

PHYSICS OF CELLULOSE XANTHATE DISSOLUTION IN SODIUM HYDROXIDE–WATER MIXTURES: A RHEO-OPTICAL STUDY

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The way cellulose xanthate (viscose) fibres dissolve in sodium hydroxide–water mixtures is studied *in situ*, under flow, using a counter rotating optical rheometer. When a bunch of viscose fibres is placed in a solvent, a visco-elastic shell is formed, slowing down the diffusion of the solvent to non-dissolved fibres. It forms a highly concentrated, visco-elastic phase that disperses slowly through a pulling mechanism sucking this visco-elastic solution into the solvent. Due to this mechanism, dispersion and distribution of cellulose xanthate into the solvent is very slow.

Keywords: viscose, cellulose xanthate, dissolution

INTRODUCTION

Cellulose derivatisation is the oldest method for producing artificial fibres, dating with the pioneering work of Count Hilaire de Chardonnet, carried out in the 1880s, near Grenoble, in France, and with the first patent on the use of cellulose xanthate preparation and subsequent regeneration, obtained by C. Cross, E. Bevan and C. Beadle in 1892. Since that time, after some economical and technical difficulties, the viscose process proved to be a very efficient and powerful method for producing fibres, films and sponges, and is still in use today, despite its difficult control of air and water pollution. The viscose process is based on the treatment of cellulose fibres from wood or cotton with sodium hydroxide and carbon disulfite, forming a cellulose derivative, called cellulose xanthate, which has the interesting property of being soluble in sodium hydroxide–water mixtures. The solution can then be shaped, followed by an acid or a thermal treatment that reverts the cellulose derivative back to cellulose, with a noticeable change in the cellulose crystal structure (transformation of cellulose I into cellulose II). Among the many key chemical reactions and physical processes characterizing this process, the dissolution step of the

cellulose xanthate fibres into a sodium hydroxide–water mixture is of great importance, since it is controlling the quality of the subsequent processing. As one can imagine, numerous scientific works have been devoted to, for example, the influence of cellulose origin, purity, molecular weight, xanthate group distribution^{1,2} or dissolution conditions (temperature,³ soda concentration, etc.) on the efficiency of the process. Equally, due to its importance in processing, the rheology of the viscose solution was studied in detail.⁴⁻⁷ What has never been studied, at least to the best knowledge of the authors, is the way the solution is forming, *i.e.* how the solid cellulose xanthate fibres are dissolved under mixing conditions. A probable reason for this lack of important data may be the absence of specific experimental tools able to perform such experiments.

The dissolution of a solid material into a solvent is a process of great importance in many fields, such as pharmacy (where it is one of the main objectives of galenics), microlithography or food. Dissolution is controlled by two different factors, of thermodynamic and kinetic nature. If thermodynamics is usually easy to master

and understand through building phase diagrams, kinetics is more complicated, being controlled by a set of several interconnected physical and chemical phenomena. In the case of polymers, dissolution is not as fast as for low molar mass materials, being controlled by either disentanglement of the polymer chains or by diffusion of chains through a boundary layer adjacent to the polymer-solvent interface.⁸ An additional, rarely studied factor is the role of flow convection on the dissolution behaviour.

When a solid (under T_g), compact, non-crystalline polymer piece is placed in contact with a fluid solvent, the solvent swells the outer part of the polymer piece, bringing it above its glass transition. Further penetration of solvent is thus eased and the polymer passes to a disentangled state that allows the movement of the chains out of the polymer and into the solvent. It is this last step that usually depends on solvent convection around the swelling and dissolving polymer. Convection acts first by removing the polymer chains out of the vicinity of the dissolving polymer piece, and bringing the new solvent close by. A second effect is to avoid the formation of a viscous polymer cake around the dissolving polymer, which usually hampers the access of the fresh solvent to the polymer piece. All these effects are well known, since stirring is nearly always applied in dissolution processes.

