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Crystallisation of cellulose/*N*-methylmorpholine-*N*-oxide hydrate solutions

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Abstract

N-methylmorpholine-*N*-oxide (NMMO) hydrates are direct solvents for cellulose used commercially in the preparation of cellulose spinning dopes for fibre and film manufacturing. The fact that the cellulose/NMMO/water solutions can crystallise under cooling is important in the process of preparing fibres and films and in their structure formation.

It is shown here that the major difference with classical polymer solutions is that the crystallisation of cellulose/NMMO/water solutions is only due to the crystallisation of the solvent, not of the cellulose. The reason for the decrease in crystallisation velocity with the increase in the cellulose concentration is the reduction in the crystallisable part of the solution. The concentration of water in solutions with the same cellulose content is found to strongly influence the crystallisation velocity and the morphology of crystallised solutions. The variation of the crystallisation velocity values with the type of cellulose can be explained by different amounts of free water bound to NMMO, that depend on the cellulose origin. © 2002 Published by Elsevier Science Ltd.

Keywords: Cellulose; *N*-methylmorpholine-*N*-oxide; Crystallisation kinetics

1. Introduction

The solving power of *N*-methylmorpholine-*N*-oxide (NMMO) hydrates for cellulose has been recognised a long time ago [1]. From the seventies, research started in industry and academia to understand what the physical characteristics of such solutions were [2–10]. This work lead to the preparation of spinnable solutions, and to the production of cellulose products, mainly fibres [11–13]. Due to environmental pressures against the use of viscose, research regained momentum these last 5 years. Among the revisited topics are the phase transitions, the state of these solutions and their rheology [14–21].

It is known that the cellulose/NMMO/water solution can crystallise under cooling. This important topic was only touched by two teams. In 1979, Chanzy et al. [6] noted that solutions of cellulose in monohydrate and anhydrous NMMO crystallise upon cooling, forming spherulites for monohydrate NMMO and cellulated textures for anhydrous NMMO. Crystallisation was found to occur after an induction time, which is increasing with cellulose concentration, a feature attributed to the effect of viscosity. More interesting was the fact that after sublimation of the NMMO and the water, the cellulose chains retained the general morphology of the crystallised solution (spherulites or cells). The conclusion of this work was that NMMO crystallises first, than does cellulose in a transcrystallised manner. A second paper by Iovleva et al. dated 1986 [19] describes the influence of cellulose DP, concentration and temperature on the rate of crystallisation. The main results are that the rate of crystallisation does not depend on cellulose degree of polymerisation (DP from 50 to 960), decreases strongly with cellulose concentration (in contrast with classical polymer solutions) and has a maximum in the temperatures range 21–25 °C for solutions with the monohydrate NMMO. The conclusion of the authors is that the predominant role in the crystallisation process belongs to the solvent, not to the cellulose.

Since crystallisation plays a role in the regeneration of cellulose (regeneration with or without crystallisation may give different end-products) and can be a method for structuring cellulose products, we revised the old data with

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Table 1
Characteristics of the cellulose used for the preparation of cellulose/NMMO/water solutions

	Kraft 1/1	Kraft 1/2	Kraft 2/1	Kraft 2/2	Kraft 3	Kraft 4
M_n (× 1000)	77.4	44.2	53.0	40.4	50	51.7
M_w (× 1000)	226.3	90.2	155.0	98.2	207	105.2
M_z (× 1000)	468.9	158.0	410.5	206.9	619.9	186.7
wt% (DP < 50)	1.1	1.6	1.5	2.3	2.6	1
wt% (DP < 200)	7.8	18.5	14.3	21.8	15.8	14.6
wt% (DP > 2000)	21	2	10.8	4	18	3.5
Crystallinity (%)	53	55	51	47	46	43

Molar mass distribution was measured by size exclusion chromatography (SEC/GPC) and crystallinity by Fourier transform infrared spectrometry (FT-IR).

the aim to clarify the role of cellulose in the crystallisation of the solutions. This article gives the results of measurements of crystallisation velocities of cellulose/NMMO/-water solutions as a function of cellulose origin, its concentration, crystallisation temperature and water content as well as of the observation of their morphologies. Viscosity measurements and X-ray scattering were used to understand the relative role of the cellulose and the solvent in the crystallisation process.

