Constitutive modeling of Poly Vinyl Alcohol-Sodium Borate gel

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Declaration

I declare that this written submission represents my ideas in my own words, and where others ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

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Approval Sheet

This thesis entitled Constitutive Modeling of Poly Vinyl Alcohol-Sodium Borate gel by Nitin Kumar is approved for the degree of Master of Technology from IIT Hyderabad.

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Dedicated to

My Parents

Abstract

PVA-SB gels have physico-chemical properties that help them find use as fracturing fluids- used to fracture deep rock formations to facilitate flow of petroleum- in the petroleum industry.

Aqueous solutions of 4% poly-vinyl alcohol (PVA), and varying concentrations (1%, 2%, 3%, 4%) of sodium borate (SB) were mixed to generate PVA-SB solutions. These solutionswere kept aside for a week for gel formation to complete.Small amplitude oscillatory shear data was obtained for the PVA-SB gel, and frequency sweep data was obtained for a strain amplitude of 1%, and angular frequency (ω) range of 0.05 sec^{-1} to 500 sec^{-1}. The storage (G') and loss modulus (G") variation with angular frequency in the range of 0.05 sec^{-1} and 50 sec^{-1} closely resembled the profile obtainable from a classical Maxwell fluid.

In order to match the data with a model, we simulated the flow of a classical Maxwell fluid under small amplitude (1%) oscillatory shear in a cone-and-plate Rheometer: we thereby obtained the predicted values of G' and G''. We fitted the parameters for the Maxwell fluid so as to match the predicted values of G' and G'' with the experimentally obtained values for PVA-SB gels.

Nomenclature

T: Total stress tensor

S: Extra stress tensor

$\mathbf{A_1}$: First Rivlin-Ericksen tensor

L: Velocity gradient tensor

λ_1: Relaxation time

μ: Dynamic viscosity

η: Complex viscosity

τ: Constant

σ: Shear stress

σ_0: Magnitude of Shear stress

ρ: Density

γ: Shear strain

$\dot{\gamma}$: Shear rate

ω: Angular frequency

G': Storage modulus

G": Loss modulus

γ_0: Magnitude of Shear strain

v_r: Velocity in r-direction

v_θ: Velocity in θ-direction

$v_\emptyset$: Velocity in ϕ-direction

Contents

Chapter 1

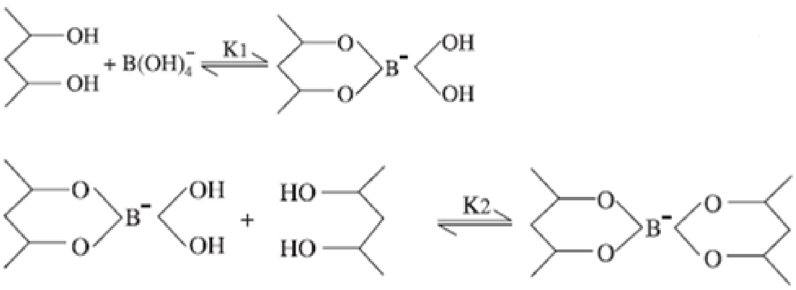
Introduction

1.1 Constitutive modeling

Constitutive modeling is a mathematical description of how materials respond to various loads. It involves the formulation of stress-deformation relationships to describe the response of a material in a specific class of processes.

1.2 Poly Vinyl Alcohol-Sodium Borate polymer gel

Poly Vinyl Alcohol is a synthetic water-soluble, cross-linked polymer. Poly Vinyl Alcohol-Sodium Borate (PVA-SB) thermo-reversible gels have attracted a substantial research interest due to their physico-chemical properties [1], leading to their applications as fracturing fluids in oil industry. Fracturing fluids are used to fracture the deep rock formations, along which gas and petroleum migrate to the well There is a sharp increase in viscosity of PVA on addition of little amount of SB due to the formation of di-diol complex between two pairs of hydroxyl groups of PVA and a borate ion. The following is the mechanism for the reaction [6]:



PVA-SB gel is a viscoelastic fluid. Viscoelastic fluids are those which have both viscous and elastic properties i.e. where a part of the stress is due to the strain field and another part is due to the shear rate. Gels, foams, soap solutions, and polymer melts are all examples of viscoelastic fluids.

1.3 Shear thickening behavior

The rheological behavior of PVA-SB solution can be changed from Newtonian behavior, at very low SB concentrations, to viscoelastic gels at higher SB concentrations. The solutions are shear-thinning at low concentrations. Practically irreversible rheological transition takes place if we increase the concentration of SB. These rheological transitions are of three types - (i) shear-thinning to shear thickening, (ii) shear-thickening to erratic and (iii) low viscosity Newtonian fluid – high viscosity Newtonian fluid [6].

1.4 Viscoelastic Behavior

Stress in a sheared state is directly proportional to strain for an ideal elastic solid. For tension, the familiar Hooke's law is applicable, and the constant of proportionality is the usual Young's modulus, G, i.e.

$$\sigma_{yx} = -G\frac{dx}{dy} = G\gamma_{yx} \quad (1)$$

Ideal elastic solid regains its original form on removal of the stress when the strain is within the elastic limit. On the other hand, for a Newtonian fluid the shearing stress is proportional to the rate of shear (and not strain). Many materials of engineering importance show both elastic and viscous effects in certain processes. In the absence of thixotropy and rheopexy effects, the material is said to be viscoelastic. Perfectly viscous flow and perfectly elastic deformation denote the two limiting cases of viscoelastic behavior [3].

1.5 Oscillatory Shear motion

Oscillatory shearing motion is a common flow used to characterize viscoelastic fluids.

