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THERMAL PROPERTIES OF CHITIN AMMONOPHOSPHATES AND THEIR COMPLEXES WITH METHANOL

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The thermal properties of chitin ammonosphosphate complexes with methanol are discussed. The endothermic effect of chitin ammonophosphate decomposition is dependent on the substitution degree. The chitin ammonophosphates have a lower ability to form complexes with methanol than chitin itself. The bonding energy of methanol with chitin ammonophosphates is dependent on the substitution degree of the ammonophosphate group. As the substitution degree increases, the quantity of methanol bonded to the chitin ammonophosphate decreases, as does the bonding energy of the methanol; this is manifested in a lower endothermic effect and a lower temperature of the maximum of this effect.

Chitin is widely distributed in living organisms, such as invertebrates, fungi, insects, molds and yeasts [1]. This mucopolysaccharide consists of chains of 2-acetamide-2-deoxy-D-glucoses linked by β-1,4 bonds. The N-acetyl-D-glucosoamine units of chitin have two reactive hydroxy groups, at the C—3 and C—6 positions. Although chitin is structurally similar to cellulose, it has poor solubility and is more resistant toward chemical reagents because of its strong micelle structure, due to inter- and intramolecular hydrogen-bonds between hydroxy and acetamide groups. The poor solubility of chitin in common solvents has been a major drawback to its utilization. However, the abundance of chitin in seafood waste, and the opportunity for promoting it as a new marine source while alleviating a pollution problem, have led to the burgeoning study of this unusual mucopolysaccharide in many research centers. Chitin has an unusual combination of properties, including toughness, bioactivity and biodegradability, which makes it an attractive specialty material. Derivatives of chitin have particularly interesting physical and chemical properties. Acylated chitins have been examined as materials for blood contact surfaces [2]. Sakaguschi and co-workers [3] have investigated the adsorption of heavy metal ions by chitin and chitosan phosphates. Chitin phosphate can be effective as a wound-healing accelerator too [4]. Austin [5] discovered that lower alcohols and carbonyl compounds from complexes with chitin. The chitin complexes of these compounds have a number of unusual properties, which make them useful in a variety of applications. They have a voluminous physical form, which allows them to be easily handled and filtered in the preparation of highly-purified chitin for pharmaceutical and other purposes. Furthermore, they are more readily dissolved in chitin solvents than natural chitin, and hence are useful in preparing chitin solutions for the fabrication of chitin in the form of films, fibers or other shaped articles; they may also contribute a plasticizing effect that enhances the cold drawing of chitin fibers and films. The chitin-methanol complex is stable at room temperature if kept in a closed vessel in the presence of a slight excess of methanol [5]. However, in the open, it loses methanol gradually.

Our results described below show how to obtain a chitin-methanol complex stable at room temperature. This paper is concerned with the thermal properties of chitin ammonophosphates and their complexes with methanol.

Experimental

Chitin was prepared from Antarctic krill by the procedure described in the literature [6]. Before use, the chitin was powdered to 50–70 mesh. Urea, phosphoric acid and methanol were purchased from BDH Chemicals LTD., Poole, England.

Experiments were carried out using chitin and chitin ammonophosphates as complexing agents for methanol. Chitin was phosphorylated by the urea-phosphate method [7], in toluene as reaction medium. The excess of the urea-phosphate and low molecular weight products of the reaction were removed from the phosphorylated chitin by washing with an aqueous solution of methanol. Before drying of the chitin ammonophosphate at room temperature, samples were washed with dry methanol several times. Samples of chitin ammonophosphate complexes with methanol, prepared in the above manner, were used for thermal analysis. Thermal investigations were made with an OD–102 (MOM, Hungary) derivatograph, using 100 mg samples of the investigated materials, in an atmosphere of air, in the temperature range 20–500°, at a heating rate of 10 deg/min. X-ray diffraction patterns were obtained with a Rigaku–Denki GF–5 diffractometer by the powder method, with the use of Ni-filtered CuK_α radiation.

