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Complex study on chitosan degradability

Summary — Results of photo- and thermodegradation of chitosan of different degrees of deacetylation (*DD*) were discussed. On the basis of the results of thermodegradation under isothermal and dynamic conditions thermal stability of chitosan films, also photochemically modified samples (UV irradiated for 1 h), was estimated. Investigations under isothermal conditions were carried out in the air atmosphere and cover the temperature range from 100°C to 200°C. Basing on the results of weight loss it was found that most susceptible to degradation was the sample of the higher *DD*; with an increase of temperature the observed changes were more distinct. Both during thermo- and photodegradation a decrease of *DD* of chitosan was observed. Modification of chitosan films by UV irradiation decreases the characteristic parameters of thermodestruction.
Key words: chitosan, deacetylation degree, thermal degradation, photochemical modification.

## VARIOUS PROCESSES OF CHITOSAN DEGRADATION — GENERAL CHARACTERISTIC

Chitosan is a natural polymer prepared from chitin by deacetylation. Physical and chemical properties of chitosan depend strongly on the molecular weight and the deacetylation degree (*DD*) [1—3]. Chitosan forms transparent, water-insoluble films which are used for packaging, preparation of membranes and biomedical materials [4, 5].

It is worth to mention that chitosan, like other biopolymers, is very sensitive to various types of degradation such as oxidative, hydrolytic, thermo-, photo- and ultrasonic degradation [6, 7]. Practical applications of pure chitosan, as well as in blends and composites with other polymers, require its exposure to heat, light, water and microorganisms with a possible degradation of the macromolecular chain. The aim of our previous [6] and present studies was to compare the photo-, thermo-, bio- and hydrolytic degradation of chitosan samples of various *DD* [8-17].

On the basis of studies on the viscosity of diluted solutions, weight loss and FTIR spectra, it was found [6, 10] that photodegradation of chitosan characterized with a higher *DD* was faster. Results of the spectroscopic studies which provide information on structural changes during the degradation process reveal significant changes in the region of deforming vibrations of -C-O-C- groups in the band of 1150-1040 cm^{-1} during both photolysis and thermal degradation. A decrease of absorbance in this wavelength range is related to scission of the chitosan chain into smaller fragments. In the case of photochemical degradation this is confirmed by the measurements of viscosity of diluted chitosan solutions. The calculated number of chain scissions (*S*) increase with the time of degradation. The rate constant of photolysis (*k*) increases with chitosan *DD*. Scission of chitosan macromolecules causes formation of free radicals that initiate oxidation. As a result of this reaction a carbonyl group appears in the band at the wave number 1730 cm^{-1}, whose increasing intensity is observed during photo- and thermodegradation. Additionally, an increased absorbance is recorded for the band of amide group at 1655 cm^{-1} (C = O vibrations) and 1560 cm^{-1} (-NH-) with a simultaneous decrease of peak intensity in the band corresponding to amine group (1590 cm^{-1}), which points to chitosan acetylation. Hence, thermo- and photodegradation results first of all in scission of the main chain and destruction of an unstable amine group. An increase of chitosan acetylation degree and macromolecules cross-linking during thermal destruction is also observed [6, 10, 18].

During the hydrolysis and biodegradation, which take place under the influence of water and microorganisms [12, 18, 19], the rate of degradation processes decreases with an increase of *DD*. This is most probably a result of a higher degree of macromolecules packing and, consequently, decreased water absorption. This in-
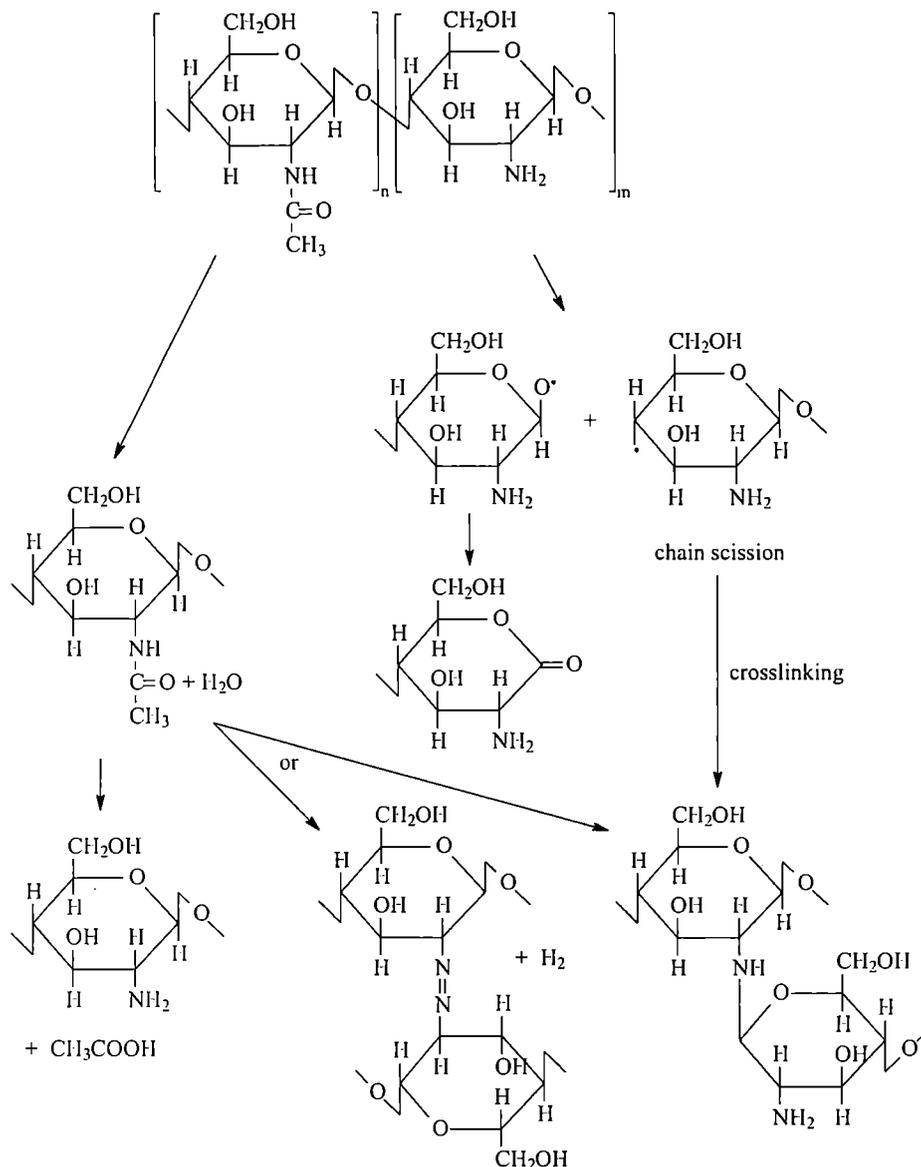
Scheme A. Possible mechanisms of transformations in chitosan macromolecules induced by degradation

