Reactions of chitosan with solid carbonyl-containing compounds under shearing deformation conditions

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Reactions of chitosan with stearic, oxalic, malonic and succinic acids and with phthalic, succinic and maleic anhydrides in the solid phase under shearing deformation conditions give the corresponding chitosan derivatives.

Chitosan is a deacetylated derivative of chitin, a natural polymer from hydrobionites. In chemical respects, this is a polysaccharide built of glucosamine residues. The natural origin of chitosan, its unique properties and the opportunity to modify it, which make it possible to expand its applications, keep attracting the attention of many researchers in various countries. Traditionally, chitosan is modified under heterogeneous conditions (in suspension) after preliminary activation of the polymer by milling, re-precipitation or swelling or by inclusion in liquid organic reagents or in aqueous acidic media.[1] We previously showed the possibility of the solid-phase modification of chitosan in the absence of solvents on exposure of the reagent mixture to a high pressure combined with shearing deformations.[2] Under these conditions, the reagents are dispersed to molecular sizes required for the chemical reactions to occur, although the reagents are solids.[3] The modification of chitosan in the solid phase offers a number of advantages in comparison with the traditional method, as it accelerates the process considerably, decreases the consumption of the reagents greatly and thus improves the ecological characteristics of the process.

In order to expand the range of solid-phase reactions of chitosan, we studied its reactions with stearic acid as an example of solid higher fatty acids and with solid two-basic carboxylic acids and their anhydrides.[†] The modification of chitosan with stearic acid and other surfactants allows one to control their hydrophilic–lipophilic balance and to enhance their surface activity and emulsifying ability,[6,7] which is an important property of chitosan and its derivatives used as structure-forming and stabilising additives for foodstuffs and cosmetic products. Modification of chitosan with bifunctional carbonyl-containing compounds should, in principle, result in its partial cross-linking and decrease its solubility in acidic aqueous media, thus expanding the potential for using chitosan as a sorbent. The products of these reactions should have

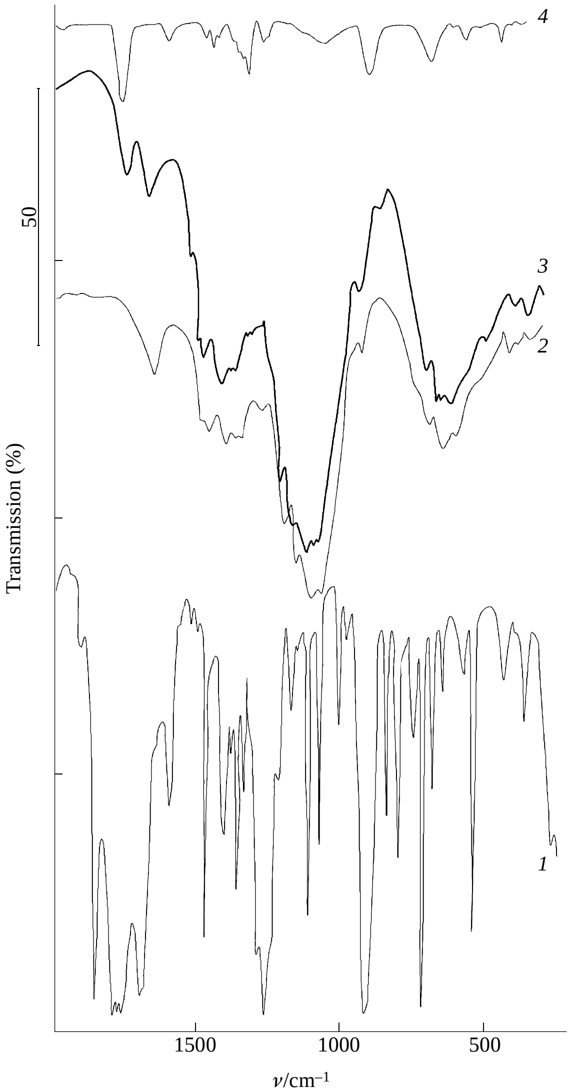


Figure 1 Regions of the IR spectra of (*1*) phthalic anhydrides and (*2*) cellulose passed through an extruder and (*3*,*4*) of the product of their solid-phase reaction at 100 °C; spectrum (*4*) was recorded against cellulose in the reference beam.

