CORRELATION BETWEEN THE ONSET OF BEADLESS CHARACTER OF NANOFIBROUS WEBS AND RHEOLOGICAL CHARACTERISTICS OF ELECTROSPUN POLYMER SOLUTIONS

Jana ZELENKOVA, Petra PEER, Petr FILIP

Institute of Hydrodynamics, Czech Academy Sciences, Prague, Czech Republic, EU,
zelenkova@ih.cas.cz, peer@ih.cas.cz, filip@ih.cas.cz

Abstract

An overwhelming majority of applications of nanofibrous webs requires sufficiently smooth character of nanofibres surface. This character is apart other parameters strongly influenced by a concentration of chosen polymeric material in the solvents. Qualitative attributes roughly depend on the prepared concentration, specifically whether it belongs to one of the four basic regions: dilute, semidilute unentangled, semidilute entangled and concentrated. A concentration separating the latter two regions is often taken as a zero-th approximation indicating an onset of beadless nanofibrous webs. The present contribution uses as a more precise indicator behaviour of so-called phase angle relating viscous and elastic moduli, in other words mutual participation of viscous and elastic components. To this aim three frequently used polymers were used: copolymer of poly(vinylidene fluoride) and hexafluoropropylene (PVDF-*co*-HFP), poly(ethylene oxide) (PEO) and poly(vinyl butyral) (PVB). For materials exhibiting first a constant behaviour or moderate decrease in a phase angle for lower concentrations, an approximation of the starting concentration is given by a concentration value where a phase angle curve starts to decrease, apparently reflecting a more progressive viscoelastic nature. As shown, such approximation provides relatively very good approximation enabling to eliminate a traditional trial-and-error method.

Keywords: Nanofibres, beadless morphology, PVDF-*co*-HFP, polymer concentration, rheology

1. INTRODUCTION

In past decades the application of nanofibrous materials has shifted from classical filters to other uses such as protective clothing, antibacterial wound dressing, antibacterial filtration membranes, and many others. The electrospinning process [1,2] represents one way to produce nanofibres in a relatively cheap manner. This process is based on applying a high voltage (in orders of tens kV) to polymer solutions or melts when ejected nanofibres are deposited on a grounded collector. Quality of the resulting nanofibres is also closely related with an appearance of so-called beads along the individual nanofibres which is mostly an unwanted phenomenon. Bead formation strongly depends on various factors such as voltage, tip-to-collector distance, additives as well as a choice of solvents.

One of the crucial parameters is represented by the polymer concentration. Its value contributes to distinguish the visual properties of the final product to three distinct cases: electrospraying (discrete drops), continuous nanofibres and the creation of spots produced by spinning due to incomplete solvent evaporation. De Gennes [3] set four consecutive regions of polymer solutions differing in concentration: dilute, semidilute unentangled, semidilute entangled and concentrated. The first two regions are separated by the so called overlap concentration c^*, the semidilute regions by the so called entanglement concentration c_e. For individual materials the multiplicative coefficients k of entanglement concentration c_e (where a semidilute entanglement region starts) are determined in such a way that for concentrations lower than k.c_e the electrospun nanofibers exhibit singularities (appearance of beads along the nanofibres) and for concentration higher than k.c_e the

beads are suppressed and the nanofibres exhibit a relatively smooth surface. The question is whether this method of evaluating an onset of concentrations for which beadless nanofibres are produced cannot be simplified. To this aim we chose three frequently used materials introduced in the Abstract. These materials are biocompatible and their application as e.g. antibacterial filtration membranes seems to be promising [4].

Based on oscillatory rheological measurements the goal of this contribution is to show a close correlation between the onset of a starting concentration for which a presence of beadless nanofibres dominates and a location of phase angle decrease, i.e. a sudden decrease from the constant course or only a moderate decrease in the curve phase angle vs. the concentration of polymer solution.

2.   MATERIALS AND METHODS

Kynar Flex® 2801 (copolymer poly(vinylidene fluoride)-*co*-hexafluoropropylene) was purchased from Arkema (France), poly(vinyl butyral) Mowital B 75H was purchased from Kuraray Specialities Europe and poly(ethylene oxide) was purchased from Sigma Aldrich (USA). The solvents N,N´- dimethylformamide (DMF) (p.a.) and ethanol (quality of p.a.) were purchased from P-LAB, a.s. (Czech Republic) and Penta (Czech Republic) respectively. All chemicals were used as obtained without further refinement.

