

## Material Properties

## Dynamic viscosity of maleate poly(vinyl alcohol) and its copolymer measured by rheometer

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## ARTICLE INFO

## Article history:

Received 9 June 2016

Accepted 12 October 2016

Available online 13 October 2016

## Keywords:

Rheometer

Water

Gel formation

Hydrogel

Water soluble polymer

Protein

## ABSTRACT

The objective of this work was to study the mechanism of gel formation for maleated poly(vinyl alcohol) (PVAM) and maleated poly(vinyl alcohol)-graft-gelatin (PVAM-g-GT) in solution form using a rheometer to monitor changes in the dynamic viscosity and shear stress-shear rate curves. The dynamic viscosity of the PVAM solution increased and then decreased with increases in the shear rate, and the dynamic viscosity of the PVAM solution decreased as a function of the MA content increased. The dynamic viscosity of the PVA solution was higher than that of the PVAM solution due to its gel formation. Moreover, the dynamic viscosity of the PVAM solution increased and then decreased over long periods. Over a storage time of 2 days, the dynamic viscosity of the PVAM decreased due to chain scission. The PVAM solution showed shear thickening in the first stage and shear thinning in the last stage of the experiment. The dynamic viscosity of the PVAM-g-GT solution continued to decrease continually at a constant rate with increases in the shear rate because the H-bonding was broken at higher shear rates. This was probably because the energy of the H-bonding interaction is less than the energy of carbon-carbon covalent bonding resulting in broken H-bonding both intra-chain and inter-chain H-bond.

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## 1. Introduction

Poly(vinyl alcohol), (PVA) is a biodegradable water soluble synthetic semi-crystalline polymer which is of interest because it is a hydrogel [2] and because of its film forming ability [1] and use as a food packaging medium [3]. PVA is a cheap water-soluble synthetic non-toxic biocompatible polymer [4]. It has good transparency in the visible range, but also demonstrates excellent oxygen barrier properties. It also exhibits film forming, emulsifying, and adhesive properties making it useful for various industrial applications such as in coating agents, drug delivery carriers, adhesives, biomedical films and packaging films [5]. However, PVA has limited moisture sensitivity and in a wet state it shows poor resistance to water molecules due to hydroxyl groups in the repeating unit of PVA. Thus, it is of restricted use in many applications.

There have therefore been many studies investigating the modification of PVA, for example, chitosan/PVA films [6], PVA/boric

acid (PVA/BA) hybrid films [5], silk/PVA blend films [7], (PVA)/tetraethyl orthosilicate (TEOS) with embedded silver nanoparticles (AgNps) [8], PVA-xanthan gum irradiated membranes [9] and PVA/gelatin blends [10].

The work described in this paper studied improvements in the water resistance of PVA using maleic anhydride as a cross-linker [11]. In previous research, maleate poly(vinyl alcohol) (PVAM) was synthesized without using an initiator. The percentage degree of grafting, dynamic viscosity, and particle size increased with the MA content, while the swelling ratio decreased due to copolymerization of the PVA and MA. The results suggested that a mass ratio of 7:3 PVA/MA was optimal for PVA-g-MA. In Ref. [12], the viscoelastic behavior of aqueous PVA-borate solutions was assessed using dynamic visco-elasticity measurements with PVA concentrations ranging from 2 to 60 g/L and borax concentrations of zero and 0.2 M at room temperature. The results suggest that PVA-borate aqueous systems with PVA concentrations of 40 g/L and above, and a borax concentration of 0.2 M produce thermo-reversible gels with a finite equilibrium life time and thermo-reversible borate-PVA di-diol cross-links. The rheological properties of aqueous solutions of PVA containing sodium borate were

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studied in Ref. [13]. The solutions exhibited a marked shear thickening at a certain critical rate of shear and the flow was unstable at higher rates of shear.

More recently, the preparation of PVAM grafted with gelatin (GT) (PVAM-g-GT) was studied using GT aqueous solutions with  $K_2S_2O_8$  as an initiator [14]. The highest tensile strength and elongation at break were found at a ratio of 8:2 PVAM:GT. The response to changing pH and temperature decreased with increases in the thickness of the sample sheet. The resulting novel smart PVAM-g-GT hydrogel was capable of controlling the rate of capsaicin release in a media with different pH values and different temperatures indicating that the hydrogel was capable of being used in the medical field.

Until now, the gel formation of PVAM and its copolymers have not been studied using a rheometer. The objective of the work described in this paper was therefore to investigate and understand the rheological properties of PVAM solutions with a rheometer. The results reported are an important complement to other studies of gel formation using a rheometer. The effects of the MA content, the reaction time and temperature, and the storage time on the rheological properties of the PVAM solutions were investigated.

## 2. Materials and methods

### 2.1. Materials

The PVA used in the experiment was purchased from Aldrich ( $M_w = 89,000\text{--}98,000$  g/mol and 99+% hydrolyzed). Maleic anhydride (MA) was purchased from Fluka. ( $M_w = 98.06$  g/mol) and used as a cross-linker.

