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Rheological Properties of Biocelsol/Viscose Blend Solutions and Properties of Regenerated Cellulose Films

This article is dedicated to the memory of Professor Henryk Struszczyk

Abstract

The dissolving of cellulose in suitable solvents to prepare fibre-forming and film-forming solutions has been a very attractive field of research for more than a hundred years. In this paper we present the rheological properties of alkali solutions of enzyme-treated cellulose (BiocelsolTM) and the blend of Biocelsol-viscose solutions. The effect of solution composition, storage temperature and time on the viscosity and deviation from the Newtonian flow were investigated. The reproducibility of the basic rheological parameters of Biocelsol alkali solutions was also investigated. The effect of the rheological properties of Biocelsol/viscose blend solutions on the tenacity of the regenerated cellulose films is discussed, as well.

Key words: rheological properties, spinning solutions viscose, Biocelsol, cellulose films.

Introduction

The dissolving of cellulose in suitable solvents to prepare fibre-forming and film-forming solutions has been a very attractive field of research for more than a hundred years. The problem is interesting from both the scientific and the industrial points of view. A series of solvents for cellulose have been developed for dissolving the chemically or enzymetreated cellulose in the last decades [1-4], because of the environmental drawbacks of the original viscose technology.

Two new technologies for regenerated cellulose products have recently been developed: Lyocel technology, based on the solution of cellulose in N-methylmorpholine-N-oxide and the cellulose carbamate technology using the alkali soluble cellulose derivative, cellulose carbamate [4, 5]. The former has been successfully employed on an industrial scale. The enzyme-treated cellulose dissolved in NaOH-water solution has proved to be a very promising, industrially exploitable spinning and film-forming solution [6]. The newest kinds of solvents for cellulose are represented by organic ionic liquids [7].

Research and the published papers on the behaviour of cellulose in alkali solutions has shown that the maximum solubility occurs in 8-10 wt% soda aqueous solution. Knowledge of the dissolving process and the structure of cellulose alkali

solutions has been elaborated in detail by Klemm et al. and Kamide et al. [8, 9]. On the other hand, there have been few papers related to the processing properties of cellulose alkali solutions, mainly the rheological behaviour of the concentrated cellulose solutions [10, 11].

The structure of the semidilute solutions of cellulose with a DP of about 300-400 in soda solutions is fully described [9, 12]. Heterogeneity on the micro- and macro-levels for aqueous NaOH solutions within the concentration range of NaOH 0-20 wt% without cellulose was found using the thermal analysis of the alkali solution. This heterogeneity consists in well-defined fractions of soda hydrate and free water. The structure of the cellulose + NaOH + H₂O mixture is more complex, and consists of three main parts: 1) free water that freezes below zero and melts at a temperature of -1 to -14 °C depending on the NaOH concentration, 2) soda hydrates composed of a 'core' of NaOH-9H2O which melts at -35 °C, and a 'shell' of amorphous water, and 3) soda hydrates bound to cellulose that do not freeze up to - 60 °C.

The soda hydrates interact with one or two groups per glucopyranose units. For the preparation of semi-dilute solutions and study of the structure and properties, the optimal concentration of NaOH in water solution was about 9 wt% and the maximum of cellulose concentration about 5 wt%. The flow of such alkali solutions of cellulose was close to that of suspensions with a power law exponent (PLE) lower than 0.5 and viscos-

ity dependences on cellulose concentration [11]. This deviation from Newtonian flow is too high for common processing solutions for fibres or films. The effort to develop the processing solutions of cellulose in recent times was aimed at increasing the cellulose concentration while at the same time decreasing the NaOH content. One of the optimised compositions of enzyme-treated cellulose solution with 7.8 wt% of NaOH, 6.1 wt% of cellulose and a small amount of additive provides solutions which can be very easily processed [13]. The aim of our work was to investigate the essential properties of Biocelsol and the Biocelsol/ viscose blend solution from the point of view of their future application in film and fibre manufacture.

The improvement of the rheological parameters of the cellulose/soda solution can be accomplished by optimising preparation conditions and using suitable additives [13, 14]. In addition, the blending of alkali soluble cellulose with viscose can lead to blend solutions with improved processing properties (rheology) and modified cellulose products.

In this paper we present the rheological properties of alkali solutions of enzymetreated cellulose (BiocelsolTM) and the blend of Biocelsol-viscose solutions. The effect of solution composition, storage temperature and time on the viscosity and deviation from the Newtonian flow were investigated. The reproducibility of the basic rheological parameters of Biocelsol alkali solutions was also investigated. The effect of the rheological properties

of Biocelsol/viscose blend solutions on the tenacity of the regenerated cellulose films is discussed, as well.

