ELECTROSPINNING OF PVB SOLUTIONS - INFLUENCE OF ELECTRORHEOLOGICAL BEHAVIOUR

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ABSTRACT

The aim of this contribution is to find an influence of shear rheological characteristics of polymer solutions on quality of spinnability. Various polyvinylbutyral (PVB) solutions are chosen for the process of electrospinning in which, under a strong electrostatic field, fibres are generated and deposited on a template as a non-woven sheet.

INTRODUCTION

In electrospinning, polymer solution or melt is ejected from a tip by a strong electric field and deposited as a fibrous mat on a grounded collector. As the charged jet travels in air, its diameter decreases due to high extension rates and simultaneous effect of stretching of the jet and evaporation of the solvent. A typical electrospinning process is described extensively in the literature [1-4]. With respect to their small diameters, the electrospun fibres have a large specific surface and the potential applications of fibres are in various areas such as filtration, nanocomposite material [3,5,6]. Viscosity, concentration, surface tension of polymer solution, molecular weight, intensity of electric field strength, temperature range among the principal parameters affecting fibre formation.

The viscosity of polymer solution has an impact on diameter of fibres, morphology and path of jet. The effect of viscosity, conductivity and surface tension has been investigated by Fong et al. [7]. Wang et al. [8] performed elongation rheology measurements with polymer solutions and they found that a slower rate of capillary thinning is expected to correlate with better spinnability of the polymer solution.

 Winslow [9,10] was the first who started research of rheological behaviour of liquids under a presence of electric field. Using quasielastic light scattering (QELS) Price et al. [11] analyzed the effect of external electric field on the dynamics of polymer chains. They found that in presence of an electric field there is a polarisation effect which is dependent on a difference in permittivity between the polymer segments and solvent.

This contribution describes the suitability of various polyvinylbutyral (PVB) solutions for the process of electrospinning. As a criterion shear rheological behaviour of these materials is taken into account, specifically a course of a curve viscosity ratio η/η_0 vs. electric field strength E. The symbols η and η_0 represent shear viscosities of a solution in the presence and absence of an electric field, respectively. In spite of high elongation rates that are imposed on jets during electrospinning, the present work focuses on a correlation between shear rheology of a polymer solution and its spinnability.

EXPERIMENTAL

The polyvinylbutyral (PVB, M_w=60,000 g/mol; Mowital, Kuraray Specialities Europe (KSE)) was dissolved in methanol, ethanol, isopropanol and butanol as 6, 10 and 14 wt% solution (basic characteristics in Table 1) at 25°C. For viscosity measurements there was used a rotational rheometer Anton Paar MCR 501 equipped with an electrorheological cell.

Table 1 Basic characteristics of the solvents used and polyvinylbutyral (PVB).

	Relative permittivity [-]	Specific conductivity [S/m]	Surface tension [mN/m]	Density [g/cm^3]
Methanol	32.7	$1.5*10^{-7}$	22.12	0.7899
Ethanol	24.5	$1.35*10^{-7}$	21.9	0.785
Isopropanol	19.9	$58*10^{-7}$	21.38	0.7813
Butanol	17.5	$9.12*10^{-7}$	24.5	0.806
PVB	3.60	$1*10^{-9}$	-	1.09

The electrospun fibres were obtained from the solution at 30kV with a tip-to-collector distance of 10 cm (=300 V/mm). The surface characteristics of the prepared nanofibre sheets were observed with a scanning electron microscope Vega TS 5130.

Hansen solubility parameters

The rheological measurement has a tight connection with solubility determined through Hansen solubility parameters [12] δ_D (representing energy from dispersion bonds between molecules), δ_P (representing energy from polar bonds between molecules), and δ_H (representing energy from hydrogen bonds between molecules) representing each molecule, see Table 2. These three parameters can be taken as orthogonal coordinates for a point in three dimensional so-called Hansen space. The nearer two molecules are in this space, the more likely they are dissolved into each other. This is exactly the situation for PVB solved in isopropanol or butanol. Both materials exhibit shorter distances in the Hansen space in comparison with ethanol and methanol, see Figure 1.