[†] Chitosan from crab shells with a degree of amination 0.90 and a molecular mass of 4.5×10^5 was used in the study. Organic acids, including stearic acid (SA, mp 70 °C), oxalic acid (OA, mp 189.5 °C), malonic acid (MA, mp 135.6 °C) and succinic acid (SU, mp 185 °C), as well as anhydrides, including phthalic anhydride (PA, mp 131.6 °C), succinic anhydride (SUA, mp 119.3–119.6 °C) and maleic anhydride (MAA, mp 54 °C), of 'chemically pure' grade were used without additional purification. The reactions were carried out as follows. A mixture of solid components was loaded in a two-screw extruder which made it possible to create a pressure and a shearing stress at various temperatures. It took the reaction mixture 3–5 min to pass along the extruder. The reaction products were purified from low-molecular-weight admixtures by extraction with ethanol in a Soxlett apparatus; the completeness of purification was monitored by UV spectrometry. The overall degree of substitution (DS) was calculated from the nitrogen : carbon (N:C) gram atom ratio; elemental analysis data were obtained on a Carlo Erba EA-1108 analyser. DS was defined as the number of reagent molecules added to a monomeric unit of the chitosan macromolecule. The type of bonds between the elementary units of chitosan and 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 degree of substitution by the ionic mechanism was calculated on the basis of the titration results. To confirm the data obtained, the content of amine nitrogen in the samples (N_{am}) was determined by the deamination of primary amino groups with nitrous acid according to Van Slyke. IR spectra were recorded in KBr pellets on a Carl Zeiss Specord M-80 spectrophotometer. The optical density (D) was calculated according to the procedure reported in ref. 4. The bands in the IR spectra were assigned according to a reported method.[5]

Table 1 Characteristics of the products of reaction of chitosan with carbonyl-containing compounds.

Reagent	Reagent: chitosan (mol/base mol)	Temperature/°C	C/N	N_{am}/N_{total}	Degree of substitution			Solubility in 0.1 M HCl (%)
					total	ionic	covalent	
Chitosan	—	—	5.56	0.90	—	—	—	100
OA	1.50	25	7.82	—	0.42	0.34	0.08	98
	1.50	50	7.85	—	0.43	0.23	0.20	94
MA	1.00	50	7.57	—	0.20	0.20	—	96
	1.50	50	8.22	—	0.40	0.36	0.04	94
	1.50	100	8.42	—	0.46	0.33	0.13	74
SU	1.50	50	7.33	—	0.10	0.05	0.05	60
	1.50	100	7.47	—	0.13	0.12	0.01	40
MAA	0.25	25	7.33	0.90	0.25	0.07	0.18	58
	0.50	50	8.30	0.81	0.50	0.36	0.14	31
SUA	0.25	50	6.93	0.89	0.16	0.08	0.08	81
	0.50	100	8.19	0.59	0.47	0.27	0.20	40
PA	0.50	100	7.96	0.89	0.21	0.07	0.14	59
	1.00	50	8.86	0.90	0.32	0.32	—	93
	1.00	100	9.95	0.53	0.45	0.23	0.22	33
SA	1.50	25	10.74	—	0.16	0.16	—	83
	1.50	50	11.29	—	0.22	0.22	—	68

complex structures, in which the substituents are linked both to hydroxyl and amino groups of the polymer by ester **1**, amide **2**, or salt **3** bonds, where R indicates C_6H_4COOH (PA), C_2H_2COOH (MAA) or C_2H_4COOH (SUA) fragments. To reveal the possibility of the formation of ester bonds under solid-phase reaction conditions, we studied the reaction of phthalic anhydride with cellulose, *i.e.* a saccharide containing, unlike chitosan, functional groups of only one type, namely, hydroxyl groups. The study of the resulting products by IR spectroscopy showed that their spectra contained weak characteristic bands corresponding to the benzene ring absorption at 1610 cm^{-1}, absorption of carbonyl groups at 1780 and 1420 cm^{-1} and absorption of aromatic esters at 1250 cm^{-1} (Figure 1, curve *2*). Elemental analysis data, in particular the content of carbon in the intact (43.98%) and modified cellulose (49.67%), indicate an increased carbon content, but the degree of O-acylation of the reagents did not exceed 10%.