Experimental

Materials

The original pulp was a dissolving grade softwood sulphite pulp delivered by Domsjoe Fabriker. The pulp is produced from a controlled mixture of Norwegian spruce (60%) and Scottish pine (40%) using a two-stage cooking and TCF-bleaching process. The original pulp was mechanically shredded for 5 hours and thereafter treated with various kinds of commercial enzymes.

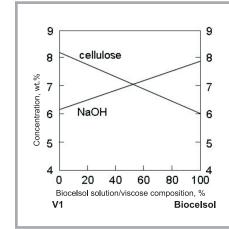
The samples of enzyme-treated cellulose are marked in the paper as B1-B6. They were treated using the following experimental enzymes BCS2 for sample B1, mixture (BCS2 + BCS10) for sample B2, BCS10 for sample B5 and commercial enzymes BCS11 with high endoglucanase activity for samples B3, B4 and B6. Sample B3 was prepared without mechanical pre-treatment, and sample B6 with lower enzyme concentration. The cellulase mixture used was a culture filtrate from a genetically modified Trichoderma reesei strain and was obtained from Primalco Ltd, Biotec, Rajama, Finland. The samples of enzyme-treated cellulose were prepared at the Tampere University of Technology (Finland) and the VTT Technical Research Centre of Finland.

Concentrated cellulose solutions

- Biocelsol solution (BS) the composition of all Biocelsol solutions was constant: cellulose: 6.0 wt.%, NaOH: 7.8 wt.%, additive 0 2 wt.%. The Biocelsol/soda solutions were prepared according to an original procedure elaborated by the IWCh, Łódź [13].
- 2) Viscose 1 (V1) composition: α-cellulose: 8.1 wt.%, NaOH: 6.1 wt.%, ripping 17.5 18.3 °H, commercial industrial product from SH Senica, Slovakia.
- 3) Viscose 2 (V2) composition: α-cellulose: 7.2 wt.%, NaOH: 4.5 wt.%, ripping 5.4 °H, commercial industrial product from Oy Visko Ab, Finland.

Biocelsol/viscose blend solutions

The Biocelsol alkali solution and viscose were blended using a laboratory stirrer. With regard to the difference in concentration of cellulose and NaOH in



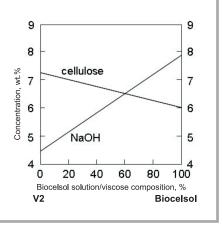


Figure 1. Change in content of cellulose and NaOH in Biocelsol/viscose blend solutions.

alkali solutions, the composition of blend solution varied according to Figure 1. Figure 1 shows that the concentration of NaOH in blend solution increases with the increase in the proportion of Biocelsol in blend solutions. An inversion of NaOH and cellulose concentrations in blend solutions is observed at about 40-60% of Biocelsol alkali solution in the blend solution.

The rheological parameters of blend solutions were evaluated. The regenerate cellulose films were prepared and their mechanical properties were measured.

Methods of measurements

Rheology of cellulose solutions

The laboratory viscosimeter Rheotest RV II (barrel – cylinder) was used to measure the rheological properties of Biocelsol/viscose blend solutions. The rheological measurements were carried out within a temperature range from 0 °C and 20 °C. The basic rheological parameters (viscosity η and deviation from the Newtonian behaviour n) of solutions were evaluated using the following equations:

$$\eta = \tau / \gamma$$
 (Newton's law)

where η - the dynamic viscosity, τ - the shear stress and γ - the shear rate, and

$$\tau = k \gamma^{\cdot n}$$
 (Ostwald-de Waale's law)

where k – the coefficient, n – the power low exponent (PLE), which determine the deviation from the Newtonian flow.

Mechanical properties of films

The mechanical-physical properties of cellulose films were measured using the Instron apparatus type 1122 according to ISO standard PN–EN ISO 527-3. The following quantities were evaluated: te-

nacity (T), calculated using the following equation:

$$T = F/(b \cdot h) = (F \cdot \rho)/(b \cdot m_s)$$
, MPa

where F – the strength at breaking, b – the width of the film slide, h – the thickness of the film, m_s – the square weight and ρ – the density of the film.

The elongation at breaking was expressed in percent.

