

## Non-degrading nitration of pinewood cellulose

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**Abstract:** *Non-degrading nitration of pinewood cellulose.* In this work, pinewood cellulose nitration was investigated, using a mixture of nitric and acetic acid with acetic anhydride. The process time and temperature were changed. Reaction products were analysed for nitrogen number and molar mass. A significant influence of temperature on degradation phenomenon of cellulose was confirmed. Low temperature of the reaction and time of 5 hours favour obtaining nitrocellulose that show the highest polymerisation degree and nitrogen number equal to 14.1%.

*Keywords:* cellulose, pinewood, nitration, molar mass

### INTRODUCTION

One of most the important properties of cellulose, as macromolecular compound, is degree of polymerisation or molar mass. For many years, scientists have been carrying out research on effective methods for its determination. Some of known methods, such as viscosity measurement in solutions of aqueous metal complexes, can cause degradation of cellulose, especially oxidised one (Strlič *et al.* 1998, Dupont & Mortha 2004). In other methods the applicability of solvent may be limited to small molar mass cellulose, as in the case of dimethylsulphoxide (DMSO). In turn, N,N-dimethylacetamide/LiCl system, used lately in chromatography, requires laborious preparation of cellulose solutions, and long procedure creates many possibilities for error (Bikova & Treimanis 2002, Dupont 2003, Strlič & Kolar 2003, Sundholm & Tahvanainen 2003).

In this situation, prior cellulose processing in order to obtain easy-soluble derivative is still competitive. The possibility of non-degrading synthesis of derivatives is fundamental condition of these methods. Their applicability to direct analysis of cellulose without its isolation from wood is another interesting perspective. Derivatives that are the most frequently used are nitrate or carbanilate (Heinze & Liebert 2001, Mormann & Michel 2002, Fischer 2004). Cellulose nitrate (nitrocellulose, NC) is the best-described derivative of cellulose from the viewpoint of synthesis and analytics (Urbański 1967, 1983, Siochi & Ward 1989). It shows good solubility in tetrahydrofuran (THF), a universal solvent for size exclusion chromatography (SEC). Since the esterification of cellulose molecule may involve up to three hydroxyl groups per glucopyranose ring, nitration product may be non-homogeneous. A complete nitration is therefore the best solution, which ensures the chemical uniformity molecules. Of the many methods of cellulose nitration, only two allow such a full substitution, without significant degradation of the product.

The first of them is based on the action of nitric and phosphoric acid, usually in the presence of phosphoric anhydride. Since phosphoric acid do not cause nitrate hydrolysis, it is possible to achieve a higher degree of esterification. Berl & Rueff (1930) applied the mixture with P<sub>2</sub>O<sub>5</sub> and obtained nitrocellulose of nitrogen content close to the maximum (about 14%).

In the case of P<sub>2</sub>O<sub>5</sub> however, some difficulties in stirring may occur due to the tendency to polyphosphoric acid gel formation, which is difficult to break up (Staudinger & Mohr 1937).

A mixture of nitric and acetic acid with acetic anhydride was used for the first time already in 1908 (Whistler 1963). This mixture was applied to cellulose trinitrate synthesis for molar mass determination. It allows to obtain the product of nitrogen number 14% or even higher and gives nitrocellulose of higher viscosity than mixtures with phosphoric acid, what indicates minimal degradation. The main disadvantages of this mixture are non-swelling of organic material, short time of safe usage and the necessity of processing at low temperatures. Bennett and Timell (1955), using a mixture of 43% HNO<sub>3</sub>, 32% CH<sub>3</sub>COOH and 25% (CH<sub>3</sub>CO)<sub>2</sub>O, nitrated linters at 0°C and obtained a product containing 14.14% of nitrogen. For 3-4 hours nitration was not cause degradation, while further extension of reaction time resulted in noticeable degradation of nitrocellulose.

## MATERIALS AND METHODS

Bleached Kraft pulp isolated from pinewood (*Pinus sylvestris* L.) was taken from the Institute of Papermaking and Printing of Technical University of Łódź.