### 2.2. Synthesis of PVAM and its copolymer

The PVAM was prepared from an aqueous solution of PVA and MA as described in previous work [14]. First, a 3%wt solution of MA was added to a 10%wt solution of PVA. This mixture was stirred at 70 °C for 2 h and the modified PVA was deposited as PVAM after 24 h. Then, a 0.5%wt KPS solution was added into the PVAM solution at 70 °C and stirred for 5 min. Finally, 10% w/w GT was added in 10% w/w PVAM at ratios of 9:1, 8:2, 7:3 and 5:5 PVAM/GT and stirred at 70 °C for 1 h to obtain a PVAM-g-GT solution. The dynamic viscosities of the PVAM and PVAM-g-GT solutions were tested using a stress-controlled rheometer (Rheometer, AR2000ex, TA Instruments, USA).

### 2.3. Characterization

The PVA, PVAM and PVAM-g-GT samples were investigated by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) using a Bruker Equinox 55 in a range of  $4000\text{--}500$   $cm^{-1}$ , and the rheological measurements were performed using the rheometer as described above. The rheological characterization of the solutions was performed by dynamic oscillatory and steady-shear tests. A standard steel parallel plate geometry (steel plate, 40 mm) was used for all the samples. The measurements were carried out using a gap distance of 500  $\mu m$ . The temperature was controlled at 25 °C using a universal temperature controller system. The start control value of the shear stress was 0.7958 Pa. The end control value of the shear stress was 79.58 Pa. The curve was built from the dynamic viscosity data averaged for each point. The rheological data were analyzed using the Data Manager software version 5.8.2.

## 3. Results & discussion

### 3.1. FTIR

FTIR was used to study the chemical structure of the PVAM, PVA and PVAM-g-GT. Fig. 1 shows the FTIR structure of the PVAM, PVA and PVAM-g-GT. The main peaks of the PVAM were observed at 1740 and 1250  $cm^{-1}$ , representing C=O and C–O stretching, respectively, and these peaks were shifted in comparison to pristine PVA, due to interactions between the PVA and the MA. The chemical structure of the PVAM was in agreement with that found in previous work [14]. A novel peak of the graft copolymer was located at 1178  $cm^{-1}$  as a result of ester linkage between the PVA and the MA [14]. In the case of the GT, there were peaks due to -NH stretching of a secondary amide at 3450 and 3423  $cm^{-1}$ , and for C=O stretching at 1680 and 1640  $cm^{-1}$ . There were also peaks due to -NH bending between 1550 and 1500  $cm^{-1}$ , -NH out of plane wagging at 670  $cm^{-1}$  and C-H stretching at 2922 and 2850  $cm^{-1}$  [14]. When the PVAM was grafted with the GT at 70 °C for 1 h, the PVAM-g-GT displayed a peak for C=O stretching at 1643  $cm^{-1}$ , for N-H bending at 1543  $cm^{-1}$ , and for C=O and C–O stretching at 1711 and 1227  $cm^{-1}$ , respectively, which were assigned to the presence of carboxylic groups in the chemical structure. Moreover, ester linkage was found at 1090  $cm^{-1}$  in the PVAM-g-GT copolymer (see Fig. 1).

### 3.2. The dynamic viscosity behavior of the PVA solution

The dynamic viscosity of the 10% wt PVA aqueous solution was observed by dynamic oscillation. The PVA solution demonstrated a change in its dynamic viscosity with four distinct stages as shown in Fig. 2. In the first stage, the dynamic viscosity of the PVA solution increased from 0.8 to 4.0 Pa s with the shear rate increasing from 1.0 to 2.5 1/s due to the formation of H-bonding and chain entanglement at a high shear rate [15]. In the second stage, the dynamic viscosity of the PVA solution decreased from 4.0 to 1.6 Pa s while the shear rate increased from 2.5 to 12.2 1/s because the H-bonding between the hydroxyl groups of the PVA molecules was easily broken at a high shear rate. However, in the third stage, the dynamic viscosity of the PVA solution increased slightly from 1.6 to 2.0 Pa s with the shear rate increasing from 12.2 to 15.8 1/s again due to the formation of H-bonding between the hydroxyl groups of the PVA molecules. Finally, in the fourth stage, the dynamic viscosity of the PVAM solution continued to decrease with the shear rate increasing from 15.8 to 64.0 1/s due to a reduction in both the H-bonding and chain entanglement. This result is consistent with the results found in previous work [15] which studied the dynamic

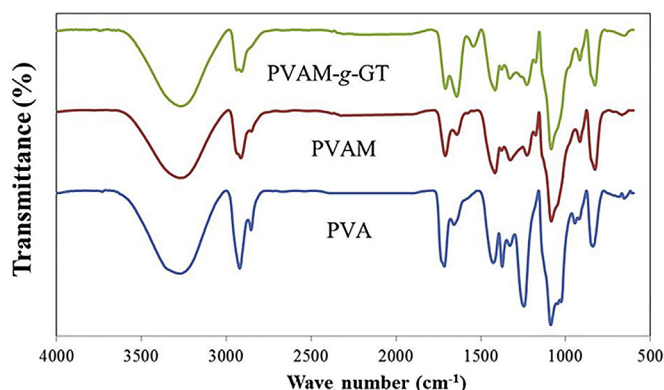


Fig. 1. FTIR spectra of PVA, PVAM and PVAM-g-GT.

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