All studies performed so far on the swelling and dissolution mechanisms of cellulose or cellulose derivative materials were performed visually, without convection (or at least without a controlled convection of the solvent) or by rheological methods involving convection, but no visualization of the dissolution process. For example, Kosan *et al.*⁹ and Michels and Kosan¹⁰ studied the rheological behaviour of a cellulose/solvent mixture and showed that it is possible to distinguish a suspension phase, when fibres are dispersed in the solvent from the dissolved phase, the latter being much more viscous. Other studies on cellulose dissolution used the measurement of the decrystallization rate through X-ray scattering.^{11,12} All these methods do not allow to observe the dissolution mechanisms while measuring the dissolution kinetics. Dissolution should be therefore observed by optical means, while controlling the solvent

convection, which can be done by rheo-optical tools, where the flowing cell is transparent to light.

The objective of this study is to use rheo-optical tools to study cellulose xanthate dissolution under flow, to investigate the involved mechanisms and to separate the influence of the intrinsic dissolution parameters from the possible formation of gels or of highly viscous layers around the dissolving cellulose xanthate materials.

EXPERIMENTAL

Cellulose xanthate with 61% CS₂, prepared in Spontex laboratories (France), was dissolved in NaOH 8%-water at three different temperatures: 0, 10 and 20 °C. Bunches of cellulose xanthate fibres were cut, to be fully visible in the field of observation.

To observe dissolution under flow, as it happens during mixing in industry, a counter-rotating rheometer was placed on a Metallux 3 (Leitz) optical microscope. The device consists of two glass plates which run in opposite directions (Fig. 1). The rotation of the two glass plates is ensured by two potentiometers, which can be controlled manually. The light source goes through the two glass plates and the sample is observed by optical microscopy, in transmission mode, linked to a recording system, *i.e.* an analogical JVC TK-C1481EG camera which provides 25 frames per second, and a DVD recorder Sony RDR-HX710. A monitor allows direct visualisation during the experiments. A frame code generator (Sony FCG-700) displays the number of frames, allowing to measure precisely the dissolution time.

The shear rate $\dot{\gamma}$ applied to one cellulose xanthate particle is given by the following formula:

$$\dot{\gamma} = \frac{(V_a + V_b) \times R}{H} \quad (1)$$

where V_a and V_b are the rotation speeds of the two glass plates, in rad/s, R is the radial position of the particle towards the rotation axis, in mm, and H is the gap between the two glass plates, in mm.

When the glass plates run in opposite directions, it is possible to keep the studied particle in the field of observation. The glass plates were cooled in an external thermal bath able to operate from 0 to 50 °C.

A small amount of cellulose xanthate (roughly 0.1-0.3% w/w, as to the solvent in large excess) was placed between the two glass plates of a counter-rotating rheometer previously placed at the test temperature. The solvent was also heated to the test temperature before being inserted in the rheometer gap. The shear rate range used was 10 to 25 s⁻¹.

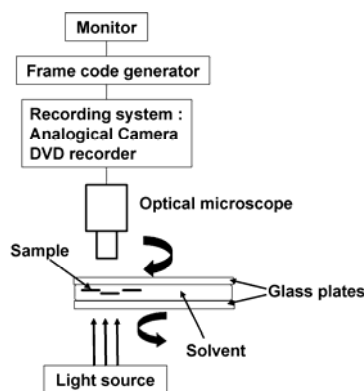


Figure 1: Schematic drawing of the counter-rotating rheometer device

RESULTS AND DISCUSSION

The dissolution of cellulose xanthahte was studied in NaOH 8%–water at 0, 10 and 20 °C. Cellulose xanthahte occurred as fibres about 15 μm in diameter, assembled into bunches containing many fibres. Cellulose xanthahte fibres are dissolved, forming a highly viscous phase, which is very elastic. Due to this, its dispersion (the fact that the highly viscous phase is breaking into smaller parts) and its distribution (the fact that the dispersed parts are homogeneously distributed in all suspending fluid) are complicated. The dissolution mechanisms are described below.