fluence on the access of microorganisms to inner regions of the film — enzymes are transported mainly with water.

FTIR spectra of chitosan of various *DD* values show no clear structural changes which take place during hydrolytic degradation. Also a spectroscopic analysis of chitosan films subjected to biodegradation shows that extent of structural changes of the polymer macromolecules is smaller than that in the case of photodegradation. A decrease of absorbance in the region of groups characteristic for chitosan depends also on the its *DD*. The strongest changes in the absorbance region of amine and amide groups as well as -C-O-C- are observed for chitosan of the lowest *DD* equal 59% [6].

Results of the viscosity measurements (in diluted solutions) of chitosan subjected to hydrolytic degradation indicate some initial increase of the viscosity. It is most probably a result of cross-linking by hydrogen bonds in

water excess. Further on a decrease of viscosity is observed as a result of slow degradation process.

Possible mechanisms of transformations of chitosan macromolecules [6, 10] were proposed (scheme A) on the basis of complex studies of chitosan degradation.

Results presented in this work give a comparison of thermal degradation of chitosan carried out in isothermal and dynamic conditions, also for the samples which were photochemically modified. For this purpose thermogravimetric and FTIR spectroscopic investigations were carried out.

EXPERIMENTAL

Materials

Chitosan [poly(2-aminoglucose-*co*-2-acetyloglu-coseamine)] samples of various *DD* values (from 59 to

86%) and viscosity—average molecular weights (M_v = 1.05 · 10^5 to 7.0 · 10^5) were prepared by deacetylation of krill chitin in the Sea Fishery Institute in Gdynia. Chitosan films were obtained by the following method: 1% chitosan solution in 1% acetic acid was filtered in a centrifuge, non-dissolved fragments of chitosan were removed and then the solution was poured onto levelled glass plates at the temperature ca. 45°C. The chitosan acetate films were extracted in ammonia water and methanol to remove thoroughly acetate residues and to obtain water-insoluble chitosan films.

Methods

Thermodegradation of chitosan films was carried out either isothermally in the air atmosphere at temperatures from 100 to 200°C or by dynamic measurements of weight loss. In dynamic thermogravimetric investigations a Mettler thermobalance was used. The measurements were conducted in the temperature range from 100 to 450°C at a constant heating rate β = 15°C/min. Chitosan films were also modified photochemically by UV irradiation emitted by a low pressure mercury lamp at λ = 254 nm (90% of light) with light intensity I = 700 Lux for 1 h.

To observe structural changes that occurred as a result of degradation, the FTIR analysis was used. It was based on the identification of the functional groups present in chitosan macromolecules, which are given below with the corresponding absorption bands (in cm^{-1}):

1. 3450 — OH group
2. 3360 — NH group stretching vibration
3. 2920, 2880, 1430, 1320 — symmetric or asymmetric CH_2 stretching vibration attributed to pyranose ring
4. 1730 — carbonyl group vibration
5. 1655 — C=O in amide group [amide I band]
6. 1560 — NH- bending vibration in amide group
7. 1590 — NH_2 in amine group
8. 1380 — CH_3 in amide group
9. 1150—1040 — C-O-C- in glycosidic linkage.

All spectra were recorded at ambient temperature at the resolution 4 cm^{-1} and 16-times scanning using Genesis II spectrophotometer (Mattson). Thickness of the films used in the FTIR studies was about 10 μm.