2. Experimental

2.1. Materials and preparation

Four different Kraft cellulose families called Krafts 1–4 were used in this work. All the cellulose samples were prepared in a similar way. Each Kraft family has the same cellulose origin, the difference being the molecular weight distribution. The properties of the cellulose samples (except Kraft 1/3 and Kraft 1/4) used in this study are given in Table 1. Cellulose solutions with 3, 6, 8 and 10 wt% (corresponding NMMO and water contents as well as the molar fractions of all components are listed in Table 2) were prepared in the following manner in the Lenzing AG research centre. A small amount of gallic acid propylester (GPE) was mixed in NMMO/water solutions and stirred during 10 min. Then, a given amount of cellulose pulp was impregnated at room temperature for 1 h in an NMMO/water/GPE solution (~50 wt% of NMMO) using a shovel kneader equipment. After the impregnation time, the excess water was distilled off by heating and evaporation. The pressure in the apparatus was fixed at 250 mbar and it was lowered every 5 min by 25 mbar until it reached 50 mbar. The dissolution process was ended when the amount of distilled water was reaching the nominal value. This value was calculated as a function of desired final water content and the water content in cellulose pulp. Finally, the pressure was brought up to 400 mbar and the temperature was fixed at 108–112 °C. The dope was maintained for 15 min under these conditions.

Table 2
Cellulose, NMMO and water contents of the samples

Cellulose		Water		NMMO	
wt%	Molar fraction	wt%	Molar fraction	wt%	Molar fraction
3	0.0123	14	0.516	83	0.471
3	0.0119	15	0.526	82	0.451
3	0.0115	16	0.555	81	0.432
3	0.0112	17	0.573	80	0.415
3	0.0109	18	0.590	79	0.398
6	0.0239	15	0.539	79	0.436
8	0.0335	13.5	0.510	78.5	0.456
10	0.0435	12.5	0.489	77.5	0.466

2.2. Equipment and experimental techniques

Cellulose/NMMO/water solutions are known to present a high tendency to exchange water with ambient air. To overcome this, all manipulations were conducted under a dry nitrogen atmosphere.

The study of the crystallisation kinetics of the cellulose/NMMO/water solutions was performed by visually following the growth of the crystals. To do this, the solution (received from Lenzing AG in the solid form) was placed on a glass slide and heated at 80 °C, then covered by another glass slide. This first heating ensures that all nuclei present in the solution are melted. Then, the sample was placed into the Linkam THMS 600 hot stage stabilised at the test temperature, using either water or liquid nitrogen as a coolant. Test temperatures were chosen between −10 and 50 °C. It was difficult to record crystallisation outside this range. The advancement of the crystallised front was observed using a Leitz Metallux 3 optical microscope in reflected light. The images were recorded with a CCD camera and a video recorder equipped with a frame counter. The propagation of the crystallisation front at a given temperature was measured versus time and the crystallisation velocity was calculated from the slope. All experiments were repeated three times.

Viscosity measurements of the 3 wt% cellulose solutions were performed on a rotational StressTech DMA rheometer equipped with two coaxial cylinders. The solid solution was quickly melted at 80 °C and then poured into the barrel kept at the same temperature. Three viscosity versus shear rate experiments were performed with each filling. The resulting

