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NITROCELLULOSE POROSITY – THERMOPOROMETRY

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Abstract

Nitrocellulose porosity was investigated by thermoporometry, based on melting point depression of liquid in limited space. Strange behaviour of water-saturated nitrocellulose was observed, which consisted of melting peak shifting of some of liquid. Thermal resistance, connected with limited contact area of nitrocellulose walls and water, is supposed as the source of phenomenon. Water is unable to completely penetrate into pores as nitrocellulose is a hydrophobic material, though prolonged stirring or boiling of mixture improves saturation. Thus total pore volume cannot be estimated correctly. In spite of this pore radius was calculated from obtained DSC curves. The results show good consistency for the same nitrocellulose materials, which proves that thermoporometry is a useful method of nitrocellulose characterisation.

Keywords: DSC, nitrocellulose, pore size, thermoporometry

Introduction

Nitrocellulose is a chemical modified naturally occurring polymer obtained from the nitration of cellulose. Cellulose structure is formed as a result of biological processes and industrial processing of raw material and shows considerable porosity. Porous structure is maintained during esterification by nitric-sulphuric acid mixture and influences properties of nitrocellulose. Products containing nitrocellulose are often stored for many years, so their cellulose substrates are inaccessible and it is necessary to apply investigation methods to nitrocellulose materials.

Thermoporometry is a method for measuring pore size and pore size distribution, based on the depression of melting temperature of the substance occurring in limited areas within small pores [1]. Analysis can be carried out by differential scanning calorimetry (DSC) [2, 3], which allows estimating pores' size of radius 2–150 nm. It is useful for polymeric materials, like foam and hollow fibers membranes [4]. Unlike mercury porosimetry it is applicable to fragile, soft or swelling materials [5, 6]. Complete filling of pores by water or another liquid is required for proper determination. Cellulose, which is a hydrophilic material, was studied by thermoporometry [7–11]. Nitrocellulose, in spite

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of having hydroxyl groups, shows far worse water wettability, which involves strange phenomena during DSC analysis.

The aim of this work was an assessment of the applicability of thermoporometry for the nitrocellulose–water system. The method is safe as conditions employed cause no decomposition of nitrocellulose. The analysis results will allow to determine the dependence of sorptive and gelatinising properties on the structure of nitrocellulose. This would enable quality assessment of nitrocellulose used in explosives and propellants industry [12].

Basis of thermoporometry

For liquid–solid phase equilibrium in conditions of complete saturation of porous material, direct dependence of melting temperature depression on curvature of interface can be described as follows [1]:

$$T=T_0-\int_0^{\gamma_{ls}C_{ls}}\frac{\nu_1}{\Delta S_m}(\mathrm{d}\gamma_{ls}C_{ls}) \tag{1}$$

where T_0 is triple point temperature for flat interface, ΔS_m is melting entropy at temperature T, ν_l is specific volume of liquid phase, C_{ls} and γ_{ls} are average curvature and tension of solid–liquid interface respectively. Solidification process of medium inside the pores advances from the meniscus of existing liquid–solid equilibrium. Interface is hemispherical and its curvature amounts to $C_{ls}=2/R_n$, where R_n is the measured curvature radius. It is lower than pore radius R_p, because of pseudoliquid layer appearance of t thickness, which does not undergo phase change ($t=R_p-R_n$). A bound layer occurs between crystal and pore walls, whose constitution changes gradually, from a structure formed by pore surface material to a condensed phase constitution through disordered state similar to liquid.

The relation between pore radius and solidification temperature depression of water can be described by Eq. (2). This relation is also correct for the melting process in spherical pores [1].

$$R_p=-64.67/\Delta T+0.57 \tag{2}$$

There is a different relation for melting in cylindrical pores, because of hysteresis:

$$R_p=-32.33/\Delta T+0.68 \tag{3}$$

Similar relations for benzene are as follows:

$$R_p=-131.6/\Delta T+1.76 \tag{4}$$

for the solidification process and melting in spherical pores and

$$R_p=-65.8/\Delta T+2.94 \tag{5}$$

for melting in cylindrical pores.

