Abstract: - The process of electrospinning is a low-cost procedure that creates nanofibres through an electrically charged jet of polymer solution or polymer melt. Electrospinning process consists schematically of a pipette holding the polymer solution, two electrodes, a DC voltage supply in the kV range, and a grounded collector. The high voltage causes drawing of the polymer drop from the tip of the pipette into a fibre. The electrically charged jets are collected as a web of fibres on the surface of a grounded collector. By virtue of their high surface-to-volume ratio, the electrospun nanofibre sheets are used as protective clothing and filtration, tissue scaffolding and other biomedical applications, reinforcement in composites, and optical, electronic and high performance applications. The emphasis will be paid to correlation between electrorheological behaviour of various polyvinylbutyral (PVB) solutions and quality of the corresponding nanofibre webs.

Key-Words: - electrospinning, electrorheology, viscosity, polyvinylbutyral solutions, nanofibres

1 Introduction
The process of electrospinning is based on an electrical charge application of which provides drawing micro- or nano-fibres from a polymer solution or melt. The electric field is generated between a tip and a grounded collector by a high-voltage power supply. The drop of a polymer solution is stored on the tip, from which, in the presence of an electric field, a Taylor cone is created, and then a single fluid jet is emitted from the apex. As the charged jet travels in air, its diameter decreases due to simultaneous effects of the stretching of the jet, the evaporation of the solvent and high extension rates. A typical electrospinning process (Fig.1) is described extensively in literature [1]-[4]. With respect to their small diameters, the electrospun fibres have a large specific surface; accordingly, the potential application of fibres sheets are in the various areas, such as tissue scaffolds, filtration, nanocomposite materials and protective clothing [3], [5], [6]. The basic parameters participating in fibre formation include viscosity, conductivity, concentration, surface tension of polymer solution, molecular weight of polymer, intensity of electric field strength, tip-to-collector distance, temperature and humidity.

Viscosity of a polymer solution represents a crucial role in the process of electrospinning. Specifically the viscosity of polymer solution can dramatically affect diameter of fibres, morphology and path of a jet, this parameter can be varied by molecular weight of polymer, concentration of a solution, type of a solvent, temperature and additives. The effect of viscosity, conductivity and surface tension has been investigated by Fong et al. [7]. They demonstrated that a usage of the polymer solution with low viscosity results in the formation of beads caused by the capillary breakup of the jet during the electrospinning due to dominating surface tension. Higher viscosity favours the formation of fibres without beads, however if viscosity of a solution is too high, electrospinning is no longer possible. Chuangchote et al. [8] applied several different solvents to electrospinning of poly(vinyl pyrrolidone) fibres and studied an influence of concentration and viscosity of solutions on a fibre diameter. Vetcher et al. [9] showed that the dependence of viscosity on molecular weight and polyacrylamid (PAA) concentration normalized to the entanglement concentration allows to predict the electrospinability of PAA solutions, mainly the quality of nanofibres.

Another parameter that ranges to the crucial one is concentration. Gupta et al. [10] observed that with an increasing concentration \( (c/c^* > 6) \) of polymer solution there were obtained uniform and bead-free fibres. The critical chain overlap concentration, \( c^* \), is the crossover concentration between the dilute and semidilute concentration regimes, for this
concentration it holds $c^*\eta \sim 1$. For polyvinyl alcohol (PVA) solutions Koski et al. [11] obtained uniform circular-shaped fibres at the concentration $5 < c/c^* < 9$. Son et al. [12] argued that minimum concentration of poly(ethylene oxide) PEO for obtaining electrospun fibres is $c/c^* \sim 10$.

Winslow [13], [14] was the first who started research of rheological behaviour of liquids under a presence of electric field. Especially viscosity $\eta$ as a dominating characteristic of so-called electrorheological (ER) fluids is studied. Generally, ER fluids are suspensions for which viscosity in presence of electric field increases intensively. Using quasielastic light scattering (QELS) Price et al. [15] 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. Wang and Huang [16] applied dynamic light scattering (DLS) for a qualitative comparison when a non-polar polymer (polystyrene) is solved either in polar or non-polar solvent. They revealed that in the latter case the effects from the externally applied electric field were negligible. This motivated Chen et al. [17] who carried out molecular dynamics simulation to predict the effects of external electric field on the diffusion dynamics of a polar or non-polar chain in polar or non-polar solvents.

Fig.1 Scheme of the electrospinning apparatus.

This contribution deals with 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, viz. a course of a curve viscosity ratio $\eta/\eta_0$ vs. electric field strength $E$. The symbols $\eta$ and $\eta_0$ 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 electrostatic spinnability.