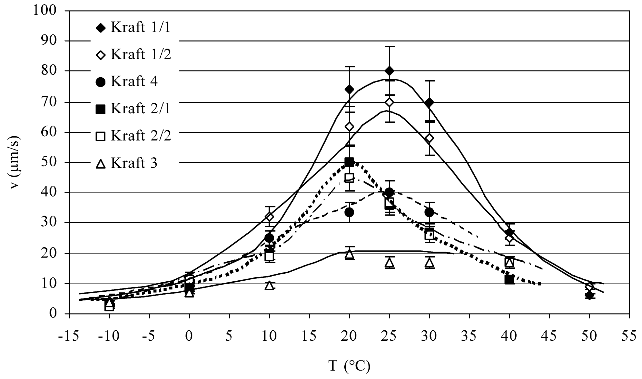

Fig. 1. Crystallisation velocity v in µm/s of the 3 wt% cellulose solutions (15 wt% of water) versus isothermal crystallisation temperature.

curves were superimposable showing that neither degradation nor water evaporation took place during the time of the experiment.

Wide angle X-ray scattering experiments were performed with a Huber (D-8219 Rimsting Germany) plane chamber, using the Debye–Sherrer method. The power of the PW 1830 Philips generator was 1200 W, using a Ni-filtered Cu Kα ($\lambda = 0.15405$ nm) beam.

3. Results and discussion

3.1. 3 wt% cellulose solutions

3.1.1. Crystallisation kinetics as a function of temperature

The crystallisation behaviour of the 3 wt% cellulose solutions (15 wt% of water) seems to follow what is known for polymer melts and solutions. Fig. 1 shows the evolution of the crystallisation velocity of solutions of various cellulose origin as a function of temperature. The crystallisation velocity is low for low temperatures because the viscosity of solutions is high. It is also low for high temperatures because the nucleation is slowed down. For the majority of solutions, the crystallisation velocity reaches a maximum around room temperature, i.e. in the temperature range 20–30 °C. This result is very similar to what was found by Iovleva et al. [19]. Most of the crystallisation curves exhibit similar behaviour even though the crystallisation velocity of the 3 wt% Kraft 3 solution presents a plateau in the temperature range 20–40 °C. For this solution it was not possible to observe a crystallisation above 40 °C, probably because the induction period was too long. The same phenomenon was observed for the 3 wt% Kraft 4 solution that did not crystallise above 30 °C.

Cellulose of different origins may have different structural morphologies that do not always allow a proper comparison. Nevertheless, it is here possible to compare two sets of samples, the Kraft 1/1 and the Kraft 1/2, as well as the Kraft 2/1 and the Kraft 2/2, of different molecular weights (Table 1). Despite their large difference in molecular weight, their growth kinetics curves are very similar, even identical within the experimental error. This absence of influence of the molecular weight of the cellulose on the crystallisation kinetics confirms the results of Iovleva et al. [19].

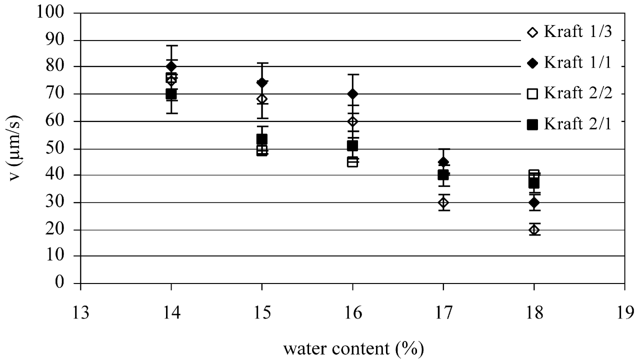

Fig. 2. Crystallisation velocity of the 3 wt% cellulose solutions versus water content, at 20 °C.