For a Newtonian fluid, the shear stress is related to the rate of shear, i.e.

$$\dot{\gamma} = \frac{d\gamma}{dt} = \gamma_m \omega \cos\omega t = \gamma_m \omega \sin\left(\frac{\pi}{2} + \omega t\right) \quad (2)$$

and here $\sigma = \eta\dot{\gamma} = \eta\gamma_m \omega \sin\left(\frac{\pi}{2} + \omega t\right) = \sigma_m \sin\left(\frac{\pi}{2} + \omega t\right)$ (3)

In this case, the resulting shear stress is out of phase by π/2 from the applied strain and the stress leads the strain. Thus, the measurement of the phase angle, which can vary between zero (purely elastic response) and π/2 (purely viscous response) provides a convenient method of quantifying the level of viscoelasticity of a substance [3]. For the linear viscoelastic region, one can define the complex viscosity η as follows:

$$\eta = \eta' + i\eta'' \quad (4)$$

where the real and imaginary parts, η' and η", in turn, are related to the storage G' and loss G" moduli as:

$$\eta'' = \frac{G'}{\omega} \qquad \eta' = \frac{G''}{\omega} \quad (5)$$

The storage modulusG' is defined as:

$$G' = \frac{\sigma_m}{\gamma_m}\cos\delta$$

(6) Thus, G' corresponds to the amplitude of in-phase stress. Likewise, the loss modulus, G", corresponds to the amplitude of out-of-phase stress, and is defined as:

$$G'' = \frac{\sigma_m}{\gamma_m}\sin\delta \quad (7)$$

Chapter 2

Rheology of Poly Vinyl Alcohol-Sodium Borate gel (Experimental)

2.1 Cone-and-Plate Rheometer

Rheometer is an instrument which measures the rheological characteristics (shear stress, viscosity, frequency, shear rate) of the material to be tested. Different types of Rheometer are Cone and Plate (CP) Rheometer, Parallel Plate Rheometer, Concentric Cylinder Rheometer.

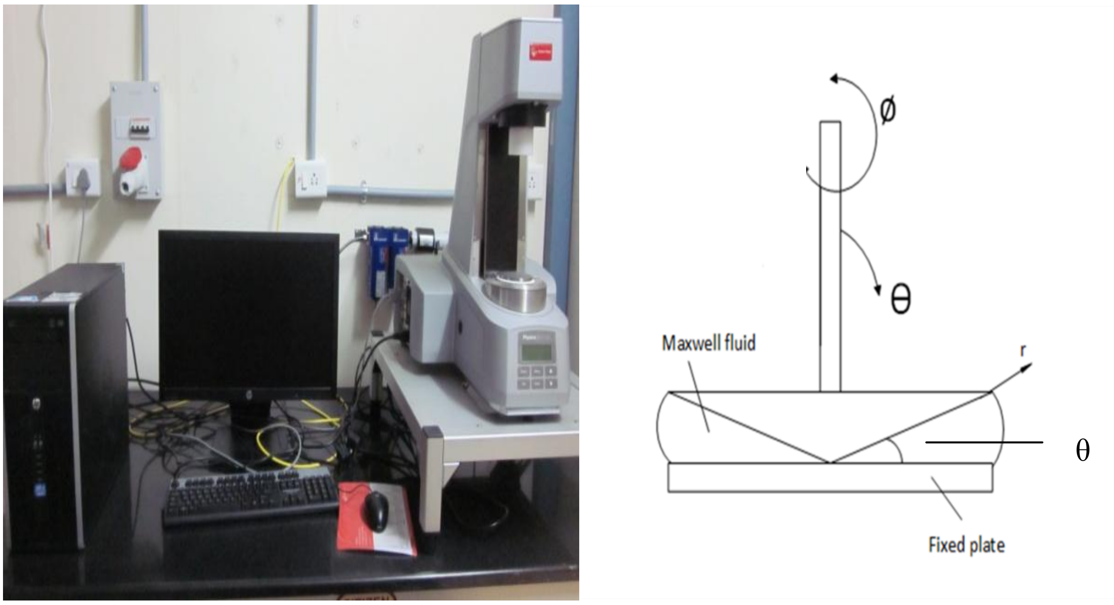


Fig 1: Cone & Plate(CP) Rheometer

A picture and accompanying schematicof the cone-and-plate geometry is shown in Fig 1. The fluid to be tested is placed in the gap between cone and plate; the cone is rotated with angular velocity ω and has oscillatory shear motion. Oscillatory Shear motion characterizes the viscoelastic fluid response to shear strain which varies sinusoidally with time. The cone diameter is 25mm and angle (θ_0) between the cone and the plate is 1^0.

There are several assumptions that have been made for experimental measurements in cone-and-plate Rheometer [2].

- Fluid intertia which tends to throw the fluid out of gap is neglected.
- Fluid-air interface is spherical.

- Secondary flows are observed in the gap for large cone angles and high rotation speeds due to competing centrifugal and normal stress effects.

- Due to viscous heating, temperature of the fluid in the gap may not be uniform.

2.2 Preparation of Poly Vinyl Alcohol-Sodium Borate gel

PVA aqueous solutions were made by slowly adding the required amount ofPVA dry powder to a known amount of water, and stirring it for 2 hours. The water was kept in a 80^{o}C water bath.Aqueous mixtures of PVA-SB were made by adding PVA solutionto SB solution kept in a 80^{o}C water bath, and stirring the mixture for 2hours. Samples were madewith PVA concentrations of 4% w/w. The concentrations of SB in the samples are 1%, 2%, 3% and 4% w/w. All the rheological measurements were done using MCR 301 Anton PaarRheometer. A cone-and-plate geometry with 25mm diameter and 1^{o}angular gap was used. Measurements weremade atleast one week after preparation of samples in order to avoid ageing effects. Frequency sweep was done at a strain amplitude of 1%: the frequency of oscillation was increased from a low value to a high value along a logarithmic ramp. Amplitudesweep was done at a frequency of 10 rad/sec: the strain amplitude was increased from a low value to a highvalue along a logarithmic ramp [6].

2.3 Linear Viscoelasticity Studies

A typical frequency sweep curve of PVA-SB systems consists of plots of thestorage and loss modulus-as calculated by the Anton PaarRheometer- versus angular frequency. Both storage and loss modulus increase with frequency at low frequencies. The storage modulus increases almost twice as fastas the loss modulus at low frequencies. At higher frequencies, there exists aplateau for storage modulus as well as for loss modulus.

