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RHEOLOGICAL CHARACTERIZATION OF CELLULOSE AND CELLULOSE/TEOS SOLUTIONS

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In order to synthesize membranes, cellulose was dissolved in a NaOH/thiourea/water system using the freezing method and further TEOS was added. Casting solutions with/without TEOS behaved as pseudoplastic fluids at different levels of operation temperature (t=25, 40 °C), number of freezing-thawing cycles (N_c=1-5), and TEOS/cellulose mass ratio (R_m=0-0.50). Characteristic flow consistency index of Ostwald-de Waele equation (K=0.406-39.349 $Pa \cdot s^n$) increased with N_c and R_m whereas the flow behaviour index (n=0.381-1) comported reversely. An increase in temperature led to lower K and larger n values for R_m=0 and had an opposite effect for $R_m \neq 0$.

Keywords: cellulose dissolution, Newtonian fluid, Ostwald-de Waele equation, shear-thinning, viscosity

1. Introduction

Neat and composite biomaterials based on cellulose have been intensively developed and used for conventional and innovative applications due to their advantages including non-toxicity, biodegrability, biocompatibility, and wide availability of the cellulose [1-3]. These biomaterials can be synthesised by dissolving the cellulose in specific solvents followed by processing the cellulose solution in order to prepare films, fibres, hydrogels or aerogels [1-7].

As effect of strong intramolecular and intermolecular hydrogen bonds as well as of hydrophobic interactions of its molecules, cellulose is difficult to be dissolved in common solvents [2-4,7-11]. Therefore, in order to improve the cellulose solubility and to facilitate the solution processing, non-derivatizing and derivatizing effective solvents have been developed and applied [12-13]. Aqueous non-derivatizing solvents include molten salt hydrates (*e.g.*, $LiSCN \cdot 2H_2O$, $LiClO_4 \cdot 3H_2O$) and aqueous solutions of inorganic metal complexes (*e.g.*, cuprammonium hydroxide (cuam), cupriethylenediamine hydroxide (cuen)), alkali

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(*e.g.*, NaOH, LiOH) with or without additives (*e.g.*, urea and/or thiourea, ZnO). Non-aqueous non-derivatizing solvents mainly are oxides of tertiary amines (*e.g.*, N-methylmorpholine-N-oxide (NMMO)), organic liquid/inorganic salt (*e.g.*, N,N-dimethylacetamide (DMA)/LiCl, dimethylsulfoxide (DMSO)/$CaCl_2$), liquid ammonia/sodium or ammonium salt (*e.g.*, NH_3/NaSCN or NH_4SCN), and ionic liquids. The most used derivatizing solvents are NaOH/CS_2, N,N-dimethlylformamide (DMF)/N_2O_4, and DMSO/paraformaldehyde.

Among these solvents, the aqueous solutions of alkali with or without urea and/or thiourea are low toxicity and cost systems which imply common reagents. Cellulose alkaline dissolution has been thoroughly studied lately [3-9,11,14-17]. The main disadvantages of aqueous solutions of alkali are the reduced ability to dissolve the cellulose and the irreversible gelation of cellulose solution with time and/or temperature increase. The gelation process occurs by associations between the cellulose chains forming an entangled network [14,16]. The freezing method, consisting in the cooling of a cellulose/alkali/water suspension at -20 °C followed by thawing the frozen solution, can be applied for improving the cellulose solubility [7,11]. Urea and thiourea as well as low temperatures (usually less than -10 °C) can enhance the cellulose dissolution and delay the gelation process by increasing the solution stability [5,7-9,11,14,15]. The following mechanism has been assumed for cellulose dissolution in NaOH/urea solution at -12 °C [8]: alkali hydrates break intramolecular and intermolecular hydrogen bonds and form new hydrogen bonds with the cellulose chains, while the urea hydrates surround the cellulose/alkali hydrates inclusion complex, preventing the cellulose aggregation by hydrogen bonds or hydrophobic interactions. Accordingly, the urea increases the stability of cellulose molecular dispersion. It has been reported that NaOH/thiourea/water and NaOH/urea/thiourea/water systems are more powerful in dissolving cellulose (up to 8 wt. %) than NaOH/urea/water [15-17].

