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INTERACTION OF WATER WITH THE REGENERATED CELLULOSE MEMBRANE STUDIED BY DSC

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Abstract

One to three endothermal peaks atributted to melting of bulk and interfacial water were observed by DSC in the regenerated cellulose – water system. The profiles of thermal effects depend on water content, time of conditioning, film pretreatment and the conditions applied during the preceding freezing-thawing cycles. The occurrence might be deduced of melting-crystallisation processes. A large amount of non-freezable strongly bounded water was also detected.

Although cellulose absorbs water quickly after immersion, the structural changes consisting on ordering of polymer fraction occur during further conditioning due to increase in strength of water binding. Using the membranes in the separation module at 90°C causes weakening of these bonds. Differences between interaction of particular cellulose films with water can be detected during the first, the second and the third heating.

Keywords: bound water, bulk water, cellulose membrane, crystallisation, DSC, interfacial water, melting, water state

Introduction

Membrane processes are involved as well in nuclear technologies as in the other industries [1–5]. Separation of various media with cellulose membranes is possible due to the interaction of the material of these membranes with solvents, especially because of differences in diffusion coefficient. Knowledge of such interaction as well as of the relation between membrane structure and mass transport through the membrane should be therefore helpful in selection of the appropriate membranes for the particular separation problems. It appears thus interesting, to study the influence of the membrane material on the properties of solvent as well as the influence of solvent on the structure of the polymer phase. The state of water in the dense hydrophilic membranes appears to be particularly interesting in regard to the fact that mass transport is considered as occurring by solution diffusion mechanism. Properties of water in such membranes are considered to be intermediate between these of bulk water and ice [6–7].

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Differential scanning calorimetry has appeared to be an appropriate method in studying interaction of polymers and biological systems with solvents [7–22]. Three types of water were discovered in membranes, differing in freezing-melting behaviour [10–14], alike in the other biochemical species [15–20]. Bulk (or ‘free’) water (present in diluted systems) melts at temperature slightly lower than pure water under the same conditions. The freezable bound water, so-called interfacial (interstitial) water (probably existing in a thick hydration shell connected to the hydrophilic polymer groups) melts at lower temperature due to the stronger connections to the polymer. Melting of the strongly bound water (non-freezable bound water considered as bound in the first hydration shell or incorporated in the micelles) was not observed at temperatures as low as –40°C.

At present, the preliminary studies of cellulose membrane – water interaction were carried out applying differential scanning calorimetry (DSC), supported by thermogravimetry (TG) and thermomechanical analysis (TMA). For determination of the state of water in membranes, examinations were carried out of melting and crystallization behaviour of water. The results were related to the structural changes in the polymer phase resulting from swelling with water.

The influence of experimental DSC parameters on the results were studied as well as the effect of pretreatment on the membrane interaction with water. In particular, we have observed what happens when the initial membrane material is placed into water at ambient temperature and the changes resulting in polymer-water interaction from prolongation of conditioning time. Tests were also done to check the influence of preceding freezing-heating cycles on DSC results. We checked then how using of the membrane in separation module at temperature as high as 90°C influences it’s interaction with water and whether it is possible to detect differences between the initial material and the membranes after usage.

Experimental

Materials

The studies were performed on the initial membrane material Tomofan (regenerated cellulose, product of Poland) 25±1 μm thick. Due to the fact that Tomofan constitutes a dense membrane, transportation of water occur due to its hydrophilicity. An active surface of the membrane equal to 19 % and average pore size equal to 17.3 nm were determined using liquid-liquid displacement porosimetry [23–26] in purpose to describe conventionally transport of water. Apart from the initial Tomofan, two other samples of the membrane were examined. These samples were used before as a filtration material in experiments with water (separation of water and heavy water). The first one was cut from the central part of the membrane and the second one from its edge (working before as a gasket). Accordingly, the first sample was exposed to the action of water under conditions of temperature up to 90°C and transmembrane pressure ca. 0.01 MPa, while the second one was subjected to a temperature treatment (up to 90°C) and mechanical pressure (clamping screws).

Methods

Differential scanning calorimetry

DSC measurements were done using the Perkin Elmer DSC instrument (Pyris) calibrated with cyclohexane (*m.p.* = 6.54°C) and indium (m.p.=156.6°C, heat of fusion=26.45 J g^{-1}).