The first fibres to dissolve are the ones at the interface with the solvent, *i.e.* the external fibres of the bunch of cellulose xanthahte fibres. They are swollen, then dissolved, thus creating a highly viscous shell that does not disperse in the sodium hydroxide–water solvent, but remains around the undissolved fibres (Fig. 2). This highly viscous shell hampers the dispersion of all fibres and prevents a fast diffusion of the solvent to the undissolved fibres.

Two competing phenomena then occur under flow. The first is the progress of dissolution with more and more fibres disappearing visually, as a result of their dissolution, while remaining in this highly viscous phase. Figures 3a and b show an advanced state, in which the dissolution of fibres is observed at two successive time periods. The second process is the dispersion of this highly viscous phase into the solvent, through the extraction of the cellulose xanthahte viscous solution phase filaments, as shown in Figures 3a and b. The origin of these filaments may be explained by the stress distribution around the dissolved phase

and by its visco-elastic character. Stress distribution occurs around this viscous phase with positive maxima at 45° to the flow direction when the suspended fluid is Newtonian,¹³ which is the case here. At these locations, pieces of the dissolving viscous phase are pulled out from this phase, forming very long filaments. The diameter of these filaments decreases when the distance from the viscous phase increases, due to the elongational flow existing between two different flow velocities in gradient direction. The fact that these filaments do not break even when reaching less than 10 microns is the clear sign that the phase is very viscous, related to its high polymer concentration, and very elastic, because it is a polymer solution. Even when gas bubbles more than five times larger than the filament diameter were attracted into it, the filament was not broken (Fig. 4), as it would have occurred for a filament with low elasticity. It has to be noticed that, if the bunch of cellulose xanthahte fibres is well-centred between the two plates, two filaments can be observed, which agrees with the analytical theory of Bagster and Tomi.¹³ However, the viscous phase was often stuck on one plate. Convection was thus applied only in one direction, involving the formation of only one filament.

Instead of having fibres dispersed in the solvent and then swollen and dissolved, the studied cellulose xanthahte sample evidences a reverse effect. It first swells and dissolves locally, forming a very visco-elastic phase embedded into the solvent, after which this phase disperses into the solvent through the described filament mechanism. It can be viewed as a slow sucking of the viscous phase by the solvent medium through these

filaments. Such a dissolution mechanism is very unfavourable from the point of view of both kinetics, since it takes much more time to disperse a very viscous phase into a fluid one than it takes to disperse solid particles, and quality of the solution, since the dispersion of these visco-elastic filaments is not easy. The convection associated to the shear distributes the filaments extracted from the viscous phase into the solvent, and

increases homogeneity of the whole mixture. As may be observed, the higher the shear rate was (between 10 to 25 s^{-1}), the faster the dissolution and the dispersion. In the explored temperature range, *i.e.* 0 to 20 °C, the dissolution time was not influenced by temperature, varying from 5 to 7 mn, as depending on the shear rate and initial size of the bunch of cellulose xanthate fibres.

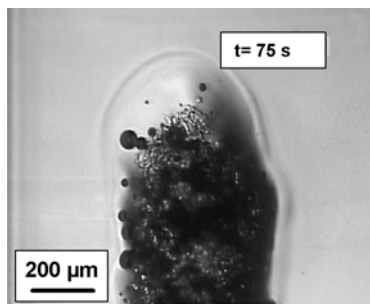


Figure 2: First step of cellulose xanthate dissolution in NaOH 8%–water, with the creation of a highly viscous shell that hampers the dispersion of all fibres and prevents fast diffusion of the solvent to undissolved fibres