3.1.2. Crystallisation kinetics as a function of the water content

In order to get more information about the growth kinetics, 3 wt% samples of Kraft 1/1, Kraft 1/3, Kraft 2/1 and Kraft 2/2 with water content of 14–18 wt% were investigated at 20 °C. Fig. 2 shows that the crystallisation velocity decreases as the water content increases. It is interesting to note that the kinetics is very sensitive to small variations of the water content of the NMMO/water solvent. A change from 14 to 18 wt% (i.e. a total variation of water content in the solution of 4 wt%) decreases the crystallisation velocity by 35%. This is due to the fact that it is the solvent that crystallises and that above the monohydrate level, there is a strong dilution factor of the NMMO/water monohydrate crystal. At water contents above 13.3% (monohydrate), the solvent is in a two-phase region below the crystallisation temperature, one phase being solid NMMO/water, the other liquid NMMO/water [8]. This dilution effect is the cause of the slowing down of the velocity. It clearly shows that if the water content of the cellulose is varying, this will have a strong effect on the crystallisation velocity of the solution.

3.1.3. Rheological behaviour of 3 wt% cellulose solutions

We saw in Fig. 1 that the crystallisation kinetics can have different behaviour as a function of temperature, and that two similar cellulose samples with very different molecular weights have nearly the same crystallisation kinetics. In order to add more information on whether it is the solvent or the cellulose that is the major player during crystallisation, we measured at 80 °C the viscosity of all the 3 wt% solutions (15 wt% of water). The results are given in Fig. 3. Crystallisation was performed in a temperature range much below the 80 °C rheological test temperature. Despite that the activation energy may slightly vary from one solution to

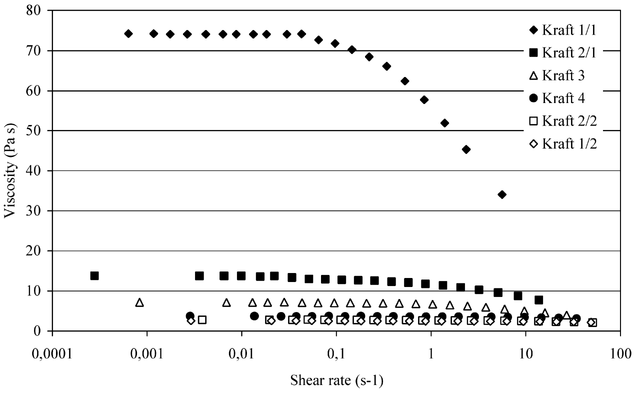

Fig. 3. Viscosity of the 3 wt% cellulose solutions at 80 °C.

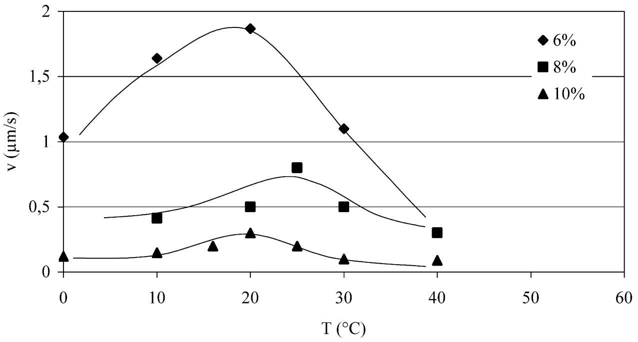

Fig. 4. Evolution of the crystallisation velocity of 6, 8 and 10 wt% Kraft 1/4 cellulose solutions with crystallisation temperature.

another when changing the origin of the cellulose, the features of Fig. 3 are so clear that the conclusions taken at 80 °C are valid for the lower temperatures at which crystallisation takes place. It can be noticed that one solution is largely more viscous than the others, namely the Kraft 1/1. In particular, it is much more viscous than the Kraft 1/2, whereas their crystallisation kinetics are very similar. Comparing Kraft 2/1 and Kraft 2/2 shows again that a large difference in viscosity does not give an effect on the crystallisation kinetics. Another surprising point is that the molecular weight of Kraft 3 cellulose in solution is close to the one of Kraft 1/1 cellulose in solution, while their viscosity and crystallisation kinetics are very different.

