AUTEX 2022 Conference Proceedings 978-83-66741-75-1

DOI: 10.34658/9788366741751.59

SYNTHESIS OF MIX CHITIN ESTERS

Anna Bednarowicz[1(*)], Nina Tarzyńska[1], Marta Patlewicz[1], Zbigniew Draczyński[1],
[1] Lodz University of Technology, Zeromskiego 116, Lodz, Poland
[(*)] *Email:* anna.bednarowicz@dokt.p.lodz.pl

ABSTRACT

The aim of this study was the synthesis of chitin esters, which at a later stage could be used to produce antibacterial textiles. The esterification of chitin was carried out using butyric anhydride, succinic anhydride and methanesulfonic acid as a catalyst. The produced products were analysed by FTIR and NMR techniques and the dynamic apparent viscosity of the spinning solutions was examined. The products containing butyl and succinic anhydride in molar ratios 95/5 and 85/15 showed the best properties.

KEYWORDS

Chitin, chitin esters, synthesis of chitin esters.

INTRODUCTION

Chitin is a natural polymer that belongs to the group of polysaccharides. It is the main component of invertebrate exoskeletons and also occurs in the cell walls of fungi and yeasts. It is easily accessible as a by-product of shellfish production [1]. Currently, this polymer is increasing its popularity. Although it possesses outstanding properties predisposing chitin to medical applications, including non-toxicity, biodegradability, gel-forming ability and antibacterial properties [2], the major problem regarding this polymer is its insolubility in well-known solvents [3]. Therefore, it is impossible to manufacture textiles from it. Nevertheless, chitin derivatives can be successfully used, the most well-known among them being chitosan, which is easily soluble in acetic, formic and lactic acid solutions [3]. Among the less known chitin derivatives are its esters. Depending on the substituents used for the synthesis, esters with different properties and capable of dissolving in many organic solvents can be produced.

Through modification of hydroxyl groups, it is possible to obtain chitin derivatives. Their physical and chemical properties will differ from the initial polymer. Many attempts have been made over the years to modify the hydroxyl groups. In 1949 Bourne [4] developed a composition consisting of trifluoroacetic acid and an organic acid, which could also be used to esterify chitin. The reaction yielded chitin monoesters and copolyesters with acetylchitin as the major component. Using the solvent combination proposed by Bourne, it was also possible to obtain butyryl, hexanionic and octanionic derivatives [5].

Research on the preparation of chitin esters has also been carried out in Poland. Researchers from the Lodz University of Technology under the direction of L. Szostand developed a method of obtaining dibutyrylchitin [6,7]. The team led by L. Szostland also succeeded in developing a method to produce mixed chitin esters. The butyryl acetyl chitin esterification reaction was carried out using perchloric acid as catalyst and a mixture of acetic and butyric anhydrides in an equal molar ratio.

Perchloric acid and methanesulfonic acid are widely used in chitin esterification [8]. They are used to obtain chitin acetate, propionate and butyrate. The produced derivative is to some extent depolymerised, however, it is soluble in organic solvents. Derivatives produced in this manner allow the creation of a spinning solution used in dry or wet spinning [9].

MATERIALS AND METHODS

Synthesis of butyryl succinyl derivative of chitin (BSC)

Chitin ground with a ball mill was used for BSC synthesis. The duration of one grinding cycle was 300 seconds at 600 rpm. The process was repeated several times to obtain higher polymer homogeneity and to accelerate and increase the reaction efficiency.

In another variant of the synthesis of butyryl succinyl derivative of chitin, methanesulfonic acid was used as a catalyst. A mixture of chitin, butyric and succinic anhydride and methanesulphonic acid was placed in a cooled reactor. The reaction was carried out for 4 h at a temperature not exceeding 4°C. After that time, the polymer was neutralised with ammonia water to remove excessive acid. The neutralised polymer was then precipitated and drained off using a fritted glass. The reaction was carried out for 4 h at a temperature not exceeding 4°C. After that time, the polymer was neutralised with ammonia water to remove excessive acid. The neutralised polymer was then precipitated and drained off using a Schott funnel. All syntheses were carried out using 25 g of chitin, 100 cm^3 of methansulfonic acid and anhydrides at different molar ratios (Table 1).

Table 1. Amount of butyric and succinic anhydride used in each synthesis.

	Butyl anhydride (mol)	Succinic anhydride (mol)
Synthesis I	0.95	0.05
Synthesis II	0.85	0.15
Synthesis III	0.75	0.25
Synthesis IV	0.65	0.35

FTIR analysis

Fourier-transform infrared spectroscopy (FTIR) analysis was performed to analyse the chemical structure. During each measurement, 64 scans were taken.

NMR analysis

The chemical structure of the synthesised polymers was analysed using H NMR spectroscopy. Only polymer samples obtained from syntheses I and II were analysed, as the reaction yields of syntheses III and IV were insufficient to obtain sufficient quantity and quality of the product.