Rheological characterization of cellulose solutions is essential for their shaping, especially into cast films. A high viscosity may lead to a inhomogeneous film and hinder its processing [1,10]. Cellulose solutions behave as Newtonian or shear-thinning fluids depending on cellulose concentration, temperature, and solvent system [1,7,10,14,16,18,19].

The present study has aimed at characterizing the rheological behaviour of casting solutions which were used to prepare neat cellulose and cellulose/ tetraethyl orthosilicate (TEOS) composite membranes applied to pervaporation separation of ethanol-water mixtures [20]. The cellulose was dissolved in a NaOH/thiourea/water system using the freezing method and TEOS was further added. Casting solutions with and without TEOS were spread as thin films which were then processed by phase-inversion method, rinsing, and drying [20]. The effect of operation temperature, number of freezing-thawing cycles, and TEOS loading on rheological parameters of casting solutions was evaluated.

2. Materials and method

Cotton cellulose powder (50 μm diameter, 0.600 g/cm^3 density), TEOS min 98 %, and crystals of thiourea were supplied by Sigma-Aldrich Chemie (Germany). NaOH pellets were purchased from Merck (Germany). All reagents were used without further purification.

Cellulose casting solutions were prepared according to the following procedure [20]: (i) cellulose powder was added to an alkaline solution (9 wt. % NaOH and 5 wt. % thiourea) forming a slurry (8.5 wt. % cellulose); (ii) cellulose slurry was vigorously stirred at 30 °C for 3 h and then frozen at about -20 °C for 24 h; (iii) frozen solution was thawed at room temperature obtaining CS; (iv) freezing-thawing cycle was repeated. A cellulose solution prepared conforming to (i)-(iv) steps was vigorously stirred with TEOS for 10 min resulting in a cellulose/TEOS casting solution.

Rheological characterization of cellulose and cellulose/TEOS casting solutions was performed using a Rheotest 2 rotary viscosimeter (MLW, Germany) equipped with coaxial cylinders. Steady-state shear flow tests were conducted at shear rates (γ) ranging from 0.5 to 122 s^{-1} and various values of process factors, *i.e.*, operation temperature (t=25, 40 °C), number of freezing-thawing cycles (N_c=1-5), and TEOS loading expressed as mass ratio between TEOS and cellulose (R_m=0-0.50).

3. Results and discussion

3.1. Rheological characterization of cellulose casting solutions

Steady-state shear flow results presented in Fig. 1 for cellulose casting solutions, *i.e.*, shear stress, τ (Pa), *vs.* shear rate, γ (s^{-1}), emphasise that for t=25 °C τ increases more sharply with γ at higher values of N_c, whereas for t=40 °C the shear flow curves are less influenced by N_c. Moreover, irrespective of N_c level, the values of τ are lower at 40 °C. For N_c=1 and t=25, 40 °C, experimental data were linearly correlated (R^2>0.995) and a line intercept of about 0 Pa was obtained, corresponding to a Newtonian fluid with a dynamic viscosity (η) equal to the line slope. For N_c=2-5 and t=25, 40 °C, the data were fitted (R^2>0.991) according to Ostwald-de Waele relationship defined by Eq. (1), where K (Pa·s^n) is the flow consistency index and n the flow behaviour index.

$$\tau = K\gamma^n \tag{1}$$

K and n rheological parameters regressed under various operation conditions are summarized in Table 1 (exp. (1)-(10)), where the Newtonian fluid

(N_c=1) is characterized by n=1 and $K=\eta$ (Pa·s). Tabulated values of flow behaviour index for N_c=2-5 (n<1) indicate a characteristic behaviour of pseudoplastic (shear-thinning) non-Newtonian fluid for which the apparent viscosity, η_{app} (Pa·s), was calculated using Eq. (2).