Melting-crystallisation processes were examined in the temperature range from –40°C to +10°C after the first fast cooling with a rate of 100°C min^{-1}. The measurements were carried out in heating – cooling – heating cycles with a heating – cooling rate of 1°C min^{-1} for the moisture containing films closed in hermetic Al Perkin Elmer DSC pans. Till 3 heating cycles were applied. Two types of experiments were carried out:

The I type procedure was applied in the preliminary experiments. The film was cut into pieces fitting well to the DSC pans and conditioned in water at ambient temperature during the required time. The samples (containing 1.5–11 mg of the wet film corresponding to 1.4–4.5 mg of the initial film) were afterwards quickly wiped dry in purpose to remove surface water before being sealed in DSC pans. The measurements were started immediately after preparation. The results (enthalpy and freezable water content) were expressed in terms of the total mass of wet films (wt%).

As it was difficult to avoid drying of the film during closing in DSC pans and to relate the results gained in this way to the presence of strongly bonded non-freezable water, the following procedure was applied during the next experiments (II type). 4–5 mg of the films were placed directly into DSC pans. The desired amount of water was added with a micro syringe. The pans were then sealed and equilibrated at ambient temperature for the required time (15, 140 min, 15 h), before starting the DSC measurements.

Water content in the samples was expressed in two modes: in terms of the mass of water added to the initial mass of the film ($m^{ad}_{H_2O}/m_f$) or in terms of the ratio of total mass of water to the mass of the anhydrous film ($m^{t}_{H_2O}/m_a$). Total mass of water $m^{t}_{H_2O}$ was calculated as that of added water ($m^{ad}_{H_2O}$) together with water present in the film stored in air at ambient temperature (equal to 8.8 wt % in the case of the initial film). The mass of anhydrous film (m_a) was determined on the way of subtracting of the mass of water adsorbed in air from the initial mass of film (m_f). In the present experiments $m^{ad}_{H_2O}/m_f$ were in the range of 0.75–1.03 ($m^{t}_{H_2O}/m_a$ in the range of 0.89–1.21). It corresponds to the total content of water in the range 47–54 wt%.

Calculations were done on the basis of two reproducible results. The contents of the particular water types were expressed in the same two modes as the water content in the system. In the experiments concerning initial film alone it was expressed as the ratio of mass of the particular type of water (total) to the mass of anhydrous film; the sum of all water type is therefore balanced to the value of $m^{t}_{H_2O}/m_a$ (the following symbols were used: F^t, $bulk^t$, I^tn_t, I^tn_1, N^t). In the experiments comparing initial film with the membranes after usage in the separation module, contents of the particular water types were expressed as the ratio of mass of the particular type of water (added) to the initial mass of film (F^{ad}, $bulk^{ad}$, $I^{ad}n_t$, $I^{ad}n_1$, N^{ad}) and balance of water is equalised then to the value of $m^{ad}_{H_2O}/m_f$.

The content of freezable water F^t (expressed in terms of total water) was determined on the basis of the ratio of total experimental heat of melting (related to the total water present in the sample) to the heat of pure water melting under the applied conditions (330 J g^{-1}). This ratio was then multiplied by a factor equal to the $m^{t}_{H_2O}/m_a$ evaluated for the individual sample. In purpose for determining the F^{ad} parameter (freezable part expressed in terms of added water), the experimental total heat of melting was related to the amount of water added into the sample and the ratio of experimental heat of melting to that of pure water was multiplied by the factor equal to $m^{ad}_{H_2O}/m_f$. The content of non-freezable water (N^t or N^{ad}) was found in each case by subtracting the freezable water content F^t from total water content (leading to N^t,), or the freezable water content F^{ad} from the amount of water introduced to the film (leading to N^{ad}). Although exact calculations of contents of the interfacial water and bulk water were not possible on the basis of the presented data, an attempt was done to relate them to the partial areas of thermal effect determined within the selected range of temperature. The high temperature part of the thermal effect with a single peak at ca. 0°C was attributed to bulk water melting, while the peaks observed at low temperature were attributed to the interfacial water. The minimum between both parts were selected as the border between the two areas. In view of describing the profile of thermal effects related to the melting of the interfacial water, the content of the water which melts in the first stage (I^tn_1, $I^{ad}n_1$ corresponding to the first endothermal maximum) was calculated apart from the total content of interfacial water (I^tn_t $I^{ad}n_t$). The same procedure was applied in each case for evaluation of bulk and interfacial water on the basis of partial areas of thermal effect as in the case of calculation of freezable water (expressed in the same mode) on the basis of total heat of water melting.

For examination of the crystallisation processes taking place in polymeric matter containing water, the cellulose was mixed with water in a mass ratio of 1:1. These samples were then hermetically closed and equilibrated at ambient temperature for the chosen time. DSC measurements were then carried out in the temperature range 10–200°C with a heating rate of 5°C min^{-1}. Moreover, melting of such sample was examined during heating in the standard closed pan and the results were compared to those obtained for the initial Tomofan, not subjected to any treatment. Enthalpies were expressed in terms of dry cellulose mass.