Fuming nitric acid, used for the nitration, was freshly obtained from a mixture of concentrated nitric and sulphuric acids in 1:2 ratio by volume, by distillation under reduced pressure, in order to avoid the temperature of the vapour to exceed 65±5°C.

Other reagents and solvents used were of analytically grade.

### Nitration procedure:

Conical flask provided with a mechanical stirrer was placed in a proper bath – water, ice or ice with salt. 29cm<sup>3</sup> of glacial acetic acid was poured into the flask and then 29cm<sup>3</sup> of acetic anhydride was added while stirring. Successively, 27cm<sup>3</sup> of fuming nitric acid was added slowly, to ensure the temperature of the mixture would not rise more than 5°C. To a nitrating mixture at a suitable temperature (-10±3, +2±2 and +12 ± 2°C) 4g of cellulose was added slowly, still stirring. The rate of adding cellulose was adjusted so that the reaction temperature increase did not exceed 5°C. After an appropriate period (2, 3 or 5 hours) nitrocellulose was filtered on a Büchner funnel and washed with water until a neutral pH of filtrate. At last, the samples were placed in round-bottomed flasks, poured with methanol and boiled for 3-4 hours to stabilise the product.

### Determination of nitrogen number of nitrocellulose:

Samples of about 4 grams of nitrocellulose were carefully grinded and vacuum dried to constant mass at 50°C. About 0.5g of each NC was weighed to the nearest 0.2mg and placed in conical flask. 50 cm<sup>3</sup> of 95% H<sub>2</sub>SO<sub>4</sub> was added and the mixture was closed and placed on magnetic stirrer in order to dissolve NC prior to titration. The mixture was titrated with a solution of Mohr's salt to change the colour from greenish-yellow to pink-yellow. The measurements were repeated to obtain three consecutive results that differ by up to 0.05% N. Titrant solution was obtained by dissolving 98g of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Mohr's salt) and 125cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> in a 500cm<sup>3</sup> flask. Titrant concentration was determined by titrating a sample of KNO<sub>3</sub> (13.85% N), dried to constant weight, according to the above procedure.

### Size exclusion chromatography (SEC):

NC samples with masses of  $0.050 \pm 0.005$ g were weighed and moved to closed vessels. The vessels were poured with  $10\text{cm}^3$  of tetrahydrofuran (THF) and placed in a rotator for 6 hours. Solutions thus obtained were subjected to analysis, using Shimadzu LC-20AD chromatograph, equipped with RID-10A refractometer. Separation was conducted on Nucleogel M-10 column at  $35^\circ\text{C}$ , with eluent (THF) flow of  $2\text{cm}^3/\text{min}$ . The samples were injected by Rheodyne 7725i manual valve with the loop  $20\mu\text{l}$ . Shimadzu LC Solution software was applied for data collection and apparatus controlling. Chromatogram processing for molar mass analysis was performed using Polymer Standard Service (PSS) software, PSS Calibrationprogram V2.99 and PSS WinGPC scientific V2.74. Polystyrene standards (Polymer Laboratories) were used of molar mass range  $6.85 \times 10^6 \div 1.70 \times 10^3$ . The values of Mark-Houwink coefficients for PS were taken from the software database (PSS) as  $K=0.01363$  and  $\alpha=0.714$ , while for high-nitrogen NC they are:  $K=0,021$  i  $\alpha=0,89$  (Radomski 2004).

## RESULTS AND DISCUSSION

The results of nitrogen number analysis of nitrocellulose samples obtained, are presented in the Figure 1. In the case of nitration at  $-10^\circ\text{C}$  for 3 and 5 hours, a high degree of cellulose esterification is yielded. Extension of time results in a small increase in nitrogen content. The result obtained for the process carried out for 2 hours is not consistent with the other results. Anticipating the next results it can be concluded that this sample was not homogeneously nitrated. Improper stirring and short reaction time were insufficient for complete nitration of the samples interior, in contrast to outer layers. For reaction carried out for five hours we get the nitrogen number of 14.10%.

