



Rheology and pressurised gyration of starch and starch-loaded poly(ethylene oxide)



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ABSTRACT

This work investigates the rheology and spinning of starch and starch-loaded poly(ethylene oxide) (PEO) by pressurised gyration in order to prepare nanofibres. The spinning dope's rheological properties played a crucial role in fibre formation. Newtonian behaviour is observed in 1–20 wt% starch suspensions and non-Newtonian behaviour is found in all the PEO–starch mixtures. Pressurised gyration of the starch suspensions produced beads only but PEO–starch mixtures generated fibres. The fibre diameter of the PEO–starch samples is shown to be a function of polymer concentration and rotating speed of the gyration system. Fibre formation can only be facilitated below a certain working pressure. The concentration of starch in the PEO–starch mixtures is crucial in defining whether beaded or continuous fibres were generated and this is related to the composition of the spinning dope. FT-IR, XRD and microscopy studies indicated very good miscibility of starch and PEO in the nanofibres. The storage modulus of the PEO–starch were also studied as a function of temperature (30–150 °C) and showed interesting results but it was not possible to deduce general trends valid for the entire temperature range.

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1. Introduction

Naturally occurring biopolymers have been used to produce nanofibres and nanofibrous structures with excellent functionality (Woodings, 2001). Of these, polysaccharides based nanofibres are shown to be of great interest to the biomedical research community (Xu, Yang, & Yang, 2009). The high surface area to volume ratio of the polymer nanofibres makes them very suitable for many biomedical applications such as scaffolds used in tissue engineering, drug release, artificial organs, wound healing and vascular grafts (Huang et al., 2011; Bhardwaj & Kundu, 2010). In addition, polysaccharide based hydrogels and microspheres are very promising for protein drug release (Pareta & Edirisinghe, 2006; Elvira, Mano, Roman, & Reis, 2002).

Starch is one of the most abundant naturally occurring polysaccharides with very good biodegradability and bioinertness. In addition, it is a sustainable and renewable biopolymer with excellent biocompatibility. Starch is found as semicrystalline granules

of various sizes and shapes in plant tissues, some algae and bacteria. It consists of two homopolymers of D-glucose, amylose and amylopectin. Amylose is a linear polymer with α -D-(1 → 4) glycosidic linkages and amylopectin is a highly branched polymer which consists of α -D-(1 → 6) glycosidic linkages in addition to α -D-(1 → 4) glycosidic linkages at the branching points (Karim, Norziah, & Seow, 2000). However, starch is too brittle to be used on its own and therefore blending it with a polymer in order to form the structures required in novel ways is a hot topic of research (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Perez, Perez, Alvarez, & Bernal, 2013; Chivrac, Pollet, Schmutz, & Averous, 2008).

A wide variety of polymeric non-woven fibres from the micro- to nano-scale are usually produced by electrospinning where basically, a nozzle carrying polymeric solution is subjected to high voltage (Edwards, Church, Werkmeister, & Rawshaw, 2009; Welle et al., 2007). The competition between the electric field force and the surface tension force has a significant influence on the fibre forming mechanism. At a critical applied voltage the electric field force can exceed the surface tension force to generate fibres (Zhang & Edirisinghe, 2006; Luo, Stoyanov, Stride, Pelan, & Edirisinghe, 2012). Several biopolymers including starch have been

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electrospun with excellent surface morphology (Kong & Ziegler, 2013; Matthews, Wnek, Simpson, & Bowlin, 2002; Huang et al., 2013). The electrospinnability of starch depends on the rheological properties and the amount of amylose/amylopectin content in the starch and the ratio of these two ingredients determines the stiffness or flexibility of the fibres (Kong & Ziegler, 2012). However, this method requires high voltage in the kV range and shows poor cost–yield efficiency as a single fibre emerges from the end of the nozzle carrying polymeric solution.

Pressurised gyration is a new technique comprised of simultaneous centrifugal spinning and solution blowing to manipulate the polymeric nanofibre size and their distribution by varying the concentration of the polymeric solution, rotating speed and the working pressure. It is a simple but efficient process allowing the formation of a multitude of parallel polymer nanofibres with regular morphology (Mahalingam & Edirisinghe, 2013). The scale up of production of nanofibres in larger quantities for various applications is very feasible through this technique. This technique makes use of the destabilising centrifugal force and the dynamic fluid flow against the stabilising surface tension of the liquid to fabricate non-woven polymeric nanofibres at very high speed. Unlike electrospinning it is independent of solution properties such as electrical conductivity and dielectric constant. Initially a jet emerges from the orifices in the face of spinneret. This jet further stretches due to centrifugal force and pressure difference at the orifice. Finally, the evaporation of the solvent leads to thinning of the fibres formed.

In this paper, we report on spinnability of starch and starch-loaded polymeric nanofibres using pressurised gyration. In order to improve the spinnability of the starch, poly(ethylene oxide) which is a synthetic semi-crystalline polymer has been added at different concentrations.

