Journal of the Mechanical Behavior of Biomedical Materials 77 (2018) 383–388

Contents lists available at ScienceDirect

Journal of the Mechanical Behavior of Biomedical Materials

journal homepage: www.elsevier.com/locate/jmbbm

Research paper

The viscoelastic response of electrospun poly(vinyl alcohol) mats

Sana Waheed, Annabel L. Butcher, Michelle L. Oyen*

Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, UK

ARTICLE INFO

Keywords:
Electrospinning
Scaffold mechanics
Viscoelasticity
Fibre diameter.

ABSTRACT

Native biological tissues are viscoelastic materials that undergo time-dependent loading in vivo. It is therefore crucial to ensure that biomedical materials have a suitable viscoelastic response for a given application. In this study, the viscoelastic properties of electrospun poly(vinyl alcohol) are investigated using tensile load relaxation testing. A five-parameter generalised Maxwell constitutive model is found to characterise the experimental response. The effect of polymer concentration and electrospinning voltage on model parameters is investigated in detail. The stiffness coefficients for the relaxation process appear to be dependent on the electrospinning conditions used whereas the time constants remain relatively unchanged. It is also observed that the stiffness parameters are linearly correlated with the equilibrium modulus, indicating that a single underlying material property dictates the relaxation moduli. Lastly, it is found that the viscoelastic model parameters are not predicted by the fibre diameter. These results provide an important understanding in designing electrospun mats with desired time-dependent properties.

1. Introduction

Ensuring the mechanical integrity of biomedical materials is critical for their success in applications such as tissue engineering (Mauck et al., 2009), wound healing (Zhong et al., 2010) and drug delivery (Sill and von Recum, 2008). Often, biomedical materials are required to mimic the mechanical properties of native biological tissues e.g. for use as tissue engineering scaffolds (Mauck et al., 2009; Sill and von Recum, 2008). Biological tissues are inherently viscoelastic materials (Fung, 1993) that undergo time-dependent loading such as pulsatile loading in blood vessels. Moreover, at the cellular level, the viscoelastic properties of the substrate material have been shown to influence cell growth and differentiation (Cameron et al., 2011; Chaudhuri et al., 2016). Therefore, it is necessary to characterise and match the viscoelastic response of biomedical materials for particular applications.

In the past two decades, a significant amount of attention has been focused on electrospinning for the fabrication of biomedical materials (Huang and Zhang, 2003; Schiffman and Schauer, 2008). Electrospinning provides a relatively simple, cost effective and versatile technique to create non-woven fibrous materials with fibre diameters in the nano- and micrometer range, making it suitable to mimic the structure of native extracellular matrix (Sill and von Recum, 2008). The properties of electrospun mats depend on a number of processing variables such as the solvent used, humidity, solution concentration and applied voltage (Huang and Zhang, 2003). While there has been some focus on the effect of these processing parameters on the resulting Young's modulus and strength of the samples (Huang et al., 2004; Lee and Deng, 2011; Butcher et al., 2017), their influence on the viscoelastic response remains to be investigated thoroughly.

Poly(vinyl alcohol) (PVA) is commonly used to fabricate electrospun mats due its easy electrospinnability, use of water as solvent and cost effectiveness (Koski et al., 2004; Zhang et al., 2005). Electrospun PVA and its derivatives have been investigated for use as tissue engineering scaffolds (Kim et al., 2006; Shalumon et al., 2009), wound healing and drug delivery patches (Taepaiboon et al., 2006; Zhou et al., 2008), antibacterial coatings (Ignatova et al., 2006) and biosensing membranes (Ren et al., 2006; Wang et al., 2010). For any of these applications undergoing time-dependent loading, the viscoelastic properties of the material become important. In this study, PVA is used as a model material and the viscoelastic response of electrospun PVA characterised using tensile load relaxation testing. In particular, the effect of solution concentration and electrospinning voltage on the time-dependent response is investigated to determine whether processing variables can be used to tune the material viscoelastic response and, if so, in what way. The sample microstructure is observed using scanning electron microscopy and compared to the corresponding mechanical response. It is found that while the electrospinning conditions do influence the viscoelastic properties of the electrospun PVA, this effect does not correlate with the fibre morphology.

* Corresponding author.
E-mail address: mlo29@cam.ac.uk (M.L. Oyen).

http://dx.doi.org/10.1016/j.jmbbm.2017.09.029
Received 4 July 2017; Received in revised form 18 September 2017; Accepted 20 September 2017
Available online 23 September 2017

2. Materials and methods

2.1. Materials

Poly(vinyl alcohol) (PVA) with 89–98 kDa molecular weight, 99 + % degree of hydrolysis and 1750 ± 50 degree of polymerisation was obtained from Sigma Aldrich, UK. PVA solutions with concentrations of 8%, 10%, 12%, 14% and 16% w/v were prepared by dissolving the appropriate mass of PVA in deionised water at 80 °C and stirring for 2 h to make transparent solutions. Each solution was allowed to cool at room temperature and used within 2 days.

