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THERMOGRAVIMETRIC ANALYSIS OF CHITINS OF DIFFERENT ORIGIN

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In this work the thermal properties of chitins of different origin were compared using a thermogravimetric technique. The α_s–α_r method, which makes possible a comparison of the thermal resistances of materials with similar thermostability, was used. The basic range of thermal conversion was determined. In this range, the thermal resistance depends on the chitin origin. The value of activation energy was calculated. No influence on the average molecular mass, crystallinity and the degree of acetylation on the thermal resistance was observed. On the other hand, it was found that the thermal stability depends on the size and perfection of crystallites as well as on the crystalline form of the chitin.

Keywords: *chitin, TG analysis, X-ray diffraction*

Introduction

Chitin is one of the most abundant and easily obtained structural biopolymer. It is a linear polysaccharide consisting of β-(1-4)-linked 2-acetamido-2-deoxy-*D*-glucopyranose units. Chitin is found as a reinforcing element in the cuticles of arthropods, cell walls of most fungi, shells of crustaceans such as crabs and shrimps, exoskeletons of krill, cuticles of insects as well as a specific component of many other living organisms.

In its native state chitin is crystalline. Chitin has been reported to occur in different crystalline forms. α-Chitin, which is the most abundant, is also thermodynamically the most stable. It occurs in the cuticles of insects, crabs and shrimps, in the exoskeletons of krill, as well as in a number of other systems. The α-form has a two-chain unit cell with a $P2_12_12_1$ space group and consequently an antiparallel arrangement of the adjacent chains [1]. β-Chitin is rather rare. It occurs for example in the extracellular spines of the euryhaline diatoms. In the β-chitin crystals, the polymer chains are arranged forming a monoclinic $P2_1$ space group with the chitin chain axis as the unique monoclinic axis. In this allomorph, there is only one chitin chain per unit cell. Therefore the β-chitin contains a parallel chain arrangement [2]. Hence, the parallelism of polymer chains within the β-chitin microfibrils is the result of unidirectional biosynthesis and crystallization [3, 4].

Due to their special chemical and biological properties and widespread availability, chitins and their derivatives have extensive applications in many industrial, medical and agricultural fields. The knowledge of their thermal pyrolysis may help to better understand and plan their industrial processing [5].

Thermogravimetry is a simple thermal decomposition analysis method of substances in solid-state. On the basis of thermal curves of investigated substances one can estimate their thermal resistance.

Thermogravimetric analyses of chitins and their derivatives are relatively rare, and existing works often even do not take into account the origin of analysed sample [6]. There are no data concerning the comparison of thermal stability of chitins from different sources.

The aim of this research was to compare the thermal properties of chitins from different sources. The analytical method proposed by Aggarwal and Dollimore [7, 8], based on the determination of the α_s–α_r factors was adopted. This method is used for the comparative investigation of substances, the TG curves of which are similar to each other.

Experimental

Materials

A commercial α-shrimp chitin was kindly supplied by Professor Seiichi Tokura, Hokkaido University, Division of Ecological Sciences, Hokkaido 060, Japan, with the viscosity-average molecular mass (M_v) equal to 378 kDa. Other α-shrimp chitin samples were supplied by France Chitin, Marseille, with M_v=612 and

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726 kDa. The samples of α-crab chitin were supplied by Professor Seiichi Tokura, (M_v=120 kDa), and by Bioengineering Centre, Russian Academy of Sciences, Moscow, Russia (M_v=395 kDa). The α-krill chitin was supplied by the See Fishing Institute, Gdynia, Poland (M_v=634 kDa). The β-squid chitin was supplied by France Chitin, with the viscosity-average molecular mass (M_v) equal to 1000 kDa.

Methods

TG analysis

The thermogravimetric analyses of all samples were carried out with Perkin Elmer TGA 7 apparatus with a platinum sample holder, using the Pyris programme for data handling. Measurements were performed in a nitrogen atmosphere at a heating rate of 15°C min^{-1}. The samples were heated up to at least 700°C, starting from 50°C. All measurements were repeated at least three times.

FTIR spectrometry

FTIR spectra were recorded for chitin samples in KBr pellets. The samples were prepared as follows: 2 mg of investigated chitin was grounded together with 200 mg of KBr into the fine powder with the particles size below 5 μm and compressed to form a clear disk. The FTIR spectra were recorded using Perkin Elmer FTIR 2000 spectrometer in the wave number 4000–400 cm^{-1}.