One can note in Fig. 3 that the two more concentrated solutions show a shear thinning region in the shear rate range investigated. This is the normal behaviour for polymers and has been already described for cellulose solutions [17]. As a conclusion, we can say that the viscosity of the solutions is not the cause of the variation of crystallisation velocities with different molecular weights or cellulose origin. As seen above, it is the water content of the solution that is influencing the kinetics. We can postulate that the different cellulose origin of the four Kraft families leads to a slightly different content of water able to bind to the solvent, thus leading to a difference in crystallisation velocity.

3.2. Crystallisation kinetics of the 6, 8 and 10 wt% cellulose solutions

Solutions with various cellulose concentration were investigated in order to clarify the role of the solvent during crystallisation. Plots of the crystallisation velocities of 6, 8 and 10 wt% Kraft 1/4 solutions are presented in Fig. 4. The crystallisation velocity decreases when the cellulose concentration in the solution increases. This phenomenon differs from the case of polymer solutions where the crystallisation velocity increases with concentration. This can be explained by considering that in classical polymer solutions, it is the polymer that is crystallising. In this case, the higher the polymer concentration is, the faster is its crystallisation. Here there is the reverse phenomenon: it is the solvent that is crystallising. So, the higher the solvent concentration (and thus the lower the cellulose concentration is), the faster is the crystallisation. The crystallisation curves are similar to the case of the 3 wt% cellulose solutions, despite their maxima are not so well marked. The maximal velocity is around room temperature, as in the case of the 3 wt% cellulose solutions. This is in agreement with the fact that it is the solvent that is crystallising.

3.3. X-ray scattering

In order to analyse the organisation of the cellulose in solutions, the following samples were investigated by X-ray scattering. Three types of sample preparation were used. First, samples of the 3 wt% Kraft 1/1, 6 wt% Kraft 1/4 and 8 wt% Kraft 1/4 solutions crystallised at room temperature were analysed. Second, the same samples were washed in a water bath at room temperature and analysed again. Third, the solvent was removed from crystallised 6 and 8 wt% Kraft 1/4 solutions by sublimation and the samples were studied. Diffraction patterns of all the samples described above are presented in Fig. 5. Diffraction pattern of the 3 wt% Kraft 1/1 crystallised solution shows a very well oriented structure, all the peaks being assigned to the crystallised solvent, with no trace of cellulose (Fig. 5a). The crystallised solvent seems to be less oriented in 6 and 8 wt% Kraft 1/4 solutions samples (Fig. 5b and c). The origin of this orientation is not clear. It may be due to the uniaxial advancing of the crystallisation front. The exposure time of the film in Fig. 5a–c is the same as for Fig. 5d–f where the NMMO has been removed either by sublimation or washing. The fact that there is no sign of crystallised cellulose in Fig. 5a–c while such signal is seen in Fig. 5d–f shows that this absence of cellulose rings was not due to the small amount of cellulose in the solution. Diffraction patterns of the water washed samples (Fig. 5d–f) can be assigned to the patterns of the cellulose II [22]. It is possible to observe the beginning of the cellulose crystallisation here but no orientation. In contrast, diffraction patterns of the samples analysed after NMMO extraction (Fig. 5g and h) show the presence of amorphous cellulose. The fact that

