JOURNAL OF THE MECHANICAL BEHAVIOR OF BIOMEDICAL MATERIALS 28 (2013) 222–231

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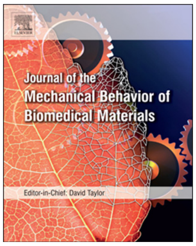

Research Paper

The effect of dilute solution properties on poly(vinyl alcohol) films

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ARTICLE INFO

Article history:
Received 27 March 2013
Received in revised form
28 July 2013
Accepted 1 August 2013
Available online 15 August 2013

ABSTRACT

Films are commonly prepared by solvent casting and accordingly it is important to investigate the relationship between the properties of the polymeric solution and the resultant solid-state properties of the film. Therefore the objective of this work was to characterise the rheological properties of aqueous solutions of PVA, containing defined co-solvents, and to relate these properties to the resultant mechanical and swelling properties of films cast from these solutions. Casting solutions were prepared using two concentrations of two molecular weights of PVA within a range of cosolvent systems. The solution properties were examined using dilute solution viscometry at 37 °C and defined in terms of the intrinsic viscosity and Huggins constant. Solutions of PVA containing each cosolvent exhibited greater intrinsic viscosities (and lower Huggins constants) than comparator aqueous solutions of this polymer. In particular propylene glycol and pyrrolidone solvents when blended with water produced thermodynamically good solvents for PVA whereas water was shown to be a thermodynamically poor solvent for PVA. Films were cast from the above solvent systems and exhibited a wide range of mechanical properties (UTS, % elongation at break and Young's Modulus) and swelling properties, both with no signs of ageing These were dependent on the nature of cosolvent used as the casting solvent. A strong correlation ($r > \pm 0.9$) was observed between the intrinsic viscosity (and Huggins constant) and the observed values of Young's modulus cast from each solvent system. These observations confirmed the importance of the chemical properties of the cosolvent on the mechanical and swelling properties of films manufactured from these solutions.

1. Introduction

Commercially, films have found use as coatings, drug delivery systems, e.g. transdermal patches, and as biomaterials (Cascone, 1997; Nechifor et al., 2009; Perfetti et al., 2010; Schroder et al., 2007). The vast majority of coatings applied to pharmaceutical dosage forms and biomaterials are polymeric and their performance is based on the intrinsic characteristics of the bulk polymer, the solvent system from which they are cast and the process conditions under which they are applied, dried and successively stored before use (Perfetti et al., 2010). Films are typically prepared by a solvent casting method and accordingly it is important to understand how the polymer and solvent interact in the solution state as this would be expected to affect

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http://dx.doi.org/10.1016/j.jmbbm.2013.08.002

their subsequent interaction in the film state. Therefore understanding the polymer–solvent interaction in the solution state will result in a more informed film-forming process. In the solution state it is possible to quantify polymer–solvent interactions using the intrinsic viscosity and Huggins constant. These parameters define the polymer coil expansion in solution and the degree of polymer–solvent interactions, with thermodynamically 'good' solvents generating greater coil expansion and more interactions (Goodwin and Hughes, 2008; Russel, 1984). If unfavourable polymer–solvent interactions occur as a result of the use of thermodynamically 'poor' solvents, polymer coils can completely collapse and become insoluble in solution (Mehrdad and Akbarzadeh, 2010). Such parameters can only be determined in dilute solutions as polymer–polymer interactions must be minimised (Goodwin and Hughes, 2008; Russel, 1984).

Poly(vinyl alcohol, PVA) is a hydrophilic, non-toxic and biocompatible polymer with excellent film forming properties (Huang and Yang, 2008; Kur et al., 2008; Pawde and Deshmukh, 2008). It is utilised in medical applications such as wound dressings, artificial skin, coatings, transdermal patches, cardio-vascular devices, and drug delivery systems (Kur et al., 2008). In order to be useful in areas of medical and pharmaceutical applications, PVA must be chemically cross-linked or stabilised using physical entaglements to help overcome the well known aging effects (Gholap et al., 2004; Kenji et al., 1993). To improve toughness various methods have been devised mostly by regulating crystallinity and the properties may also be 'tuned' with careful addition of solvent (Cho et al., 2009; Drappel et al., 1997; Hong et al., 1998, 2001, 2009; Matsuda et al., 1998; Park et al., 2001; Sandell and Doring, 1970).