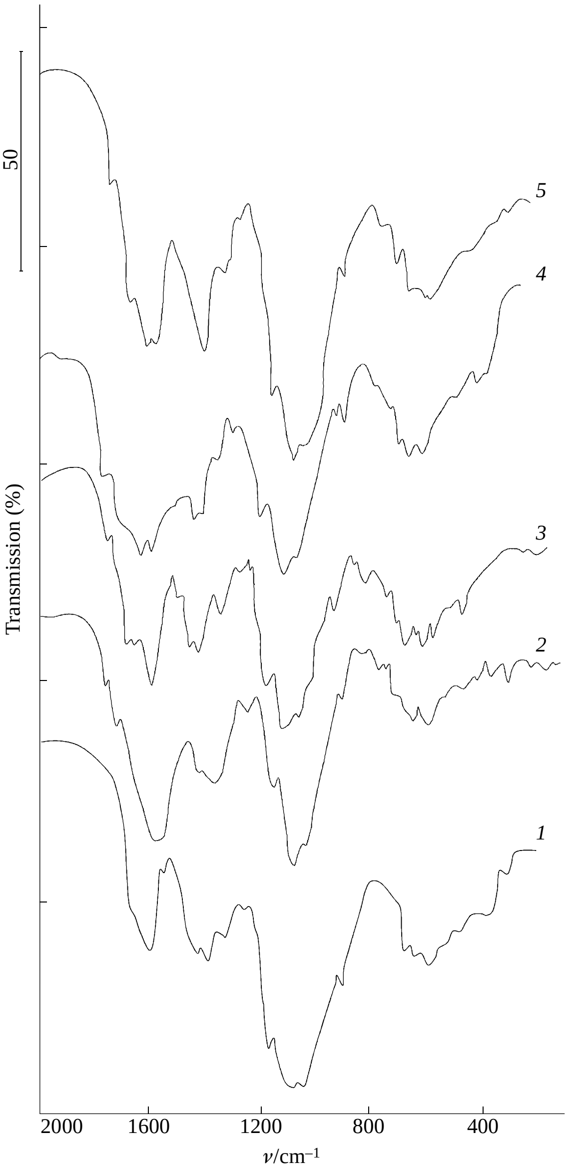
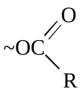
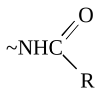


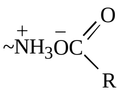
Figure 2 Regions of the IR spectra of (*1*) chitosan and products of its reactions with (*2*) malonic and (*3*) succinic acids at 100 °C and with (*4*) maleic and (*5*) phthalic anhydrides at 50 °C and 100 °C, respectively.


$\sim\mathrm{OC}(=\mathrm{O})\mathrm{R}$

1


$\sim\mathrm{NHC}(=\mathrm{O})\mathrm{R}$

2


$\sim\overset{+}{\mathrm{N}}\mathrm{H_3}\overset{-}{\mathrm{O}}\mathrm{C}(=\mathrm{O})\mathrm{R}$

3

Table 1 lists the parameters of some products of the reaction of chitosan with carboxylic acids and anhydrides under shearing deformation conditions at temperatures varied from 25 to 100 °C. In the temperature range specified and under ordinary conditions, the starting compounds do not react and do not change. It can be concluded from a comparison of the data presented in Table 1 that in the presence of a considerable excess of the reagent, the addition occurs by a mixed mechanism, preferentially through salt bonds. The number of substituents added increases as the excess of the reagent and temperature increase. The increase in temperature affects the formation of covalent bonds to the greatest extent. The amide bonds are formed only when a considerable excess of the reagent is used, as indicated by a decrease in the N_{am}/N_{total} ratio in the products of reaction of chitosan with PA and SUA obtained at 100 °C. The reaction of chitosan with MAA occurs quantitatively both at room and enhanced temperatures. Under solid-phase conditions at the same temperature and with a constant molar ratio of the components, the reactivity in the series of two-basic carboxylic acids and anhydrides changes as follows: oxalic acid > malonic acid > succinic acid (see, *e.g.*, samples 2, 4, 6); maleic anhydride > succinic anhydride > > phthalic anhydride (samples 9, 11, 12). Succinic acid, which is the weakest, reacts by no more than 10%, while succinic anhydride, as could be expected, has much higher reactivity. The reaction of chitosan with the higher fatty (stearic) acid occurs according to the ionic mechanism, and the degree of substitution of chitosan stearates obtained at enhanced temperature reaches 0.22.