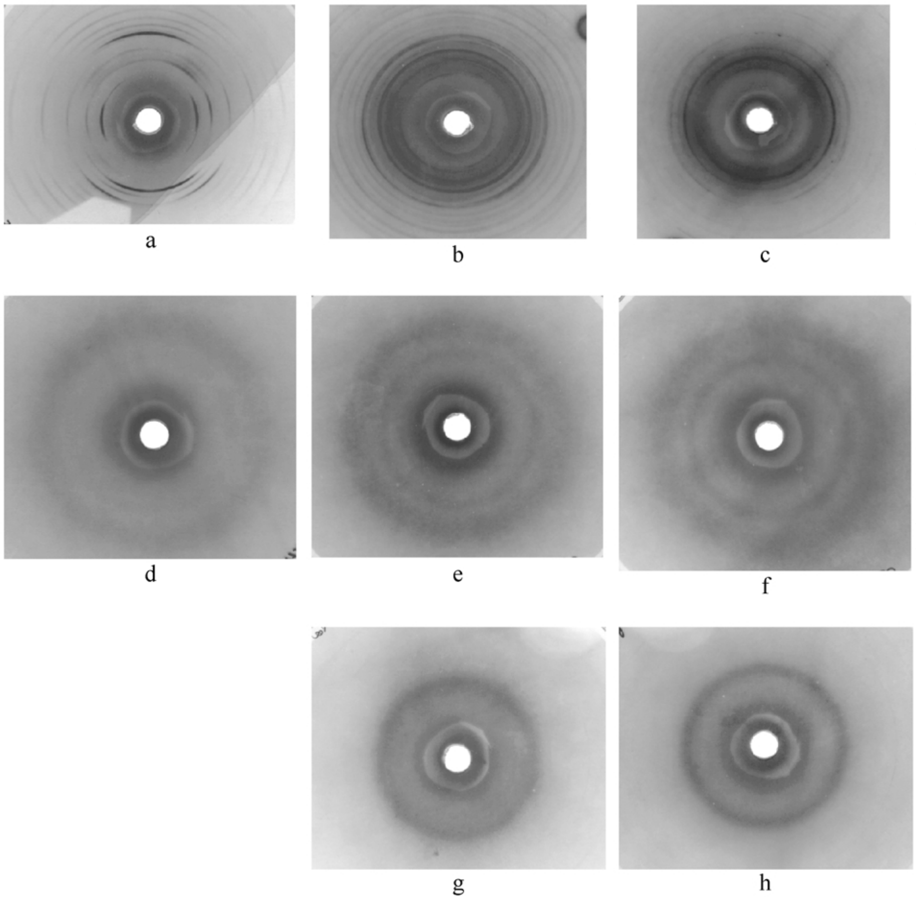

Fig. 5. X-ray diffraction patterns of the 3, 6 and 8 wt% cellulose solutions: (a) crystallised 3 wt% Kraft 1/1 solution; (b) crystallised 6 wt% Kraft 1/4 solution; (c) crystallised 8 wt% Kraft 1/4 solution; (d) 3 wt% Kraft 1/1 solution after water washing; (e) 6 wt% Kraft 1/4 solution after water washing; (f) 8 wt% Kraft 1/4 solution after water washing; (g) 6 wt% Kraft 1/4 solution after NMMO sublimation; (h) 8 wt% Kraft 1/4 solution after NMMO sublimation.

there is no trace of crystalline cellulose in the crystallised solutions is not in agreement with the paper by Chanzy et al. [6] where the authors suggested that the solvent crystallises first and cellulose after, in a transcrystalline manner. We found no evidence of such cellulose crystallisation, in accordance with our results of crystallisation kinetics.

3.4. Morphologies of the crystalline cellulose solutions

The morphology of crystallised cellulose solutions has not attracted much work in the past. It was noted by Chanzy et al. [6] that solutions in NMMO monohydrate crystallise mainly in the form of spherulitic morphologies. In fact, pure NMMO monohydrate forms also large spherulites under cooling [23]. The finding that in cellulose/NMMO/water solutions, it is the solvent that is crystallising explains easily why a spherulitic morphology is often observed with the cellulose solutions (despite that it is also a common feature for molten or in solution crystallisable polymers [24,25]).

The crystallisation of low molecular weight materials, polymer and melts is well documented [24–26]. The morphology, for a given material, is a strong function of the degree of supercooling. As was already said, there is an easy nucleation and a slow growth at high supercooling while it is the contrary at low supercooling. In general, this will favour spherulitic morphologies at low crystallisation temperatures, and elongated needle-like morphologies at high temperatures.

