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Polymer Degradation and Stability

The storage stability of polyvinylbutyral solutions from an electrospinnability standpoint

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ABSTRACT

The quality of electrospun fibres is subject to many factors ranging from the characteristics of the materials used to processing conditions. Although an important parameter for applicability, less attention has been paid to the storage stability of applied polymer solutions and its impact on the quality of electrospun webs. The aim of this study is to analyse the storage stability of polyvinylbutyral solutions in methanol and ethanol for the formation of undisturbed nanofibres. The quality of nanofibrous mats produced over a period of 197 days, during which the solutions were stored under constant conditions, was investigated. Using rheological measurements, SEM, FTIR, and DSC techniques, it was shown that the storage period for the solutions used had almost no influence on the quality of electrospun fibres, which is a positive result for practical use.

1. Introduction

The quality of nanofibrous webs created by an electrospinning process plays a crucial role for their application in various fields such as filters, nanocomposite materials, membranes, and in medical areas [1–5]. In the electrospinning process, single jets are ejected from the apices of Taylor cones created at the surface of a drop of polymer solution (Fig. 1). Jet forming is initialised by an electric field generated by a high-voltage power supply between the tip of the stick where the drop is stored and the grounded collector. In principle, the charged polymer jets are, during their passage from the tip onto the collector, simultaneously exposed to two basic factors reducing their diameters: high extension rate, the magnitude of which should not result in a jet disruption, and the rate of solvent evaporation optimally corresponding to the situation in which the solvent is completely evaporated at the moment of reaching the collector.

Polyvinylbutyral (PVB) is a useful material in the electrospinning process. PVB is frequently added to increase the spinnability of the prepared solutions. This procedure was applied to the production of boron nitride nanofibres [6]. Mullite nanofibres were obtained through an optimal dosage of PVB [7]. PVB was used as a spinnable carrier for manufacturing luminescent ceramic fibres [8]. Mesoporous silica nanofibres were prepared with the assistance of PVB during the process of electrospinning [9]. Composite nanofibres were fabricated from PVB/silica [10] as well as multiwalled carbon nanotube/PVB [11]. The addition of PVB proved crucial in the preparation of bead-free resol fabrics [12] as well as in the production of composite fibres containing yttrium and cerium [13,14]. Using a PVB/inorganic salt solution, it is also possible to prepare well-aligned and highly-ordered nanofibrous architecture [15]. PVB in combination with polyaniline and polyethylene oxide was used in the construction of humidity sensors [16,17]. However, in this case the formation of beads in nanofibres was beneficial, as it enabled good adhesion to the electrode.

Polyvinylbutyral also plays an important role if used separately. For example, it is possible to introduce interlayers connecting glass plies in laminated glass. The properties of the interlayers were improved by using electrospun nanofibres composed of PVB and carbon nanotubes [18]. Recently, pure commercial polyvinylbutyrals were also analysed [19]. Analyses of electrospinning processes, when only pure PVB (+solvents) was used, are discussed, e.g., in Refs. [20–24].

Practically all studies on electrospinning have focused on four basic groups of factors participating in the creation and affecting the quality of nanofibrous webs. These include the polymer (molecular weight, molecular weight distribution, topology of macromolecules), solvent (surface tension, solubility parameters, relative

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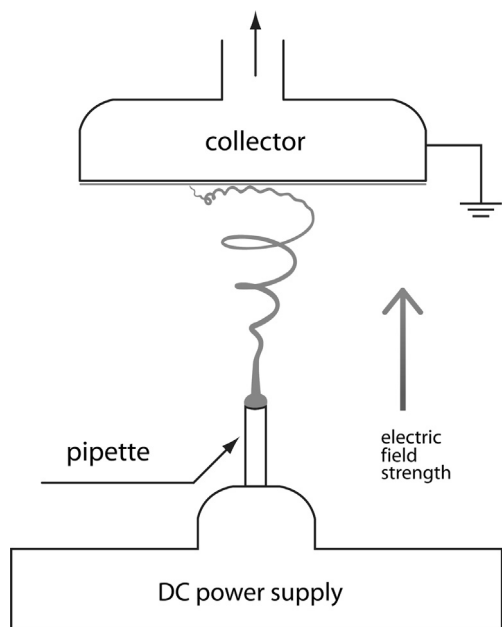E-mail address: peer@ih.cas.cz (P. Peer).

Fig. 1. Schematic sketch of an electrospinning apparatus.

permittivity), solution (viscosity, concentration, specific conductivity), and process parameters (electric field strength, tip-to-collector distance, temperature, humidity).