Apparatus and materials

DSC analysis was carried out on a ‘Pyris 1’ apparatus produced by Perkin-Elmer. Nitrocellulose samples were investigated in hermetically sealed aluminium vessels. Water samples were examined in hermetic steel vessels. All analysis data was collected at a temperature range –50–20ºC. Liquid nitrogen was used as the cooling medium.

Three kinds of nitrocellulose were used in our study, containing 12.4, 13.2 and 13.51% of nitrogen respectively. Wet nitrocellulose samples were pressed under 250 MPa in order to ensure good sample contact with measuring vessel walls. Hand pressed and non-pressed samples were investigated as well.

Results and discussion

Water penetrating a porous material can be divided into three classes:

- Pore filling water, which undergoes depression of phase change temperature.
- Bulk water, which occurs in boundless space and does not show a temperature depression effect.
- Non-freezing water, thin layer of water bound to the walls of pores.

In our investigations of nitrocellulose samples another class of water was noticed, represented by a very broad peak of melting in the range over 0°C. It overlaps with the narrow peak of melting, which can be related to bulk water. Simultaneously the effect of melting temperature depression in pores is barely noticeable for most samples. Comparison of results obtained at various heating rates is displayed on Fig. 1. It is visible, that the effect of temperature increase for the broad peak diminishes significantly with the lowering of the heating rate, while significant shifting of peak maximum temperature is not observed for the sharp peak, corresponding to typical melting process in unlimited space. Taking into consideration the lamellar structure of nitrocellulose it may be supposed that the prior-mentioned phenomenon is connected with heat flow retardation in samples. In order to obtain good thermal conduction samples were pressed in measuring vessels.

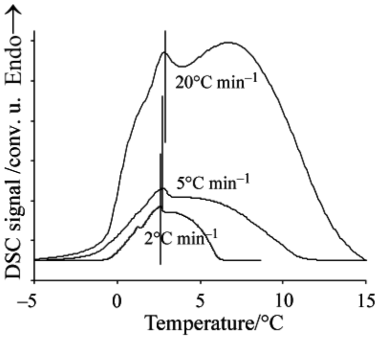


Fig. 1 DSC curves of water melting in nitrocellulose, obtained for various heating rates, β=2, 5 and 20°C min^{-1}

Nitrocellulose is an elastic material, which may undergo relaxation after pressing, while distances between near fibrils of nitrocellulose increase. At that point a situation may occur, in which water present in macropores of nitrocellulose takes the form of separate drops rather than a continuous phase (Fig. 2). Spherical shape of water drops is supposed, due to hydrophobic properties of nitrocellulose. The distances between nitrocellulose fibrils amount to 10–100 μm and size of the water phase among them exceeds the applicability range of thermoporometry. In unperturbed heat flow conditions melting of such water takes place like for bulk water. However if the contact area of the nitrocellulose fibril and the water drop is limited, retardation of heat flow may occur through interface, which involves water melting at seemingly higher temperature.

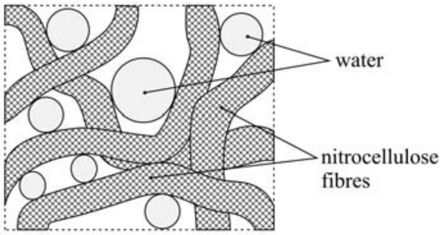


Fig. 2 Macroporous structure of nitrocellulose containing ice

The effect of contact area limitation with drop size lowering is shown in Fig. 3. When surface tension exceeds significantly deformational forces of a liquid, drops take shape close to spherical. Then interface contact area is minimal. If drop size is further lowered the contact area decreases slower than drop mass, so the rate of phase change may be relatively higher. The effect of melting peak shifting is expected then to concern of larger water drops melting rather than mesopore melting.

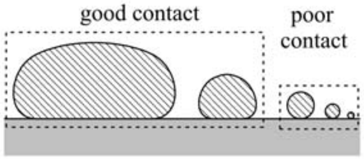


Fig. 3 Scheme of drop size and shape dependence on contact area of fibre walls and liquid drops

DSC investigations were conducted on wet nitrocellulose samples, pressed under various charges and non-pressed as well. No clear relation between sample preparation method and melting retardation was observed. These results prove that even in the non-pressed sample water takes a form, which hinders heat flow. Poor water wettability of nitrocellulose is concluded as the main source of the obtained results.

It has to be noticed, that elimination of heat flow retardation by lowering the heating rate during analysis is not the proper solution. Possible water migration in low stiffness material must be considered, which was observed in cellulose [7, 8]. Noticeable dependence of heating rate on determined ratio of water amount in pores and outside them was found.

When water alone melting was investigated in steel vessels the effect of temperature shifting of melting peak was observed as well. Poor wettability of vessel walls was noticed during water filling, as water strongly tended to form separate drops of different diameters. Figure 4 shows an example of a DSC curve of water melting. On the registered DSC curve two separate peaks of melting are showed. Shifting of the second peak corresponds to water drops of very little contact with measuring vessel walls. Water occurrence in drop form is concluded as the sufficient source of poor thermal conductivity, for limited contact area of water and vessel walls.

DSC investigations were conducted on nitrocellulose samples saturated with benzene, which like water does not solve nitrocellulose. The prepared sample was impressed from benzene extent ('A' sample) and paper dried additionally ('B' sample). Results presented on Fig. 5 show similar behaviour of benzene and water in tested samples. Two partially overlapping effects of melting were observed for this solvent, the first represented by a narrow peak and corresponding to bulk melting of benzene and the second represented by broad peak, shifted up to higher temperatures. In spite of the same conditions of analysis lower temperature of bulk melting peak was found for sample 'A'. This observation suggests worse heat conduction in sample 'B', connected to nitrocellulose properties, but not to the heating rate. The occurrence of a larger peak of shifted temperature for sample 'B' is in good agreement with

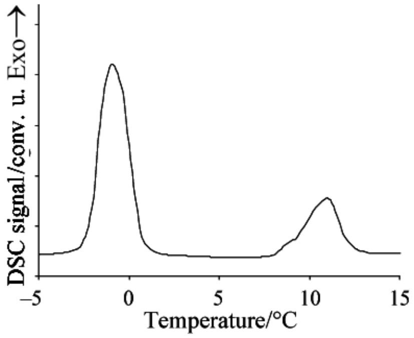


Fig. 4 DSC curve of water melting in steel vessel, β=10°C min^{-1}

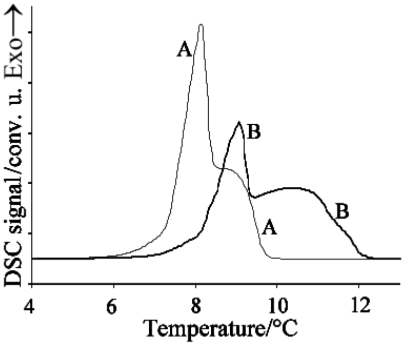


Fig. 5 DSC curves of benzene melting in nitrocellulose, β=2°C min^{-1}

the explanation provided above. Benzene contents in both samples are similar and amount to 64% for ‘A’ sample and 53% for ‘B’ sample. Though differences are not very high, the sample with lower benzene content shows higher peak temperature shifting than expected. Surface drying causes a decrease of solvent amount in unlimited space of good contact to nitrocellulose fibres, as may be suggested from comparison of DSC curves and determined benzene contents.

On the base of considerations presented above the occurrence of a broad peak of maximum shifted up to higher temperatures may be assumed as a typical phenomenon in DSC investigation of nitrocellulose saturated by poorly wettable liquid.

The next investigations were conducted in order to confirm the origin of melting peak shifting and to test possibility of its reduction. Nitrocellulose samples were boiled for 30 min in order to facilitate water penetration into pores. DSC curves of such prepared samples are shown in Fig. 6. A significant influence of boiling on the melting peak shifting effect was not found, but additional peaks appeared below the narrow peak of bulk melting. The enlarged part of Fig. 6 presents low, but clear peaks in range of –6 – –2°C as well. This shows possibility of water penetration into mesopores, although elimination of melting peak shifting phenomenon failed.