Fig. 6 shows morphologies of the 3 wt% cellulose solutions with cellulose of various origins crystallised in temperatures range between −10 and 50 °C. Almost all samples have a spherulitic morphology at low crystallisation temperatures. This spherulitic morphology exhibits either radial needle-like structure (Fig. 6c–f) or radial lamellar structure (Fig. 6b). Only one sample presents parallel lamellae morphology at low crystallisation temperatures (Fig. 6a). Near room temperature, where the rate is the largest, the crystallisation starts always at the edges of the sample and a needle-like morphology predominates. In general, the lower the crystallisation velocity, the larger and perfect the needles are. At high crystallisation temperatures, the presence of curved sheaf-like arrays (Fig. 6c) or small dendritic crystals (Fig. 6e) appearing after at least 1 h is observed. These entities are the precursors of the spherulites.

In order to clarify the influence of the water content,

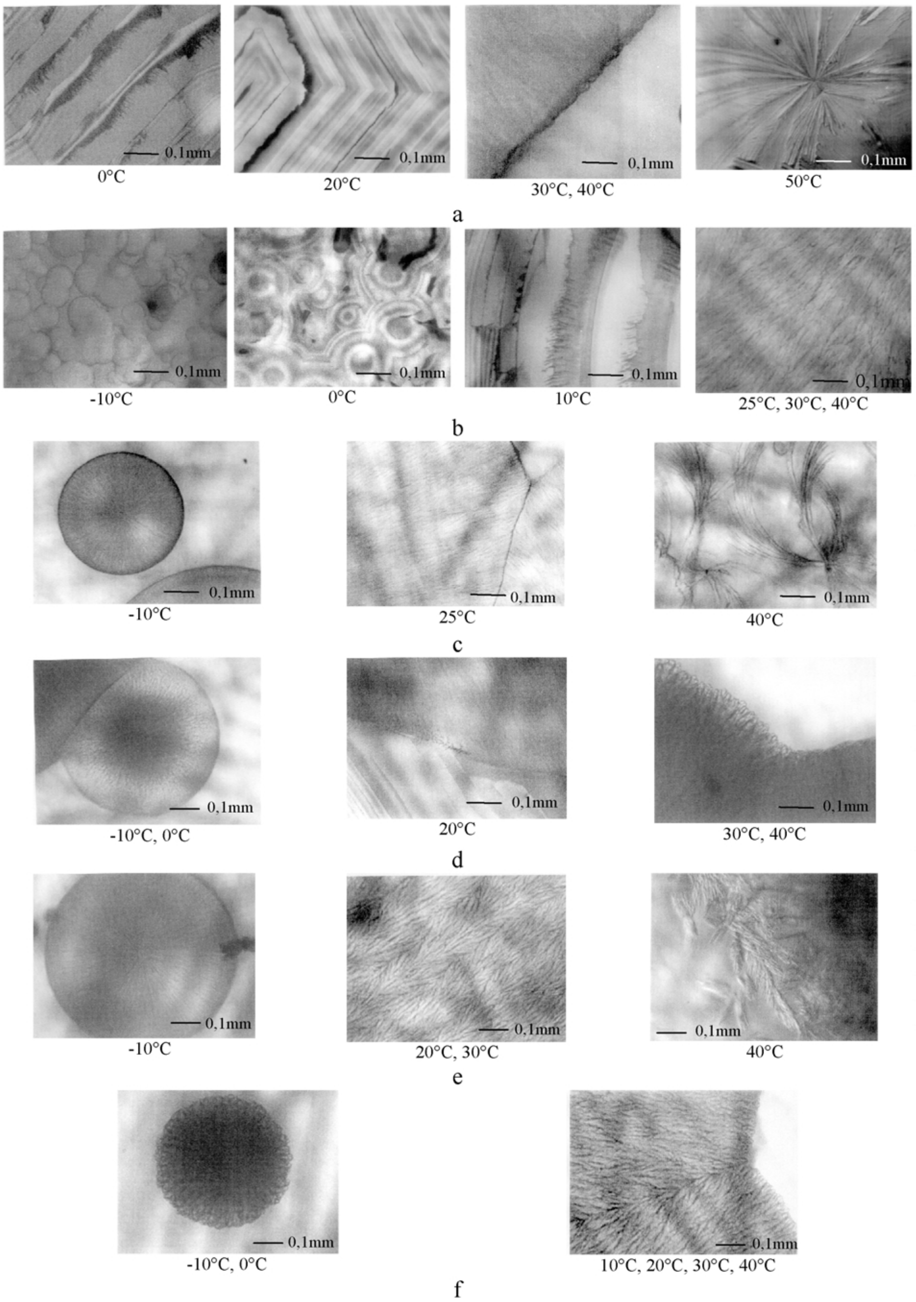

Fig. 6. Micrographs of the 3 wt% cellulose solutions crystallised at various temperatures: (a) Kraft 1/2; (b) Kraft 1/1; (c) Kraft 2/2; (d) Kraft 2/1; (e) Kraft 4 and (f) Kraft 3.

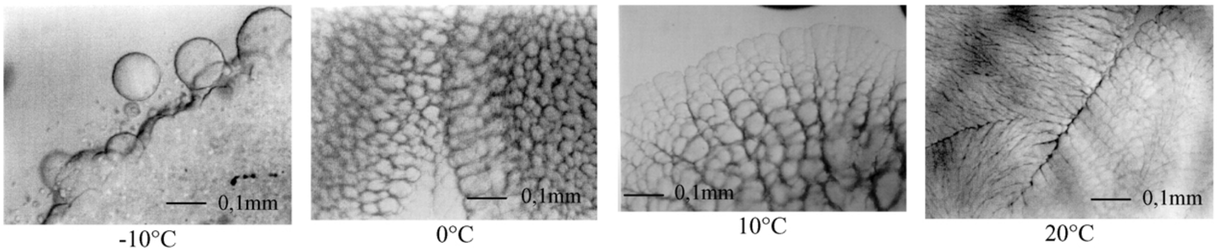

Fig. 7. Micrographs of the 6 wt% Kraft 1/4 solution crystallised at various temperatures.

3 wt% Kraft 1/1, Kraft 1/3, Kraft 2/1 and Kraft 2/2 solutions with various water content (14–18 wt%) were crystallised at 20 °C and their morphologies were examined. It was observed that the morphology of solutions with low water content is characterised by the presence of parallel lamellae while solutions containing high amount of water present a needle-like morphology. Samples with intermediate water concentration may exhibit both parallel lamellae and needles (as it is shown in Fig. 6d). This large sensitivity of the morphology of crystalline solutions to water content may be due to this sensitivity to viscosity. Large change in viscosity is strongly influencing morphology.

The morphology of 6 wt% Kraft 1/4 solution crystallised at various temperatures is shown in Fig. 7. At low crystallisation temperatures, spherulites appear in the bulk of the sample and their coalescence makes the recording of the crystallisation velocity impossible. At higher temperatures the growth of lamellae can be observed. Once crystallised, solution has a globular morphology aspect. The morphologies of 8 and 10 wt% cellulose solutions are very similar although the size of the observed globules seems to be larger.

4. Conclusions

Solutions of cellulose in NMMO/water crystallise under cooling, with a maximum crystallisation velocity around room temperature. The crystallisation is not due to the cellulose, which stays in an amorphous state. The crystallisation kinetics is very sensitive to the amount of water in the solution. The higher the water content above the monohydrate level, the slower is the crystallisation velocity. The crystallisation velocity does not depend on the molecular weight of the cellulose. It is rather interesting to note that the crystallisation velocity is not a function of the overall viscosity of the solution, in contrast with most materials. It seems to depend only on the properties of the solvent (water content, amount, probably topological arrangement) that is lying around the cellulose chains. The solvent viscosity is very sensitive to water content. Since the viscosity is a major factor controlling the morphology of the crystallised solution, this morphology will in turn be very sensitive to water content.

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