The complementary methods

Thermomechanical (TMA) analyses were carried out using a TMA7 Perkin Elmer instrument. A 3 mm quartz probe was used in expansion mode (parallel plate) with a force of 50 or 10 mN. The piece of membrane was put under the probe and immersed in an excess of water one minute after the start of data collection. The probe position was measured at 20°C during 18 h. Additionally experiments in extension mode were done.

Water content in Tomofan sample hold in air at ambient temperature was determined on the basis of the loss of mass taking place after several days of storage in dessicator over P_2O_5. The result was confirmed by thermoanalytical analysis carried out using a TGA7 Perkin Elmer thermobalance. The mass of sample was measured during heating from ambient temperature till 100°C with a rate of 5°C min^{-1} and afterwards during isothermal heating continued for two hours at 100°C.

X-ray diffraction (WAXS) pattern was recorded using a URD6 Diffractometer (Freiberger Precisionmechanik, Germany) with IRYS-3M generator and Geiger-Müller counter. The $\mathrm{Cu}_{\mathrm{K}_\alpha}$ radiation (Ni filtered, wavelength λ= 1.54178) was used with a tube voltage of 35 kV and a tube current of 20 mA. The measurement was done in the range from 5 to 64 2θ with a step of $\Delta 2\theta = 0.05$ and counting time 25 s. Crystallinity was evaluated applying the Herman's integral method [27]. The line was plotted in the diffraction pattern separating crystalline peaks from the amorphous peak and background (shown in Fig. 1). The upper field is attributed to the crystalline regions and the bottom field of the amorphous regions in the sample. Crystallinity was determined as the percentage of the 'crystalline' area in the total field under the diffraction line.

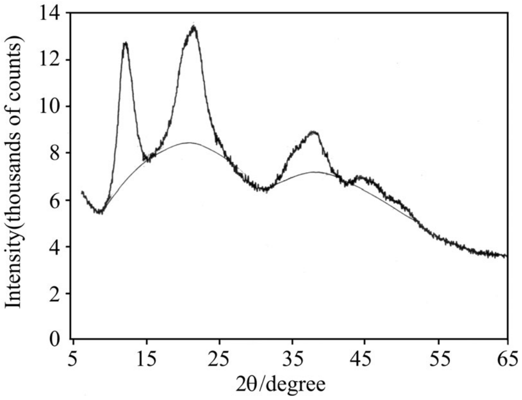

Fig. 1 Diffraction pattern recorded for the initial membrane material Tomofan. The line is shown separating the 'crystalline' and the 'amorphous' regions

Results and discussion

A crystallinity of 11±1% was determined for the initial Tomofan film on the basis of the WAXS pattern (Fig. 1).

Water interaction with the initial Tomofan film. Melting and crystallisation of water

Initial Tomofan film stored in air at ambient temperature contains 8.8 wt% of water. Such residual water is strongly bounded with polymer and therefore does not crystallise during cooling (till –40°C) nor during slow heating. No thermal effect of water melting was thus observed for that film before it was conditioned with liquid water.

Tomofan absorbs water quickly after immersion. Different profiles of endothermal effects of water melting with two to three peaks were observed depending on conditions of film treatment (equilibration time, water content). It might be concluded, on the basis of the profile of thermal effect of melting, that the appearance of several peaks in DSC curves (as well as of minima separating these peaks) is connected to the occurrence of recrystallisation simultaneously with melting of the interfacial water. Due to the partial recrystallisation in the melt, an exothermal effect of crystallisation is recorded simultaneously with the prevailing endothermal effect of melting. The evidence of exothermal process is clear in the curve presented in Fig. 2b.

I type experiments

Endothermal effect corresponding to melting of interfacial water appears at temperature lower than that observed for distilled water under the same condition already after immersing of the sample into water for 1 min (Fig. 2). The melting enthalpy indicates the presence of 10.8 wt% of such water. Only the negligible peak at ca. 0°C corresponds to melting of the residual surface (bulk) water. After further conditioning (15 min) a single melting endotherm of water was still observed but with maximum at a higher temperature (Fig. 2). The larger amount of freezable interfacial water (14.8 wt%) was also detected. Part of this water melts at higher temperature thus has properties more similar to these of bulk water. The existence of strongly bounded freezable water might be however stated as well after 1 min as after 15 min on the basis of the ascending of the DSC