2 Experimental

2.1 Material and experimental devices

The polyvinylbutyral (PVB) was chosen for this experiment, the commonly used polymer as the mesopore template, which is non-toxic, odourless and environment friendly. PVB (Mw=60,000 g/mol; Mowital, Kuraray Specialities Europe (KSE)) was consecutively dissolved in methanol, ethanol, isopropanol and butanol as 6, 10 and 14 wt % solution (for details see Svrcinova et al. [18]). The PVB solutions were prepared by a laboratory shaker at 25°C overnight. For viscosity measurements there was used an Anton Paar rotational rheometer MCR 501 equipped with an electrorheological cell C-PTD200/E (bob and cup arrangement, diameter 17mm). The surface characteristics of the prepared nanofibre sheets were observed with a scanning electron microscope Vega TS 5130.

2.2 Hansen solubility parameters

For the prediction of PVB solubility in various solvents there were used Hansen solubility parameters (HSP) [19] $\delta_D$ (representing energy from dispersion bonds between molecules), $\delta_P$ (representing energy from polar bonds between molecules), and $\delta_H$ (representing energy from hydrogen bonds between molecules) representing each molecule, see Table 1.

<table>
<thead>
<tr>
<th>Hansen solubility parameters</th>
<th>$\delta_D$ [MPa$^{1/2}$]</th>
<th>$\delta_P$ [MPa$^{1/2}$]</th>
<th>$\delta_H$ [MPa$^{1/2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>15.1</td>
<td>12.3</td>
<td>22.3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>15.8</td>
<td>8.8</td>
<td>19.3</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>16.0</td>
<td>6.8</td>
<td>17.4</td>
</tr>
<tr>
<td>Butanol</td>
<td>16.0</td>
<td>5.7</td>
<td>15.8</td>
</tr>
<tr>
<td>PVB</td>
<td>18.6</td>
<td>4.4</td>
<td>13.0</td>
</tr>
</tbody>
</table>

These three parameters can be visualized using a spherical representation. The radius of the sphere, $R$ (radius of interaction), indicates the maximum difference in affinity for which a good interaction takes place. The HSPs of the good solvents are located closer to a centre of the sphere, the poorer ones approach the radius, and non-solvents are located outside of the sphere. In our case...
isopropanol and butanol exhibit shorter distance to the centre in the Hansen space in comparison with ethanol and methanol, see Fig. 2.

2.3 Shear viscosity

Using the experimental devices mentioned in Section 2.1 there were measured the shear viscosities of all solutions in the absence and presence of an electric field, see Figs. 3 and 4. The PVB solutions with good solvents exhibit an almost constant curve of $\eta/\eta_0$ vs. $E$, whereas the viscosity curves for the poor solvents are increasing.

Fig. 3 Shear viscosity of PVB solutions (absence of electric field strength).

Fig. 4 Dependence of shear viscosity ratio $\eta/\eta_0$ on electric field strength for PVB solutions.

Fig. 5 depicts slightly increasing viscosity curves for PVB dissolved in methanol (poor solvent) whereas the viscosity curves of PVB in butanol (good solvent) shown in Fig. 6 are constant. The enhancement of viscosity is dependent on time and this effect is not reversible.

The electrospun fibres were obtained from the solutions at a voltage of 30 kV and a tip-to-collector distance was fixed to 10 cm (=300 V/mm). The quality of electrostatic spinnability of these materials was evaluated using SEM analysis by Vega TS 5130. It was shown that with increasing curve $\eta/\eta_0$ vs. $E$ the spinnability of the solution improves, see Fig. 7. This result corresponds to an
interaction radius $R$ (of a given polymer (PVB) and solvents) generated by the Hansen solubility parameters $\delta_D$, $\delta_P$, and $\delta_H$ in the sense that the solvents for which their locations in the Hansen space generated by PVB are close to or exceed the radius $R$, are suitable for the process of electrospinning as documented by the SEM images. On the other hand, those solvents which locations in the Hansen space are closer to its centre, i.e. they are good solvents of PVB, exhibit an almost constant curve of $\eta/\eta_0$ vs. $E$, and do not exhibit good spinnability. Based on the above findings it was shown that, unlike butanol and isopropanol, ethanol and methanol as the solvents of PVB are suitable for electrospinning.

![Fig. 5 Enhancement of shear viscosity of PVB dissolved in methanol (poor solvent).](image)

![Fig. 6 Shear viscosity values independent on electric field strength for butanol (good solvent).](image)

![Fig. 7 SEM images of PVB electrospun from 10 wt% solution: a) PVB in butanol, b) PVB in isopropanol, c) PVB in ethanol, d) PVB in methanol.](image)
3 Conclusion
The electrospinning process is affected by a number of entry parameters. This contribution focused on the impact of an electric field on shear viscosity of the polymer solutions. It was shown that PVB dissolved in a poor solvent exhibited viscosity enhancement in the presence of an electric field and its electrospinning formed nonporous circular-shaped fibres without defects. It can be deduced that these solvents are suitable for electrospinning. The influence of concentration was found, but it is negligible for the poor solvents whereas quality of electrospinning of the polymer solutions with the good solvents is dependent on concentration.

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 electrostatic spinnability. Structure of nanofibres was documented by the SEM images.

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References: