Extensional rheology of crosslinked poly(vinyl alcohol) films

Sunilkumar Khandavalli · Abhijit P Deshpande

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Abstract Elongational behavior of crosslinked ionic polymer swollen with water was investigated. Poly(vinyl alcohol) is crosslinked with an ionic crosslinker (sulfosuccinic acid) and a non-ionic crosslinker (glutaraldehyde) and the elongational behavior was compared. Preliminary material characterization such as swelling and ion exchange capacity studies (IEC) were carried out. Elongational behavior of PVA-SSA and PVA-GA showed strain hardening similar to crosslinked polymers, due to finite extensibility of the network. Elongational behavior of PVA-SSA and PVA-GA was examined varying charge density and crosslinker concentration.

Keywords Poly(vinyl alcohol) · Sulfosuccinic acid · Non-linear rheology · Large amplitude oscillatory shear · Polyelectrolyte gels

Introduction

Ionic polymers have potential applications in myriad fields such as - proton conducting membranes in fuel cell technology (Choudhury et al 2009), pervaporation membranes in separation technology (Kusumocahyo et al 2000; Wang et al 2009), actuators and sensors (Lee et al 2012), MEMS systems, bio-mimetic applications (Bahramzadeh and Shahinpoor 2011), superabsorbent polymers (Ono et al 2007), ion-exchange resins (Anand et al 2001) and desalination applications (Xie et al 2011). Due to their superabsorbent characteristics (Ono et al 2007), they have become an attractive material in biomedical and pharmaceutical applications such as drug delivery, cell encapsulations, disposable diapers, biosensors, and tissue engineering (Hong et al 2010; Plunkett et al 2005).

However, the fundamental understanding of the intrinsic nature of ionic polymers A small fraction of ionic content in polymers show a dramatic effect in the physical and mechanical properties, such as mechanical strength, conductivity, solubility, and glass transition
temperature ($T_g$) (Li et al 1989; Li and Nemat-Nasser 2000; Ignac 2005). The fundamentally challenging aspect of ionic polymers has been to understand the microscopic structure, self-assembly of polymers chains under the influence of ionic interactions. The presence of charged groups in ionic polymer create long range electrostatic interactions (coulombic), in addition to the excluded volume effects. The highly repulsive electrostatic forces strongly influence the self-assembly and morphology of polymer chains. The electrostatic potential energy of the charged groups can be estimated from Debye-Huckel theory (Dikeos 1978). Odijk (Odijk 1977) and Skolnick and Fixman (Skolnick and Fixman 1977) introduced the concept of electrostatic persistence length ($L_e$), in addition to the intrinsic persistence length ($L_p$), to describe the charge induced bending stiffness of the polymer chain. Numerous investigations on ionic polymer melts and solutions revealed a phase segregation of polymer chains into hydrophilic and hydrophobic regions called as clusters, which are believed to enhance the properties of ionic polymers (Takahashi et al 1995; Li et al 1989). However, accurate description of structure and morphological changes induced by ionic interactions could not be made.

Elongational behavior is commonly observed in many industrial applications such as blow moulding, melt and fibre spinning, film moulding. With growing interest in ionic polymers as potential material in many applications (Ignac 2005), it is essential to investigate the elongational behavior of ionic polymers. Crosslinked ionic polymers have improved mechanical properties and have applications in many fields (Rhim et al 2004; Basak and Adhikari 2009). Investigation of elongation behavior exists for ionic polymer melts (Takahashi et al 1994a), polyelectrolyte solutions (Andrews et al 1998; Borisov et al 1995), neutral crosslinked networks. To our knowledge there exists very limited literature on the elongational behavior of crosslinked ionic polymers in the presence of solvent (Myung et al 2007; Miquelard-Garnier et al 2009). The presence of long range Coulombic interactions in the solvent-network network system strongly influences the structure and self-assembly of the polymer network (Guan et al 2011).