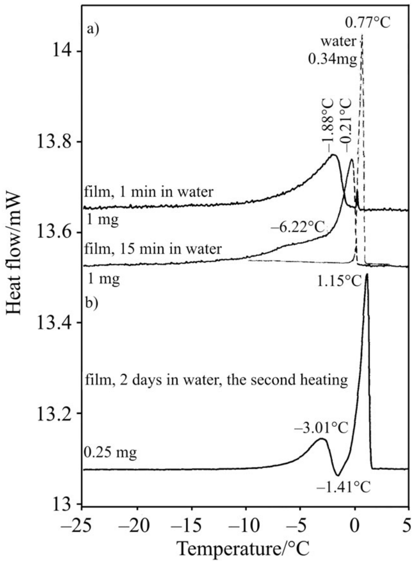

Fig. 2 The examples of DSC curves, obtained during the first type experiments. The curves were calculated per the selected total mass (shown in the cuves): a – the first heating of pure water and the Tomofan samples conditioned with water during 1 min and during 15 min. Ca. 10.8 and 14.8% of freezable water was found after 1 and 15 min, respectively. b – clearly separated endothermal and exothermal effects recorded during the second heating of the sample containing of 62.7% of total water ($m^{t}_{H_2O}/m_a \approx 1.69$) while ca. 47% of freezable water was detected both during the first and the second heating

curve starting from ca. –15°C. Two melting endotherms were observed after conditioning during 15 h corresponding to bulk and interfacial water.

II type experiments

Figure 3 presents the influence of treatment time on the melting processes occurring during heating the films at $m^{\mathrm{t}}_{\mathrm{H_2O}}/m_{\mathrm{a}} \approx 0.92$ ($m^{\mathrm{ad}}_{\mathrm{H_2O}}/m_{\mathrm{f}} \approx 0.75$). A larger fraction melts at a lower temperature with increasing treatment time. Two endothermal maxima connected to melting of interfacial water appear on the DSC curves after 140 min, while only one was observed after 15 min. It indicates the stronger differentiation of water in that state and the higher possibility of occurrence of crystallisation in melt. The evaluation of the particular types of water presented in Table 1 indicates that freezable water content (both bulk and interfacial) decreases between 15 and 140 min, while the content of the strongly bonded nonfreezable water increases. Although no essential differences might be found between particular types of water in the samples conditioned during 140 min and 15 h (Table 1), differences between the state of interfacial water might be deduced on the basis of the profiles of thermal effects shown in Fig. 3. Apart from the peaks connected to the melting of interfacial water also these connected to bulk water melting are observed at lower temperature after longer conditioning (Fig. 3). Crystallisation during cooling also occurs at lower temperature after longer treatment. The peaks of exothermal effects of crystallisation were, therefore, observed at –10.7±0.1°C after 15 min and 13.3±0.4°C after 140 min. The results presented in Fig. 3 and in Table 1 together with the above data concerning crystallisation during cooling show all that water becomes stronger bound to the film with increasing time of treatment. It might be expected, therefore, that the membranes will gain better efficiency in processes, based on their hydrophilic properties, after longer conditioning at ambient temperature (till 15 h) although their swelling occurs very fast.

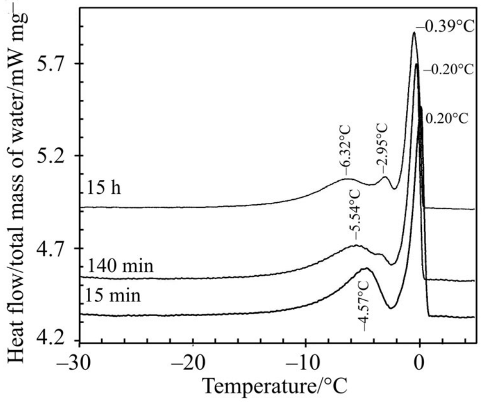

Fig. 3 The examples of DSC curves recorded during the first heating for the initial Tomofan kept in water at $m^{\mathrm{t}}_{\mathrm{H_2O}}/m_{\mathrm{a}}$ equal to ca 0.92 ($m^{\mathrm{a}}_{\mathrm{H_2O}}/m_{\mathrm{f}} \approx 0.75$) at ambient temperature during: 15 min ($m^{\mathrm{t}}_{\mathrm{H_2O}}/m_{\mathrm{a}} = 0.924$), 140 min ($m^{\mathrm{t}}_{\mathrm{H_2O}}/m_{\mathrm{a}} = 0.911$) and 15 h ($m^{\mathrm{t}}_{\mathrm{H_2O}}/m_{\mathrm{a}} = 0.937$)

Table 1 The content of bulk, interfacial (total and in the first stage) and non-freezable water as evaluated on the basis of heat of thermal effect of melting (total and the particular partial areas) recorded on the first heating of the samples conditioned during the selected period at $m^t_{H_2O}/m_a \approx 0.92$ and 1.07.