RESULTS AND DISCUSSION

Isothermal thermodegradation studies

Weight loss measurements

Weight loss results of chitosan show (Fig. 1) that the process of the polymer thermodegradation depends on its DD value. The most susceptible to thermal degradation appears to be the sample of the highest DD (unstable amine group). With increasing temperature from 100°C (Fig.1a) to 200°C (Fig.1b) more intensive changes of chitosan relative weight are observed.
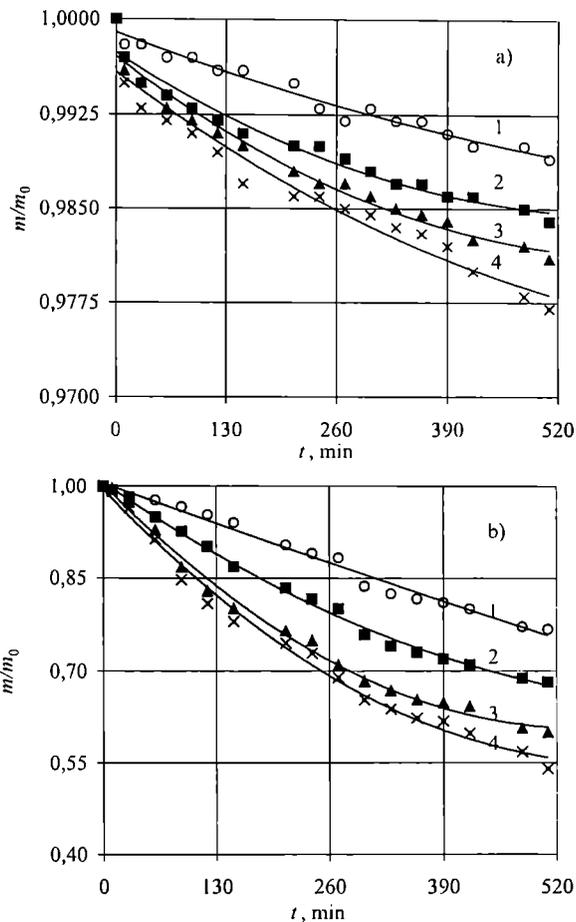

Fig. 1. Relative weight loss versus time for chitosan samples of various deacetylation degrees (DD): 1 — 59%, 2 — 67%, 3 — 78%, 4 — 86% during isothermal thermodegradation at a) 100°C and b) 200°C

FTIR spectra

Interesting results were obtained when carrying out a spectroscopic FTIR analysis of chitosan films subjected to thermodegradation at the temperature 100°C, 130°C, 160°C and 200°C. Fragments of FTIR spectra in Fig. 2 obtained for chitosan of DD = 78% after various thermodegradation times at the temperature 200°C reveal changes of absorbance in the bands corresponding to selected functional groups. This enables an analysis of structural changes that take place in chitosan during thermodegradation.