Poly(vinyl alcohol) (PVA) based polymers are of great interest, owing to their excellent bio-compatibility, good film forming abilities and high water absorbent characteristics (Bolto et al 2009). For the present study, polyvinyl alcohol is used as a base polymer for the synthesis of crosslinked films. Sulfosuccinic acid (SSA) is used as an ionic crosslinker where, crosslinking occurs between -OH of PVA and -SO$_3$H of SSA via esterification reaction. For comparative study, PVA films crosslinked with glutaraldehyde (GA) were also prepared where, -OH of PVA and -CHO of GA react to form acetal bridge. In the present study, we aim to investigate the elongational behavior of crosslinked ionic polymers in the presence of solvent to gain insights of the role of solvent-network interactions in the elongational behavior of ionic polymers.

Theoretical Background

Swelling

Polymer network swells when immersed in a solvent. The equilibrium swelling of the network is governed by the osmotic pressure and the elasticity of the network. One of the classical theories that describes equilibrium swelling is Flory-Rehner theory (Flory and John Rehner 1943). Using Flory Rehner theory, network parameters such as, the molecular weight between crosslinked junctions ($M_c$), can be estimated using the following equation:
where $M_{np}$ is the number average molecular weight of the polymer chains, $V_s$ is the molar volume of the solvent, and $\chi$ is the Flory-Huggins interaction parameter between the polymer and solvent, $\nu_s$ is polymer volume fraction after equilibrium swelling.

The above equation is valid for polymer networks synthesized in solid state. Peppas and Merrill (Peppas and Merrill 1976) modified the Flory-Rehner equation for a system where crosslinking reaction of the polymer chains occurs in the presence of solvent, and is given by:

$$\frac{1}{M_c} = \frac{2}{M_{np}} - \frac{\nu_s}{\rho V_s} \frac{\left[\ln(1 - \nu_s) + \nu_s + \chi V_s^2\right]}{[\nu_s^{1/3} - \frac{1}{2}]} \left[\nu_s^{1/3} - \frac{1}{2}(\frac{\nu_s}{\rho})^{2/3}\right]^{1/3}$$

(1)

where $\nu_s$ is polymer volume fraction in relaxed state.

The above equations assume Gaussian chain distribution of the network. But real networks are associated with network heterogeneities. Peppas and co-workers developed another equation that takes into account of non-Gaussian characteristics of crosslinked polymer networks which is given by (Peppas and Barr-Howell 1986):

$$\frac{1}{M_c} = \frac{2}{M_{np}} - \frac{\nu_s}{\rho V_s} \frac{\left[\ln(1 - \nu_s) + \nu_s + \chi V_s^2\right]}{[\nu_s^{1/3} - \frac{1}{2}]} \left[\nu_s^{1/3} - \frac{1}{2}(\frac{\nu_s}{\rho})^{2/3}\right]^{1/3} \left[\frac{\nu_s}{\rho} - \frac{1}{2}(\frac{\nu_s}{\rho})^{2/3}\right]^{2/3} \left[1 + \lambda (\frac{\nu_s}{\rho})^{1/3}\right]^{1/2}$$

(2)

where $N$ is given by:

$$N = \frac{\lambda M_c}{M_n}$$

(4)

where, $M_n$ is the molecular weight of the repeating unit and $\lambda$ is the number of links per repeating unit.

By solving equations 3 and 4, we can obtain the average molecular weight between crosslinked junctions ($M_c$). Crosslink density ($\rho_c$) is determined from $M_c$ using the following equation:

$$\rho_c = \frac{1}{\bar{v} M_c}$$

(5)

where $\bar{v}$ is the specific molar volume of the polymer.

Theoretical crosslink density ($\rho_t$) can be estimated as (6),

$$\rho_t = \frac{c f}{2}$$

(6)

where $c$ is the crosslinker concentration (mol/cm$^3$) and $f$ is the crosslinking agent functionality.
Experimental

Materials

Atactic Poly(vinyl alcohol) (a-PVA; M.W = 125,000 g mol$^{-1}$, degree of hydrolysis of 88%) was obtained from Sd Fine Chemicals Ltd Mumbai, India. Sulfosuccinic acid (SSA; 70 wt% solution in water) was obtained from Sigma Aldrich Chemicals, USA. Glutaraldehyde (GA; 25 wt% solution in water) was obtained from Loba Chemie Ltd. Mumbai, India).