Time		15 min	140 min	15 h	15 h
I		II	III	IV	V
Water content in the examined samples and melting enthalpies					
Added water	$m^{ad}_{H_2O}/m_f\cdot 100$	75.3±1.5	74.2±1.3	76.7±2.1	88.8±1.5
Total water	$m^t_{H_2O}/m_{fa}\cdot 100$	92.3±1.8	91.1±1.5	93.7±2.5	107.0±1.8
Heat of endothermal effect of melting, J g^{-1}:					
– expressed in terms of added water content		184.5±0.3	165.5±0.4	172.2±5.3	155.7±4.6
– expressed in terms of total water content		206.1±0.4	185.1±0.3	192.0±5.9	171.3±5.1
Calculated content of the particular types of water expressed in terms of the ratio of mass of water (total) to the mass of anhydrous film ($m^t_{H_2O}/m_a\cdot 100$, mg/mg)					
Freezable (F^t)		51.6±0.1	45.7±0.1	48.9±1.5	50.5±1.5
bulk^t		26.4±0.3	23.6±0.1	23.5±1.0	23.0±1.3
Interfacial, total (I^tn_t)		25.2±0.3	22.1±0.1	24.3±1.0	27.9±1.0
Interfacial, I stage (I^tn_1)		25.2±0.3[a]	18.7±0.2	18.2±1.0	23.5±1.0
Non-freezable (N^t)		40.8±1.0	45.4±1.0	45.9±1.5	56.5±1.5
Bounded (non-freezable and interfacial) $N^t+I^tn_t$		67.9±1.3	67.5±1.1	69.4±1.5	84.5±2.5

[a] only single stage in heat transfer might be attributed to the interfacial water

Figure 4 shows examples of DSC curves recorded for samples conditioned with various amounts of water during the same time of 15 h. From the comparison of these curves and the data presented in Table 1 (columns IV and V), it can be concluded that more interfacial water appears in the system when the total water content increases. The first maximum connected to the interfacial water melting is larger and recorded at higher temperature, because of the larger amount of such water in the system. Further crystallisation of the larger amount of water result in the larger exothermal effect but noticed at a higher temperature. Therefore, two maxima and two minima are observed at $m^t_{H_2O}/m_a \approx 0.94$ while due to the increase in both endothermal and exothermal effects, the smaller second maximum surrounded by two deep minima were observed at $m^t_{H_2O}/m_a \approx 1.07$. The higher content of the interfacial phase present at $m^t_{H_2O}/m_a \approx 1.21$ is evident from the endothermal and exothermal effects. Simultaneously, higher and more narrow endothermal maximum connected to bulk water melting is observed at higher temperature (Fig. 6). The higher content of the non-freezable water was found at $m^t_{H_2O}/m_a \approx 1.07$ than at $m^t_{H_2O}/m_a \approx 0.94$ (Table 1) (apart from the higher content of the interfacial water). It might be stated therefore that increase of $m^t_{H_2O}/m_a$ ratio from 0.94 to 1.07 results in an increase of the amount of as well non-freezable as interfacial water.

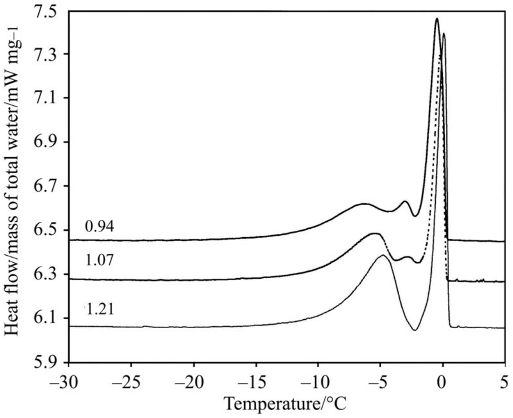

Fig. 4 The examples of DSC curves recorded during the first heating of Tomofan sample conditioned during 15 h at $m^{t}_{H_2O}/m_a$ equal to 0.94, 1.07 and 1.21 (shown on the particular curves; $m^{ad}_{H_2O}/m_f$: equal to 0.77, 0.89 and 1.03, respectively)

Water interaction with the initial Tomofan film. Swelling in water and crystallisation of polymer matrix

In regard of the evidence of the influence of time of conditioning on the state of water in the membrane, it appeared interesting to examine also the swelling of the membrane in water and to study the influence of the conditioning with water on the structural properties of the cellulose matrix.