Polymer materials were dissolved in corresponding solvents (**Table 1**) using a magnetic stirrer MR Hei-Tec (Heidolph, Germany) with the help of a teflon-coated magnetic cross under these conditions: mixing rate was set to 250 rpm, temperature 25 °C and time of mixing was 48 hours (24 hours in the case of Kynar Flex® 2801). The sufficiently wide and dense concentration range ensured that the full palette of nanofibres was at disposal and moreover, it ensured an acceptable approximation of a location where a phase angle started to decrease.

Table 1 Ranges of concentrations of the individual polymer solution

Polymer	Solvent	Molecular weight [g/mol]	Concentration [wt.%]
PVDF-*co*-HFP	DMF	455,000[a]	8, 10, 12, 13, 15, 17, 18, 20 – 29 in steps of 1 %
PVB	ethanol	75,000[a]	3 – 10 in steps of 1 %, 12, 14
PEO	distilled water	637,500[b]	0.3, 0.5, 0.6, 0.8, 1, 1.2, 1,5, 1.8, 2 – 6 in steps of 0.5 %, 7, 7.5, 8, 9

[a] molecular weight provided by the producer, [b] molecular weight determined by SEC (Size Exclusion Chromatography)

The nanofibres were spun (see **Table 2** presenting the conditions) using our laboratory needleless device equipped with a high-voltage power supply SL70PN150 (Spellman, USA), a carbon steel stick (10 mm in diameter) with a semispherical hole for depositing of 0.2 mL of polymer solution and a motionless flat metal collector.

Table 2 Summary of the entry parameters of the electrospinning process

Material	Voltage [kV]	Tip-to-collector distance [cm]	Temperature [°C]	Humidity [%]
PVDF-*co*-HFP / DMF	18	10	23 ± 1	34 ± 1
PVB / ethanol	20	10	21 ± 1	40 ± 1
PEO / distilled water	12 - 25	20	22 ± 1	39 ± 2

A rotational rheometer Physica MCR 501 (Anton Paar, Austria) equipped with the concentric cylinder geometry (the inner and outer diameters were 26.6 and 28.9 mm, respectively) was used both for oscillatory

measurements (frequency sweep within 0.1 – 100 Hz at strain 1 %) providing elastic G' and viscous G'' moduli, and for shear viscosity measurements (a range 0.01-300 s^{-1}). The value of shear rate $\dot{\gamma}$ = 0.12 s^{-1} belonging to a linear viscoelastic region was chosen for measurement of shear viscosity of polymer solutions with different polymer concentrations, and consequently applied to a determination of specific viscosity. The phase angle δ (tan $\delta = G''/ G'$) was determined at frequency of 10 Hz. Temperature was set to 25 °C. Each measurement was carried out at least three times and the individual runs were more or less identical.

A high resolution scanning electron microscope Vega 3 (Tescan, Czech Republic) was used for characterization of nanofibrous mats. Prior to imaging, the samples were sputtered by a conductive coating layer using a sputter Quorum Q150R (Quorum Technologies Ltd, UK).