A significant decrease of peak intensity is observed at 1150—1040 cm^{-1} corresponding to deforming vibrations of -C-O-C- groups (Fig. 2c), which points to scission of the chitosan chain. The decrease of absorbance in the band of hydroxyl groups OH at 3450 cm^{-1} (water release) and in the bands corresponding to symmetric and non-symmetric vibrations of methylene groups CH_2 at 2920 cm^{-1} and 2880 cm^{-1} is also significant (Fig. 2a). In absorption bands at the wave number 1320 cm^{-1} and 1420 cm^{-1} the intensity drop is related to changes that occur within the methylene groups (Fig. 2b). Like in the case of photodegradation, there is a significant decrease of absor-
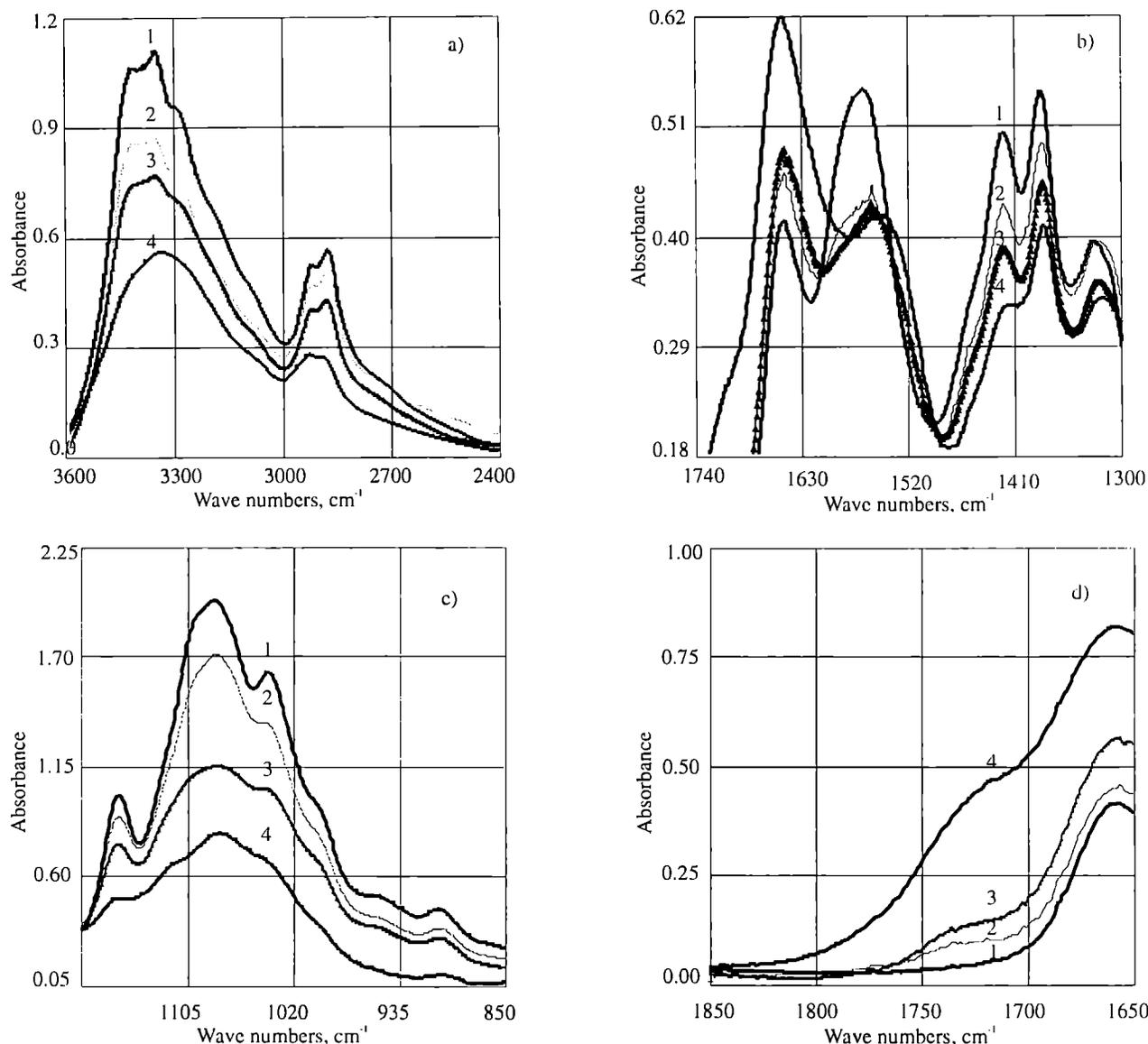
Fig. 2. a—d. FTIR spectra at various band absorption obtained for chitosan of DD = 78% after various times of thermodegradation at 200°C; time: 1 — 0h, 2 — 1h, 3 — 2h, 4 — 9h

bance at 3360 cm^{-1} related to scission of hydrogen bonds present between N-H groups of adjacent molecules. An increase of absorbance in the band of amide group is also recorded at 1655 cm^{-1} (C = O) and 1560 cm^{-1} (-NH-) with a simultaneous decrease of peak intensity in the band corresponding to the amine group at 1590 cm^{-1} (Fig. 2b). Cross-linking of macromolecules is followed by the destruction of amine group (see scheme A).

In Fig. 3 the decrease of DD due to chitosan degradation during thermal degradation at the temperature 200°C was compared with changes observed during of photochemical degradation.

DD was calculated in accordance to the following equation:

$$DD = \left(1 - \frac{A_{1655}}{A_{3450}}\right) \cdot \frac{1}{1.33} \cdot 100\% \qquad (1)$$

where: A_{1655} — C=O absorbance in amide group band, A_{3450} — absorbance in OH group band.

So, the changes of DD caused by the thermal degradation are proceeding much more fast.

In the band of carbonyl groups with the wave number 1730 cm^{-1}, as in the process of photochemical oxidation, an increase of absorbance during thermodegradation in air atmosphere is observed (Fig. 2d).

Changes in absorbance ΔA in this region caused by the appearance of carbonyl group in the chitosan molecule being a result of oxidation are shown in Fig. 4. So, the increase of DD values leads to limitation of ΔA in carbonyl band.

The largest weight loss (Fig. 1) and the smallest changes within functional groups (Fig. 5) are reported for the sample of the higher DD. During thermodegradation at the temperature 200°C the amine group is destroyed, which in the connection with remarkable mobility of the chain may lead to cross-linking of chitosan macromolecules (an increase of gel fraction). Chitosan of
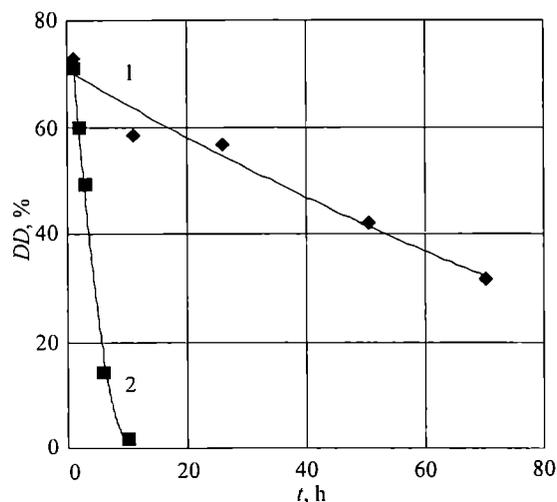
Fig. 3. Changes of DD of chitosan during its photo- (1) and thermal degradation at the temperature 200°C (2)
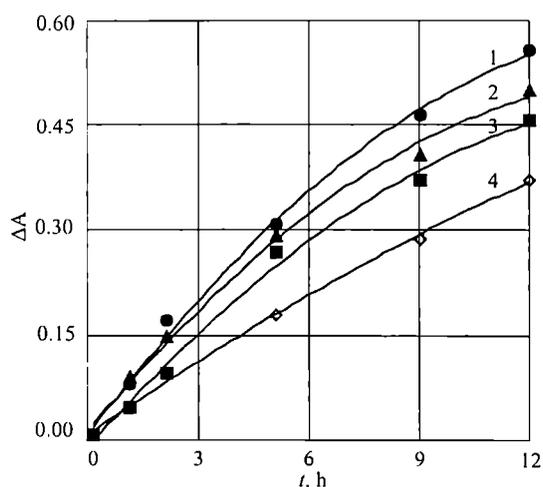