Figure 5 presents TMA results obtained for the initial Tomofan (expansion mode, 50 mN). After one minute the sample is immersed in water. A sharp increase in volume with a factor of ca. 1.8 is observed within 5 min. The increase levels off and is almost

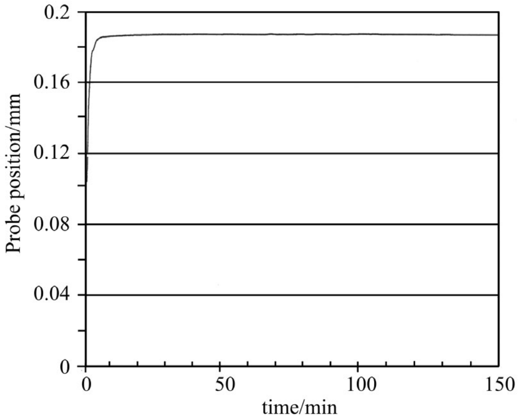

Fig. 5 TMA curve recorded for the initial Tomofan film with a force of 50 mN (expansion mode)

stable after 100 min. The exact behaviour of the film depends, however, on the stress applied on it via the probe. For smaller stresses (10 mN) an overshoot was observed with a steady decrease afterwards. In this case stabilisation was not reached within the experiment (18 h). The increase in volume is in the normal direction to the film and not in the film direction. This was checked with an experiment in extension (not shown).

A broad endothermal effect was noticed in the range of 61–131°C of the moisture containing samples ($m^{t}_{H_2O}/m_a \approx 1.07$, $m^{ad}_{H_2O}/m_f \approx 0.90$) after conditioning during 18 h (Fig. 6) with an enthalpy equal to 15±1.5 J g^{-1}. This endothermal effect seems to be connected to the melting of the polymer phase and therefore indicates the ordering resulting in cellulose-water system after prolonged water treatment [11], similarly to that taking place in starch after hydrothermal crystallisation [28–29]. It might be supposed that creation of the new type of ordering occurs in the amorphous phase. In fact, an exothermal effect probably connected to crystallisation was reported by Kimura *et al.* [21] in the similar temperature range during heating of amorphous cellulose submitted to conditioning at high water vapour pressure.

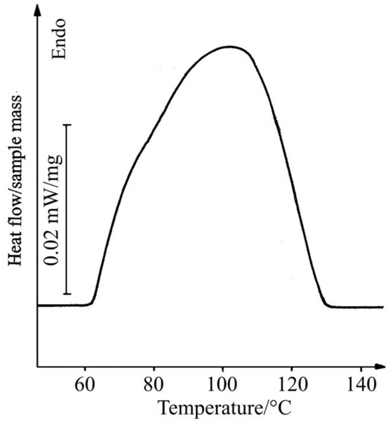

Fig. 6 Thermal effect of melting of cellulose matrix recorded under hydrothermal conditions for the initial Tomofan film stored in water during 18 h ($m^{t}_{H_2O}/m_a = 1.07$, $m^{ad}_{H_2O}/m_f = 0.89$). No thermal effect was observed in this temperature region after 15 min of storage

For the samples which were conditioned with water for a short time (15 min) no thermal effect was observed during heating till 200°C. It might be concluded, therefore, that rapid swelling observed by TMA in the preliminary stage of the experiment does not induce ordering of the polymer matrix.

The influence of film pretreatment on the further interaction with water

Evident differences between physical properties of the initial film and both parts of the membrane after usage in the separation module arises from comparison of their electrostatic interactions. Particularly strong repulsive forces were observed for the central part of the membrane, active during the separation processes, but also in the case of the edge of the membrane. No such interactions were observed for the initial film.

More water melts at higher temperature in the case of the membrane after usage as compared to the initial film submitted to water treatment under the same conditions ($m^{ad}_{H_2O}/m^f \approx 0.89$, 15 h) (Fig. 7, Table 2). A larger amount of freezable water was detected and more bulk water is present in this sample than in the initial film. The DSC profiles of endothermal effects and maxima observed at higher temperature, indicate also that more interfacial water melts at higher temperature. It might be concluded, therefore, that using the membrane in a separation module at temperatures as high as 90°C causes weakening of the bounds between water and membrane. It might be expected, consequently, that separation capacity of this hydrophilic membrane deteriorates after prolonged usage. As expected, mechanical pressure of several atmospheres applied at elevated temperature (edge of the membrane) influences the further state of water more than the treatment applied to the central part of the membrane active in the separation processes (contact with solvent under the conditions of heat treatment and transmembrane pressure (0.01 MPa)). This indicates that weakening of bonds between the edge of the membrane and water is larger than in the case of the centre.

