

Influence of polymer solution properties on the characteristics of electrospun fibers

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ABSTRACT

The influence of polymer solution composition on the properties of electrospun fibers of poly (lactic-co-glycolic acid) (PLGA) solutions were studied. The polymer solutions were more elastic and had higher viscosity when DMF-CHL was used compared to DMF-THF. As a result, the electrospun PLGA fibers had a higher stiffness and tensile strength when they were electrospun from DMF-CHL.

INTRODUCTION

Micro- or nanoscale fibers have been used for biomimetic structures, such as tissue scaffolds, wound dressings and drug delivery carriers¹⁻³. Electrospinning is a versatile, cost effective and simple process for producing micro- or nanoscale fibers by exposing polymer solution/melt to a high voltage. Electrospinning has been widely used for tissue engineering and wound healing^{4, 5}. Electrospun fibre structures have shown boundless advantages in biomedical applications, due to their high porosity and biomimetic structure of the extracellular matrix of the body. Various materials can be used for electrospinning, including both natural and synthetic polymers². Recently, the electrospinnability of different polymers was investigated, and sufficient chain overlap and entanglements of the polymer solution were regarded as the prerequisite for electrospinning^{6, 7}.

Mechanical properties are very important for tissue engineering and wound healing^{8, 9}. Electrospun fibers should be strong enough to provide a physical barrier to protect the wound area or equivalent to the replaced tissue in the body. The three dimensional structure with high porosity can provide a support for cell growth and migration.

In this study, PLGA was electrospun, by dissolving it in the binary solvents of DMF-THF and DMF-CHL. The surface tension and rheological properties of polymer solutions, as well as the morphology and mechanical properties of the resulting electrospun fibers were studied.

MATERIALS AND METHODS

PLGA (LA: GA, 75:25, molar ratio) with inherent viscosity (25°C, 0.1% chloroform [CHL]) in the range 0.8-1.2 dl/g was purchased from Evonik (Darmstadt, Germany). Molecular biology grade N, N-dimethylformamide (DMF), HPLC grade tetrahydrofuran (THF), and CHL were obtained from Sigma-Aldrich (Denmark). All materials were used as obtained.

PLGA was dissolved in the binary solvent DMF- THF (1:1, v:v) or DMF-CHL (1:1, v:v) at concentrations of 10% and 30% (w/v), respectively, at room temperature.

The viscoelastic properties of different polymer solutions were investigated using DHR-3 Rheometer (TA instruments, USA). All samples were analysed using the cone-

plate geometry (diameter 40 mm, cone angle 1°) at 10°C, using a solvent trap to create a thermally stable vapour barrier, eliminating solvent loss during rheological experiments. Oscillatory amplitude sweep tests were conducted to determine the linear viscoelastic region of each solution. Subsequently, oscillatory frequency sweeps from 0.1 to 100 rad/s were performed at the strain amplitude within the linear viscoelastic region. The shear viscosity of the solutions was investigated through a logarithmic steady shear rate increase from 0.1 to 1000 s⁻¹.

The surface tension of the polymer solutions was measured by pendant drop method using a KRUSS Drop Shape Analyzer – DSA100 (Hamburg, Germany). A drop of the measured solution was suspended in the air from a needle of a syringe. The needle was inserted into a transparent glass box which had been saturated with the same solvent as the one dissolving the polymer at room temperature (22-23°C). The shape of the drop results from the interplay between the surface tension and gravity. In the pendant drop method, the surface tension was calculated from the shadow image of a pendant drop using drop shape analysis.

The morphology of the electrospun samples was characterized using scanning electron microscope (SEM, Hitachi High-Tech HITACHI, USA). The samples were mounted on metal stubs with double-sided adhesive tape and coated under vacuum with gold in an argon atmosphere prior to observation. The specimens were then imaged at an accelerating voltage of 5kV.

The tensile strength measurements were carried out by TA.XT plus texture analyzer (Stable Micro Systems LTD., UK), equipped with a load cell which had a maximum load of 50 N and a resolution of 1N. The test speed was 0.04mm/s and the gripping distance was 40mm. In order to avoid breakage of the sample during the sample fixing, the fibers were inserted into

the gripping part together with an aluminium foil, which was cut before the measurement.