$$\eta_{app} = K\gamma^{n-1} \qquad (2)$$

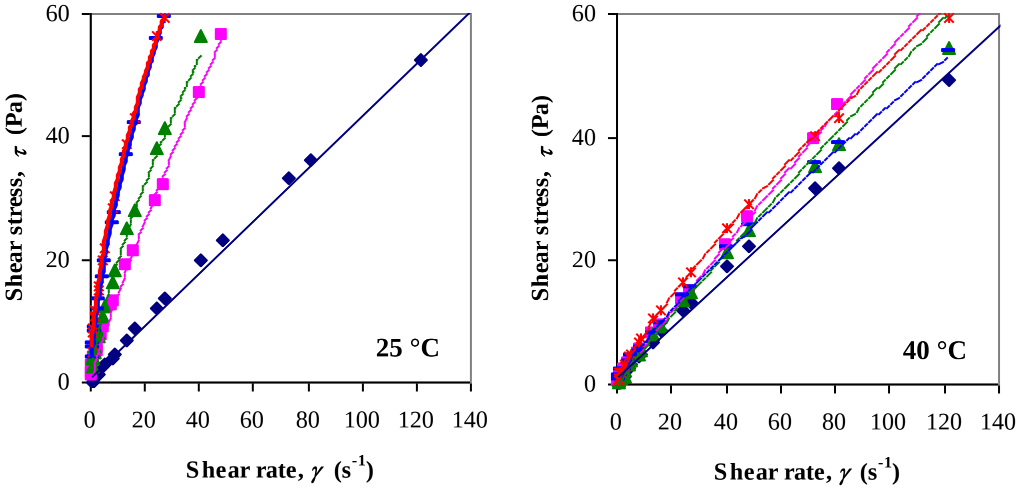

Fig. 1. Shear stress, τ, *vs.* shear rate, γ, for various values of number of freezing-thawing cycles (bullets: experimental, line: calculated with Eq. (1)): N_c=1 (♦), N_c=2 (■), N_c=3 (▲), N_c=4 (—), N_c=5 (∗)

Variation of η_{app} with γ for different levels of process factors is shown in Fig. 2, where $\eta_{app}=\eta=K$ for the Newtonian fluid (N_c=1). Depicted curves reveal that η_{app} values decrease with an increase in γ (shear-thinning non-Newtonian fluid) and t as well as they increase with N_c. Moreover, the influence of N_c on η_{app} at t=40 °C is almost negligible. The shear-thinning behaviour may be due to a disentanglement of cellulose polymer chains and/or an increase in chain orientation in the flow direction during the rotational measurements [1,10,16,18]. A decreasing variation of η_{app} on t has been reported for cellulose-NaOH solution with additives [16,19] and it may be caused by reducing the entanglement of polymer chains at higher temperatures [16], whereas an increase in η_{app} with N_c could be an effect of gelation induced by freezing [7].

Table 1

Rheological parameters of casting solutions depending on process factors

Exp.	Process factors			Rheological parameters	
	R_m	t (°C)	N_c	K (Pa·s^n)	n
1	0	25	1	0.427	1
2			2	1.992	0.862
3			3	3.905	0.707
4			4	6.178	0.684
5			5	8.246	0.597
6		40	1	0.406	1
7			2	0.658	0.958
8			3	0.673	0.936
9			4	1.025	0.823
10			5	1.263	0.809
11	0.25	25	1	3.839	0.687
12			2	5.405	0.645
13		40	1	17.109	0.521
14			2	20.674	0.472
15	0.50	25	1	8.580	0.601
16			2	9.589	0.579
17		40	1	37.053	0.399
18			2	39.349	0.381