Essential differences were noticed between the profile of thermal effects connected to the first and the second melting of ice (Fig 8a). More freezable water was detected during the second than during the first heating with clear increase in the bulk water content (evaluation is given in Table 3). This is probably caused by the feasi-

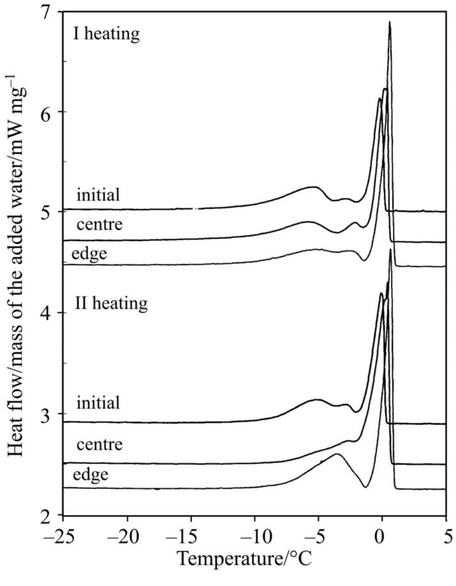

Fig. 7 Comparison of the melting endotherms recorded during the first and the second heating for the initial Tomofan, and both parts of the membrane removed from the separation module. The measurements were done after conditioning during 15 h at $m^{ad}_{H_2O}/m_f \approx 0.89$ ($m^{t}_{H_2O}/m_a \approx 1.07$)

Table 2 Distribution of water introduced to the initial Tomofan film and the both parts of the film used in the separation on the way of conditioning at $m^{ad}_{H_2O}/m_f$=0.89 for 15 h (expressed in terms of added water)

Sample		Initial Tomofan	Centre of membrane	Edge of membrane
I		II	III	IV
Water content in the examined samples and melting enthalpies				
Added water	$m^{ad}_{H_2O}/m_f\cdot 100$	88.8±1.5	88.6±1.3	89.5±0.6
Total water	$m^{t}_{H_2O}/\mathrm{m}_{fa}\cdot 100$	107.0±1.8[b]	106.8±1.6[b]	107.8±0.7[b]
Heat of endothermal effect of melting, J g^{-1}:				
- expressed in terms of added water content		155.7±5.1	188.3±1.3	192.4±1.0
- expressed in terms of total water content		171.3±4.6	207.5±1.5	211.3±1.1
Calculated content of the particular types of water expressed in terms of ratio of the mass of added water to the mass of the initial film ($m^{t}_{H_2O}/m_a$ x 100, mg/mg):				
Freezable (F^{ad})		46.1±1.4	55.7±0.4	57.3±0.3
bulk^{ad}		21.0±1.2	28.4±0.5	34.6±0.5
interfacial (total; $I^{ad}n_t$)		25.1±1.0	27.3±0.7	21.3±0.3
interfacial (I stage, $I^{ad}n_1$)		22.9±1.0	22.4±1.0	15.6±0.1
Non-freezable (N^{ad})		42.7±1.5	32.9±0.3	32.2±0.2
Bounded (non-freezable and interfacial) $N^{ad}+I^{ad}n_t$		67.9±1.5	60.1±1.0	53.5±0.5

[b] The values are calculated with assumption of 8.8% of water in each membrane

bility of crystallisation of a larger water fraction during slow than during fast cooling (preceding the second and the first heating, respectively) as fast cooling enables to preserve water in a form more similar to the one in the primary state. It seems to be more likely than reduction of bound water content in result of application of freezing-thawing cycles [15], especially as no essential differences could be noticed between melting endotherms recorded during the second and the third heating, after the same directly applied thermal treatment.

The influence of freezing – melting – freezing cycles was noticed as well in the case of the initial Tomofan as in the case of both parts of used membrane (Figs 8a, b, c). Moreover, it seems to be the larger when the film pre-treatment in separation module has caused larger influence on the primary film interaction with water. Therefore, the higher sensitivity of the membrane after usage might be deduced to the freezing – thawing conditions as compared to the initial film. This confirms also the conclusion concerning structural changes taking place in the membrane under use. Comparison of the content of the particular types of water detected during the first, and the second heating of the initial Tomofan and both parts of the membrane during the same experimental cycle, is given in Table 3. During the third heat-