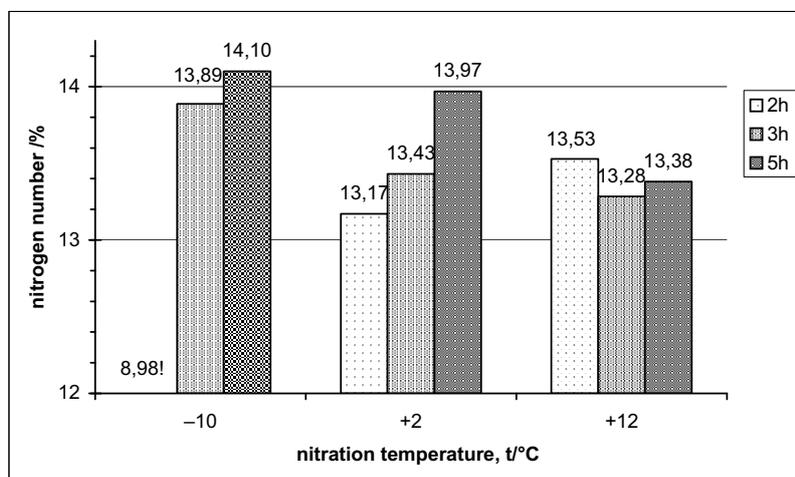


Fig. 1 Nitrogen numbers of nitrocelluloses obtained

In the case of the nitration process conducted in the temperature range  $0 \div 4^\circ\text{C}$ , there is a clear relationship between the reaction time and nitrogen number of the product. The longer the nitration, the higher nitrogen number is yielded. After 5 hours of nitration, the result is close to 14%. In the case of nitration at the highest temperature, it was found that the

reaction seems to reach equilibrium, as the extension of time does not increase the degree of substitution. The maximum nitrogen number is 13.53%. Further reaction causes a slight decrease of its value, which may be due to decomposition of nitrating mixture at process temperature.