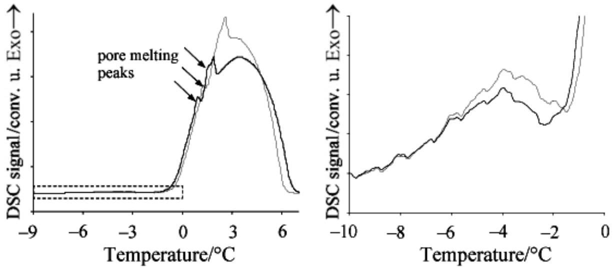


Fig. 6 DSC curves of water melting in nitrocellulose after 30 min boiling, $\beta=2°\mathrm{C\ min^{-1}}$; arrows point peak of larger pores’ melting; at right marked fragment in enlargement

It has to be noticed, that peak shifting up to higher temperatures (above the temperature of water melting) is connected with heat conductivity of a sample. Phase change occurs at normal melting temperature, but considering the high thermal resistance melting proceeds at significantly higher temperature of the environment.

Samples of nitrocellulose were investigated after mechanical stirring in water suspension. DSC curves in Fig. 7 show the obtained results. In this case, subtle structure of DSC curves below bulk melting peak is worse visible, while peaks in range of –6 – –2°C are more sharply outlined. Compared to boiled nitrocellulose, far better water penetration of mesopores takes place. The effect of melting peak shifting is still observable. Heat conductivity improvement is noticeable for the sample submitted to longer stirring. It is visible as the temperature of the sharp peak of bulk melting is lower and the shifted melting peak is less broad. Melting peaks below the narrow peak of bulk melting are at different positions, but temperature difference (about 1°C) is similar to that of bulk melting peaks. Temperature depression of both samples is almost the same.

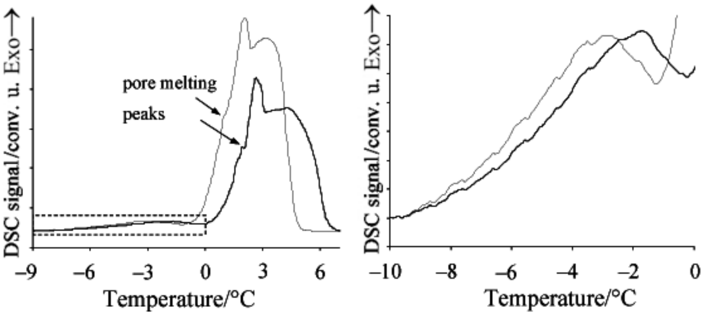


Fig. 7 DSC curves of water melting in nitrocellulose after stirring in suspension, thick line 10 h, thin line 60h, β=2°C min^{-1}; arrows point peak of larger pores' melting; at right marked fragment in enlargement

DSC curves of water melting in nitrocellulose based granulated products were analysed. Granular nitrocellulose was prepared from water suspension with addition of ethyl acetate, evaporated during granules' formation. Two lots of product were analysed, marked as 'I' and 'II'. Samples were submitted to water soaking for 30 min at 50°C. Extent of water was then removed from surface by filter paper and these samples were compared with the ones directly drawn from water.

DSC curves of water melting for product I, presented in Fig. 8, show that minimal shifting of melting peak occurs for non-dried sample, while after removal of water extent a violent increase of melting peak temperature shifting takes place. Bulk melting peak is shifted up to higher temperatures and an additional broad peak clearly appears. Results for product II are similar, as shown in Fig. 9. The wet sample shows good heat conduction, while drying involves typical phenomenon of melting peak temperature shifting. Moreover, stronger drying causes further retardation of heat flow in the sample, which can be observed as shifting of bulk melting peak and broadening of the second shifted melting peak as well. As expected, superficial water removal has no influence on subtle structure decay of DSC curves below bulk melting peak, which corresponds to melting of water inside mesopores.