Fig. 4. Changes of absorbance ΔA of chitosan carbonyl band versus time at T = 200°C, for samples of various DD values; DD: 1 — 59%, 2 — 67%, 3 — 78%, 4 — 86%

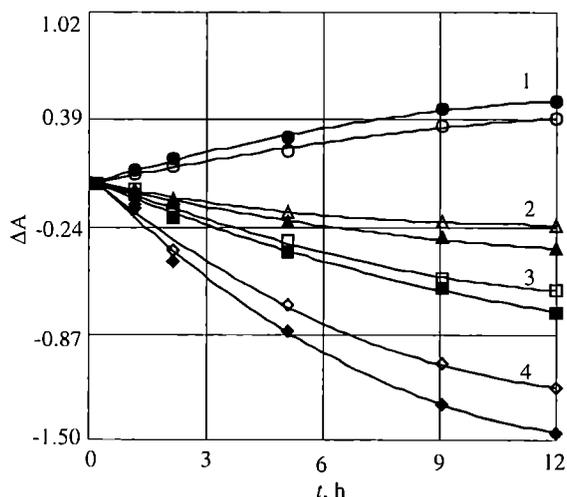*Fig. 5. Changes of absorbance ΔA of some chitosan bands versus time at T = 200°C; bands: 1 — 3450, 2 — 2920, 3 — 1655, 4 — 1070 cm⁻¹ (DD values of chitosan samples: 86% — open points and 59% — full points)*

higher *DD* values is subjected to the cross-linking to a larger extent, its structure becomes less flexible and more stable and the resulting structural changes become weaker.

Dynamic thermodegradation studies

Beside the isothermal studies an attempt was made to estimate stability of the chitosan chain by carrying out dynamic thermogravimetric measurements. Thermograms obtained were used for the analysis of chitosan degradation kinetics. Important elements of the kinetic model of degradation process include activation energy and reaction order. Figure 6 illustrates the dependence of
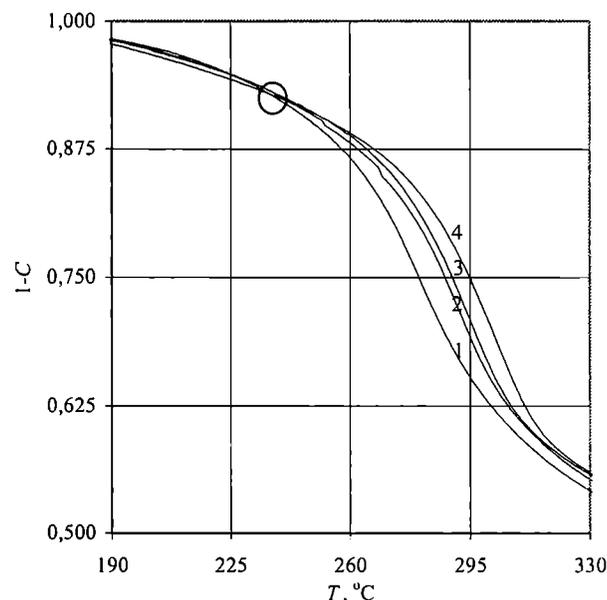

Fig. 6. TG curves obtained for chitosan of various DD (heating rate = 15°C/min); DD: 1 — 59%, 2 — 67%, 3 — 78%, 4 — 86% (C — conversion degree)

chitosan films weight loss during heating (chitosan of various *DD* values) on temperature (TG curves). At the beginning of the process (to 230°C) more susceptible to degradation seem to be the films of higher *DD* (a similar relationship was observed previously when studying the degradation of chitosan in isothermal conditions at the temperature from 100 to 200°C). Thermal degradation leads to cross-linking of the chitosan structure, in particular of a high *DD*, by destroying the amine group. Then, the cross-linked system becomes more stable to further degradation. At the next stage of the process of thermomodegradation (above 230°C) the samples of higher initial *DD* seem to be more stable.