Table 2 hansen solubility parameters of the solvents used and polyvinylbutyral (PVB).

	Hansen solubility parameters		
	δ_D [MPa$^{1/2}$]	δ_P [MPa$^{1/2}$]	δ_H [MPa$^{1/2}$]
Methanol	15.1	12.3	22.3
Ethanol	15.8	8.8	19.3
Isopropanol	16	6.8	17.4
Butanol	16	5.7	15.8
PVB	18.6	4.4	13.0

Shear viscosity measurements

The shear viscosities of all solutions were measured in the ramp mode using bob and cup arrangement, diameters of 27 and 17 mm in absence and presence of electric field, respectively. Figure 2a depicts shear viscosity of PVB dissolved in alcohols as 10 wt% solutions. PVB dissolved in good solvents shows shear thinning behaviour at high shear rates > 100 s^{-1} and its zero shear viscosity is higher. On the contrary, for poor solvents the viscosities are constant, zero shear viscosity is lower. For each solution there was determined the curve relating the viscosity ratio η/η_0 to the electric field strength E (Figure 2b). The good solvents of PVB exhibit an almost constant curve of η/η_0 vs. E, whereas viscosity curves for the poor solvents exhibit enhancement.

Effect of concentration on viscosity enhancement

Gupta et al. [13] showed that uniform and bead-free fibres were obtained with increasing concentration ($c/c^* > 6$) of polymer solution.

In this case the critical chain overlap concentration, c^*, was calculated from $c^* \sim 1/[\eta]$, where the intrinsic viscosity $[\eta]$ was determined from a slope in the plot of reduced viscosity η_{red} (a specific viscosity-to-concentration ratio, also denoted as

viscosity number) as a function of concentration c in the low concentration limit. Effect of concentration on viscosity of polymer solutions is depicted in Figure 3. PVB was not dissolved as 14 wt% solution in butanol and isopropanol due to high viscosity, formation of gel.
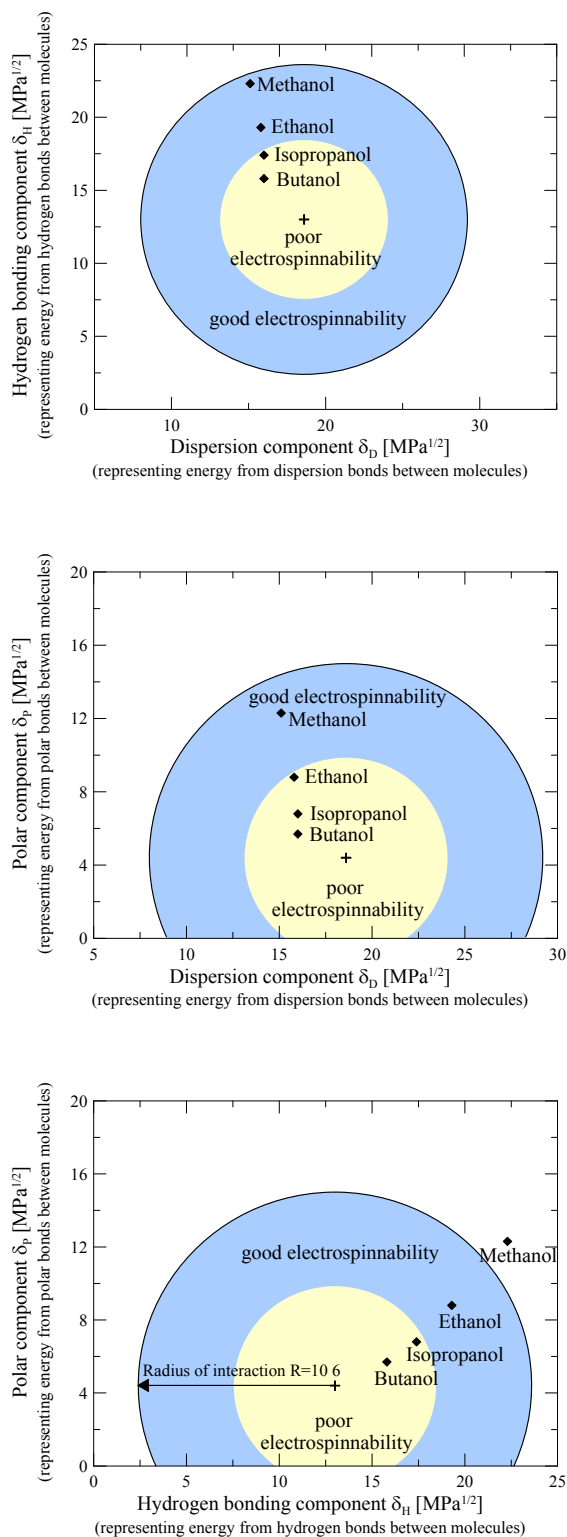