Film preparation

PV A-SSA films were prepared following the procedure found in literature (Rhim et al 2004). PV A was dissolved in distilled water at 80 °C with continuous stirring at least for 6 h until a homogeneous solution was obtained. The resulting PVA solution was mixed rigorously with a desired amount of sulfosuccinic acid for 24 h. Films were cast by pouring the solution on a petri dish and evaporated at 60 °C for 24 h. To induce partial crosslinking the films were heated for another 2 h at 60 °C. The crosslinked films were peeled off from the petri dish. The thickness of the films obtained was 200 microns.

PV A-GA film preparation is well reported in literature (Mansur et al 2008). A desired amount of glutaraldehyde was added to 10 wt% PVA solution and stirred at room temperature for 1 h. To catalyze the reaction between PVA and GA, HCl was added in 3:2 mole ratio with respect to GA. The solution was then poured into the petri dish and allowed it to crosslink at room temperature for 5 days. The crosslinked films were peeled off and washed thoroughly to remove any unreacted GA and HCl. The reaction scheme of PV A-SSA and PV A-GA is shown in Figure 1. The resulting films showed a thickness of 200-800 microns. Films were cut into rectangular shape of width 5 - 2.5 mm and length 5 - 10 mm for performing extensional rheology.

Degree of Swelling

Swelling studies were carried out to study the water absorption characteristics and strength of the films. Degree of swelling was determined by immersing the pre-weighed dried film in distilled water at 25 °C for 24 h to reach equilibrium swelling. The swollen film was then wiped carefully with a tissue paper and immediately weighed. Degree of swelling can be calculated by:

\[
\text{Degree of Swelling} = \frac{(W_s - W_d)}{W_d} \times 100\% \tag{7}
\]

where, $W_s$ is the weight of the swollen film and $W_d$ is the weight of the dry film.

Charge density

Charge density is estimated from ion exchange capacity (IEC), which is a measure to quantify the moles of ionic groups (-SO$_3$H) in the crosslinked polymer film. A classic titration procedure is followed to determine the Ion Exchange Capacity (Seo et al 2009). The
crosslinked ionic film was immersed in 1 M HCl for minimum 12 h to convert into H⁺ form (Kim et al 2005). It was washed thoroughly to remove HCl and then soaked in 1 M NaCl aqueous solution for a day to exchange protons with Na⁺ ions. The ion-exchanged solution was then titrated with 0.01 M standardized NaOH solution. The IEC was determined using the following equation.

\[ IEC = \frac{V \times M}{W_d} \ (\text{mmol} \ g^{-1}) \]  

(8)

\( W_d \) is the weight of the dry film, \( V \) is the volume of NaOH consumed and \( M \) is the molarity of NaOH.

From IEC, charge density \( f \) can be calculated as;

\[ f = IEC \times MW_n \]  

(9)

where \( MW_n \) is the molecular weight of the repeating unit (vinyl alcohol).

**Rheological measurements**

Rheological experiments were carried out using SER Universal Testing Platform, an accessory of Anton Paar Physica MCR 301 Rheometer. It is a dual windup drum extensional rheometer that was designed to used as a detachable fixture on conventional rheometers (Sentmanat 2004). Extensional rheology was conducted at 25 °C on PVA-GA and PVA-SSA films swollen with water at different elongational strain rates.
Results and discussion

Preliminary characterization of crosslinked PVA systems

![Graph a) Degree of swelling (%) vs. crosslinker content for PVA-GA and PVA-SSA b) Charge density vs. crosslinker content of PVA-SSA](image)