RESULTS AND DISCUSSION

Rheological characterization of PLGA in different solvents

A strain amplitude within the linear viscoelastic region, identified in oscillatory strain sweep tests, was selected for the dynamic oscillatory frequency sweep tests. The results demonstrated a concentration dependent loss modulus (Fig. 1), which was independent of strain, and increasing approximately 2 orders of magnitude with PLGA concentration increasing from 10% to 30%. For the polymer solutions at concentration of 30% (w/v), the linear viscoelastic region was between 0.1 to 100% strain. No LVR was obtained for the polymer solutions at 10% (w/v) concentration.

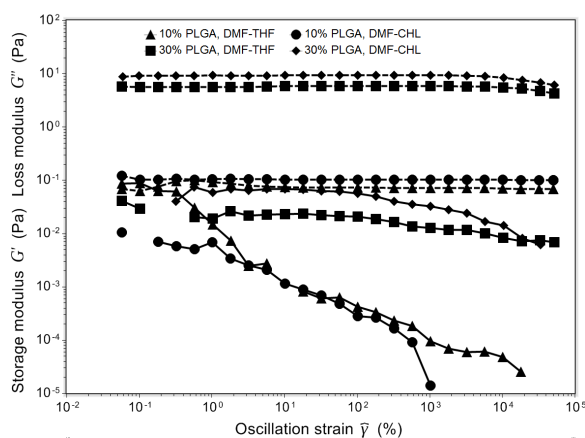


Figure 1. Oscillatory strain sweep of PLGA solutions in different solvents at concentrations of 10% and 30%.

Oscillatory frequency sweep measurements were performed at 5% strain at 10 °C. Within the frequency range measured, the loss modulus G'' was always higher than the storage modulus G' (Fig. 2). Both G' and G'' showed significant increase in response to increasing angular frequency with typical concentration dependence behaviour, except

for the G' at 10% concentration, which was nearly constant at low frequencies, and had erroneous negative values at higher frequencies, due to the high sample inertia. Both the viscous and elastic moduli of the solutions were higher when dissolved in DMF-CHL, than those dissolved in DMF-THF.

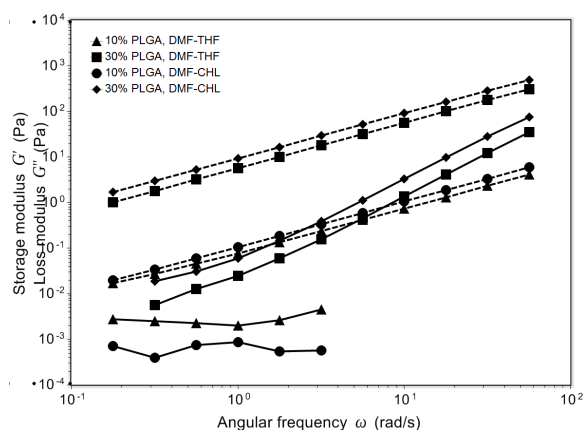


Figure 2. Storage and loss moduli of PLGA solutions dissolved in different solvents at concentrations of 10% and 30%. At higher frequency (> 5 rad/s), the data points of G' of 10% polymer solutions had erroneous negative values which are not shown.

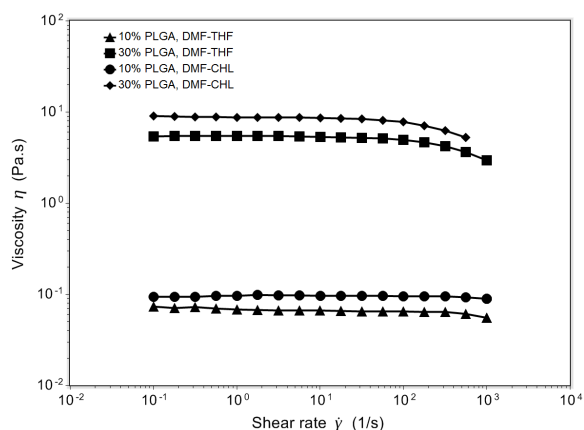


Figure 3. Shear viscosity of PLGA solutions dissolved in different solvents at 10% and 30% concentrations

Flow sweep was used to evaluate the shear induced changes in molecular entanglements, interaction, deformation and orientation. As expected, increasing PLGA concentration yielded a solution with higher

shear viscosity, due to increased molecular interaction within the solution (Fig. 3). In the range of about 1 to 1000 s^{-1} , the solutions showed Newtonian behavior, except for the 30% polymer solutions, an apparent onset of shear thinning was observed at high shear rate. The solutions in DMF-CHL had a higher viscosity than those in DMF-THF.