2.4 Test performed

Two repetitions of the tests were done but one of test data was taken

The following Samples were tested:

- 4%PVA-1%SB
- 4%PVA-2%SB
- 4%PVA-3%SB
- 4%PVA-4%SB

2.4.1 Amplitude Sweep [5]

Frequency: 10rad/sec

Amplitude range: 1-1000%

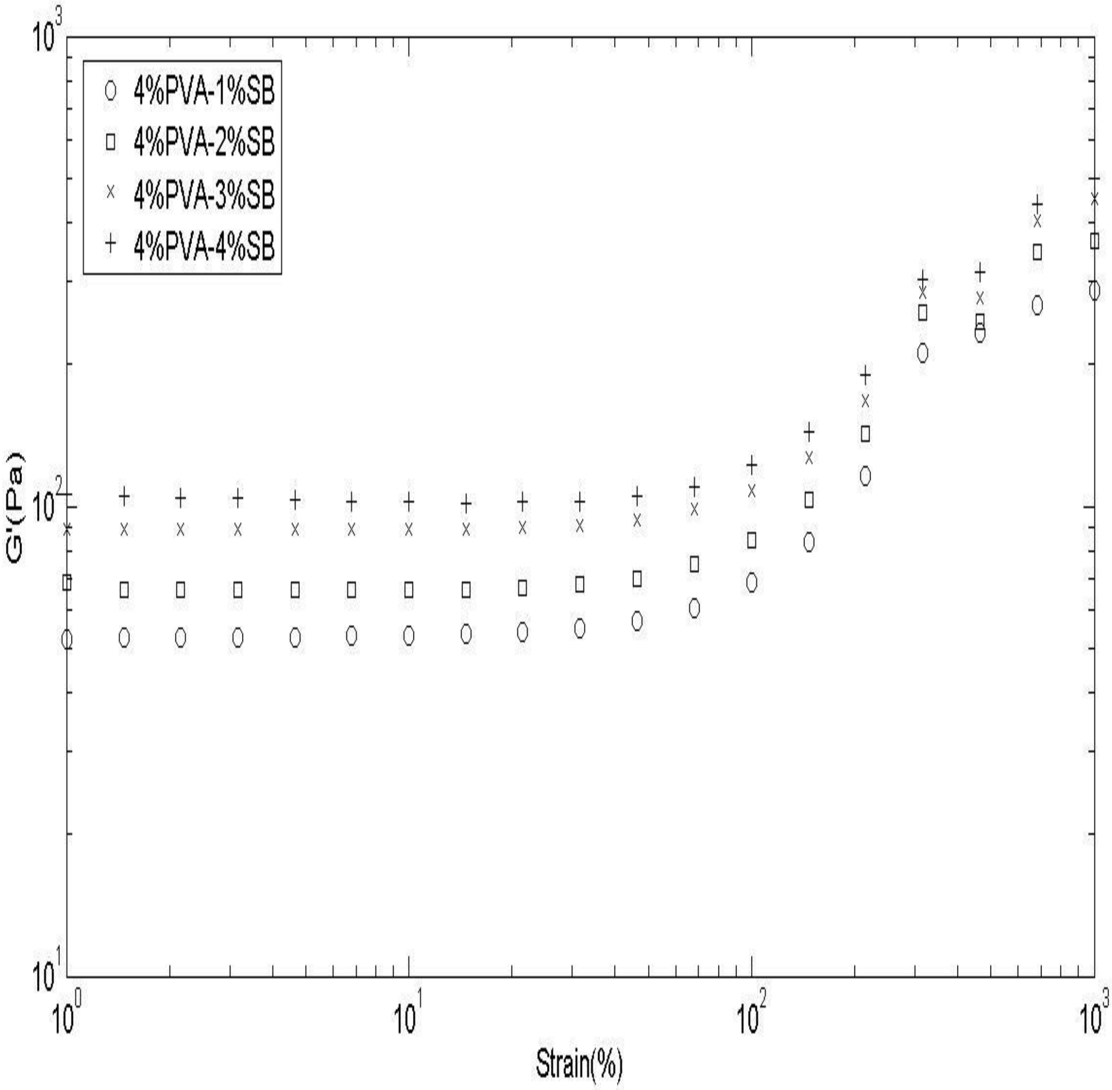


Fig 2: Comparison of G’ for PVA-SB gel for amplitude sweep measurements

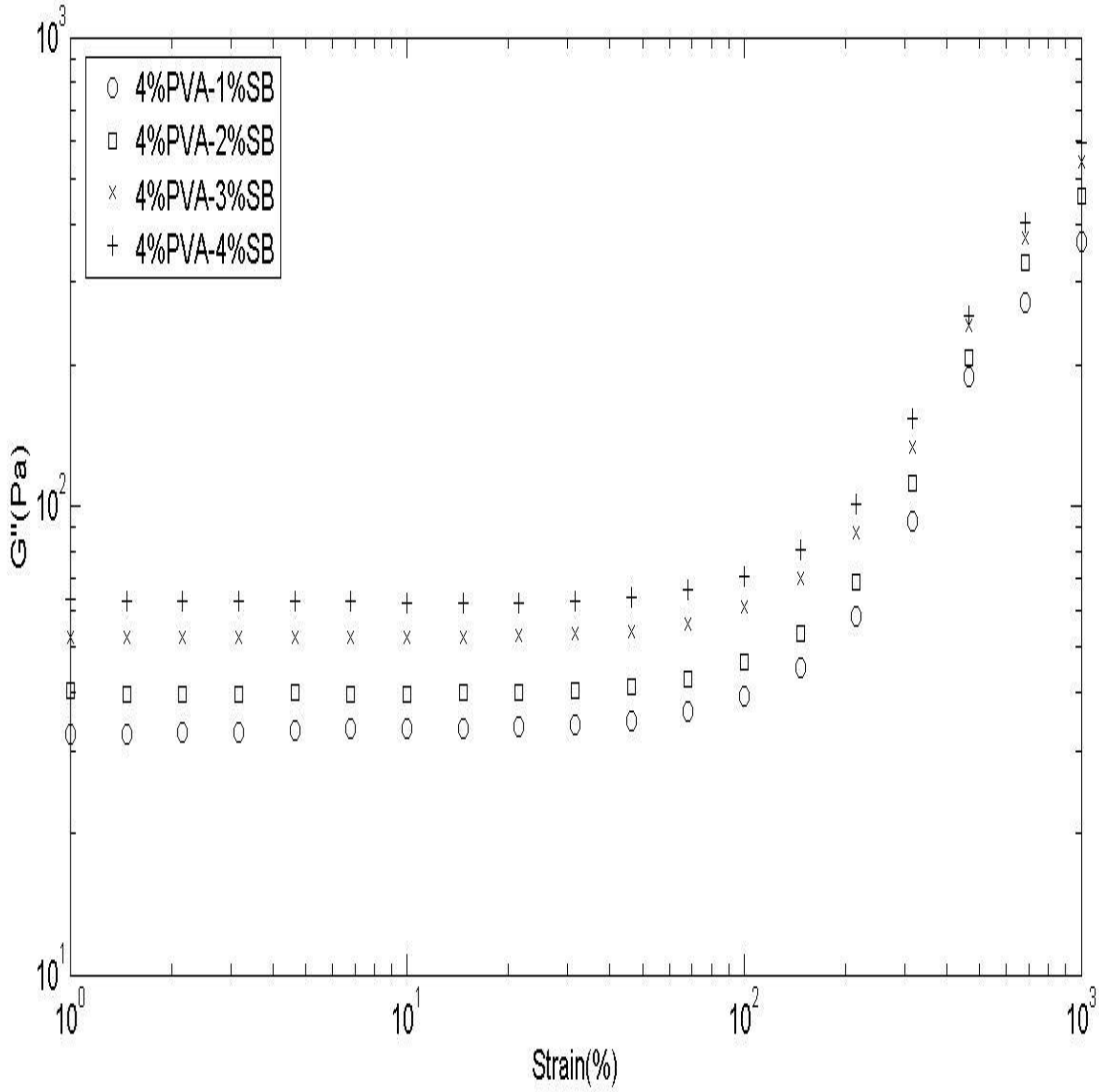


Fig 3: Comparison of G" for PVA-SB gel for amplitude sweep measurements

2.4.2 Frequency Sweep data [5]

Amplitude: 1%

Frequency range: 0.05-50 rad/sec

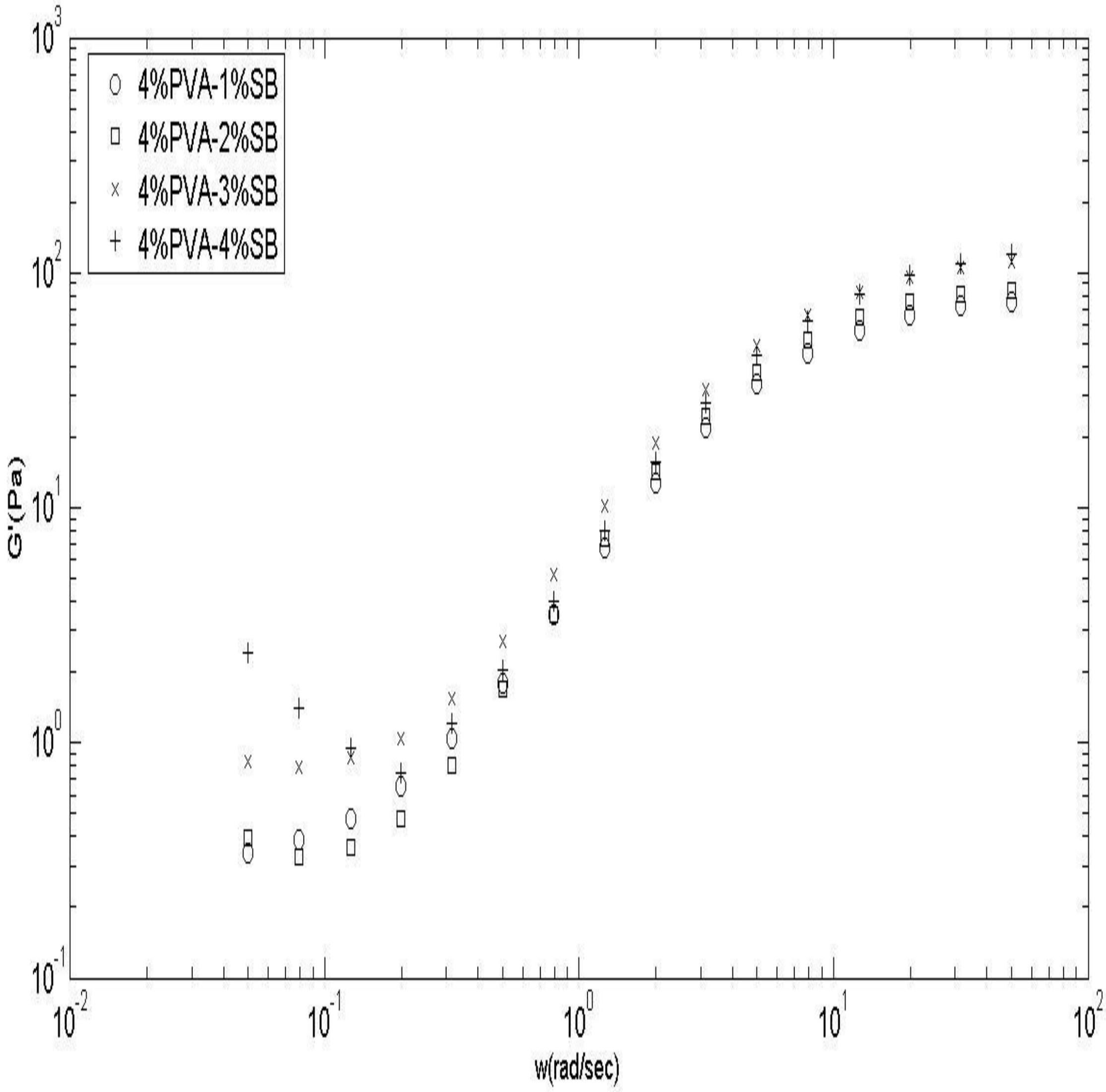


Fig 4: Comparison of G’ for PVA-SB gel for frequency sweep measurements

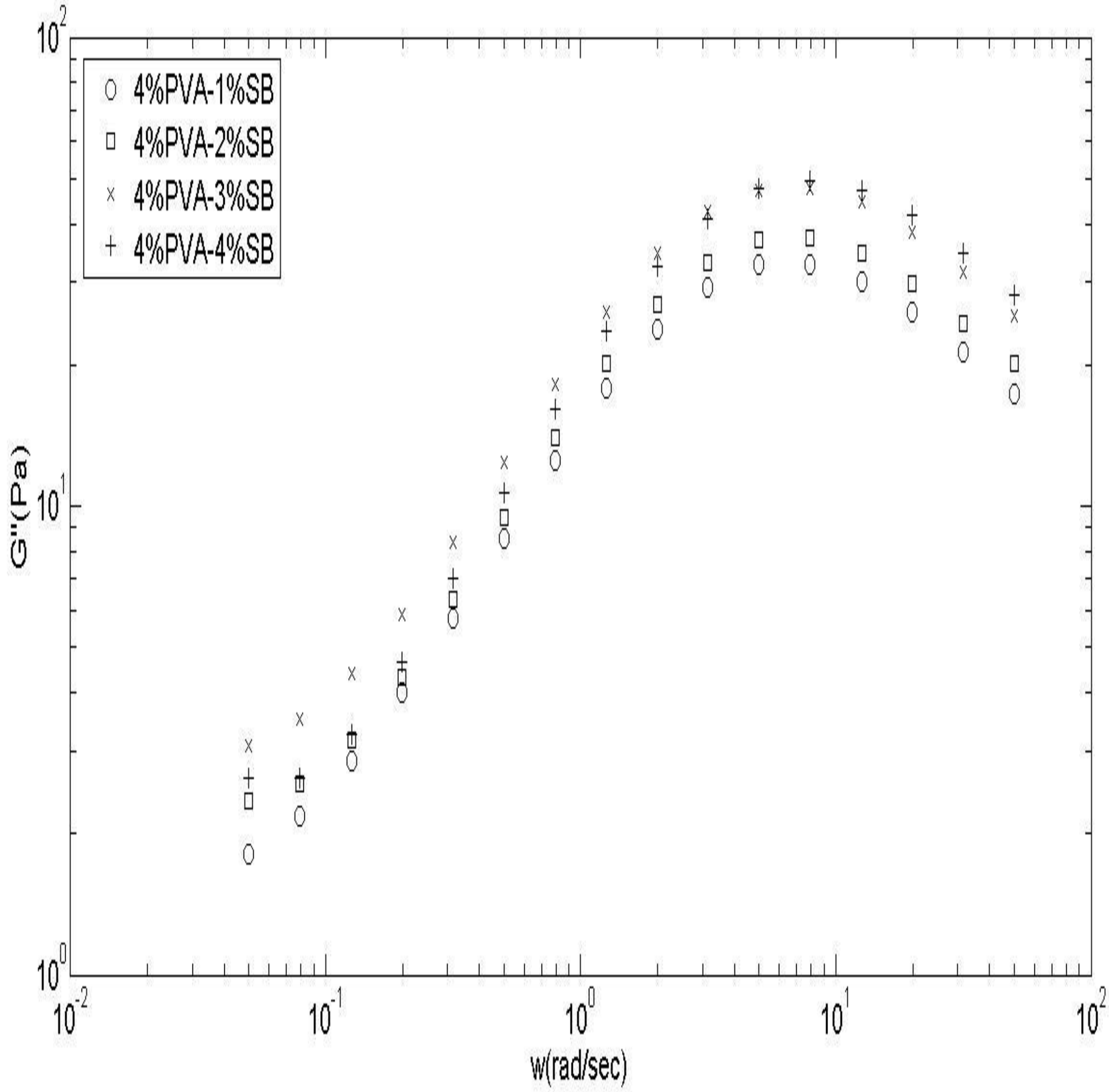


Fig 5: Comparison of G" for PVA-SB gel for frequency sweep measurements

2.4.3 Viscosity variation with shear rate [5]

Strain rate range: 1-30 sec^{-1}

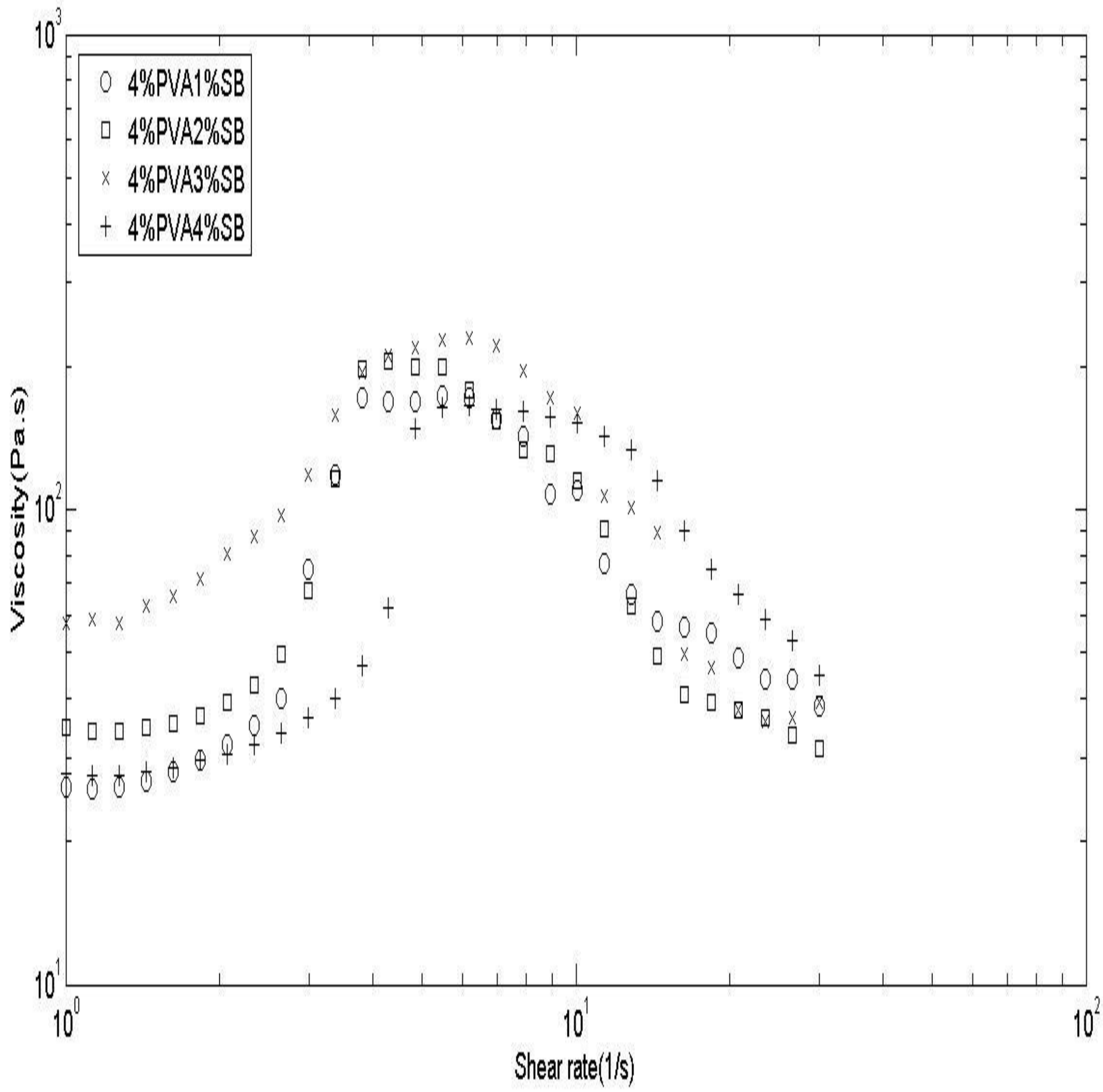


Fig 6: Viscosity variation with shearrate for PVA-SB gel

Chapter 3

Rheology of PolyVinyl Alcohol-Sodium Borate gel (theory)