Results and discussion

Typical DTA curves for chitin and chitin ammonophosphates with different degrees of substitution are shown in Fig. 1. Curve A shows two endothermic effects: the first, with maximum at 80°, characterizes the thermal decomposition of the chitin-methanol complex, and the second, with maximum at 317°, is a result of the thermal decomposition of chitin. Changes in the range 20–100° confirm the previous observation [4, 5] that the chitin complex with methanol can be unstable. The weight lose in the first endothermic effect range is about 10%. This proves that the sample is a methanol complex of chitin. By calculation, 0.65 mol methanol is bonded to 1.0 mol chitin. This complex indicated considerable stability, for the maximum rate of its decomposition is at 80°, i.e. about 15.3° higher than the boiling point of methanol. The decomposition of this complex gives an endothermic effect with $\Delta T = 19.2°$ (Table 1). However, the chitin ammonophosphates have a lower ability to form complexes with methanol than that of chitin. The bonding energy of methanol with chitin ammonophosphates is dependent on the degree of

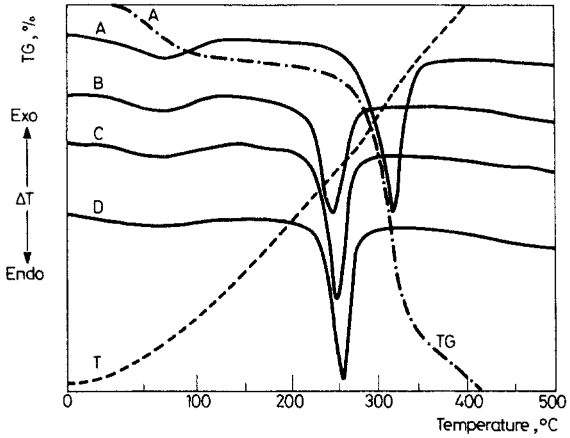

Fig. 1 TG and DTA curves of: A-chitin; and DTA curve of B, C, D-chitin ammonophosphates with different substituted degree

Table 1 Thermal properties of cithin ammonophosphate with different substitution degree

Sample	Polymer type	Degree substitution (DS)	Temp. of endothermic effect, °C		Δt of endothermic peak, °C	
			Peak I	Peak II	Peak I	Peak II
A	Chitin	—	80	317	19.2	174.0
B	Chitin ammonophosphate	0.6	80	242	19.1	122.7
C	Chitin ammonophosphate	0.9	71	245	10.9	163.6
D	Chitin ammonophosphate	1.0	62	251	8.2	169.1

substitution of the ammonophosphate group. If the substitution degree increases, then the quantity of methanol bonded to the chitin ammonophosphate decreases, as does the bonding energy of the methanol; this is manifested in a lower endothermic effect and a lower temperature of the maximum of this effect. Thus, the endothermic effect for chitin ammonosphosphate with DS = 1.0 lies at 62°, with $\Delta T = 8.2°$. Hence, the bonding energy of methanol with this ammonophosphate is much lower than the bonding energy in the chitin-methanol complex.

As shown by the curves in Fig. 1 and the data in Table 1, chitin ammonophosphates have lower thermal resistances than unmodified chitin. The maximum thermal decomposition rate for the above chitin ammonophosphate derivatives lies in the temperature range 240–250°, whereas for chitin it is much higher, at 317°. The endothermic effect of chitin ammonophosphate decomposition is dependent on the substitution degree, and from $\Delta T = 122.7$ for DS = 0.6 increases to $\Delta T = 169.1°$ for DS = 1.0.

Figure 2 shows the curve for chitin ammonophosphate with substitution degree 0.6, which has a similar ability to form a complex with methanol as that of chitin. To

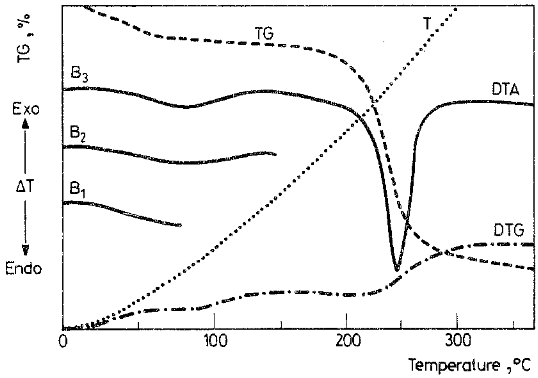

Fig. 2 Thermal curves of: B_1, B_2, B_3-chitin ammonophosphate with substituted degree equal 0.6

Table 2 Composition of chitin ammonophosphate after heating to different final temperature