Analysis of apparent dynamic viscosity

For the dynamic apparent viscosity study, the polymer, in powder form, was dissolved in dimethylformamide (DMF). The study was carried out on a rotational viscometer at shear rates of 10, 30, 50, 70 and 100 1/s at 25°C, using an R7 spindle. The obtained measurements were used to plot the dependence of shear rate on apparent dynamic viscosity using a double logarithmic scale.

RESULTS AND DISCUSSION

The spectrum presented below (Figure 1) shows significant differences between chitin and the chitin esters obtained.

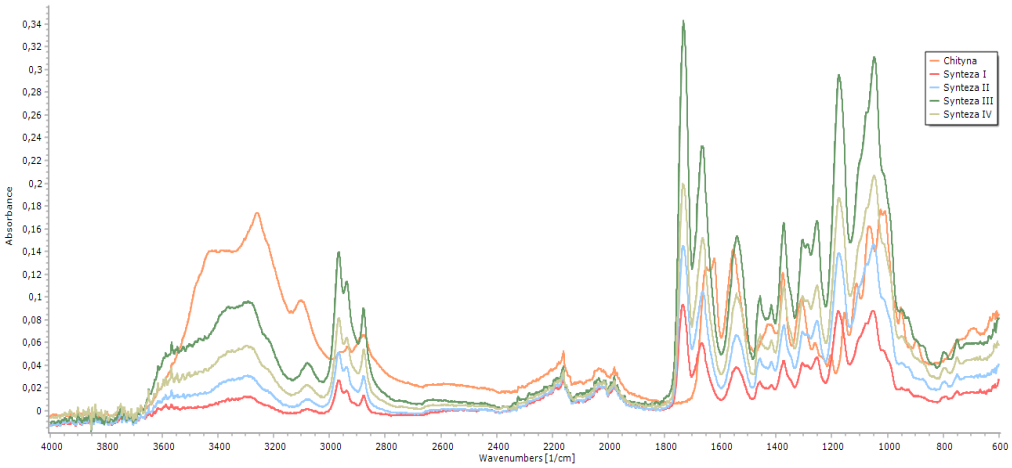

Figure 1. FTIR ATR spectra of obtained chitin esters.

In the chitin spectra, signals with a maximum at 3443 cm^{-1} can be identified. These match the -OH groups present in chitin. In the case of the maximum at 3280 cm^{-1}, it corresponds mainly to the -NH group. The broad band visible in the range 3000-2800 cm^{-1} originates from signals of >CH, $-CH_2-$ and $-CH_3$ groups present in chitin. In the presented spectra intensive signals of amide groups, characteristic for chitin, are also present, a band with maximum at 1656 cm^{-1} for amide group I and 1554 cm^{-1} for amide group II. The peak at 898 cm^{-1} represents the characteristic glycosidic bond.

The absorption bands at 3450 cm^{-1} originate from -OH groups of chitin disappears. The disappearance is not complete, which may indicate insufficient substitution with butyryl and succinic groups.

Besides FTIR ATR analysis, the obtained chitin esters were analysed by NMR. The analysis was performed only on the polymer samples from syntheses I and II, as the reaction yields for syntheses III and IV were found to be insufficient to obtain adequate quantity and quality of the product.

Based on these measurements of proton signals the theoretical degrees of substitution was determined (Table 2), using of Eq. [1]:

$$DS_M = \frac{{}^1/_3\, I_{\gamma CH_3}}{{}^1/_6\, I_{H_2-H_6}} \qquad [1]$$

where, $I_{\gamma CH_3}$ - integer value of signal intensity, originating from protons in methyl group of butyric acid residue at 0.60 ppm, $I_{H_2-H_6}$ - integral value of signal intensity in the range 3.0-4.2 ppm, originating from H2 - H6 protons in glucosamine moiety of polymer.

Table 2. Degree of substitution with butyryl groups and with succinic groups.

	Ratio of reagents in the mixture (mol)		Degrees of substitution determined by H NMR		Theoretical degrees of substitution	
	Butyric acid anhydride	Succinic acid anhydride	DS_B	DS_S	DS_B	DS_S
Synthesis I	0.95	0.05	1.74	0.05	1.90	0.10
Synthesis II	0.85	0.15	1.48	0.30	1.70	0.30

For the polymer produced in synthesis I, the degree of substitution calculated with respect to butyryl groups is 1.74, while in the case of total substitution it should be 1.9. However, the degree of substitution calculated with respect to succinyl groups is 0.05, and at the assumed anhydride content it should be 0.1. In the case of the polymer produced in synthesis II, the degree of substitution calculated with respect to butryl groups is 1.48, and at the assumed anhydride content it should be 1.7. The degree of substitution calculated with respect to succinyl groups is 0.3, and this is its maximum value at the assumed anhydride

content. On the basis of integration, the degree of deacetylation of chitin was also calculated, which in this case was 0.25.