As far as the authors are aware and in spite of the fact that PVB exhibits various forms of degradability, no attention has been paid to the possible time degradation of the polymer solutions in connection with the corresponding quality of electrospun nanofibres [25—31]. The aim of this study is to analyse and qualitatively compare nanofibrous mats prepared by electrospinning from PVB solutions with methanol and ethanol within a period of almost 7 months, simulating the durability of these solutions in practical applications. During this time, the PVB solutions were kept under constant storage conditions. Methanol and ethanol, although poor solvents of PVB, contribute to higher quality of the electrospun nanofibres in comparison to a situation when good solvents are used, e.g. [21].

2. Experimental

For a qualitative comparison of the solutions of PVB in methanol and ethanol and corresponding nanofibrous mats over a period of almost 7 months (1, 8, 15, 29, 57, 87, 113, 141, 169, and 197 days), the following characterisation techniques were used: conductivity and rheological measurements, a scanning electron microscopic (SEM) analysis of electrospun nanofibres, infra-red spectroscopy, and differential scanning calorimetry (DSC) measurements.

2.1. Materials

Polyvinylbutyral (Mw = 60,000 g/mol; Mowital B 60H, Kuraray Specialities Europe) was dissolved in methanol and ethanol (quality of p.a., Penta, Czech Republic) at 10 wt.% concentration. The structure of Mowital B 60H is composed of vinyl butyral, vinyl alcohol and vinyl acetate, in this case 75—81, 18—21 and 1—4%, respectively. Basic characteristics of the entry components are summarised in Table 1, including the Hansen solubility parameters (HSP). To homogenise both solutions, a magnetic stirrer was used at 150 rpm at 20 °C over 5 days. Afterwards, the solutions were poured into flasks, which were placed into a tempered dark box (20 °C) and taken out just before each measurement.

Table 1
Characteristics of PVB and solvents used.

Property		PVB	Ethanol	Methanol
Relative permittivity		3.6	24.5	32.7
Specific conductivity [S/m]		1.0×10^{-9}	1.4×10^{-7}	1.5×10^{-7}
Surface tension [mN/m]		–	21.9	22.1
Density [kg/m^3]		1090	785	789
HSP [MPa$^{1/2}$]	δ_D	18.6	15.8	15.1
	δ_P	4.4	8.8	12.3
	δ_H	13.0	19.3	22.3

A choice of 10 wt.% concentration was based on the trend relating concentration vs. quality of electrospun nanofibres. For 6 wt.% concentration, the electrospun webs exhibit a quantity of non-fibrous formations (beads, etc. — their appearance attained approximately 90 pcs/50 × 50 square micrometres) for both polymer solutions (PVB in methanol and PVB in ethanol). These imperfections disappear with an increasing concentration. The quality of webs corresponding to 10 wt.% concentration is very good as documented in the next section.

2.2. Conductivity measurements

The conductivity of both solutions (Table 2) was measured using a Conductivity Meter Lab 960 (SCHOTT Instruments, Germany) before each rheological measurement. As the maximal experimental deviation of the device used is approximately 0.5%, the deviation of conductivity for both solutions was approximately 1% during the whole testing period.

2.3. Rheological measurements

The rheological measurements, carried out with a Bohlin Gemini rotational rheometer (Malvern, U.K.) equipped with a bob and cup (25 mm and 27.4 mm in diameter) arrangement, included both steady shear and oscillatory modes. The temperature was kept constant at 20 °C during all experiments.

2.4. Electrospinning

The prepared PVB solutions were electrospun using a proposed laboratory device (see Fig. 2) at a voltage of 25 kV with a tip-to-collector distance of 100 mm. The laboratory device is assembled with the materials exhibiting very low conductivity to ensure that an electric field is not affected by the device itself. The basic construction is formed by aluminium rods, the lower (1 × 1.16 m) and upper (0.5 × 1.16 m) mm thick tables are made of fibre-glass reinforced thermoset polyester material Glastic UTR (Röchling Glastic Composites, USA; insulation resistance 3.1×10^{12} Ohm) as well as the nuts and bolts fixing a draw with a collector to the upper plate. The pieces forming the draw are only glued. A distance between a replaceable tip of carbon steel stick (SAE designation 11xx, a diameter 10 mm) and the collector is handled manually with a linear guidance preserving perpendicularity between a stick axis

Table 2
Conductivity of prepared PVB solutions.

Time [days]	Conductivity PVB-ethanol [mS/m]	Conductivity PVB-methanol [mS/m]	Temperature [°C]
1	1.26	3.62	21.7
113	1.29	3.64	22.9
197	1.28	3.60	23.0