Results and discussion

Rheological behaviour of Biocelsol concentrate solutions. Influence of temperature and storage time

Samples B1 to B4 were used for dissolving in soda solution according to the defined procedure, and so solutions BS1 to BS4 were prepared. The viscosity and PLE were evaluated on the basis of rheological measurements (Table 1). Small differences were found between the viscosity of the Biocelsol solutions, excluding BS2 solution, where the lower viscosity is due to the higher hydrolysis (lower molecular weight) of cellulose. However, the PLEs of these solutions are very low (\sim 0.4), and the solutions had a tendency to gel. With regard to the non-Newtonian flow of the solution, the expression of viscosity is convenient

Table 1. Viscosity η [Pa.s] and PLE n of Biocelsol solutions at 0 °C.

	Rheological parameters				
Biocelsol solutions	Viscosit	n			
	$\gamma = 25 \text{ s}^{-1}$	γ = 150 s-1	"		
BS1	13.9	4.7	0.39		
BS2	4.4	1.6	0.47		
BS3	10.6	3.5	0.37		
BS4	11.4	4.2	0.39		

Table 2. Dynamic viscosity η and PLE n of the Biocelsol soda solutions in dependence on storage time at 10 °C.

Biocelsol		motor	Temperature, °C	Storage time, h at 10 °C		
solution	Parameter			0	21	42
BS1	η, Pa·s	γ = 25 s-1	0	5.8	6.5	6.6
			20	2.9	3.6	3.3
		γ = 150 s ⁻¹	0	2.9	2.9	2.9
			20	1.5	1.7	1.6
	n		0	0.61	0.58	0.54
			20	0.62	0.57	0.57
BS5	η, Pa·s	γ = 25 s ⁻¹	0	8.1	8.2	9.4
			20	3.9	4.1	4.7
		γ = 150 s ⁻¹	0	4.4	4.0	4.1
			20	2.0	2.0	2.1
	n		0	0.61	0.57	0.54
			20	0.63	0.59	0.55

in the region with a clear change of the viscosity on the shear rate $(25 - 250 \text{ s}^{-1})$. Viscosity in Tables 1 and 2 is expressed in accordance with the coefficients of variation of viscosity.

In the next step, the BS1-BS4 solutions were blended with viscose V1 in a concentration range of 20 to 60 wt.% of BS in the blend solution. Blending the Biocelsol solutions with viscose V1 provided the blend solutions with a significant decrease of PLE relative to viscose (n=0.9). The PLE decreased with the increase of the ratio of Biocelsol to viscose solution (Figure 2).

The critical value of n for the processable solutions was estimated for $n \ge 0.60$. The blend viscosity is required to be close to that of the additive value. An acceptable composition of blend solutions regarding the rheological properties for all the investigated enzyme treated pulps and viscose V1 is represented by the content of Biocelsol solutions 0 to 40 wt%. The BS2/V1 blend solution exhibited the best rheological

properties in this case (n = 0.90 - 0.72, viscosity 5.4 - 3.5 Pa.s for 150 s^{-1}), (Figure 3).

The blend solutions exhibited clear heterogeneity, with a strong influence of the majority phase on the rheological parameters. The viscosity of the blend solutions decreased slightly in comparison with the additive values of the Biocelsol and viscose solutions.

It is interesting that the viscosity of the blend solution with a share of 40% of the BS has a tendency to increase to a level close to that of the additive solution (Figure 3).

Influence of storage time on rheological properties

On the basis of previous results of rheological measurements (Table 1, Figures 2 & 3) the best procedure was selected and used to prepare BS1 and BS6 soda solutions. The prepared Biocelsol solutions were stored at 10 °C for 42 hours. The rheological measurements were carried out at 0 °C and 20 °C. The dependence

Table 3. Average activation energy of flow of BS1 and BS5 (0 - 20 °C) for constant shear rate in dependence on storage time at 10 °C.

Biocelsol	Shear rate, s ⁻¹	E _f , kJ·mol ⁻¹			
solution		0 h	21 h	42 h	
BS1	25	22.4	19.7	23.3	
	50	22.5	19.8	22.7	
	100	22.6	19.5	21.7	
	150	22.6	19.2	21.1	
BS5	25	22.4	18.8	22.1	
	50	21.6	18.6	21.4	
	100	20.9	19.5	20.6	
	150	20.5	20.5	20.5	

of the shear stress on the shear rate of the Biocelsol solutions revealed that the non-Newtonian behaviour of solutions improved, and PLE values of 0.55 - 0.62 were obtained, (Figure 4), (Table 2).