PVA is a water soluble polymer due to the presence of OH groups in the backbone chain. Crosslinked PVA films swells when immersed in water. The degree of swelling reaches equilibrium until the osmotic pressure is balanced by the elasticity of the network. The presence of charged groups results in an additional osmotic pressure due to ionic contribution which increases the degree of swelling. In Figure 2a, degree of swelling for PVA-SSA and PVA-GA are compared with varying crosslinker content. The degree of swelling decreased with increase in crosslinker content in both cases as expected. PVA-SSA showed a higher degree of swelling compared to PVA-GA due to the presence of sulfonic groups in the backbone chain (Frusawa and Hayakawa 1998). The OH groups of PVA interact with water and form hydrogen bonded structures. The aggregated structure of water molecules around SSA groups, due to the electrostatic interactions of the ionic groups, is significantly different compared to
the structure around OH groups (Guan et al 2011). Charge density of PVA-SSA determined from ionic exchange capacity is shown in Figure 2b. Charge density increased with increase in ionic crosslinker content as expected. Before discussing the rheological behavior at small and large deformations, the equilibrium modulus of different films is described in the next section.

Analysis of network structure

Crosslinked network structure is analyzed through network parameters such as crosslink density ($\rho_c$) and average molecular weight between crosslinked junctions ($M_c$). In Table 1, network parameters estimated from swelling measurements are shown. Equation 3 proposed by (Peppas and Barr-Howell 1986) is used to estimate the average molecular weight between network junction ($M_c$). From ($M_c$), crosslink density was determined using Equation 5. The following experimental parameters are used for the estimation of network parameters: weight average molecular weight $M_{wp} = 125,000$ for PVA, which was used in the place of number average molecular weight ($M_{np}$); molar volume of water ($V_s$) = 18 cm$^3$/mol; Flory-Huggins interaction parameter between the PVA and water $\chi = 0.49$ (Sakurada et al 1959); number of links per repeating unit $\lambda = 3$, specific molar volume of the PVA $\bar{v} = 0.788$ cm$^3$/g, volume fraction of polymer in relaxed state $v_r$ is assumed as 1 for PVA-SSA due to negligible water content after PVA-SSA film formation. Crosslinking functionality (f) of sulfosuccinic acid (SSA) and glutaraldehyde (GA) is taken as 2. The network parameters were estimated at different crosslinker content of PVA-GA and PVA-SSA. As expected, the average molecular weight between crosslinked junctions ($M_c$) decreases with increasing crosslinker content of PVA-SSA and PVA-GA and therefore the crosslink density increases with the crosslinker content. The theoretical crosslink density ($\rho_c$) estimated from crosslinker concentration is also shown in Table 1 to compare with the crosslink density ($\rho_c$) estimated experimentally using swelling theory. Generally, theoretical crosslinking is expected to be higher than the actual crosslinking due to wastages of the crosslinker content in the crosslinking process. But the crosslink density estimated swelling measurements are greater than the theoretical values for both PVA-GA and PVA-SSA. The disagreement with the theory could be due to the use of swelling theories, which assume ideal network assumptions (Quesada-Perez et al 2011). The crosslink density values of PVA-GA are greater than PVA-SSA. We have further estimated the crosslink density from zero shear storage modulus ($G_o$) using the theory of rubber elasticity given by the following equation (Flory 1953; ?)

$$G = \frac{\rho M}{RT} \left( v_r \right)^{2/3} \left( \frac{1}{\bar{v}} \right)^{1/3}$$

(10)

The crosslink density ($\rho_m$) estimated using rubber elasticity theory are lower than the theoretical crosslink density and also the crosslink density estimated from swelling measurements. Higher estimates of crosslink density from swelling than from rubber elasticity theory are also reported in literature (Martens and Anseth 2000; ?).