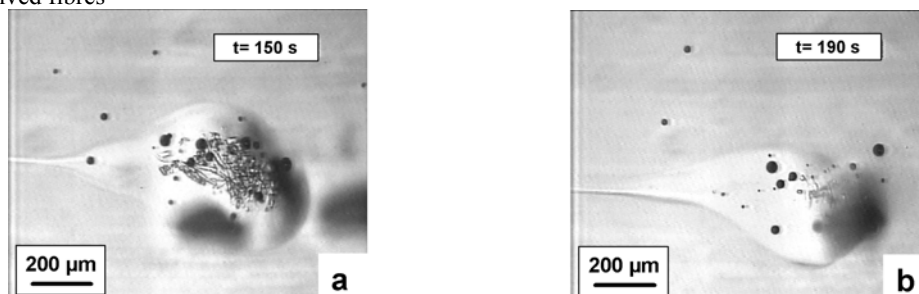


Figure 3: Advanced step of dissolution of cellulose xanthate in NaOH 8%–water under flow (shear rate – about 20 s^{-1}) observed with the counter-rotating rheometer, at two successive dissolution time periods (a) 150 s, (b) 190 s. An increasing number of fibres dissolve and the highly viscous phase disperses into the solvent in the form of filaments

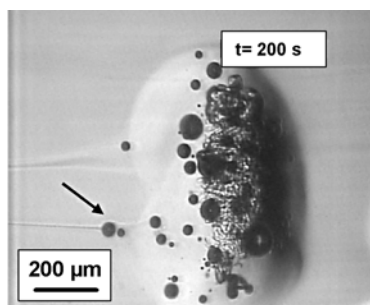


Figure 4: Advanced step of cellulose xanthate dissolution in NaOH 8%–water under flow (shear rate – about 20 s^{-1}) observed with the counter-rotating rheometer. As gas bubble (black arrow) is more than five times larger than the filament diameter, it is attracted into the filament, yet without breaking it

CONCLUSIONS

The dissolution of cellulose xanthate fibres in sodium hydroxide–water under shear flow first involves a highly concentrated and highly visco-elastic phase,

which slows down the dispersion into the solvent by a sucking mechanism, through filament pulling. Such a process does not favour quick obtaining of a good solution.

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REFERENCES

¹ A. Rußler, T. Lange, A. Potthast, T. Rosenau, E. Berger-Nicoletti, H. Sixta and P. Kosma, *Macromol. Symp.*, **223**, 189 (2005).

² A. Rußler, A. Potthast, T. Rosenau, T. Lange, B. Saake, H. Sixta and P. Kosma, *Holzforschung*, **60**, 467 (2006).

³ G. N. Musatova, E. M. Mogilevskii, M. A. Ginzberg and D. N. Arkhangelskii, *Fibre Chem.*, **2**, 451 (1972).

⁴ T. E. Hopkins and J. W. Whatley, *J. Appl. Polym. Sci.*, **6**, 600 (1962).

⁵ V. G. Kulichikhin, E. Z. Kipershlak and A. Ya. Malkin, *Fibre Chem.*, **2**, 417 (1972).

⁶ D. Lodesová and A. Lodes, *Rheol. Acta*, **22**, 396 (1983).

⁷ N. Simeonov, G. Peev, D. Parigvozdeva and A. Nikolova, *Cellulose Chem. Technol.*, **27**, 497 (1993).

⁸ B. A. Miller-Chou and J. L. Koenig, *Prog. Polym. Sci.*, **28**, 1223 (2003).

⁹ B. Kosan, C. Michels and F. Meister, *Cellulose*, **15**, 59 (2008).

¹⁰ C. Michels and B. Kosan, *Lenzinger Berichte*, **84**, 62 (2005).

¹¹ Y. Wang and Y. Deng, *Biotechnol. Bioeng.*, **102**, 1398 (2009).

¹² G. A. Marson and O. A. El Seoud, *J. Polym. Sci., A*, **37**, 3738 (2000).

¹³ D. F. Bagster and D. Tomi, *Chem. Eng. Sci.*, **29**, 1773 (1971).