2.2. Scaffold fabrication by electrospinning

An in-house electrospinning set-up was used in this study. The polymer solution was contained in a 20 ml plastic syringe (BD Plastipak, Spain) with a 21G stainless steel blunt needle (BD Plastic, UK). A high voltage power supply (Glassman High Voltage, UK) was connected to the PVA solution via an alligator clip attached to the syringe needle. The flow rate was set at 0.2 ml/h using a syringe pump (Alaris Medical, UK) and a square 8 × 8 cm collector covered in aluminium foil was used to collect the electrospun fibres with a tip-to-collector distance of 10 cm. Electrospinning was then performed for approximately 8 h for each set of conditions. The average temperature and humidity recorded during the fabrication of all electrospun samples was 21 °C and 43%, respectively. Samples were prepared at applied voltages (V_o) of 10, 12, 14, 16, 18 and 20 kV. No cross-linking was performed. Of the entire parameter space considered, the 16% PVA, 10–12 kV samples could not be prepared due to high solution viscosity leading to blockages in the syringe pump, and the 8% PVA concentration produced flaky samples without a suitable film structure which could not be mechanically tested but were included in the morphology assessment.

2.3. Microstructure characterisation

The morphology of electrospun PVA meshes was observed using a scanning electron microscope (EVO LS 15, Carl Zeiss, UK) at an accelerating voltage of 10 kV after gold coating. The images obtained were analysed using the software ImageJ (Schneider et al., 2012). The mean fibre diameter value, d, was calculated by averaging the diameter of 100 fibres to obtain a statistically representative value.

2.4. Mechanical testing

The viscoelastic response of electrospun PVA was investigated using displacement controlled tensile load relaxation tests. To this extent, at least $n = 3$ mechanical test specimens with grip-to-grip gauge dimensions of 20 mm × 5 mm were prepared from each electrospun mat. Each strip was placed in between two glass slides and the average strip thickness obtained from a set of five readings using a pair of digital vernier callipers (Hangzhou Maxwell Tools, China). Care was taken to avoid compression of the samples. Laboratory tape was applied to the ends of the specimens and the specimens gripped using custom made stainless-steel clamps.

All mechanical testing was performed on a universal testing machine (model 5544, Instron, Canton, MA) with a 500 N load cell (also Instron). A strain-to-failure test was carried out only on the 8%, 18 kV sample with an extension rate of 0.05 mm/s. From the tensile response thus obtained, it was determined that load relaxation tests were to be performed at 1.0% and 1.5% engineering strains ($\triangle l/l$). Two hold strains were used to check whether the material response was linear or non-linear viscoelastic. For the load relaxation tests, specimens were extended at 1.5 mm/s to the peak strain followed by a 150 s hold and return to gauge length. The specimen was allowed to equilibrate for 5 min before the test was repeated for the second hold strain.

2.5. Material model

As will be shown later, the electrospun PVA demonstrated a linear viscoelastic response in the testing regime investigated in this study. A generalised Maxwell model (also called Maxwell-Wiechert model or Prony series), commonly used for linear viscoelastic materials, is used to characterise the relaxation response. The constitutive relationship for the generalised Maxwell model with N chains is:

$$\sigma(t) = E(t)\varepsilon_o \tag{1}$$

$$E(t) = E_e + \sum_{i}^{N-1} E_i \exp\left(\frac{-t}{\tau_i}\right) \tag{2}$$

where $\sigma(t)$ is the observed stress response with time t, ε_o is the hold strain and $E(t)$ is the relaxation response defined as a function of the equilibrium modulus E_e, the time constant τ_i for a relaxation process and the corresponding stiffness modulus E_i for the particular relaxation process.

The experimental load data $P(t)$ is converted to nominal stress $\sigma(t)$ by dividing by the original cross-sectional area A_o (= thickness × width) of each strip to give the engineering stress. Assuming an instantaneous response and a step increase in strain, the initial ramp response was removed from the experimental data. A non-linear curve fitting program (OriginPro 9.1, OriginLab, Northampton, MA) was then used to fit Eq. (2) with an increasing number of chains (N) to the relaxation response.

3. Results and discussion

3.1. Fibre size and morphology

Representative SEM images of samples prepared at an applied voltage of 14 kV and different PVA concentrations are shown in Fig. 1. The 8% PVA concentration samples produced beaded nanofibres at all electrospinning voltages, presumably leading to the flaky sample structure, and were therefore not included in the load relaxation testing. Higher concentration samples produced continuous fibres due to the increased solution viscosity allowing the surface tension to be overcome. For high PVA concentration and high applied voltage, a few thick non-fibrous ribbon-like structures were also observed in the morphology. The average fibre diameter, d, for samples prepared at different electrospinning conditions is shown in Fig. 2. Connecting lines are only shown as a visual aid. The applied voltage does not appear to have a consistent effect on the average fibre diameter whereas increasing solution concentration leads to an overall increase in the fibre size, consistent with previous studies (Supaphol and Chuangchote, 2008).

3.2. Viscoelastic response of electrospun mats

For linear viscoelastic response, the relaxation modulus $E(t) = \sigma(t)/\varepsilon_o$ is independent of hold strain ε_o. Fig. 3(a) shows that the relaxation modulus of a representative specimen for both 1.0% and 1.5% ε_o are nearly identical, indicating that the specimen response is within the linear viscoelastic regime. Generalised Maxwell models with three, five and seven parameters were then fitted to the relaxation response to find the suitable constitutive relationship. From Fig. 3(b), it can be seen that a standard linear solid model (three-parameter fit) does not give a suitable fit to the experimental data whereas a seven-parameter fit is not significantly better than the five-parameter fit. Thus, the five-parameter model was deemed appropriate to characterise the viscoelastic behaviour of electrospun PVA with the constitutive equation as follows:

$$E(t) = E_e + E_1 \exp(-t/\tau_1) + E_2 \exp(-t/\tau_2) \tag{3}$$

Previous studies on electrospun polycaprolactone (Sethuraman