Elongational behavior

In Figure 3, the elongational viscosity ($\eta_e$) is plotted against time (t) for 0.25 PVA-GA sample at various strain rates. We can observe that the elongational viscosity ($\eta_e$) increases
Table 1: Structural parameters of PV A-GA and PV A-SSA at various crosslinker content estimated from swelling and mechanical measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \rho_t ) (mmol/g PV A-X)</th>
<th>( M_c ) (g/mol)</th>
<th>( \rho_c ) (mmol/cm(^3))</th>
<th>( \rho_m ) (mmol/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 PV A-SSA</td>
<td>0.32</td>
<td>2425</td>
<td>0.52</td>
<td>0.024</td>
</tr>
<tr>
<td>0.37 PV A-SSA</td>
<td>0.48</td>
<td>1615</td>
<td>0.84</td>
<td>0.055</td>
</tr>
<tr>
<td>0.50 PV A-SSA</td>
<td>0.64</td>
<td>1107</td>
<td>1.15</td>
<td>0.071</td>
</tr>
<tr>
<td>1.00 PV A-SSA</td>
<td>1.26</td>
<td>544</td>
<td>2.30</td>
<td>0.076</td>
</tr>
<tr>
<td>0.25 PV A-GA</td>
<td>0.31</td>
<td>479</td>
<td>2.60</td>
<td>0.020</td>
</tr>
<tr>
<td>0.50 PV A-GA</td>
<td>0.63</td>
<td>310</td>
<td>4.10</td>
<td>0.054</td>
</tr>
<tr>
<td>1.00 PV A-GA</td>
<td>1.26</td>
<td>184</td>
<td>6.50</td>
<td>0.057</td>
</tr>
</tbody>
</table>

\( \rho_t, \rho_c, \rho_m \) are crosslink densities estimated from theory, swelling and mechanical measurements respectively.

with time. The variation of elongational viscosity (\( \eta_E \)) shows two regions - I. \( \eta_E \) a gradual increase, called as linear region II, a rapid increase in \( \eta_E \), called as non-linear region. The non-linear region is called as strain-hardening behavior and is a sensitive indicator of microstructure of the polymer. Strain hardening due to long chained branching in many polymer melts such as polystyrene (Hepperle, Jens and Munstedt, Helmut 2006), polybutadiene (Kasehagen and Macosko 1998), polyethylenes (Munstedt et al 1998), was widely investigated. Strain-hardening is also shown by crosslinked networks such as crosslinked rubbers (Lotti et al 2012), PVC gels (Aoki et al 2010), acrylamide based gels (Wei et al 2010) and poly(acrylic acid) gels Myung2007, Garnier2009. In the case of crosslinked polymers, strain-hardening phenomena was attributed to the finite extensibility of the polymer network (Lotti et al 2012). A similar strain-hardening behavior in PVA-GA as can be observed in Figure 4 due to the finite extensibility of the crosslinked network. Elongation viscosity is conducted at different elongational strain rates (0.01s\(^{-1}\), 0.1s\(^{-1}\), 1s\(^{-1}\)). The onset of strain hardening varies with strain rates. Strain hardening appears earlier with increasing strain rates. To further understand the effect of strain rate on elongational behavior, tensile stress versus Hencky strain are plotted in Figure 4 at different strain rates for 0.25 PVA-GA. We can observe that the stress-strain curves overlap at all rates indicating that the strain hardening behavior is independent of strain rate i.e strain hardening appears in PVA-GA appears at the same Hencky irrespective of strain rate.

In Figure 5, (\( \eta_E \)) versus time (t) for 0.25 PVA-SSA is plotted at different strain rates. We can observe that PVA-SSA shows strain-hardening behavior similar to PVA-GA at all the strain rates. Further, tensile versus tensile strain is plotted in Figure 6 at different strain rates. We can observe a overlap in the behavior at all strain rates indicating a strain rate independent strain-hardening behavior. In the next section, the elongation behavior of PVA-SSA and PVA-GA are compared in detail.
Comparison of PVA-SSA and PVA-GA

The solvent-network interactions in PVA-GA are associated with weak polar interactions and in PVA-SSA the interactions are associated with long range Coulombic interactions which may have an important influence in the structure of polymer-network system. However, comparing the elongational behavior of 0.25 PVA-GA and 0.25 PVA-SSA in Figure 7, both PVA-GA and PVA-SSA show qualitatively similar behavior (strain-hardening) though the solvent-network quite different in both the systems. This suggests that the elongational behavior is predominantly governed by the crosslinked network and less on the solvent-network polar/ionic interactions. Investigations on the elongation behavior of ionomer melts, varying neutralization degree and counter ions, showed strain hardening behavior due to the effect of ionic interactions (Takahashi et al 1994b). However, further investigations varying water content or charge density may give insights of the role of ionic interactions in the solvent network system. However, a noticeable difference in the failure strain can be observed. At all strain rates, PVA-SSA fails at larger strains compared to PVA-GA. This suggests that
the solvent-network interactions may have a greater role in the failure mechanisms rather than the strain-hardening effect.