X-ray diffraction

The degree of crystallinity and the size of crystallites were determined by means of X-ray diffraction (XRD) method. Diffraction patterns were recorded in a symmetrical reflection mode using URD-6 Seifert diffractometer and a copper target X-ray tube (λ=1.54 Å) operated at 40 kV and 30 mA. CuK$_\alpha$ radiation was monochromized with a graphite monochromizer and a Ni filter. WAXS curves were recorded in the 2θ range 4–60°, with a step size of 0.1°. Investigated chitins were powdered and pressed into a sample holder. Samples with the radius of 2 cm and the thickness of 1 mm thick were prepared.

Results and discussion

A comparison of the thermal stability of chitin with different origin

The thermal degradation of chitin takes place within 300 to 460°C (Fig. 1). The TG curves for all the samples show one-step degradation and the differences between chitin of different origins are relatively small.

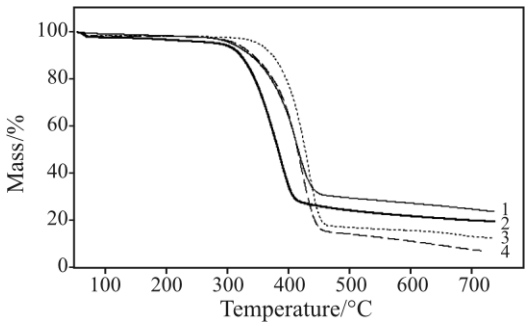

Fig. 1 TG plots of investigated chitins in nitrogen atmosphere (1 – crab; 2 – squid; 3 – krill, 4 – shrimp)

The processes of the thermal degradation of chitins were compared using the α_s–α_r method of evaluation [7, 8], which determines the thermal reactivity of different substances on the comparison base. The data obtained from the TG of shrimp chitin were used as the reference base and denoted by α_r, whereas the other three by α_s.

The α coefficient was determined according to the following equation:

$$\alpha = \frac{w_i - w}{w_i - w_f} \quad (1)$$

where w is the mass fraction of a substance at a given temperature, w_i is the mass fraction of the substance at the initial temperature and w_f is the mass fraction of the substance at the final temperature.

The plots of α_s *vs.* α_r (Fig. 2) were prepared for the main transformation range of TG run.

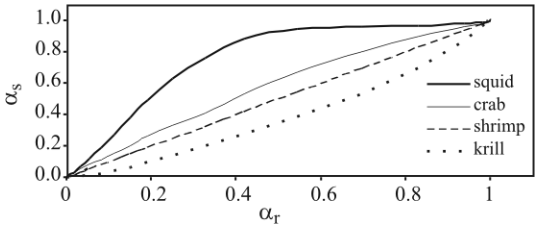

Fig. 2 α_s–α_r plots for the investigated chitins with the shrimp chitin taken as the reference sample (α_r)

As one can see in Fig. 2, the krill chitin has higher thermal stability than the reference sample, whereas the other samples are less stable. The sample of squid chitin is the least stable one. A similar conclusion can be drawn from the α_s coefficient temperature plot (Fig. 3).

TG measurements show that from the point of view of their thermal stability, the investigated chitins can be ranged as follows: krill>shrimp>crab>squid. As it can be seen in Fig. 3 and Table 1, this order does not change throughout the whole course of the main thermal degradation stage.

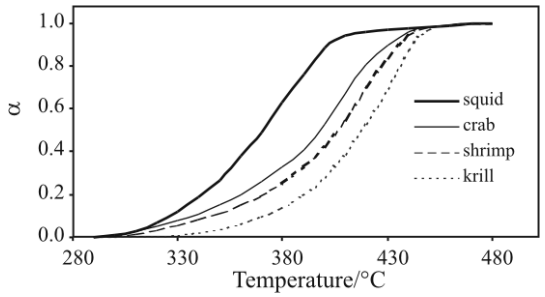

Fig. 3 α_s coefficient plots of the investigated chitins *vs.* temperature

Table 1 α_s coefficient of chitins at α_r=0.5 and α_r=0.90

Source of chitin	α_s at α_r=0.5	α_s at α_r=0.90
Krill	0.36	0.80
Crab	0.62	0.94
Squid	0.93	0.98

To exclude the influence of molecular mass of the investigated samples on the obtained results, thermoanalysis of samples with definitely different molecular masses were performed. On the obtained TG curves of the same chitin origins with different molecular masses (from 378 to 726 kDa α-shrimp chitin and 120–395 kDa for α-crab chitin) the differences were not observed. On the basis of these data one can conclude that in the analysed range, the differences in molecular mass do not influence essentially the thermal stability of the samples.