Analysis of the TG (Fig. 6) and DTG curves (Fig. 7) allows us to specify the characteristic parameters of thermomodegradation, namely:
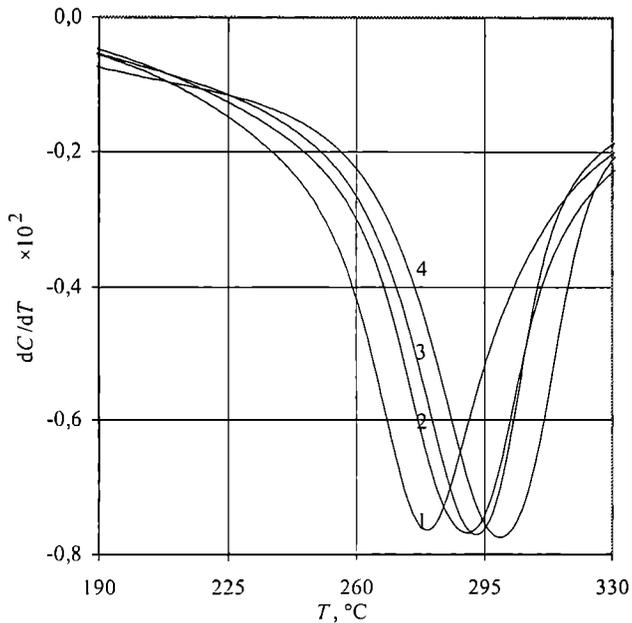
Fig. 7. DTG curves obtained for chitosan of various DD (heating rate = 15°C/min); DD and C as on Fig 6

— temperature of the degradation onset T_{pr} on the basis of TG curve deviation from the initial run for zero value of conversion degree C_0;

— temperature of the maximum degradation rate T_{mr} (minimum of DTG curve);

— temperature of 50% degradation T_{50}.

Values of these parameters for chitosan films of different *DD* are given in Table 1.

Modification of chitosan films by preliminary UV irradiation decreases the characteristic parameters of thermodestruction (Table 1 and Fig. 8).

T a b l e 1. Thermodegradation parameters determined for photochemically modified (thermo + UV) and nonmodified (thermo) samples of chitosan films of different *DD* values

Parameter	T_{pr}, °C[*]		T_{mr}, °C[*]		T_{50}, °C[*]	
DD, %	Thermo	Thermo + UV	Thermo	Thermo + UV	Thermo	Thermo + UV
59	103	101	279	278	353	337
67	109	102	289	284	360	345
78	111	102	293	287	362	346
86	116	104	299	289	363	339

[*] The meanings of symbols — see text.

The reaction order (*n*) and activation energy (E_a) of thermodegradation were calculated according to Freeman-Carrol method, using the following equation [20]:

$$\frac{\Delta \log \beta \frac{dC}{dT}}{\Delta \log(1-C)} = n - \frac{E_a}{2.3R} \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \log(1-C)} \qquad (2)$$

where: $C = (m_0 - m)/m_0$ — conversion degree; m_0 and m — initial and final mass of the sample, respectively; β — heating rate.
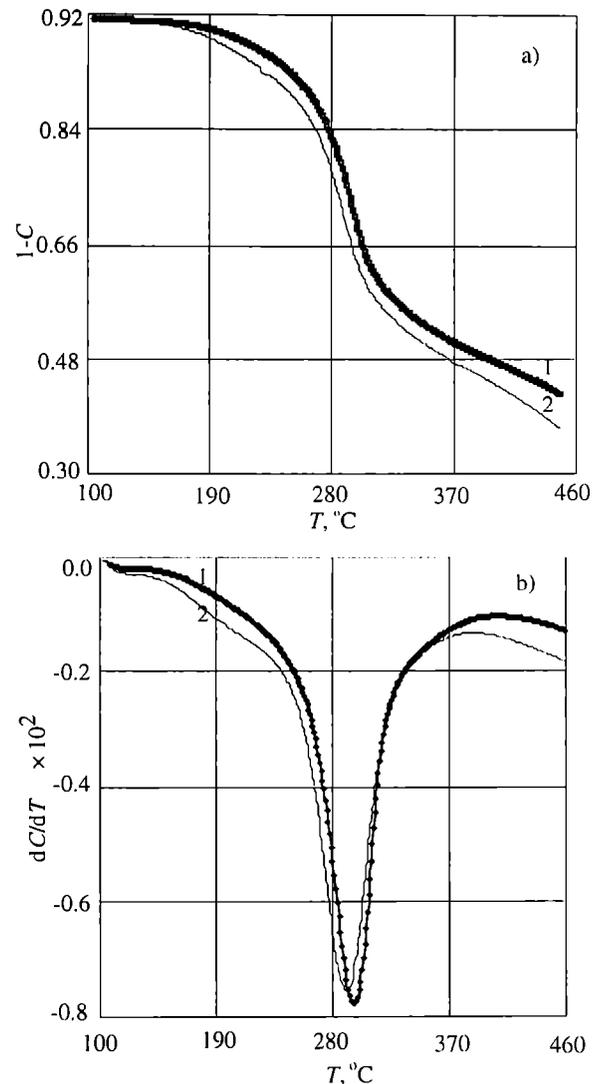

