	94
20	Malonic acid	1.5	100	8.42	0.46	0.33	0.13	74
21	Succinic acid	1.5	50	7.33	0.10	0.05	0.05	60
22	Succinic acid	1	100	7.33				50
23	Succinic acid	1.5	100	7.47	0.13	0.12	0.01	40

^a Molar ratio polysaccharide reagent.

Table III Ratio Between the Optical Densities of the Characteristic Adsorption Bands of the Products of the Solid-phase Reaction Between Chitosan and Anhydrides of Carboxylic Acid and the Internal Standard ($D = 1070 \text{ cm}^{-1}$)

Sample	D_{2950}	D_{1760}	D_{1650}	D_{1600}	D_{1420}	D_{1300}
Starting chitosan	0.51	0.02	0.14	0.41	0.37	0.27
5	0.62	0.13	0.57	0.47	0.61	0.35
7	0.59	0.44	0.55	0.48	0.73	0.53
8	1.3	0.38	2.24	0.54	0.84	0.63
9	0.58	0.15	0.47	0.49	0.41	—
10	0.60	0.17	0.36	0.45	0.43	—
11	0.61	0.47	0.50	0.42	0.50	—
12	0.52	0.27	0.46	0.51	0.52	—
13	0.57	0.29	0.60	0.74	0.51	—

bility. For these products, the formation of gel-like solutions in acid–water solutions takes place, which makes difficult the exact evaluation of its solubility.

We made an attempt to perform semiquantitative analysis of the IR spectra, using the method of the baseline and internal standard.⁵ As an internal standard, we used the absorption band due to C—O—C bands at 1070 cm^{-1} of the chitosan pyranose cycle. The IR spectra of chitosan modified by phthalic and other anhydrides, unlike those of cellulose derivatives, contain strong characteristic absorption bands of nonionized carboxyl groups ($1760\text{--}1710 \text{ cm}^{-1}$) and the band due to the ionized carboxyl groups at 1650 cm^{-1} and that of the benzene ring (1600 cm^{-1}). The spectra of chitosan modified with malonic and succinic acids or with maleic anhydride contain characteristic absorption bands of alkyl groups at 2950 and $700\text{--}720 \text{ cm}^{-1}$ (Fig. 1, curves 4–6).

In Tables III and IV are given the ratio be-

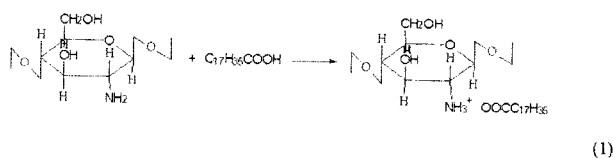
tween the optical densities of some characteristic absorption bands of the obtained products and the internal standard. As seen from the tables, this ratio (the amount of added substituents) is increased with increase of the temperature and molar ratio. This is evidenced also by the data of Tables I and II, which show the DS of the obtained derivatives. Stronger oxalic acid shows higher reactivity. The degree of utilization of the weakest acid (succinic) does not exceed 10%, the extent of substitution of the obtained chitosan derivatives virtually being independent of the conditions of the solid-phase reaction.

These data confirm the conclusion that the acids and anhydrides react with chitosan. A significant increase in the intensity of the bands characteristic of the amide groups in these spectra and the appearance of the absorption bands due to ionized carboxyl and amino groups allow us to suggest that the addition proceeds through both ionic and covalent bonds.

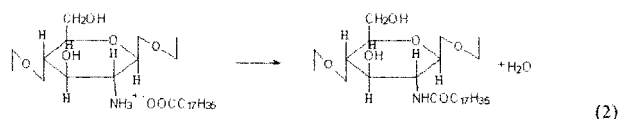
Table IV Ratio Between the Optical Densities of the Characteristic Adsorption Bands of the Products of the Solid-phase Reaction Between Chitosan and Carboxylic Acid and the Internal Standard ($D = 1070 \text{ cm}^{-1}$)

Sample	D_{2950}	D_{1720}	D_{1640}	D_{1550}	D_{1408}	$D_{800\text{--}720}$
4	0.97	0.08	0.45	0.42	0.52	0.26
15	0.99	0.09	0.55	0.46	0.55	0.43
16	0.50	0.38	0.81	0.92	0.67	0.18
19	0.60	0.33	0.71	0.85	0.51	0.19
20	0.69	0.56	0.82	0.92	0.61	0.20
21	0.64	0.16	0.52	0.55	0.48	0.22
23	0.66	0.25	0.57	0.82	0.58	0.24

The reaction of chitosan with fat stearic acid presumably proceeds according to the following scheme:



and leads to the formation of chitosan stearate. It is not excluded, however, that under the conditions of shear deformation at temperatures above 60°C dehydration of the salt bonds can take place and amide bonds can form between the chitosan macromolecules and the moieties of stearic acid:



Thus, the products, in principle, may contain alkyl groups linked by both salt and covalent bonds [eqs. (1) and (2), respectively].