Calculation of the activation energy of chitin samples

The most important parameter of the thermal pyrolysis of a polymer is its activation energy (E_A) [9, 10]. The activation energy (E_A) of the chitin samples was calculated using the Friedman method [11]. The results are given in Table 2.

Table 2 Activation energy of chitins of different origin calculated by Friedman method [11]

Chitin	E_A/kJ mol^{-1}
Krill	102±2
Shrimp	87±1
Crab	73±1
Squid	54±1

The activation energy calculated for the krill chitin has the highest value from the others chitins. This result is in accordance with the earlier established hierarchy of the thermal stability of chitins according to which the krill chitin is the most stable one. The activation energies values calculated for the remaining samples also agree with this hierarchy.

Determination of the degree of N-acetylation (DA) of chitin based on FTIR spectra

The FTIR spectra of the α-chitin from krill (Fig. 4a) and of β-chitin from squid (Fig. 4b) are shown in Fig. 4. In both spectra there are strong absorption bands at ca. 3443 cm^{-1} due to –OH groups, at ca. 3280 cm^{-1} related mainly due to the –NH– groups, and very intensive band in the range of ca. 3000–2800 cm^{-1} mainly due to CH–, –CH_2– and –CH_3 groups present in the chitin of both types. Intensive double absorption bands appear at ca. 1696–1607 cm^{-1}, assigned to amid I, and isolated band at ca. 1554 cm^{-1}, corresponding to amid II absorption. FTIR spectra confirm the chemical similarity of α- and β-types of chitin.

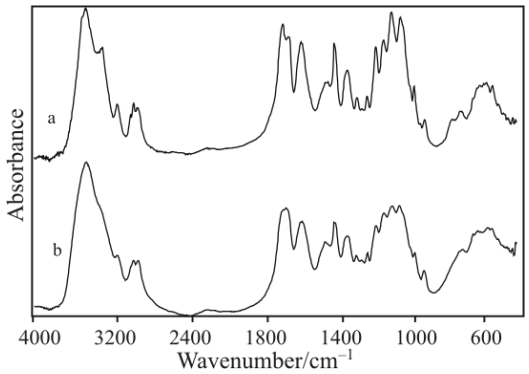

Fig. 4 FTIR spectra: of a – α-form chitin and b – β-form chitin

Based on FTIR spectra the degree of N-acetylation were calculated from the equation proposed by Domard [12] and shown in Table 3:

$$\%\text{N-acetylation} = (A_{1655}/A_{3450}) \cdot 115 \qquad (2)$$

where A_{1655} – absorbance of I amid band (analytical band) 1655–1660 cm^{-1}; A_{3450} – absorbance of hydroxyl band (reference band) ca. 3450 cm^{-1}.

Table 3 Degree of N-acetylation of chitins

Chitin	DA/%
Krill	89
Shrimp	93
Crab	85
Squid	68

As it is seen in Table 3, the DA values of α-type chitins are in the range of 85–93%. This fact indicates that all samples of the α-form chitin have similar

amount of N-acetylamido groups in the main chain. The highest DA has the chitin from shrimp (93%), and the lowest that one from crab (85%). In the Table 3 only the β-chitin from squid has clearly lower DA of 68% but this value still qualify this sample as a chitin.

Results of XRD method

The analysis of XRD curves and calculations of the degree of crystallinity were performed using WAXSFIT [13], a new version of the Optifit [14] computer program. In the first stage, a linear background was determined based on the intensity level at small and large angles and subtracted from the diffraction curves. Next, the curves of all samples were normalized to the same value of integral intensity scattered by a sample over the whole range of scattering angle recorded in the experiment. Finally, the diffraction curves were resolved into crystalline peaks and amorphous component. To obtain this, a theoretical curve was constructed, composed of functions related to individual crystalline peaks and amorphous halos. The theoretical curve was fitted to the experimental one using a multicriterial optimization procedure and a hybrid system [14], which combines a genetic algorithm and a classical optimization method of Powell. Both crystalline peaks and amorphous halos, were represented by a linear combination of Gauss and Lorentz profiles:

$$F_i(x) = f_i H_i \exp\left\{-\ln 2\left[\frac{2(x-x_{oi})}{w_i}\right]^2\right\} + \frac{(l-f_i)H_i}{1+[2(x-x_{oi})/w_i]^2} \quad (3)$$

where x – scattering angle 2θ, H_i – peak height, w_i – width at half height, x_{oi} – peak position, f_i – shape factor, f_i equals 0 for Lorentz profile 1 for Gauss profile.