Rheology is the study of the flow of materials. Fluids are different from solids, because fluids deform continuously when there is an applied stress, while solids undergo a finite deformation and then stop. The objective of Rheology is to determine the fluid flow that would be produced due to applied forces.

3.1 Maxwell fluid model

Many Viscoelastic models like Maxwell model, Oldroyd-B model and Kelvin-Voigt model can be considered but we assume Maxwell model because of experimental results.

We first assume that the PVA-SB gel can be modeled using a Maxwell fluid model.

We will motivate the Maxwell fluid model using the building blocks of springs and dashpots commonly used to describe linear Viscoelastic response of materials[3].

The stress–strain relationship for the spring element (fig 7a) is

$$\sigma_e = G\gamma \qquad (8)$$

elementand the relationship for the dashpot (fig 7b) is:

$$\sigma_v = \eta\dot{\gamma} \qquad (9)$$

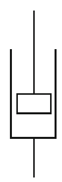


Fig 7a: Elastic element Fig 7b: Viscous element

The two elements can be connects as shown in fig 8, where same stress is transmitted through these elements and the total strain is the sum of both elements' respective strains.

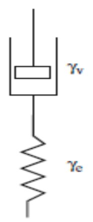


Fig 8: Maxwell model

This combination is called the 'Maxwell model'. In this case, the stresses in the two elements are

$$\sigma = G\,\gamma_E \;=\; G\dot{\gamma}_V \qquad (10)$$

The above relations are used to obtain the stress–strain relationship

$$\sigma + \lambda_1\dot{\sigma} = \;\eta\dot{\gamma} \qquad (11)$$

where $\lambda_1 = \eta/G$ is the relaxation time constant for this model.
We can represent the sinusoidal strain applied to a complex fluid sample as

$$\gamma = \;\gamma_0 \sin\omega t \qquad (12)$$

The linearresponse of material in terms of stress can be written as

$$\sigma = \;\sigma_0 \sin(\omega t + \delta) \qquad (13)$$

where$\delta$is the phase lag. Different waveforms, such as triangular, square, and trapezoidal, have also been used in oscillatory shear.
In small amplitude oscillatory shear (SAOS), material functions are defined to quantify the material behavior based on the strain imposed and the stress response.
For SAOS, the response of Maxwell model is:

$$G' = \frac{\eta\omega^2\lambda_1}{1+\omega^2{\lambda_1}^2}, \qquad\qquad G'' = \frac{\eta\omega}{1+\omega^2{\lambda_1}^2} \qquad (14)$$

where λ_1 (the relaxation time) and η are the model parameters

From above equations, the material response at very low frequencies is $G' \propto \omega^2$ and $G'' \propto \omega$ signifying viscous response. At very high frequencies, material response is $G' = \eta/\lambda_1$ and $G'' \propto \omega^{-1}$. The constant value of storage modulus is $G'(=\eta/\lambda_1)$ and is called the elastic modulus. At frequency $\omega = \eta/\lambda_1$ a crossover between G' and G'' occurs.

3.2 Governing Equations of Maxwell fluid in Cone-and-PlateRheometer

As stated previously, we will assume that the PVA-SB samples in the CP Rheometer can be modeled as Maxwell fluids.

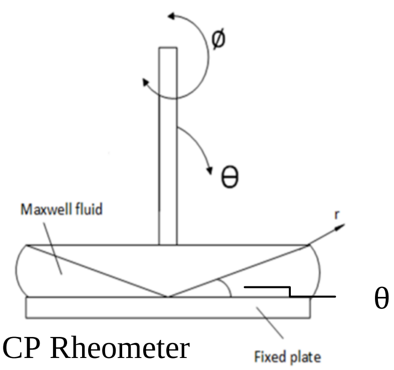


Fig 9: Schematic of CP Rheometer

The 3-D frame-invariant Maxwell model is a generalization of the linear viscoelastic Maxwell model and is written as:

$$\mathbf{T} = -p1 + \mathbf{S}(\cong \tau) \quad (15)$$

$$\mathbf{S} + \lambda_1 \overset{\nabla}{\mathbf{S}} = \mu \mathbf{A_1} \quad (16)$$

$$\mathbf{A_1} = \nabla v + \nabla v^t \quad (17)$$

$$\overset{\nabla}{\mathbf{S}} = D\mathbf{S}/Dt - \mathbf{LS} - \mathbf{SL}^T \quad (18)$$

$$\frac{D\mathbf{S}}{Dt} = \frac{\partial \mathbf{S}}{\partial t} + (\text{grad } \mathbf{S})v \quad (19)$$

It must be noted that the 3D generalization is capable of describing non-linear response whereas the spring-dashpot analog is restricted to describing linear viscoelastic response.

3.2.1 Semi-inverse approach

In semi-inverse approach we assume that there exists a flow field satisfying the boundary conditions. This flow field is then substituted in the mass balance and momentum balance equations. We then check if there is a solution to the equations that matches the form initially assumed.
We assume that the following flow field exists in the fluid sample placed between the cone and plate:

$$v = v_r \hat{e}_r + v_\theta \hat{e}_\theta + v_\emptyset \hat{e}_\emptyset \quad (20)$$

$$v_r = v_\theta = 0 \quad (21)$$

$$v_\emptyset = r\omega \quad (22)$$

$$v = r\omega \hat{e}_\emptyset \quad (23)$$

3.2.2 Kinematics

$$\mathbf{A_1} = \begin{bmatrix} 2\frac{\partial v_r}{\partial r} & \frac{\partial v_\theta}{\partial r} + \frac{1}{r}\frac{\partial v_r}{\partial \theta} - \frac{1}{r}v_\theta & \frac{\partial v_\emptyset}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial v_r}{\partial \emptyset} - \frac{1}{r}v_\emptyset \frac{\partial v_\emptyset}{\partial r} - \frac{1}{r}v_\emptyset \\ \frac{\partial v_\theta}{\partial r} + \frac{1}{r}\frac{\partial v_r}{\partial \theta} - \frac{1}{r}v_\theta & 2\left(\frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{1}{r}v_r\right) & \frac{1}{r}\frac{\partial v_\emptyset}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial v_\theta}{\partial \emptyset} - \frac{\cot\theta}{r}v_\emptyset \\ \frac{\partial v_\emptyset}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial v_r}{\partial \emptyset} - \frac{1}{r}v_\emptyset & \frac{1}{r}\frac{\partial v_\emptyset}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial v_\theta}{\partial \emptyset} - \frac{\cot\theta}{r}v_\emptyset & 2\left(\frac{1}{r\sin\theta}\frac{\partial v_\emptyset}{\partial \emptyset} + \frac{1}{r}v_r + \frac{\cot\theta}{r}v_\theta\right) \end{bmatrix} \quad (24)$$

$$\theta = \frac{\pi}{2}\text{-}\theta_0\theta_0 = 1^0 \approx 0 \qquad\qquad \theta = \frac{\pi}{2}$$

$$\mathbf{A}_1 = \begin{bmatrix} 0 & 0 & \frac{\partial v_\emptyset}{\partial r} - \frac{1}{r}v_\emptyset \\ 0 & 0 & -\frac{\cot\theta}{r}v_\emptyset + \frac{1}{r}\frac{\partial v_\emptyset}{\partial \theta} \\ \frac{\partial v_\emptyset}{\partial r} - \frac{1}{r}v_\emptyset & -\frac{\cot\theta}{r}v_\emptyset + \frac{1}{r}\frac{\partial v_\emptyset}{\partial \theta} & 0 \end{bmatrix} \quad (25)$$

$$[A_1]_{r\emptyset} = \frac{\partial v_\emptyset}{\partial r} - \frac{1}{r}v_\emptyset$$

$$= \omega - \frac{r\omega}{r} = 0$$

$$\gamma = \gamma_m \sin\omega t \quad (26)$$

$$\dot{\gamma} = \gamma_m \omega\cos\omega t \quad (27)$$

$[\mathbf{A}_1]_{\theta\emptyset} = \frac{1}{r}\frac{\partial v_\emptyset}{\partial \theta}$and this is usually referred to as $\dot{\gamma}$

Thus, from the above, we may equate $[\mathbf{A}_1]_{\theta\emptyset}$ to the sinusoidal shear rate as follows

$$[\mathbf{A}_1]_{\theta\emptyset} = \gamma_m \omega\cos\omega t$$

$$A_1 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \gamma_m\omega\cos\omega t \\ 0 & \gamma_m\omega\cos\omega t & 0 \end{bmatrix} \quad (28)$$

$$\mathbf{L} = \begin{bmatrix} \frac{\partial v_r}{\partial r} & \frac{1}{r}\frac{\partial v_r}{\partial \theta} - \frac{1}{r}v_\theta & \frac{1}{r\sin\theta}\frac{\partial v_r}{\partial \emptyset} - \frac{1}{r}v_\emptyset \\ \frac{\partial v_\theta}{\partial r} & \frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{1}{r}v_r & \frac{1}{r\sin\theta}\frac{\partial v_\theta}{\partial \emptyset} - \frac{\cot\theta}{r}v_\emptyset \\ \frac{\partial v_\emptyset}{\partial r} & \frac{1}{r}\frac{\partial v_\emptyset}{\partial \theta} & \frac{1}{r\sin\theta}\frac{\partial v_\emptyset}{\partial \emptyset} + \frac{1}{r}v_r + \frac{\cot\theta}{r}v_\theta \end{bmatrix} \quad (29)$$