Fig. 7: Comparison of 0.25 PVA-SSA and 0.25 PVA-GA at various strain rates
Effect of charge density

In previous section, the comparison of the elongational behavior between ionic and neutral crosslinked PVA showed no difference in the strain-hardening phenomena suggesting the possibility of predominant role of network over the solvent-network interactions. Therefore, to examine the effect of ionic interactions in more details, the elongational behavior of PVA-SSA is compared at various crosslinker content in Figure . We observe a qualita-
ative behavior similar elongational behavior (strain-hardening) at all crosslinker content. This will confirm the predominant network influence. However, with increase in crosslinker both the crosslink density and charge density are increased. Therefore, there exists a possibility of predominant influence of network rather than ionic interactions. In order to check the role of solvent-network interactions, examining the elongational behavior varying the strength of interactions at fixed crosslink density by adding salt may give insights of the role of ionic interactions in elongational behavior. The effect of salt water in PVA-SSA is discussed in the next section.

0.1 Effect of salt water

To investigate the effect of ionic content on elongational behavior, PVA-SSA films are swollen in salt water to screen the charged interactions reducing the effective electrostatic interactions of the solvent-network system. 0.5 PVA-SSA and 1.0 PVA-SSA films were swollen in 1 M NaCl to equilibrium and extensional rheology was conducted at different strain rates. In Figure 9, the elongation viscosity versus time compared between 1.0 PVA-SSA films swollen in water and salt at different strain rates. No qualitative difference in the elongational behavior was observed, however a difference in the strain failure can be observed. In salt at 0.01 and 1.0 strain rates, 1.0 PVA-SSA films fail at earlier time than films swollen in water. A similar early failure of PVA-GA was observed when 0.25 PVA-GA and 0.25 PVA-SSA were compared in the previous section 7. Thus, as the charge in PVA-SSA films is neutralized with NaCl ions, PVA-SSA films behave close to non-ionic such as PVA-GA. This further corroborates the earlier observation that the solvent network interactions play a less role in the strain-hardening effect but strongly influences the failure mechanisms. Additionally, effect of salt water was also investigated for 0.5 PVA-SSA as shown in Figure 10 at different strain rates. Both in salt and water, similar strain hardening behavior was observed. But a difference in strain failure was observed as in 1.0 PVA-SSA. Film swollen in salt showed early failure at 0.01 and 1 strain rates compared to the films swollen in water.

Conclusions

The elongational behavior of crosslinked ionic and non-ionic poly(vinyl alcohol) films was investigated varying the crosslinker content and charge density. Effect of salt concentration on the elongational behavior was also examined. PVA-GA and PVA-SSA films showed strain-hardening behavior similar to crosslinked rubbers due to finite extensibility of the network. No qualitative difference in the elongational behavior between PVA-GA and PVA-SSA was observed suggesting a predominant role of the network in strain-hardening effect over solvent-network interactions. However, a difference in failure strain was observed between PVA-GA and PVA-SSA. PVA-GA showed an early failure compared to PVA-SSA indicating the critical role solvent-network interactions in failure mechanisms rather than the strain-hardening effect. Study of the effect of charge density and salt water on the elongational behavior showed similar nature further supporting the observations.
Fig. 9: Extensional viscosity vs. time plot for 1.0 PVA-SSA swollen in 1 M NaCl at different strain rates

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Fig. 10: Extensional viscosity vs. time plot for 0.5 PVA-SSA swollen in 1 M NaCl at different strain rates.

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