Fig. 8. Comparison of curves: TG (a) and DTG (b) obtained for original (1) and photochemically modified chitosan (2) of DD = 78% (modification time 1 h); C — conversion degree
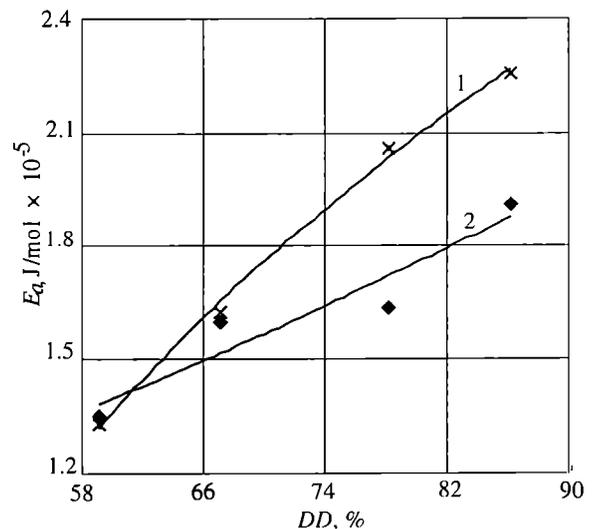

Fig. 9. Dependence of activation energy (E_a) of thermodegradation on chitosan DD values for original (1) and photochemically modified samples (2)
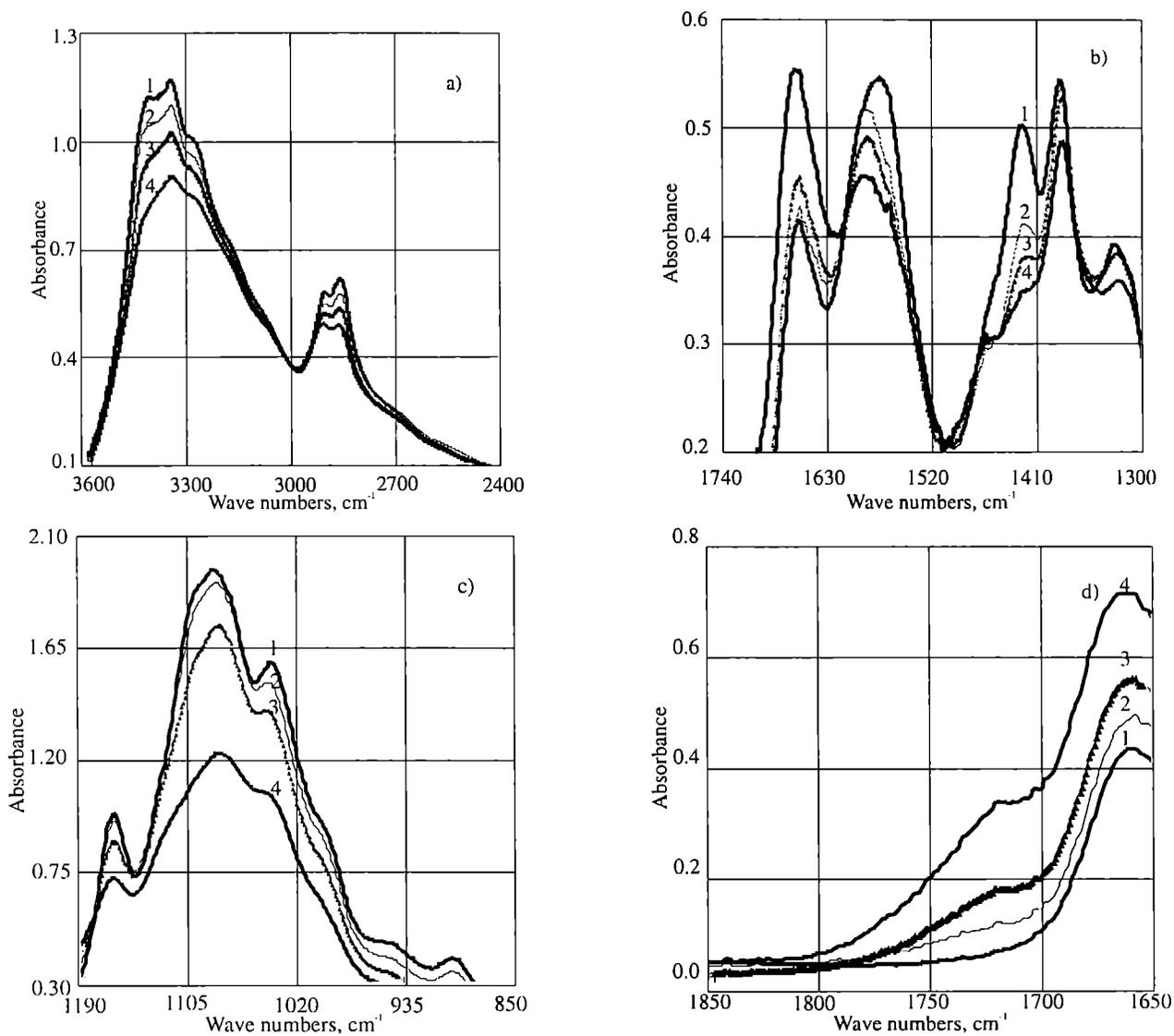
Fig. 10. FTIR spectra obtained for chitosan of DD = 78% after various times of photodegradation (UV radiation); time: 1 — 0 h, 2 — 10 h, 3 — 25 h, 4 — 75 h
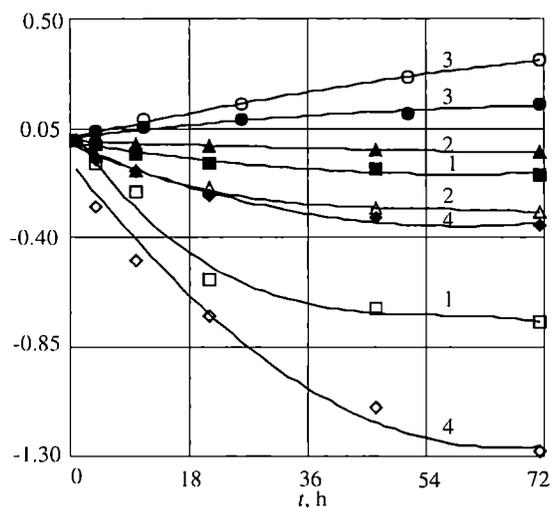