To verify whether it would be possible to form fibres from the produced polymers, the apparent dynamic viscosity of the solutions was examined (Table 3). 10% solutions of polymers from syntheses I and II in dimethylformamide were tested for apparent dynamic viscosity. The solutions were also tested after 14 days. After 1 day there are no significant differences between the viscosity values. However, solutions of polymer from synthesis I are characterised by a lower value of dynamic apparent viscosity.

Table 3 Values of dynamic apparent viscosity of polymer solutions from synthesis I and II.

		Shear speed (rpm)				
		10	30	50	70	100
		dynamic apparent viscosity (mPa·s)				
Synthesis I	day 1	485	636	681	715	741
	day 14	627	838	880	901	918
Synthesis II	day 1	701	708	727	762	777
	day 14	633	735	764	779	805

However, after 14 days, the dynamic apparent viscosity increased in both cases. This was possibly caused by evaporation of the solvent. In the case of another chitin copolyester, BAC, the following conditions need to be met to obtain porous fibres by the wet solution method: the concentration of the spinning solution should be between 10.6-12.8% and the apparent dynamic viscosity should be between 22700-26500 mPa·s. Therefore, it can be concluded that for BSC the concentration of the spinning solution could be higher.

CONCLUSION

In the case of synthesis III (75/25) and IV (65/35), the yield was insufficient, which made further analysis impossible. Thus, it can be concluded that:

- The synthesis of chitin copolyesters using methanesulfonic acid, butyric and succinic anhydride is possible. However, it is crucial to maintain the correct ratio of anhydrides.
- FTIR ATR analysis shows a different structure of the produced polymers compared to chitin. In all spectra obtained for chitin esters, new intense absorption bands appear, originating from carbonyl bond >C=O in ester groups at 1740 cm^{-1}.
- H NMR analysis confirms that in the majority of cases the degree of substitution with butyryl and succinic groups does not reach its maximum value.
- The values of dynamic apparent viscosity of the solutions of the produced chitin copolyesters enable to conclude that there would be a possibility to produce fibres from them using the wet solution method.
- The products made of the obtained polymer could find application in the medical industry, due to their excellent antibacterial, anti-inflammatory and haemostatic properties. Moreover, compared to chitin, they are characterised by better solubility in organic solvents, which would significantly improve their processing.
- Using different ratios of butyric and succinic anhydrides could lead to an even better polymer property and higher reaction efficiency.

ACKNOWLEDGMENT

This work was partially supported by statutory research fund of the Institute of Material Science of Textiles and Polymer Composites no. I-42/501/4-42-1-3.

REFERENCES

[1] Søltoft-Jensen J., Hansen F., *New Chemical and Biochemical Hurdles*, Emerg. Technol. Food Process. An Overv., 2005, pp. 387–416, doi: 10.1016/B978-012676757-5/50017-7.
[2] Hu J., *Cosmetics Applications of Adaptive and Functional Polymers* [in:] *Adaptive and Functional Polymers, Textiles and Their Appllications*, Imperial College: London 2011, pp. 252–283, doi: 10.1142/9781848164765_0008.
[3] Sabatier P., Senderens J., It C., Sachs R.K., Wolfe A.M., *Dictionary of Science* (6th Edition), 1941, p. 781.
[4] Bourne E.J., Stacey M., Tatlow J.C., *Studies on Trijluoroacetic Acid*, Part, J. Chem. Soc. 1949, vol. 268, pp. 2976–2979.
[5] Draczyński Z., *Kopoliester Butyrylo-Acetylowy Chityny Jako Nowy Aktywny Składnik Nanokompozytów Polimerowo-Włóknistych*, Zeszyty Naukowe, Wydaw. Politechniki Łódzkiej, Łódź 2013.
[6] Szosland L., *Soluble Chitin Mixed Esters: Synthesis And Characteristic*, Prog. Chem. Appl. Chitin its Deriv. 1999, vol. 27.
[7] Szosland L., *Synthesis of highly substituted butyryl chitin in the presence of perchloric acid*, J. Bioact. Compat. Polym. 1996, vol. 11, no 1, pp. 61–71, doi: 10.1177/088391159601100105.
[8] Muzzarelli C., Francescangeli O., Tosi G., Muzzarelli R.A.A*., Susceptibility of dibutyryl chitin and regenerated chitin fibres to deacylation and depolymerization by lipases*, Carbohydr. Polym. 2004, vol. 56, no 2, pp. 137–146, doi: 10.1016/j.carbpol.2004.01.002.
[9] Yang B.Y., Ding Q., Montgomery R*., Preparation and physical properties of chitin fatty acids esters*, Carbohydr. Res. 2009, vol. 344, no 3, pp. 336–342, doi: 10.1016/j.carres.2008.11.006.