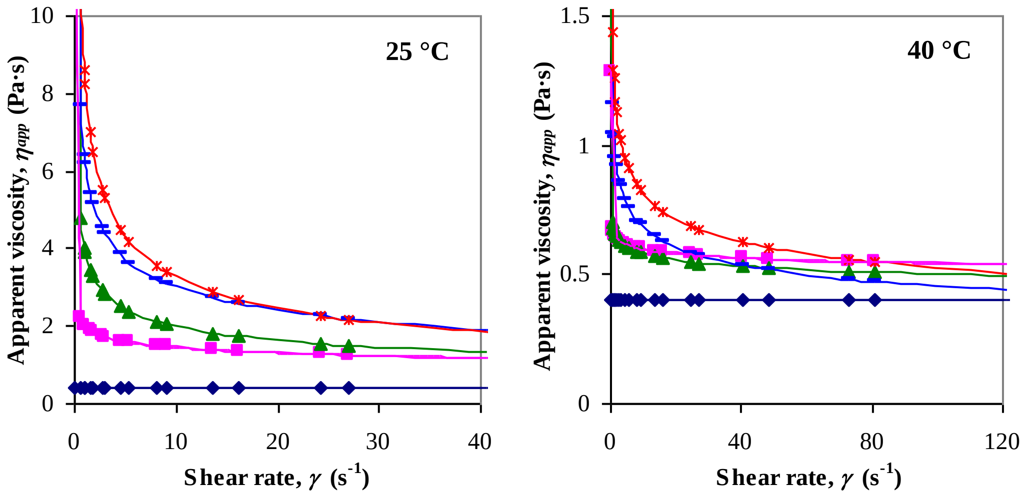

Fig. 2. Apparent viscosity, η_{app}, *vs.* shear rate, γ, for various values of number of freezing-thawing cycles: N_c=1 (♦), N_c=2 (■), N_c=3 (▲), N_c=4 (—), N_c=5 (∗)

Results presented in Fig. 3 referring to the effect of process factors on rheological parameters highlight that: (i) K values are higher for t=25 °C and increase linearly (R^2>0.94) with N_c; (ii) the influence of N_c on K may be neglected for t=40 °C; (iii) n values are lower for t=25 °C and decrease linearly (R^2>0.93) with N_c. Cellulose casting solutions were spread as thin films which were further processed by the phase-inversion method followed by rinsing and drying in order to prepare cellulose membranes, as shown elsewhere [20]. The films based on less viscous solutions obtained after 1 and 2 freezing-thawing cycles (N_c=1, 2) were more homogeneous, whereas those cast from more viscous solutions (N_c=3-5) exhibited a non-homogeneous structure with bubbles. Accordingly, in order to obtain high quality cellulose/TEOS composite membranes, only these less viscous solutions (N_c=1, 2) were selected for preparing casting solutions with TEOS.

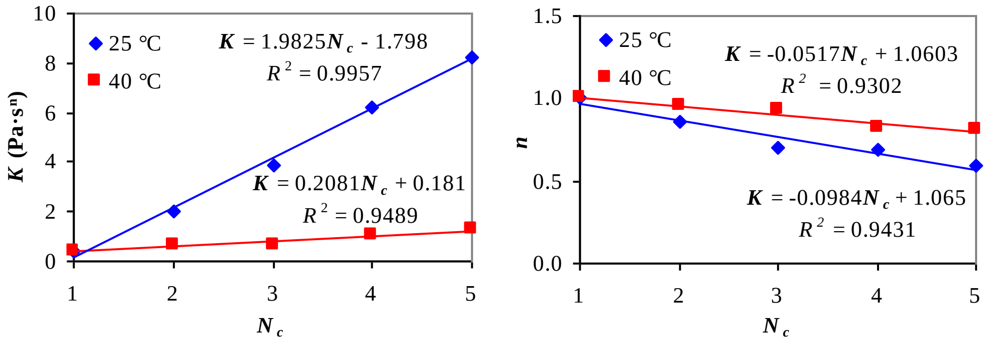

Fig. 3. Flow consistency index, K, and flow behaviour index, n, *vs.* number of freezing-thawing cycles, N_c (bullets: values fitted based on shear flow experimental data, line: linear regression)

3.2. Rheological characterization of cellulose/TEOS casting solutions

Experimental shear flow data depicted in Fig. 4 for cellulose/TEOS casting solutions (R_m=0.25, 0.50; t=25, 40 °C; N_c=1, 2) were fitted (R^2>0.995) using Ostwald-de Waele equation and the values of K and n rheological parameters are specified in Table 1 (exp. (11)-(18)).

Variation of η_{app} with γ shown in Fig. 5 indicates a shear-thinning fluid for which η_{app} increases with R_m, t, and N_c. Depicted curves highlight a significant effect of t, whereas the influence of N_c is almost negligible, especially for R_m=0.50. Moreover, it is observed that characteristic η_{app} values of cellulose solutions (R_m=0), which are also included in Fig. 5, are lower than those corresponding to cellulose/TEOS solutions under the same conditions. Higher values of η_{app} in the presence of TEOS ($Si(OCH_2CH_3)_4$) may be due to the hydrogen bonds formed between –OH groups of cellulose and silanol (–Si–OH) groups obtained by TEOS hydrolysis. Moreover, it seems that a high temperature favoured the occurrence of these hydrogen bonds.