The starting values of crystalline peaks positions were calculated from the unit cell dimensions of α-chitin and β-chitin given by Minke and Blackwell [1] and Blackwell [2]. According to [1], the unit cell of α-chitin is orthorhombic with dimensions a=0.474 nm, b=1.886 nm and c=1.032 nm. The unit cell of β-chitin is monoclinic [2] with dimensions a=0.485 nm, b=0.926 nm, c=1.038 nm and γ=97.5°. In both cases the c axis corresponds to the molecular chain axis. With these data, the interplanar distances d_{hkl} for individual families of lattice planes were calculated. For α-chitin:

$$d_{hkl} = \left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2\right]^{-\frac{1}{2}} \quad (4)$$

and for β-chitin:

$$d_{hkl} = \left[\frac{(h/a)^2 + (k/b)^2 - (2hk/ab)\cos\gamma}{\sin^2\gamma} + \left(\frac{l}{c}\right)^2\right]^{-\frac{1}{2}} \quad (5)$$

Next, using Bragg's law:

$$2d_{hkl}\sin\theta = n\lambda \quad (6)$$

where n is a natural number, the positions of peaks related to a given family of planes were calculated.

The amorphous component was approximated by means of two broad maxima. The first maximum, located at lower diffraction angles results from the intermolecular scattering and the second one observed at higher angles results from intramolecular scattering [15, 16]. In the case of α-chitin, the maxima were located at 2θ≈20.5° and 2θ≈40.5° while in the case of β-chitin at 2θ≈20.5° and 2θ≈39°.

The diffraction curves of krill chitin (α-type) and squid chitin (β-type) resolved into components are shown in Figs 5 and 6.

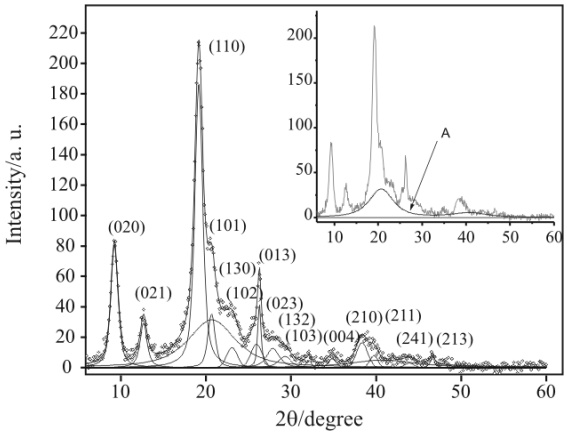

Fig. 5 X-ray diffraction curve of krill chitin (α-chitin) resolved into crystalline peaks and amorphous component. The amorphous component is shown in the insert

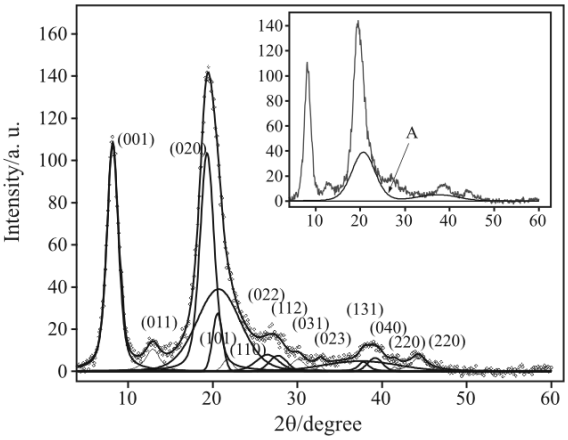

Fig. 6 X-ray diffraction curve of squid chitin (β-chitin) resolved into crystalline peaks and amorphous component. The amorphous component is shown in the insert