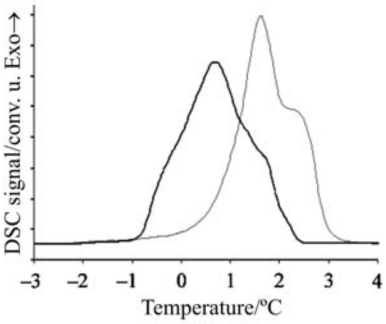


Fig. 8 DSC curves of water melting in granulated nitrocellulose I: thick line – directly drawn from water, thin line – after paper drying, β=2°C min^{-1}

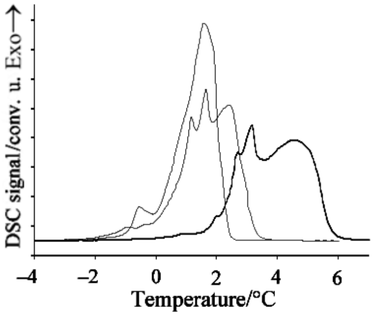


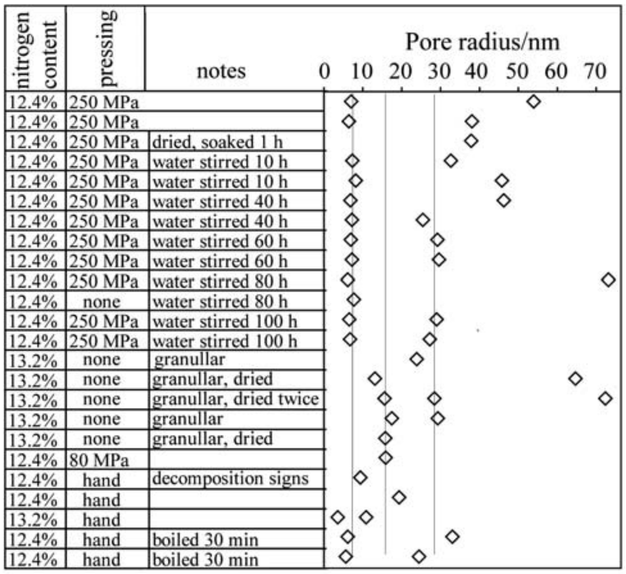
Fig. 9 DSC curves of water melting in granulated nitrocellulose I: thin line – directly drawn from water, dotted line – after first paper drying, thick line – after second drying, β=2°C min^{-1}

On the base of obtained results calculation was made to estimate nitrocellulose pores' size. It was assumed that the last narrow peak of DSC curve corresponds to bulk water melting of good contact with the rest of the sample (0°C). In this manner, internal temperature calibration of each sample was made. ΔT values of melting point depression in pores were estimated this way, pores' size was then determined from the Eq. (3) for cylindrical pores. The shape of pores was assumed arbitrarily, but it has no influence on the comparison of nitrocellulose samples. The shape factor estimation from hysteresis investigation of melting – solidification processes in pores is strongly hindered in this case, because of broad melting peak of water of poor contact with the rest of the sample. Taking into account the rough peak outline of pore melting, determination of pore distribution would be burdened with strong deviation. Thus pore sizes were determined on the base of observed temperatures of peak maximum.

It has to be noticed, that estimated pore sizes are burdened with high uncertainty, considering small ΔT values and deviation of peak temperature determination. In spite of the mentioned difficulties, results show very good convergence, excellent for the smallest pores. A dependence on the type of nitrocellulose studied may be found. For nitrocellulose samples of nitrogen content 12.4% the size amounted to 6.8±0.9 nm is typical, which moreover converges with 6 nm values for cellulose [7] and may be a proof of cellulose structure stability during nitration process. For granulated nitrocellulose, which was treated by solvent (ethyl acetate), most samples show pores of radius 15.4±2.0 nm. For both nitrocellulose kinds value 29.0±0.6 nm was obtained. Values described may be noticed as multiples, which is in good consistence with the layer structure of nitrocellulose.