Fig. 11. Changes of absorbance ΔA of some chitosan bands versus time of UV degradation; bands: 1 — 3450, 2 — 2920, 3 — 1655, 4 — 1070 cm⁻¹ (DD values of chitosan samples: 86% — open points, 59% — full points)
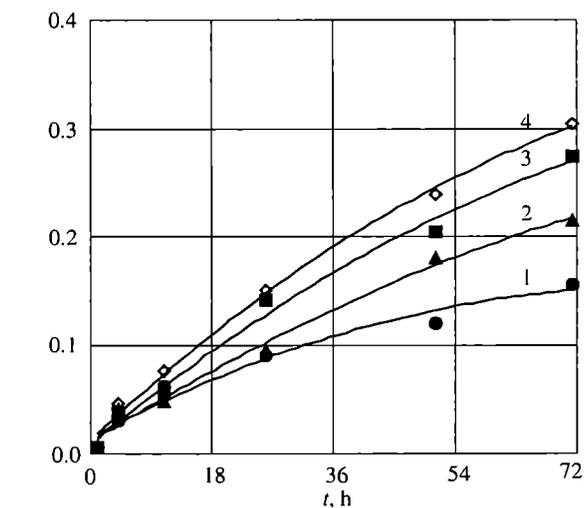
Fig. 12. Changes of absorbance ΔA of chitosan carbonyl band versus time of UV degradation for samples of various DD values; DD: 1 — 59%, 2 — 67%, 3 — 78%, 4 — 86%

From the plot (which should be a straight line) of the left-hand side of equation 2 on $\Delta(1/T)/\Delta\log(1 - C)$ the activation energy E_a of thermodegradation and reaction order n can be obtained from the slope and value of ordinate, respectively.

Figure 9 illustrates dependence of the activation energy of thermodegradation on chitosan DD values. The activation energy of the samples UV modified is much lower. Reaction order (n) was equal approximately to 2.

FTIR studies of the photochemical stability of chitosan

To determine changes caused by a photochemical modification of chitosan FTIR measurements were carried out.

The pertinent FTIR spectra are shown in Fig. 10 (obtained for chitosan of $DD = 78\%$). With increasing time of photodegradation the more distinct changes are observed within the characteristic functional groups.

Figure 11 shows changes of absorbance of characteristic groups in chitosan macromolecules found for two samples of various DD values after various periods of photodegradation.

Changes of the absorbance in the band of carbonyl group (at the wave number 1730 cm^{-1}) depending on the photodegradation time, observed for the samples, are shown in Fig. 12.

More distinct changes in the polymer structure are observed in the case of sample of higher DD, both as the results of chain scission (rate constant of chain scission increases with an increase of DD) and of destruction of less stable amine group.

CONCLUSIONS

On the basis of presented in this paper results of weight loss and FTIR spectra investigations it was found that there was a definite effect of the deacetylation degree of chitosan on the rate of degradation processes which took place under the influence of ultraviolet light or at high temperatures.

In the case of photodegradation, the chitosan of the highest DD value is degraded the fastest rate which is due to the largest contribution of chromophore amine groups that absorb UV radiation. Results of spectroscopic studies show that both photodegradation and thermal degradation lead first of all to scission of the main chain and destruction of the unstable amine groups. A decrease of chitosan DD is observed in the process of thermodestruction; cross-linking of chitosan macromolecules takes place which improves thermal stability of the polymer in the next stage. At the temperature range up to 230°C thermodegradation rate is higher for chitosan samples of larger DD (higher weight loss in dynamic and isothermal measurements). At the tem-

perature range at a maximum rate of weight loss, the chitosan sample of higher DD is more stable (also the activation energy of the reaction is higher). Modification of the chitosan films using UV irradiation decreases characteristic parameters of the process of thermodestruction: T_{pr}, T_{mr}, T_{50} and activation energy E_a of thermodegradation of chitosan. Thermodegradation of chitosan in the air atmosphere causes oxidation of the sample (absorbance of carbonyl groups band increases). The higher DD the lower is the rate of oxidation. The higher weight loss of chitosan sample of higher DD at 200°C the smaller the change of the sample structure observed in FTIR studies.

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