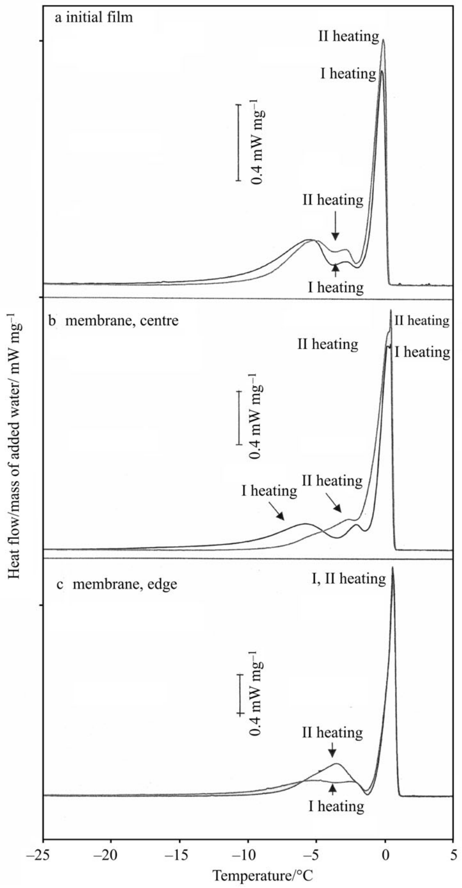

Fig. 8 Comparison of the DSC curves recorded during the first and the second heating (carried out within the same experiment) for: a – the initial Tomofan, b – centre of the membrane, c – edge of the membrane

ing (performed as the second one after slow cooling at 1°C min^{-1}), similar results were obtained as during the second one. This confirms the conclusion concerning the validity of the conditions applied during the preceding freezing cycles on the endothermal effects of melting recorded during the foregoing heating.

Consequently, the differences between the cellulose films, initial and subjected to pretreatment in separation module are easily detected during the second and the third heating as well as during the first heating (Fig. 7a,b).

The result shows the importance of taking care about reproducibility of the freezing - thawing conditions, in purpose of studying and comparing interaction of various membranes with water. Moreover, it might be concluded on the basis of the similarity of the results obtained during the second and the third heating, that comparison of water interaction with various films might be better observed during heating taking place after slow

Table 3 Distribution of water in the initial Tomofan film and in the membranes after usage as detected during the first and the second heating of the individual samples presented in Fig. 9 ($m^{\mathrm{ad}}_{\mathrm{H_2O}}/m_{\mathrm{f}} = 0.89$, conditioning for 15 h). The content of the particular water types is expressed in terms of the ratio of the added water to the initial mass of the film ($m^{\mathrm{ad}}_{\mathrm{H_2O}}/m_{\mathrm{f}}$ x 100, mg mg^{-1})

Sample	Process	Heat of melting/ J g^{-1}	Type of water			
			Bulk/ 100x mg mg^{-1}	Interfacial		Non-freezable/ 100x mg mg^{-1}
				Total100x mg mg^{-1}	I stage 100x mg mg^{-1}	
I	II	III	IV	V	VI	VII
Initial film	I heating	168.7	20.5	25.0	22.9	42.9
Initial film	II heating	178.7	28.5	19.7	12.7	40.6
Membr. centre	I heating	203.6	29.0	25.9	20.4	32.3
Membr. centre	II heating	207.6	41.2	14.8	13.8	31.2
Membr. edge	I heating	213.9	36.9	20.8	15.7	32.3
Membr. edge	II heating	227.7	35.5	25.9	not detected	31.2

freezing cycles (applied at present before the second heating) than after heating taking place after fast freezing (applied before the first heating).

Conclusions

One to three endotherms attributed to melting of bulk and interfacial water were observed during the first, the second and the third heating of regenerated cellulose membrane – water system, depending on water content, equilibration or treatment time and sample history. These thermal effects occur at lower temperature than melting of pure water. Moreover, a large amount of non-freezable strongly bounded water was detected. The profiles of endothermal effecs of ice melting depend on the conditions applied during the preceding freezing-thawing cycles. It might be deduced that several peaks on melting endotherms correspond to the occurrence of melting-crystallisation processes.

Although an extremely rapid swelling was detected immediately after the sample was placed into water, structural changes still occur during prolonged treatment. These changes may include the creation of crystalline ordering in the polymer fraction as deduced from the increase in strength of water binding. Such increase in hydrophilicity is expected to influence efficiency of separation.

Strength of bounds between the membrane and water was smaller in the case of the membranes which were used in separation module before examination. It might be expected, therefore, that separation ability of these hydrophilic membranes deteriorates after prolonged usage.The content of strongly bounded water was lower in the case of the film subjected to mechanical pressure than to the membrane active in separation process and subjected to transmembrane pressure at the same temperature (90°C). The state of water in the material obtained after such usage seems to be the more sensitive to conditions of freezing than that in the initial Tomofan film.

Differences between interaction of particular cellulose films with water can be detected as well during the second and the third heating as during the first heating.

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