Surface tension of polymer solutions

The results of surface tension are showed in Table 1. At low concentration, the surface tension was nearly unchanged compared to the pure solvent, while it increased when the polymer concentration reached 30% (w/v).

Table 1. The surface tension of different polymer solutions

Sample (1:1, v:v)	PLGA (w/v%)	Surface tension (298.15K) (mN/m)
DMF- THF	--	28.9±0.2
DMF- THF	10	28.6±0.3
DMF- THF	30	31.1±0.3
DMF- CHL	--	30.3±0.5
DMF- CHL	10	30.2±0.4
DMF- CHL	30	32.1±0.1

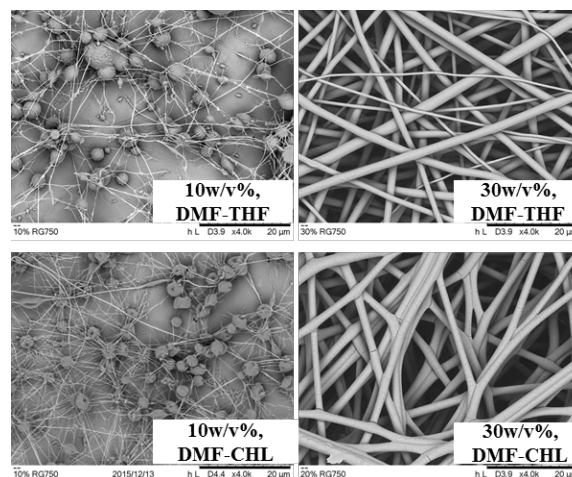


Figure 4. The morphology of electrospun fibers from different polymer solutions

Morphology of electrospun fibers

Both beaded and uniform fibers were obtained from the polymer solutions in this

study (Fig. 4). The surface of samples prepared from solutions in DMF-THF was smoother than the ones prepared from DMF-CHL. At low concentration, the viscosity of polymer solutions could not overrule the effect the surface tension completely. As a result, the samples tended to break into droplets and beaded fibers formed. At the higher concentration, the viscosity had a dominating role, overpowering the surface tension and resulting in uniform fibers.

Mechanical properties

The stress-strain curves of electrospun fibers prepared from different polymer solutions are presented in Fig. 5. The fibers showed the typical ductile behaviour, an initial linear region followed by an elongation region. The elastic modulus calculated from the slope in the linear region was higher for the fibers prepared from the solution with DMF-CHL than for the ones prepared from DMF-THF. This might be caused by the higher viscosity of the polymer solution in DMF-CHL. More intermolecular interactions existed in the polymer DMF-CHL solution, which could resist the deformation caused by an external force, thereby creating stronger fibers in the electrospinning process.

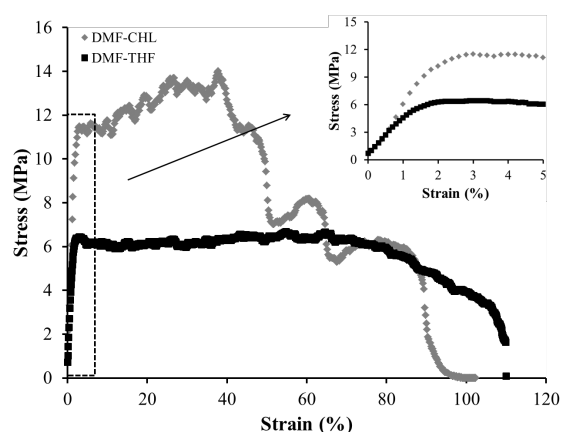


Figure 5. The stress-strain curves of electrospun fibers from 30% solutions of PLGA in different solvents

CONCLUSION

The polymer solutions at 30% concentration, and thereby with higher viscosity, were able to form uniform fibers, whereas the lower viscosity 10% solutions resulted in beaded fibers. In addition, the fibers spun from the solutions in DMF-CHL proved have better mechanical properties than the ones in DMF-THF.

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