2. Experimental

2.1. Materials and rheology

Starch, derived from potato ($(C_6H_{10}O_5)_n$, average molecular weight $M_w \sim 10^6$ g/mol, amylose:amylopectin 25%:75%) was obtained from Sigma Aldrich, UK and used in this investigation. 1 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt% and 25 wt% of starch was dissolved in deionised water (laboratory grade) and dimethyl sulphoxide (DMSO, Sigma Aldrich, UK) using a water:DMSO weight ratio of 50:50. These were prepared in an air tight bottle and stirred using a magnetic bar at 80 °C for 60 min. Although starch possesses excellent functionality with a diverse range of applications, the poor mechanical properties of the natural polymer led to the development of starch composites (Pereira et al., 2011). Poly(ethylene oxide) (PEO, molecular weight 200 000 g/mol, Sigma Aldrich, UK) was used as a binding polymer. PEO solutions were prepared in deionised water and DMSO using a weight ratio of 50:50. The weight ratio of PEO to starch was varied from 0 to 50% to prepare the PEO–starch mixtures. All these contained 15 wt% of solids, however, the PEO:starch ratio in these was varied (90:10, 70:30 and 50:50). Therefore, the PEO:starch ratio in these are 13.5 wt% PEO and 1.5 wt% starch (90:10), 11.5 wt% PEO and 4.5 wt% starch (70:30) and 7.5 wt% PEO and 7.5 wt% starch (50:50). These were prepared in an air tight bottle and stirred using a magnetic bar at 80 °C for 60 min.

The concentrations of PEO chosen in this work were based on the viscoelastic nature of the polymer. Generally, a lower concentration promotes bead or droplet formation and a higher concentration results in polymer melts where extrusion of fibres is difficult or promotes thicker fibre formation (Katti, Robinson, Ko, & Laurencin, 2004). The viscosity of the starch

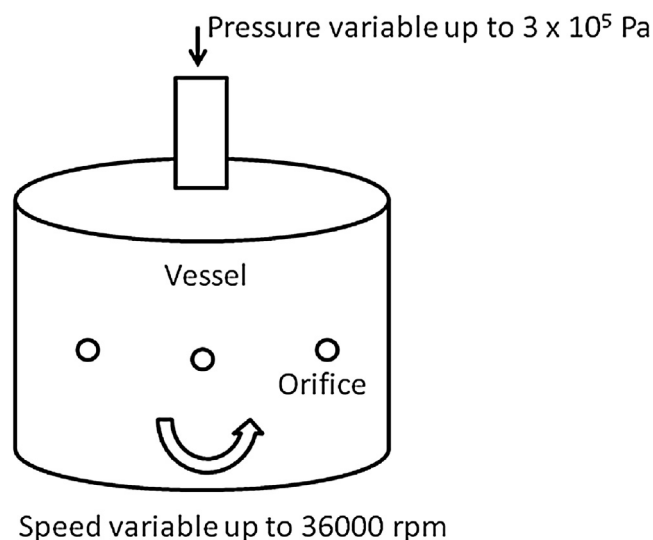


Fig. 1. Schematic diagram illustrating the experimental set-up used for pressurised gyration.

solutions and PEO–starch suspensions was measured using a Brookfield viscometer. Viscosity data were collected in the shear rate range from 1.32 to 330 s⁻¹ at the ambient temperature (~20 °C).

2.2. Pressurised gyration

The experimental set up operating at ambient temperature used in this study is shown in Fig. 1. It consists of a rotary aluminium cylindrical vessel (~60 mm in diameter and ~35 mm in height) containing orifices (~20) on its face. The size of one orifice is 0.5 mm. The vessel and orifice dimensions (including the number of orifices) can be varied to suite. One end of the vessel is connected to a motor which can generate speeds up to 36 000 rpm. The other end is connected to a gas stream (e.g. N₂), the pressure of which can be varied up to 3 × 10⁵ Pa. The high speed of the rotating vessel forms a polymer solution jet. This jet subsequently stretches into fibres through an orifice. This stretching can be enhanced by blowing of gas into the vessel. The polymer solution formed in this way undergoes evaporation of the solvent to generate the fibres. To facilitate the collection of polymeric fibres there is a stationary collector made of aluminium foil placed around the spinning vessel.

2.3. Characterisation

The characteristics of the spinning dopes' (whether solution or suspension) and the morphology of fibres formed was studied by optical microscopy (Nikon Eclipse ME600). The latter was also investigated with scanning electron microscopy (SEM, Hitachi S-3400n) at an accelerating voltage of 5 kV. The samples were coated with gold using a sputtering machine (Edwards Sputter S1 50B) for 150 s to minimize charging effects prior to imaging. Statistical analysis on average fibre diameter and diameter distribution of nanofibres was obtained from SEM images. The fibre diameter was calculated using high magnification images with IMAGE J software using ~100 measurements which were made at different locations of the coated samples to calculate the average fibre diameter. For this purpose histograms were made and Gaussian distribution was fitted using Origin software. This was verified by goodness of the fit which was close to 1. The maximum value of the fitted Gaussian distribution curves was noted and taken as the average value. High resolution imaging of the nanofibres was performed using

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