Good consistency of obtained results is an indication that the assumption about the location of bulk melting peak of small heat resistance is correct and testifies to the applicability of thermoporometry in nitrocellulose investigation.

Among the investigated nitrocellulose samples there were some, which did not show melting peak temperature shifting, while the effect of melting in pores was exceptionally high. Those samples revealed decomposition symptoms, as yellowing



nitrogen content	pressing	notes
12.4%	250 MPa	
12.4%	250 MPa	
12.4%	250 MPa	dried, soaked 1 h
12.4%	250 MPa	water stirred 10 h
12.4%	250 MPa	water stirred 10 h
12.4%	250 MPa	water stirred 40 h
12.4%	250 MPa	water stirred 40 h
12.4%	250 MPa	water stirred 60 h
12.4%	250 MPa	water stirred 60 h
12.4%	250 MPa	water stirred 80 h
12.4%	none	water stirred 80 h
12.4%	250 MPa	water stirred 100 h
12.4%	250 MPa	water stirred 100 h
13.2%	none	granullar
13.2%	none	granullar, dried
13.2%	none	granullar, dried twice
13.2%	none	granullar
13.2%	none	granullar, dried
12.4%	80 MPa	
12.4%	hand	decomposition signs
12.4%	hand	
13.2%	hand	
12.4%	hand	boiled 30 min
12.4%	hand	boiled 30 min

Fig. 10 Pore sizes obtained for investigated nitrocellulose samples

and smell of nitrogen dioxide. DSC curves of water melting in those samples are shown in Fig. 11. Nitric acid and nitrogen oxides released during nitrocellulose decomposition are supposed to facilitate water penetration into pores. Additionally, peaks of bulk melting show no significant temperature depression, which indicates low fouling level of water by decomposition products. The ‘X1’ sample was derived from the ‘X2’ sample by pressing, which involves some water removal. Both samples differ distinctly in porosity, which also demonstrates the usefulness of thermoporometry to characterise nitrocellulose samples. For the sample marked ‘X1’ pore volume amounts to only 0.19 $cm^3 g^{-1}$, while for sample ‘X2’ 0.57 $cm^3 g^{-1}$. Pore sizes, calculated from Eq. (3) is another difference. Pore radius estimated at peak maximum

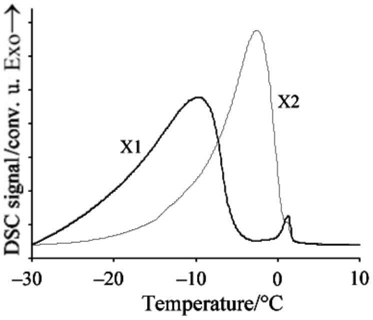


Fig. 11 DSC curves of water melting in nitrocellulose revealing decomposition symptoms, thin line – non pressed sample, thick line – pressed sample, β=2°C min^{-1}

amounts to 3.9 nm for sample 'X1' and 9.8 nm for 'X2'. Taking into consideration the differences in water content in the samples, occurrence of the same small pores can be noticed for both samples, while sample 'X2' shows occurrence of larger pores as well. On the base of sample preparation method, pressing is supposed to remove of water from the larger pores only.

Conclusions

The conducted investigations indicate high hydrophobic properties of nitrocellulose, which coupled with high surface tension of water makes free penetration of water into pores almost impossible. This is an important limitation of studies on nitrocellulose using thermoporometry. Prolonged stirring or boiling of nitrocellulose in water suspension facilitates water penetration into pores. Temperature shifting of melting observed as broad peak above narrow peak of melting in unlimited space of small thermal resistance, is a typical phenomenon in wet nitrocellulose samples. The experiments' results point to heat flow hindrance as the source of the mentioned phenomenon, connected with limited contact area of condensed phases. In spite of the above-described difficulties, thermoporometry has proven a useful investigation method for the comparison of nitrocellulose based materials. Benzene shows similar behaviour in nitrocellulose when used instead of water.

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