3.   RESULTS

Based on measurement of shear viscosities for individual concentrations of PVDF-co-HFP, the specific viscosities were calculated using the relation $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$, where η_0 is the zero shear rate viscosity (measured at $\dot{\gamma}$ = 0.12 s^{-1}) and η_s is the solvent (DMF) viscosity (= 0.807 mPa.s). Consequently, the first three concentration regions according to de Gennes [3] were determined separated by the overlap concentration c^* (≈ 12 wt.%) and entanglement concentration c_e (≈19 wt.%). These two concentrations correspond to the intersection points of linear segments optimized with respect to the experimental points, see **Figure 1**.
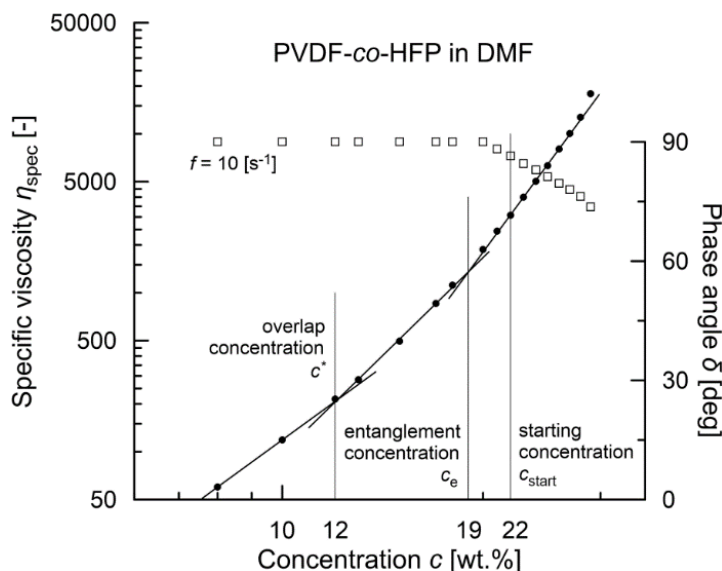

Figure 1 Correlation between an onset of viscoelasticity (a decrease of phase angle, open circles) and a starting concentration corresponding to an onset of beadless PVDF-co-HFP nanofibres

Based on elastic (storage) G' and viscous (loss) G'' moduli, a course of the phase angle δ (tan$\delta = G''/ G'$) is depicted in **Figure 1**. A value of concentration for which the phase angle starts to decrease (slightly more than 20 wt.%) corresponds to the formation of network structures among the polymer chains and exceeds a location of the entanglement concentration (≈ 19 wt.%).

The morphology of PVDF-co-HFP nanofibres was correlated with the rheological characteristics of measured solutions. **Figure 2** documents that up to the overlap concentration (c^* ≈ 12 wt.%) no nanofibres are formed and as a result only a disordered set of blobs are received. Starting with the overlap concentration the primary forms of nanofibres are indicated mixed with the blobs, and finally a passage from bead to bead-free nanofibres is apparent round the entanglement concentration. It seems that an adequate quality of nanofibres is achieved for c_{start} = 22 wt.% and higher. This value closely corresponds to a concentration for which the phase angle starts to decrease as elasticity begins to manifest.
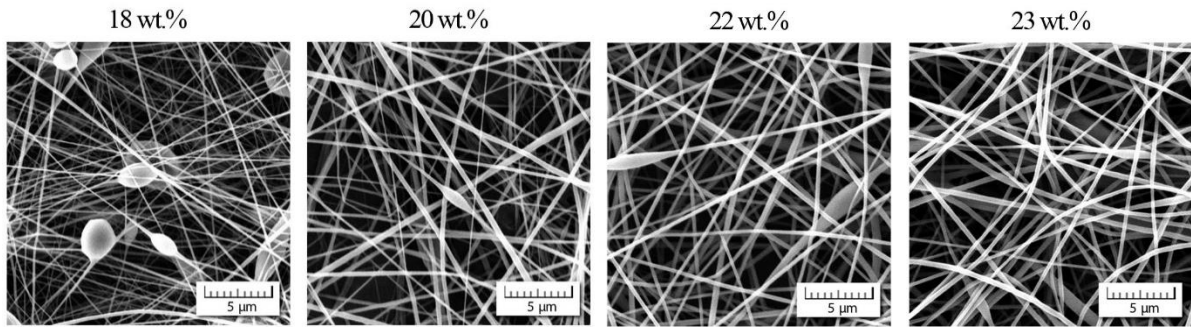
Figure 2 Morphology of individual nanofibres in dependence on PVDF-*co*-HFP concentration