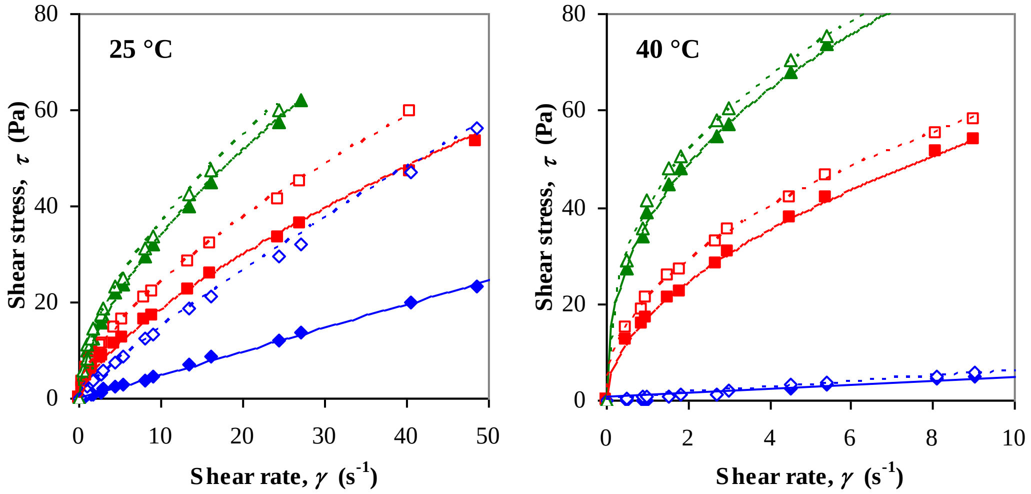

Fig. 4. Shear stress, τ, *vs.* shear rate, γ, for various values of TEOS loading and number of freezing-thawing cycles (bullets: experimental, line: calculated with Eq. (1)): R_m=0, N_c=1 (♦); R_m=0.25, N_c=1 (■); R_m=0.50, N_c=1 (▲); R_m=0, N_c=2 (◊); R_m=0.25, N_c=2 (□); R_m=0.50, N_c=2 (Δ)

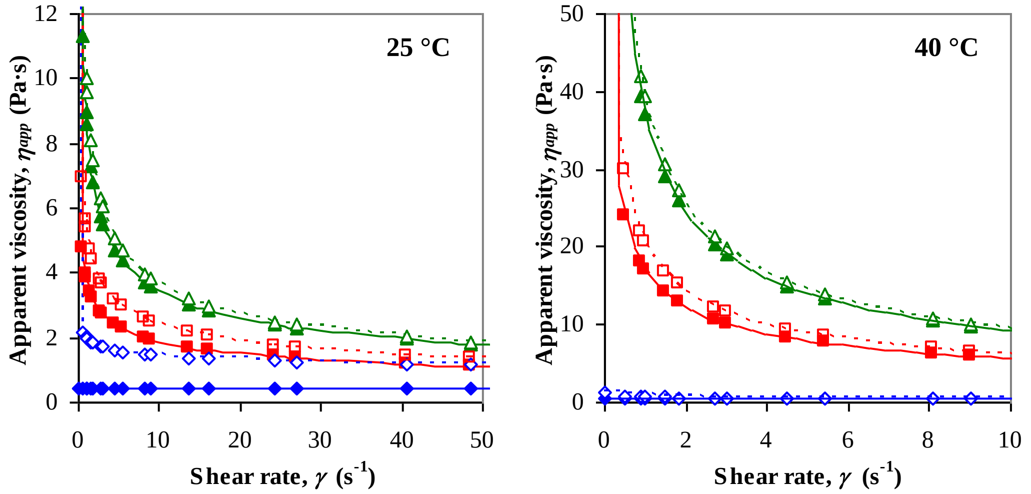

Fig. 5. Apparent viscosity, η_{app}, *vs.* shear rate, γ, for various values of TEOS loading and number of freezing-thawing cycles: R_m=0, N_c=1 (♦); R_m=0.25, N_c=1 (■); R_m=0.50, N_c=1 (▲); R_m=0, N_c=2 (◊); R_m=0.25, N_c=2 (□); R_m=0.50, N_c=2 (Δ)

In order to establish the effect of process factors on K and n parameters, the data associated to rheological measurements of cellulose/TEOS casting solutions were processed according to a 2^3 factorial experiment, where the dimensionless process factors (x_i=±1, i=1..3) were determined by Eqs. (3)-(5). Regression correlations expressed by Eqs. (6) and (7) indicate that K increases with x_1, x_2, and x_3 (R_m, t, and N_c, respectively) whereas n behaves reversely.