Using PVA as a model polymer, this study investigates the rheological properties of this polymer in the solution state and the relationship between these and the mechanical and swelling properties of films cast from these solutions. Furthermore the effect of annealing, a technique used to engineer the mechanical properties of PVA films, on this relationship was investigated. From this information the relationship between the thermodynamic quality of the solvent and the effects on film properties may be generated, information that is relevant to the use of this biomedical and pharmaceutical uses of this polymer.

2. Materials and methods

2.1. Materials

PVA (Sigma-Aldrich) M_w 13,000–23,000, 98% hydrolysed (low molecular weight). PVA (Sigma-Aldrich) M_w 31,000–50,000, 98–99% hydrolysed (medium molecular weight). Deionised water from an Elga water purifier. The solvents were: DMSO, dimethyl sulphoxide, (VWR) analytical grade; PG, propylene glycol, (VWR) analytical grade; DPG, dipropylene glycol, (Sigma-Aldrich) analytical grade; 2-pyrrolidone (Sigma-Aldrich) analytical grade; NMP, *N*-methyl pyrrolidone, (VWR) analytical grade; NEP, *N*-ethyl pyrrolidone (Sigma-Aldrich) analytical grade. All solvents were used without further purification.

2.2. Solution preparation

Dilute solutions of 5, 2.5, 2, 1.5, 1, 0.75 and 0.5% w/w PVA were prepared in various water/solvent compositions for characterisation using dilute solution viscometry. In this the required mass of PVA was added to the solvent combination (water, water and 10% w/w solvent or water and 20% w/w solvent) and left to heat/stir at 90 °C for 24 h in a sealed container prior to testing. The solutions were removed from the heat and allowed to cool to room temperature, in sealed containers, for ca. 3 h before analysis.

2.3. Film preparation

The various PVA solutions were prepared in a pre-cleaned wide mouth, sealable bottle with stirring at 90 °C for 24 h until a homogenous solution formed. These were then removed from the heat and cast into 9 cm diameter plastic Petri dishes then allowed to air cool to room temperature for five days within a fume cupboard. Following film formation, samples of each formulation were annealed by placing in an oven at 90 °C for 10–15 min.

2.4. Dilute solution viscometry

The rheological properties of dilute solutions of PVA were determined at 37 ± 0.02 °C using an A or B tube Ubbelohde viscometer. The tubes were thoroughly cleaned with cold water prior to initial measurements being recorded with the pure solvent mix without polymer (t_0). The flow time of the polymer solution (t) was then recorded and the reduced and intrinsic viscosity were then calculated as follows:

Kinematic viscosity (ν) = Flow time x tube constant
Relative viscosity (η_r) = $\upsilon_{\text{solution}}/\upsilon_{\text{solvent}}$
Specific viscosity (η_{sp}) = $\eta_r - 1$
Intrinsic viscosity (η) = $\lim_{c\to 0} \eta_{sp}/C$ where C is the solution concentration (g/100 mL)
Inherent viscosity (η_i) = $\ln(\eta_r)/C$

Calculations of the intrinsic viscosity (η) and the Huggins and Kraemer constants (K_H and K_K, respectively) were performed using both the Huggins equation and the Kramer equation as follows:

Huggins equation

$$\frac{\eta_{sp}}{c} = [\eta] + K_H\left[\eta^2\right]C$$

(Huggins, 1942).

Kraemer equation

$$\frac{In(\eta_r)}{c} = [\eta] + K_K\left[\eta^2\right]C$$

(Kraemer, 1938).

2.5. Film testing

2.5.1. Tensile analysis

Tensile analysis of the various polymer samples was performed using a Stable Micro Systems TA-XT2 Texture Analyser