Sample	Heating time, min.	Final temp., °C	Content of elements, % C	H	N	P	Crystal. index %
A	—	—	45.30	6.60	6.60	0.28	—
B	—	—	41.77	6.77	6.43	7.49	84
B_1	20	80	32.95	6.51	7.35	8.66	82
B_2	40	150	30.52	6.24	7.79	10.57	81
B_3	70	370	22.23	4.19	8.13	16.55	0.0

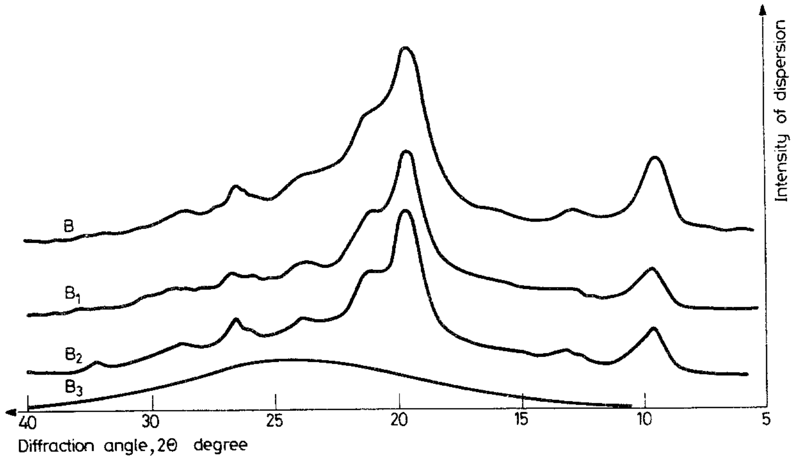

Fig. 3 X-ray diffraction curves of chitin ammonophosphate with substituted degree equal 0.6; B-used for experiments, B_1-heated to 80 °C, B_2-heated to 150 °C, B_3-heated to 370 °C

elucidate the chemical composition differences during heating of this chitin ammonophosphate, thermal investigations were carried out with samples heated to different temperatures. The first sample was heated for 20 min to 80° (curve B1), the next one for 40 min to 150° (curve B2), and the last one for 70 min to 370° (curve B3). All heated samples had different chemical compositions (Table 2) in comparison with the chitin and chitin ammonophosphate used for thermal analysis. The high decrease in the carbon content of the sample heated to 80°, with increases in the phosphorus and nitrogen contents, can be explained only by hydrolysis of a covalent bond in the amido group of the chitin ammonophosphate. At the same time, the methanol complex of chitin ammonophosphate is decomposed. This conclusion was confirmed by X-ray investigation (Fig. 3). On decomposition of the chitin ammonophosphate complex with methanol liberation, there was a decrease in the degree of crystallinity for all heated samples (Table 2).

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Zusammenfassung — Die thermischen Eigenschaften von Chitinammoniumphosphat-Komplexen mit Methanol werden diskutiert. Der endotherme Effekt der Zersetzung von Chitin-ammoniumphosphat hängt vom Substitutionsgrad ab. Chitin-ammoniumphosphate haben eine geringere Neigung zur Ausbildung von Komplexen mit Methanol als Chitin selbst. Die Bindungsenergie der Chitin-ammoniumphosphat-Komplexe mit Methanol hängt vom Substitutionsgrad der Ammoniumphosphatgruppe ab. Mit steigendem Substitutionsgrad wird sowohl die Menge des an Chitin-ammoniumphosphat gebundenen Methanols als auch die Bindungsenergie des Methanols kleiner; dies kommt in einem verminderten thermischen Effekt und einer tieferen Temperatur für das Maximum dieses Effektes zum Ausdruck.

Резюме — Обсуждены термические свойства комплексов хитин аммонофосфата с метанолом. Эндотермический эффект разложения хитин аммонофосфата зависит от степени замещения. Хитин аммонофосфаты обладают меньшей способностью к образованию комплексов с метанолом по сравнению с хитином. Энергия связи метанола с хитин аммонофосфатами зависит от степени замещения аммонофосфатной группы. С увеличением степени замещения уменьшается количество метанола, связываемого с хитин аммонофосфатом, а также их энергия связи. Это проявляется в понижении эндотермического эффекта и понижении температурного максимума этого эффекта.