The analogous experimental approach was carried out with PVB dissolved in ethanol (a measured value η_s = 1.087 mPa.s). The results are introduced in **Figures 3** and **4**. In this case the starting concentration is slightly lower than the entanglement concentration.
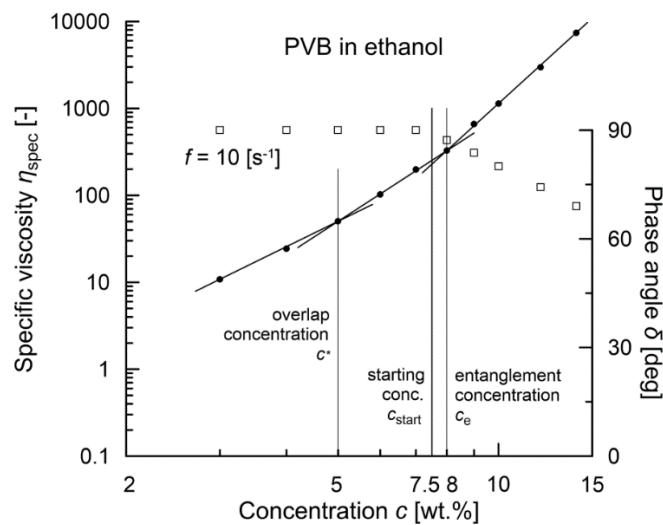

Figure 3 Correlation between an onset of viscoelasticity (a decrease of phase angle, open circles) and a starting concentration corresponding to an onset of beadless PVB nanofibres
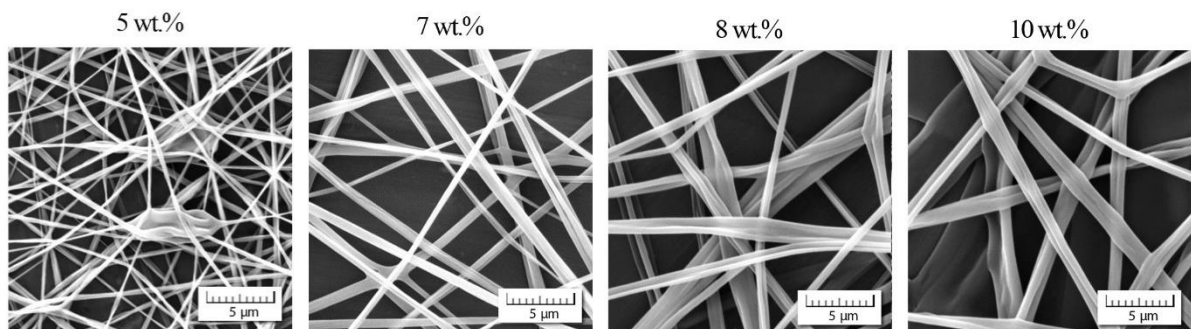

Figure 4 Morphology of individual nanofibres in dependence on PVB concentration

The analogous experimental approach was also carried out with PEO dissolved in distilled water (η_s = 0. 890 mPa.s). The results are summarized in **Figures 5** and **6**. In this case (M_w = 637,500 g/mol) the polymer solutions exhibit viscoelastic behaviour also for lower concentrations due to higher molecular weight. First, a decrease in the relation phase angle vs. concentration is rather moderate. Then, at the concentration of

approximately 6 wt.% a sudden drop is apparent. Hence, this value (c_{start}) indicates the region from which the nanofibres have dominantly bead-free character.
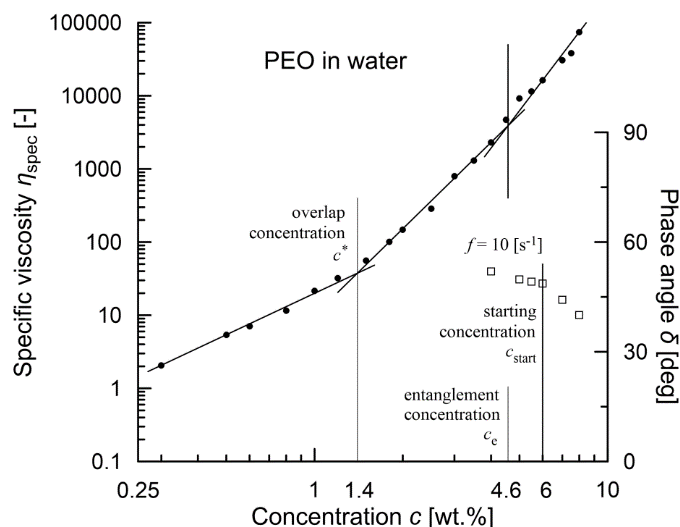