Furthermore, a significant influence of x_2 and a less important effect of x_3 are observed. Simplified relationships given by Eqs. (8) and (9), which were validated after eliminating the non-significant coefficients [21-23], reveal that K increases with x_1 and x_2 factors as well as with their interaction, whereas n increases with a decrease in all process factors as well as in x_1x_2 and x_1x_3 interactions.

$$x_1 = \frac{R_m - 0.375}{0.125} \tag{3}$$

$$x_2 = \frac{t - 32.5}{7.5} \tag{4}$$

$$x_3 = \frac{N_c - 1.5}{0.5} \tag{5}$$

$$K = 17.7 + 5.943x_1 + 10.847x_2 + 1.054x_3 + 3.712x_1x_2 - 0.228x_1x_3 + 0.411x_2x_3 - 0.089x_1x_2x_3 \tag{6}$$

$$n = 0.536 - 0.045x_1 - 0.092x_2 - 0.016x_3 - 0.0076x_1x_2 - 0.0065x_1x_3 - 0.0006x_2x_3 + 0.0014x_1x_2x_3 \tag{7}$$

$$K = 17.7 + 5.943x_1 + 10.847x_2 + 3.712x_1x_2 \tag{8}$$

$$n = 0.536 - 0.045x_1 - 0.092x_2 - 0.016x_3 - 0.0076x_1x_2 - 0.0065x_1x_3 \tag{9}$$

4. Conclusions

The cellulose was dissolved in NaOH/thiourea/water using the freezing method in order to synthesize neat cellulose membranes. TEOS was further added to cellulose casting solutions for obtaining cellulose/TEOS composite membranes. Rheological tests of casting solutions with and without TEOS were performed at various values of operation temperature (t=25, 40 °C), number of freezing-thawing cycles (N_c=1-5), and TEOS loading (R_m=0-0.50).

Experimental shear flow data, *i.e.*, shear stress (τ) *vs.* shear rate (γ), indicated for R_m=0 and N_c=1 a Newtonian fluid with a viscosity of about 0.4 Pa·s and for other operation conditions a shear-thinning behaviour characterized by an apparent viscosity (η_{app}) calculated depending on γ and two rheological parameters, *i.e.*, flow consistency index (K=0.658-39.349 Pa·s^n) and flow behaviour index (n=0.381-0.958). The shear-thinning behaviour may be caused by a disentanglement of cellulose polymer chains and/or an increase in chain orientation in the flow direction. The influence of process factors on its responses, *i.e.*, τ, η_{app}, K, and n, was evaluated.

It was established that τ, η_{app}, and K increased with N_c and R_m, whereas n exhibited an opposite trend. An increase in η_{app} with N_c could be an effect of gelation induced by freezing, while higher values of η_{app} in the presence of TEOS may be due to the hydrogen bonds between –OH groups of cellulose and –Si–OH groups formed by TEOS hydrolysis. Regarding the temperature influence, a high level of t led to lower values of τ, η_{app}, and K as well as larger values of n for cellulose solutions (R_m=0), whereas cellulose/TEOS solutions behaved reversely. A decreasing in η_{app} at higher temperatures could be determined by reducing the entanglement of cellulose polymer chains in cellulose solutions, whereas TEOS enhanced the occurrence of hydrogen bonds between –OH groups of cellulose and –Si–OH groups leading to an increase in η_{app}.

Characteristic rheological parameters of cellulose/TEOS solutions were processed according to a 2^3 factorial experiment and regression equations expressing the variation of K and n parameters with the process factors were obtained. The equations emphasized higher K and lower n values with an increase in all process factors as well as an almost negligible effect of N_c.

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