Table 4 XRD results for α-chitin samples

Sample	Crystallinity	Size of crystallites/nm					α_s at α_r=0.50
		D_{020}	D_{110}	D_{021}	D_{013}	D_{ave}	
Krill	0.66	8.7	8.7	9.3	19.3	11.5	0.36
Shrimp	0.75	8.7	7.0	6.8	17.1	9.9	0.50
Crab	0.74	9.7	8.1	6.8	14.2	9.7	0.62

Table 5 XRD results for β-chitin sample

Sample	Crystallinity	Size of crystallites/nm				α_s at α_r=0.50
		D_{001}	D_{020}	D_{011}	D_{ave}	
Squid	0.68	5.5	4.5	4.5	4.8	0.93

The degree of crystallinity was calculated as the ratio of the total, integral intensity comprised in the crystalline peaks to the total, integral intensity scattered by a sample over the whole range of measurements.

Moreover, using the Sherrer's formula:

$$D_{hkl} = \frac{\lambda}{w\cos\theta} \quad (7)$$

where w – width at half height of a peak related to (*hkl*) lattice planes.

The size D_{hkl} of crystallites in the direction perpendicular to the lattice planes related to the most pronounced crystalline peaks were calculated.

Calculated crystallinity values and sizes of crystallites are given in Tables 4 and 5.

The crystallinity of krill chitin is the lowest among all samples. A comparison of the normalized XRD curves of krill and crab is shown in Fig. 7. It is easy to notice, that the integral intensity comprised in the crystalline peaks of krill is clearly smaller than that one of crab chitin.

On the other hand, TG experiments have shown that the thermal stability of krill chitin is the highest. The results of XRD investigations presented in Tables 4 and 5 suggest that the thermal stability of investigated samples is not related to the degree of crystallinity but to the size and perfection of crystallites. The sizes of α-chitin crystallites in the directions perpendicular to polymer chain axis (D_{020} and D_{110}) do not differ too much from one another (Table 4). However, in the direction perpendicular to (013) plane, which is close to the polymer chain axis, the crystallites of krill chitin are the longest, resulting in the biggest average dimension D_{ave}. Moreover, the (021) and (013) peaks in XRD curve of krill chitin are clearly higher than in the case of remaining α-chitin samples (Fig. 7). This fact indicates on a higher perfection of crystallites in krill chitin.

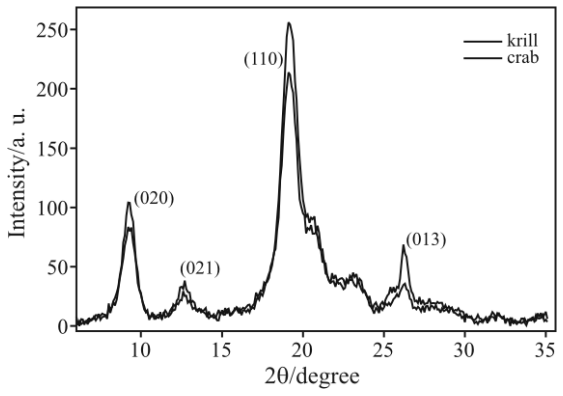

Fig. 7 A comparison of XRD curves of crab and krill samples

In the light of XRD results, a considerably lower thermal stability of squid chitin is connected not only to its different crystalline structure (β-chitin) but also with much smaller size of crystallites (Tables 4 and 5).

Conclusions

The investigations performed in this work have shown that the basic range of the thermal degradation of chitin is 300–460°C. It was also shown, that the α_s–α_r method can be successfully used in the determination of the thermal resistance of chitins. In the investigated temperature range the thermal resistance depends on the origin of this biopolymer and can be arranged as follows: krill chitin>shrimp chitin>crab chitin>squid chitin. No deviations from this order were observed in the basic range of the thermal degradation. It was found, that the monoclinic β-chitin obtained from squid is thermally much less stable than the orthorhombic α-chitins originating from krill, crab and shrimp. XRD investigations have proved that apart from the type of the crystalline structure of chitin, the size and perfection of crystallites are the most important factors influencing its thermal stability. As it could be expected, the activation energy of the thermal degradation of chitin is clearly higher for the samples of higher thermal resistance. No influence on the average molecular mass, the degree of crystallinity and the degree of acetylation on the thermal resistance of investigated samples was observed.

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