Modification of chitosan with carboxylic acids and anhydrides did not make them soluble in water and organic solvents, as

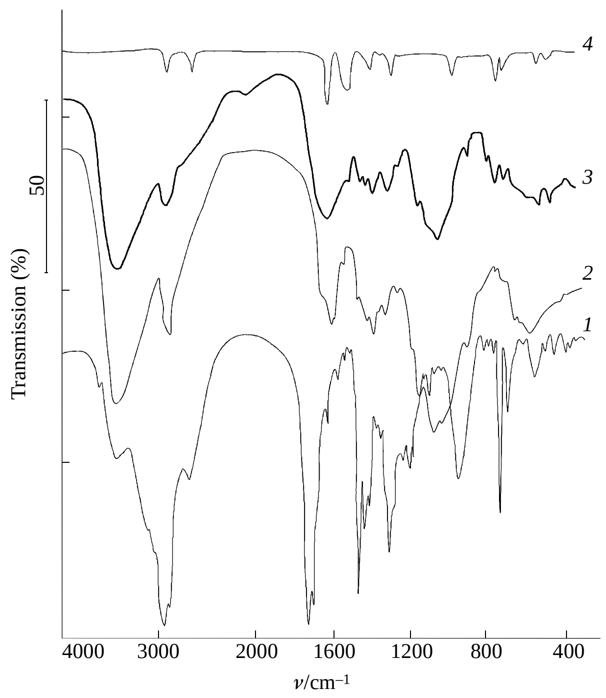


Figure 3 IR spectra of (*1*) stearic acid, (*2*) starting chitosan and (*3*,*4*) chitosan stearate; spectrum (*4*) was recorded against chitosan in the reference beam.

could be expected taking into account the fact that the structure regularity is violated considerably and hydrophilic carboxyl groups and hydrophobic methyl groups are introduced in the products. The considerable decrease in solubility of some of the products in acidic aqueous media is probably due to the formation of both intramolecular and intermolecular cross-linking.

The structure of the products obtained was also studied by IR spectroscopy. The IR spectra of chitosan modified by phthalic and other anhydrides, unlike those of cellulose derivatives, contain strong characteristic absorption bands of carboxyl groups (1740–1710 cm^{-1} and 1550 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 CH at 2950 cm^{-1} and 720–700 cm^{-1} (Figure 2, curves *2*–*4*). The IR spectrum of the reaction product of chitosan with stearic acid (Figure 3, curves *3* and *4*), as opposed to the spectrum of the initial chitosan (curve *2*), displays stronger absorption at 3000–2500 and 1700–1500 cm^{-1} and new bands, *e.g.*, 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 SA (curve *1*) and result from vibrations of alkyl groups, confirms that SA residues have been added to chitosan. On the other hand, the absence of a considerable change in absorption at 1720 cm^{-1} (non-ionised COOH groups) and the presence of a wide complex band at 1700–1500 cm^{-1} in spectrum *3*, which is resolved in spectrum *4* into a number of bands at 1640, 1540 and 1520 cm^{-1} resulting from vibrations of ionised carboxyl and amino groups, may indicate that addition involves the carboxyl groups of the acid and the amino groups of chitosan and results in the formation of salt-type bonds between the polymer and stearic acid.

Thus, the possibility of solid-phase modification of chitosan with carboxylic acids and their anhydrides under combined pressure and shearing deformations, as demonstrated in this work, confirms once again the potential of this method for the further chemical modification of chitosan.

The derivatives obtained from chitosan and dicarboxylic acids or their anhydrides have a polyampholyte structure and can be used as selective sorbents and carriers for acetic acids, enzymes and other biologically active compounds. The soluble fractions of chitosan hydrophobised with stearic acid can find use as emulsifiers and stabilisers for foams and emulsions.

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