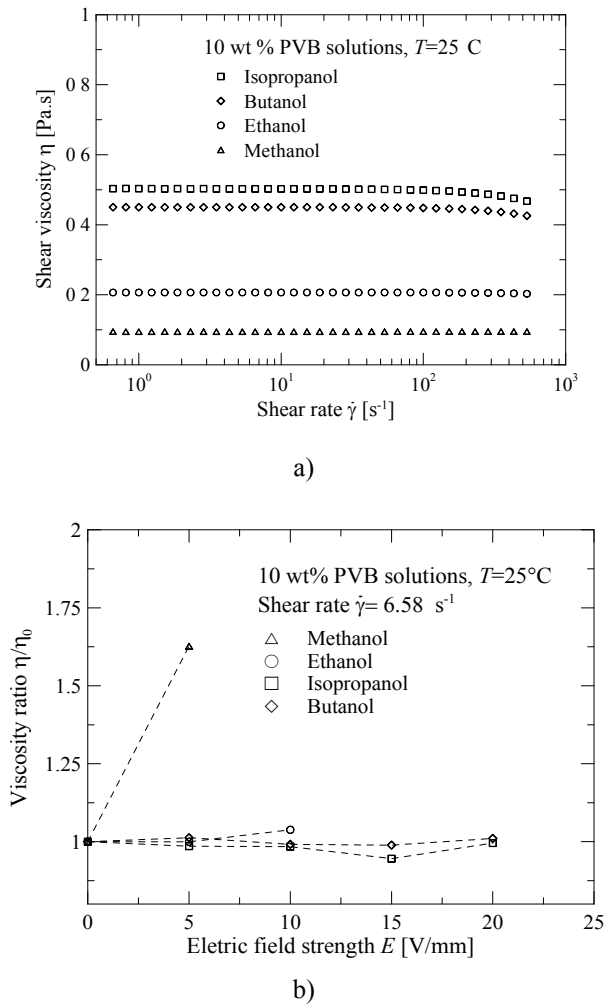**Figure 1**. Hansen solubility parameters for PVB and solvents.

a)

b)

Figure 2 a) Shear viscosity of PVB solutions (absence of electric field strength), b) Dependence of viscosity ratio η / η_0 on electric field strength for PVB solutions.
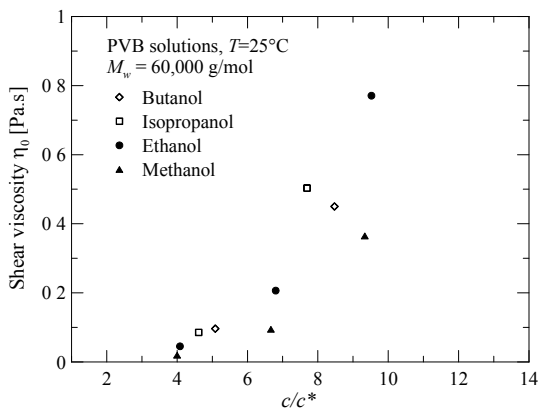

Figure 3. Zero shear viscosity vs. c/c* for PVB in different solvents.