Experimental results in Table 2 reveal that the difference in PLE of BS solutions for 0 °C and 20 °C is negligible. Similarly, a very small decrease in PLE was obtained with a storage time of alkali solutions at 10 °C. The viscosity of solutions at 0 °C was found to be about 2-3 times higher in comparison with those for 20 °C for both samples along the whole scale of the shear rate.

Average values of activation energy of flow at a constant shear rate decrease slightly with the increase of storage time, and exhibit a moderate minimum at 20 hours of storage time; this is connected with a change in the structure of solution (ageing) see Table 3.

Concentrated alkali solutions of enzyme treated cellulose BS1 and BS5 were used

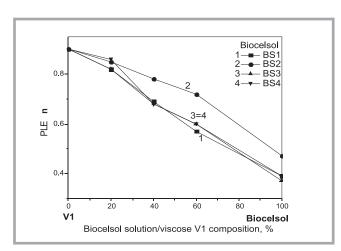


Figure 2. Dependence of PLE n of Biocelsol/V1 blend solutions on Biocelsol/viscose V1 composition at 15 °C.

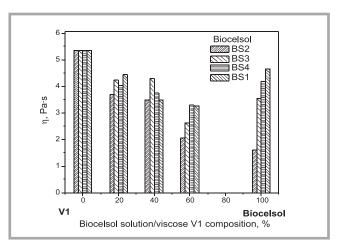
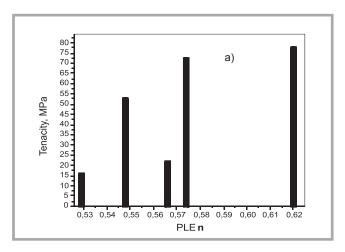


Figure 3. Dependence of viscosity of Biocelsol/V1 blend solutions on Biocelsol/viscose V1 composition 15°C, $\gamma = 150 \text{ s}^{-1}$.



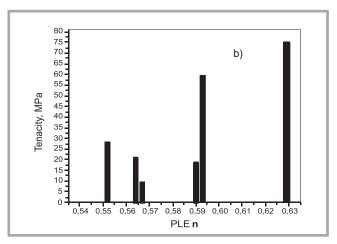


Figure 5. Correlation of the PLE n of the Biocelsol BS1 (a) and BS5 (b) solutions with tenacity of the cellulose films prepared using these solutions.

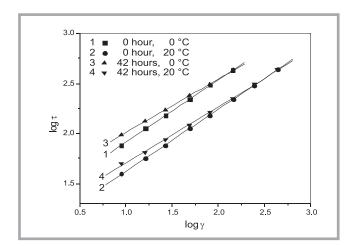


Figure 4. Flow curves $\log \tau$ vs. $\log \gamma$ for alkali solutions of BS1 measured and evaluated for 0° C and 20° C for storage time 0 and 42 hours at 10° C.

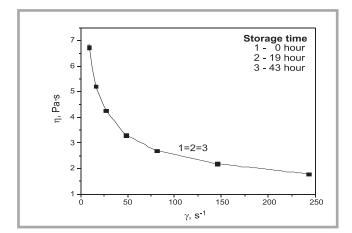
Figure 6. Dependence of viscosity η on shear rate γ for BS6 at 15 °C after dissolving.

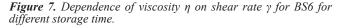
to prepare films of regenerated cellulose. The correlation of the tenacity of regenerated Biocelsol films and PLE for BS1 and BS5 are presented in Figures 5.a and 5.b.

The results reveal the significant effect of the PLE of Biocelsol solutions

on the films' structure and mechanical properties. The tenacity of cellulose films prepared from alkali solutions at constant conditions grows with the increase of the PLE. At approximately n above 0.6, the tenacity of Biocelsol films of above 50 MPa was obtained.

Thus, the experimental results confirmed our preliminary assumptions based on initial trials concerning the critical PLE value for good processing of the Biocelsol solution ($n \ge 0.6$). These showed a decrease of light transmittance through the blend solution (heterogeneity) and a





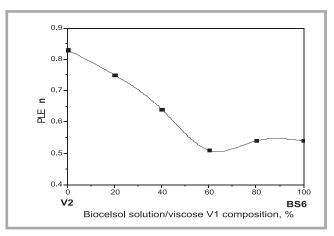


Figure 8. Dependence of PLE n of BS6/V2 blend solution on Biocelsol/viscose V2 composition at $15\,^{\circ}\text{C}$.

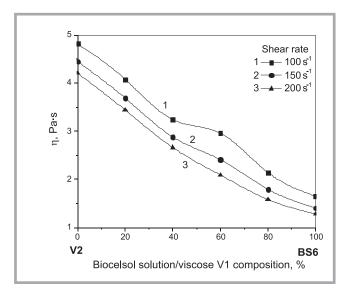


Figure 9. Dependence of Viscosity of BS6/V2 blend solutions on concentration of BS6 in V2 at 15°C.