Figure 2 shows the curves for titration of stearic acid (curve 1) and chitosan stearate (curve 2) in a dilute HCl solution. Stearic acid virtually is not titrated under the conditions used; there-

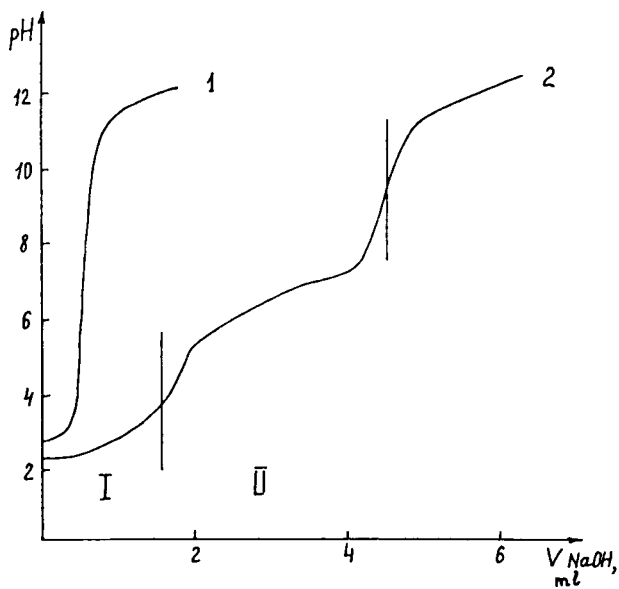


Figure 2 Potentiometric titration curves for the suspensions of (1) stearic acid and (2) chitosan stearate in HCl solution.

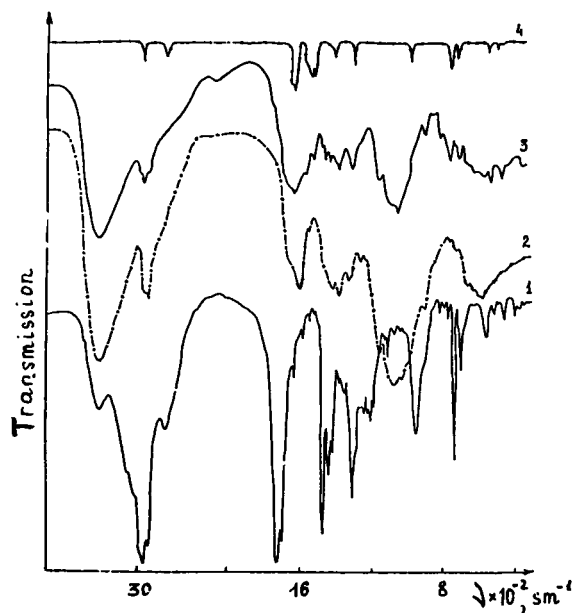


Figure 3 IR spectra of (1) stearic acid, (2) starting chitosan, and (3,4) chitosan stearate; spectrum (4) was recorded against chitosan in the reference beam.

fore, portion II on the titration curve of chitosan stearate should be assigned to the titration of amino groups of chitosan, free (as hydrochloride in titrating a suspension of the product in hydrochloric acid) and linked by ionic bonds to the moieties of stearic acid (stearate), because it is impossible to titrate covalent bonded moieties. The total amount of the titrated amino groups in chitosan stearate is 3.8 mmol/g. This corresponds to a DS equal to 0.22, taking into account their content in the starting chitosan (5.2 mmol/g).

The DS calculated from the data of titration and elemental analysis should be related to the moieties of stearic acid linked by ionic bonds and to the total amount of the moieties of stearic acid linked by ionic and covalent bonds, respectively. Therefore, it can be concluded (see Table II) that the addition reaction of stearic acid to chitosan under the chosen conditions proceeds only via the ionic mechanism.

The IR spectrum of the reaction product of chitosan with stearic acid (Fig. 3, curves 3 and 4), displays stronger absorption at 2500–3000 and 1500–1700 cm^{-1} and new bands, for example, at 800 cm^{-1} . The presence of bands at 2950, 2650, 1308, 929, and 760 cm^{-1} in spectra 3 and 4, which are also present in the spectrum of stearic acid (curve 1) and result from vibrations of alkyl

groups, confirms that stearic acid residues have been added to chitosan. Chitosan modification by carboxylic acid and anhydrides does not give them the capacity to dissolve in water and organic solvents, which may be expected, taking into account the significant breach of structure regularity and the products hydrophilic carboxylic and hydrophobic methyl groups. The considerable decrease of solubility of some obtained products in acid–water media is connected apparently to the formation of intermolecular and intramolecular crosslinks.

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