Figure 5 Correlation between a sudden decrease of phase angle (open circles) and a starting concentration corresponding to an onset of beadless PEO nanofibers
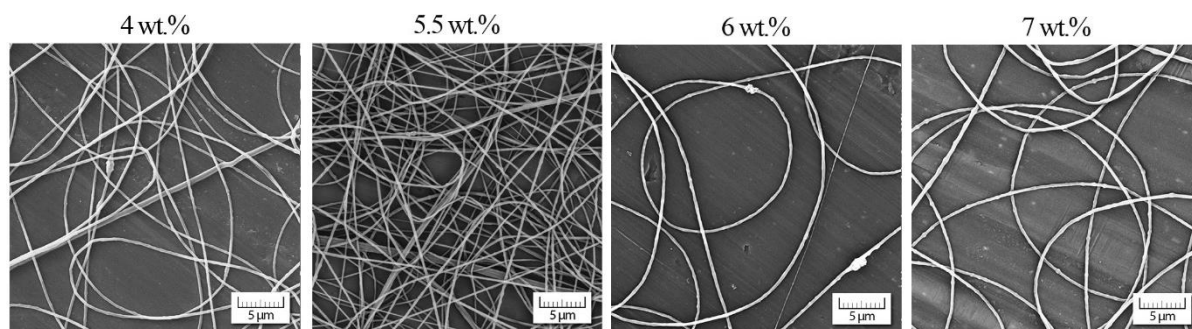

Figure 6 Morphology of individual nanofibres in dependence on PEO concentration

The following **Table 3** summarizes the results for all three materials. The differences between the individual polymers also subject to topology of macromolecular chains and their possible entanglement.

Table 3 Summary of the overlap, entanglement and starting concentrations for used polymeric materials

Material	Overlap concentration c^* [wt.%]	Entanglement concentration c_e [wt.%]	Starting concentration c_{start} [wt.%]
PVDF-*co*-HFP / DMF	12	19	22
PVB / ethanol	5	8	7.5
PEO / distilled water	1.4	4.6	6

4. DISCUSSION

The determination of the starting concentration for the PEO solution is not so strict as for the remaining two materials as PEO solutions exhibit viscoelastic behaviour also for lower concentrations due to relatively high molecular weight. A more pronounced decrease of the phase angle starts from already mildly decreasing curve phase angle vs. concentration which contrasts to the PVDF-*co*-HFP and PVB solutions for which the phase

angle attains a constant value (90°) for lower concentrations. This also results in relatively gradual passage of PEO nanofibres from beaded to beadless character.

Possible electrospinnability of polymeric materials and quality of the resulting nanofibres is subject to a number of entry parameters which can be roughly distributed into four categories: polymer characteristics (molecular weight, viscosity, etc.), solvent characteristics (rheological parameters, etc.), polymer solution characteristics (concentration, Hansen solubility parameters, etc.), and process characteristics (e.g. voltage, tip-to collector distance, temperature, humidity).

The topic of this study is a participation of polymer concentration on the appearance of singularities (beads) along the electrospun nanofibres. It is well known that characterization of polymeric materials differs from batch to batch [5]. It results in a variable value of the concentration separating beaded and beadless nanofibres. The primary factor causing these discrepancies is represented by variable molecular weight modifying rheological characteristics. It means that the experimental findings valid for one batch cannot be automatically applied for the other and the whole evaluation process should be repeated. The rheological procedure presented in the preceding section substantially accelerates acquiring new data (starting concentrations) with new batches eliminating hitherto necessity to repeat the individual experiments using a spinning device.

5.   CONCLUSION

Determination of a starting concentration of electrospinnable polymer solutions for which the obtained electrospun nanofibres exhibit a bead-free surface is usually carried out by a trial-and-error method. The proposed method using oscillatory rheological measurements provides a very good approximation of the starting concentrations. For materials exhibiting first a constant behaviour or moderate decrease of a phase angle for lower concentrations, an approximation of the starting concentration is given by a concentration value where a phase angle curve starts to decrease apparently reflecting more progressive viscoelastic nature. It was documented using solutions of three often used polymers: PVDF-*co*-HFP, DMF and PEO.

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