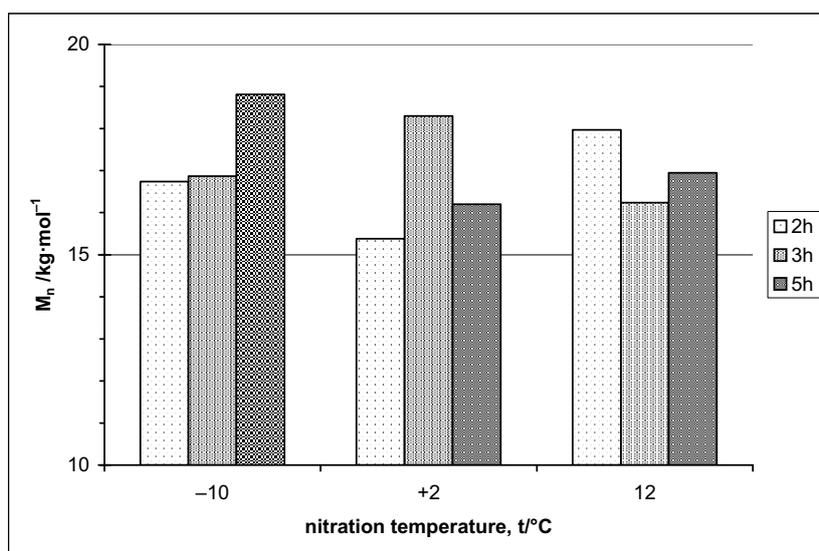


Fig. 2 Numbers average molar mass of nitrocelluloses obtained

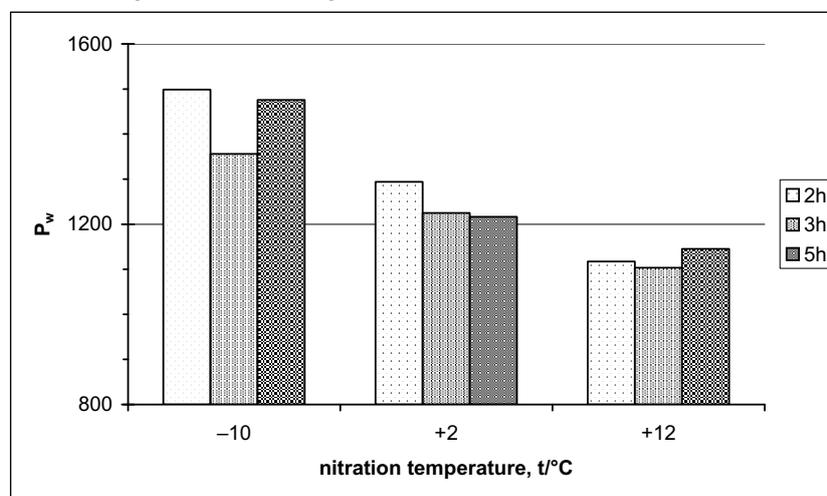


Fig. 3 Weight average polymerisation degree of nitrocelluloses obtained

The results of SEC determination of molar mass distribution were presented as averages comparison, in the Figure 2 and 3. In the case of number average molar mass ( $M_n$ ), differences between individual samples seem to be random and no clear dependence can be concluded. Weight average, presented as polymerisation degree ( $P_w$ ), is more sensitive to

changes in the fraction of the largest molecules. When reactions were conducted at +2°C, molecules size decrease with prolonged reaction time, which indicates some degradation during the nitration. The first of the samples nitrated at -10°C is inappropriate for comparison due to incomplete substitution. Similar polymerisation degree indicates, however, the heterogeneity of the nitration. One part of cellulose sample was highly nitrated, while the other one was only slightly nitrated, so it remained insoluble. The samples nitrated at -10°C for 3 or 5 hours do not show evidence of degradation. Their polymerisation degree are higher than for the samples obtained at +2 and +12°C. The last samples, obtained at +12°C, do not show the downward trend in  $P_w$  with increasing time of nitration. However, due to much lower nitrogen number of NC, the results cannot be treated with the same reliability as the previous one, since the Mark-Houwink coefficients were optimised for highly nitrated cellulose.

Another parameter that strongly affects the quality of nitration product is the reaction temperature. The highest molar masses are obtained when nitration is conducted below zero temperature. The increase in temperature causes a clear decrease in polymerisation degree of NC, regardless of the time of the nitration. Comparison of the results shows clearly that degradation of nitrated cellulose may occur, especially at temperatures above zero. NC obtained at -10°C shows polymerisation degree above 1300, while nitrated at +12°C has it at much lower level of about 1100. Such a difference is significant and it should be taken into consideration when applying nitration to molar mass analysis of cellulose.

In addition, as there is no clear dependence of number average molar mass of NC on nitration conditions, the process can be recognised as concerning mainly the largest molecules. The longest chains fragmentation reduces significantly the weight averages and has significantly lower influence on number averages.

## CONCLUSIONS

A general conclusion for the application of the method presented is the necessity of providing the optimal conditions of nitration, from the viewpoint both eliminating possible degradation of NC and complete esterification of hydroxyl groups. Special care has to be paid at the following questions:

- Low water content in nitrating mixture is critical. During the distillation of nitric acid, a key concern is to maintain the lowest temperature of the process. This prevents the decomposition of fuming nitric acid on the oxides of nitrogen, oxygen and water.
- Adequate stirring during nitration is very important to ensure, otherwise there may be heterogeneous substitution of cellulose.
- Temperature of nitration plays a key role in the degradation of nitrocellulose. Nitrating at -10°C ensures decrease in this phenomenon. Only weight average molar mass shows significant dependence on temperature, which indicates the degradation to be concerned with the largest molecules.
- When nitration is conducted at -10°C, a time of nitration should not be too short due to possibility of incomplete nitration. As there is no significant risk of cellulose degradation, reaction time should be extended to about 5 hours, which yield maximum nitrogen number of nitrocellulose.

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**Streszczenie:** *Niedegradująca nitracja celulozy z drewna sosny.* W pracy badano proces nitrowania celulozy z drewna sosny mieszaniną kwasu azotowego, octowego i bezwodnika octowego. Zmieniano czas i temperaturę procesu. Produkty reakcji były analizowane pod kątem liczby azotowej oraz masy molowej. Stwierdzono istotny wpływ temperatury na proces degradacji celulozy podczas nitrowania. Niska temperatura i czas procesu 5h sprzyjają otrzymaniu nitrocelulozy o najwyższym stopniu polimeryzacji oraz liczbie azotowej wynoszącej 14,1%.

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