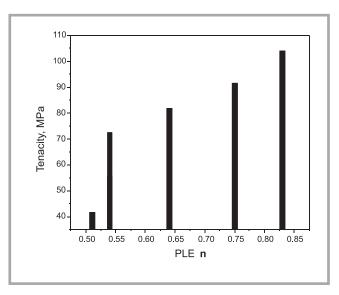


Figure 10. Correlation of the PLE n of the Biocelsol BS6/V2 blend solutions and tenacity of the regenerated cellulose films prepared using BS6/V2 blend solution.

significant decrease in the tenacity of the regenerated cellulose films prepared from cellulose (or blend) alkali solutions with a PLE below 0.6. The exact border between 'processing' and 'non-processing' was not found to be sharp. A small deviation from defined parameters during preparation of solutions and films can have a negative effect on the films' tenacity (Figure 5.b). The influence of viscosity of the solution at constant composition on the films' tenacity has not been found to be so unambiguous.

Reproducibility and stability of Biocelsol concentrated solutions

This part of the research was aimed at investigating the reproducibility of the rheological properties of the Biocelsol alkali solutions, as well as the stability of the rheological properties in dependence on mixing time during preparation and storage time at 5 °C.

To evaluate the reproducibility and stability of the rheological properties of the solutions, six BS6 alkali solutions were prepared. The standard concentrations of components were used.

The rheological properties of solutions were evaluated within 0 to 60 min of mixing time and within 0 to 43 hours of storage time at 5 °C. The rheological parameters of cellulose alkali solutions were obtained at 15 °C.

The results in Figures 6 and 7 show that the reproducibility of the rheological properties of BS6 solution from the point of view of the method of preparation is very good and fully acceptable. The coefficient of varia-

tion for viscosity was evaluated within \pm 6.2% to \pm 9.5%, and the variation of viscosity decreases for the higher shear rate (Figure 6). The PLE did not change in dependence on the storage temperature, and decreased only slightly with storage time. Similarly, the rheological parameters of the BS6 solution in dependence on the storage time of 0 to 43 hours at 5 °C are very stable, and their change is negligible (Figure 7).

Rheological properties of Biocelsol/viscose V2 blend solution and the mechanical properties of the blend film

The BS6 was used for blending with viscose V2, and blend solutions throughout the whole concentration range were prepared. The dynamic viscosity and deviation from the Newtonian flow of the BS6/V2 blend solutions in dependence on the blend composition and on the shear rate are given in Figures 8 and 9. The Biocelsol/viscose blend solutions were prepared with good reproducibility of their rheological properties (viscosity and PLE). The PLE of blend solutions decreases from n = 0.83 for viscose V2 with the increase of the content of BS6 in viscose, passes through a minimum at 60% of BS6 alkali solution (n = 0.51) and slightly increases to 100% of BS6 solutions (n = 0.54), (Figure 8).

The viscosity of viscose V2 is about twice as high in comparison with BS6;

for the blend solution, it decreases with the increase proportionally of BS6 in blend solutions (Figure 9). The results show that the poorest processing of solutions is expected for the blend solution with a minimum of PLE (60 wt% of BS6 solution in blend BS6/V2 solution).

The dependence of the tenacity of the regenerated cellulose films based on BS6/V2 blend solutions on their PLE reconfirmed previous experiments which led to the conclusion that the higher is the PLE, the higher is compatibility of the blend solutions, and thus the higher tenacity of the blend cellulose film (Figure 10).

Conclusions

- The concentrated Biocelsol/soda solutions exhibit a significant deviation from Newtonian behaviour, with a PLE n ranging from 0.55 to 0.62. The PLE of the Biocelsol/viscose blend solutions increases proportionally to the content of viscose in the blend solutions.
- The viscosity values of the Biocelsol/ viscose solution are close to the additive values using Biocelsol solution with low viscosity or slightly below them (at higher viscosity of Biocelsol solutions).
- The tenacity of the regenerated cellulose films based on Biocelsol and Biocelsol/viscose solutions decreases significantly with the solutions' increased deviation from the Newtonian flow within the examined range of PLEs.

Acknowledgment

This work was supported by the EC project 'Biocelsol' FP6 505567-1/NHP2-CT-2003-50-5567.

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- Received 08.03.2007 Reviewed 13.04.2007

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