Figure 4 shows slightly increasing viscosity curves for PVB dissolved in methanol (poor solvent) whereas the viscosity curves of PVB in butanol (good solvent) are constant. The enhancement of viscosity is dependent on time and this effect is not reversible.
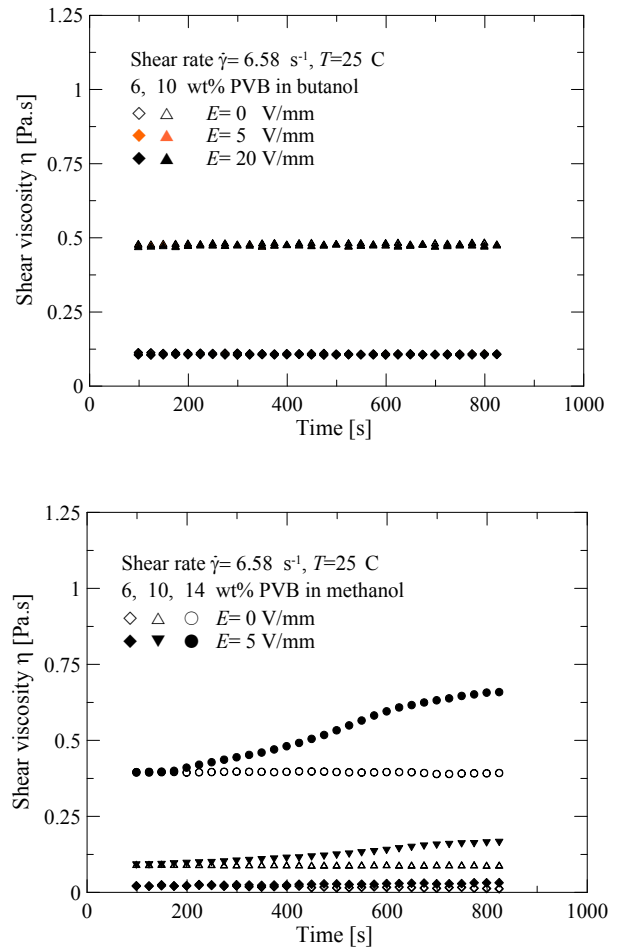

Figure 4 Enhancement of shear viscosity of PVB dissolved in methanol (poor solvent), no change of shear viscosity values with electric field strength for butanol (good solvent).

Electrospun fibres of PVB

Quality of spinnability of these materials was evaluated using the SEM analysis. Effect of concentration of polymer solution in electrospinning process is depicted in Figures 5-7. The fibres were obtained from 6 wt% PVB solutions of isopropanol, ethanol and methanol, in contrast to PVB in butanol where no fibres were obtained. Fibres with higher diameters were obtained from PVB dissolved in ethanol and methanol (poor solvents) as 14 wt% solutions.

This shows that with increasing curve η/η_0 vs. E the spinnability of the respective solution improves.
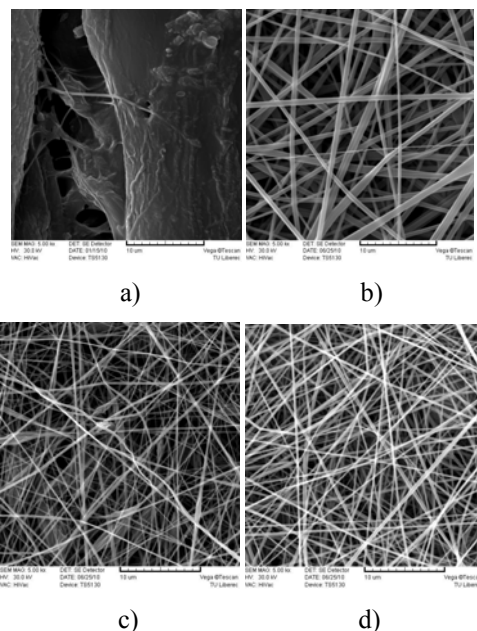
Figure 5 SEM micrographs of PVB electrospun from 6 wt% solution: a) PVB in butanol, b) PVB in isopropanol, c) PVB in ethanol, d) PVB in methanol.
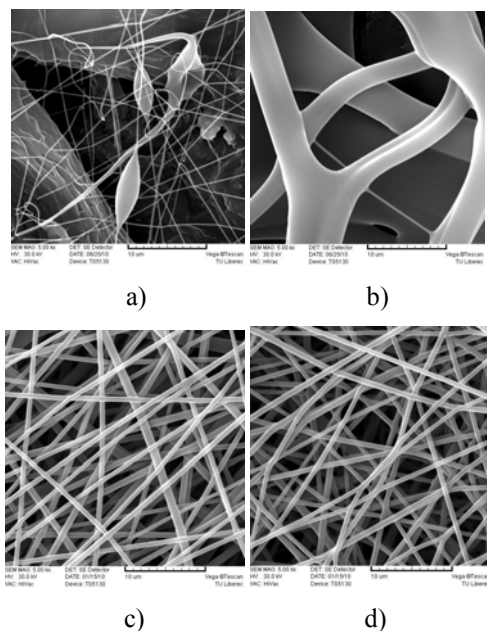

Figure 6 SEM micrographs of PVB electrospun from 10 wt% solution: a) PVB in butanol, b) PVB in isopropanol, c) PVB in ethanol, d) PVB in methanol.

RESULTS AND DISCUSSION

Impact of the solvents on spinnability is validated through the SEM images (Figures 5-7). From PVB dissolved in butanol and isopropanol (good solvents) there were obtained no fibres, whereas for PVB dissolved in ethanol and methanol (poor solvents) there were developed fibre sheets. The tight connection to spinnability and solubility determined through the Hansen solubility parameters was validated, see Figure 1. The shape of the polymer chain depends on solubility of polymer in a solvent. If the individual polymer chains in good solvent are free to uncoil and stretch, viscosity of a solution is high. On the contrary when polymer chains stay coiled and grouped together into microscopic clusters then this topology reflects in lower viscosity. If the external electric field is applied, the polymer chains uncoil and stretch, therefore the viscosity of solution increases and the process of electrospinning is much easier. If the polymer chain in good solvent is uncoiled and stretched then in presence of electric field polymer chain will not react.
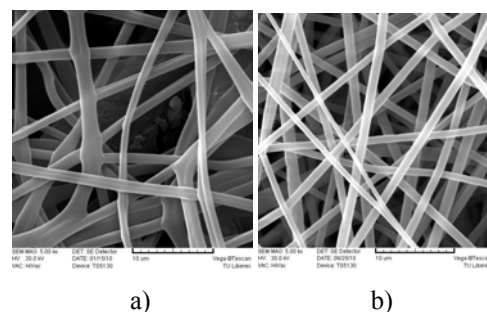

Figure 7 SEM micrographs of PVB electrospun from 14 wt% solution: a) PVB in ethanol, b) PVB in methanol.

A series of the papers documented an influence of concentration of the solutions on the quality of electrospun fibres. In this case the uniform bead-free fibres from PVB dissolved in poor solvent were obtained at the concentration range $4 < c/c^* < 10$. PVB dissolved in poor solvents as 6, 10, 14 wt% solutions are suitable for the process of electrospinning. It was found that viscosity enhancement of a polymer solution in the presence of an electric field increases with concentration of a polymer solution. The behaviour of two good solvents was different when compared with two poor solvents, which increased viscosity in presence of an electric field. The uniform fibres were obtained from PVB dissolved in isopropanol as 6 wt% solution ($c/c^* \sim 4$), whereas polymer droplets were obtained from PVB dissolved in butanol at the same concentration.

CONCLUSION

The electrorheological properties of the individual solvents play a substantial role in the process of electrospinning. It was found the correlation between shear viscosity and spinnability. Shear viscosity enhancement in a presence of an electric field corresponds to good spinability. Structure of nanofibres was documented by the SEM images.

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