$$\mathbf{L} = \begin{bmatrix} 0 & 0 & -\omega \\ 0 & 0 & 0 \\ \omega & \gamma_m \omega \cos\omega t & 0 \end{bmatrix} \tag{30}$$

$$\mathbf{S} = \begin{bmatrix} \mathbf{S}_{rr} & \mathbf{S}_{r\theta} & \mathbf{S}_{r\emptyset} \\ \mathbf{S}_{r\theta} & \mathbf{S}_{\theta\theta} & \mathbf{S}_{\theta\emptyset} \\ \mathbf{S}_{r\emptyset} & \mathbf{S}_{\theta\emptyset} & \mathbf{S}_{\emptyset\emptyset} \end{bmatrix} \tag{31}$$

$$\mathbf{LS} = \begin{bmatrix} -\omega\mathbf{S}_{r\emptyset} & -\omega\mathbf{S}_{\theta\emptyset} & -\omega\mathbf{S}_{\emptyset\emptyset} \\ 0 & 0 & 0 \\ \omega\mathbf{S}_{rr}+\gamma_m\omega\cos\omega t\mathbf{S}_{r\theta} & \omega\mathbf{S}_{r\theta}+\gamma_m\omega\cos\omega t\mathbf{S}_{\theta\theta} & \omega\mathbf{S}_{r\emptyset}+\gamma_m\omega\cos\omega t\mathbf{S}_{\theta\emptyset} \end{bmatrix} \tag{32}$$

$$\mathbf{SL^T} = \begin{bmatrix} -\omega\mathbf{S}_{r\emptyset} & 0 & \omega\mathbf{S}_{rr}+\gamma_m\omega\cos\omega t\mathbf{S}_{r\theta} \\ -\omega\mathbf{S}_{\theta\emptyset} & 0 & \omega\mathbf{S}_{r\theta}+\gamma_m\omega\cos\omega t\mathbf{S}_{\theta\theta} \\ -\omega\mathbf{S}_{\emptyset\emptyset} & 0 & \omega\mathbf{S}_{r\emptyset}+\gamma_m\omega\cos\omega t\mathbf{S}_{\theta\emptyset} \end{bmatrix} \tag{33}$$

3.2.3 Constitutive Model

$$\mathbf{T} = -p1 + \mathbf{S}(\cong \tau) \tag{34}$$

$$\mathbf{S} + \lambda_1 \overset{\triangledown}{\mathbf{S}} = \mu\mathbf{A_1} \tag{35}$$

$$\frac{D\mathbf{S}}{Dt} = \frac{\partial\mathbf{S}}{\partial t} + (\text{grad }\mathbf{S})v \tag{36}$$

$$\left(\frac{D\mathbf{S}}{Dt}\right)_{rr} = \frac{\partial\mathbf{S}_{rr}}{\partial t} + v_r\frac{\partial\mathbf{S}_{rr}}{\partial r} + v_\theta\left(\frac{1}{r}\frac{\partial\mathbf{S}_{rr}}{\partial\theta} - \frac{2}{r}\mathbf{S}_{r\theta}\right) + v_\emptyset\left(\frac{1}{r\sin\theta}\frac{\partial\mathbf{S}_{rr}}{\partial\emptyset} - \frac{2}{r}\mathbf{S}_{r\emptyset}\right)$$
$$= \frac{\partial\mathbf{S}_{rr}}{\partial t} + \omega\frac{\partial\mathbf{S}_{rr}}{\partial\emptyset} - 2\omega\mathbf{S}_{r\emptyset} \tag{37}$$

$$\left(\frac{D\mathbf{S}}{Dt}\right)_{r\theta} = \frac{\partial\mathbf{S}_{r\theta}}{\partial t} + v_r\frac{\partial\mathbf{S}_{r\theta}}{\partial r} + v_\theta\left(\frac{1}{r}\frac{\partial\mathbf{S}_{r\theta}}{\partial\theta} + \frac{1}{r}(\mathbf{S}_{rr} - \mathbf{S}_{\theta\theta})\right)$$
$$+ v_\emptyset\left(\frac{1}{r\sin\theta}\frac{\partial\mathbf{S}_{r\theta}}{\partial\emptyset} - \frac{1}{r}\mathbf{S}_{\theta\emptyset} - \frac{\cot\theta}{r}\mathbf{S}_{r\emptyset}\right)$$
$$= \frac{\partial\mathbf{S}_{r\theta}}{\partial t} + \omega\frac{\partial\mathbf{S}_{r\theta}}{\partial\emptyset} - \omega\mathbf{S}_{\theta\emptyset} \tag{38}$$

$$\left(\frac{D\mathbf{S}}{Dt}\right)_{\theta\theta} = \frac{\partial\mathbf{S}_{\theta\theta}}{\partial t} + v_r\frac{\partial\mathbf{S}_{\theta\theta}}{\partial r} + v_\theta\left(\frac{1}{r}\frac{\partial\mathbf{S}_{\theta\theta}}{\partial\theta} + \frac{2}{r}\mathbf{S}_{r\theta}\right) + v_\emptyset\left(\frac{1}{r\sin\emptyset}\frac{\partial\mathbf{S}_{\theta\theta}}{\partial\emptyset} - 2\frac{\cot\theta}{r}\mathbf{S}_{\theta\emptyset}\right)$$

$$= \frac{\partial \mathbf{S}_{\theta\theta}}{\partial t} + \omega \frac{\partial \mathbf{S}_{\theta\theta}}{\partial \emptyset} \tag{39}$$

$$\left(\frac{D\mathbf{S}}{Dt}\right)_{r\emptyset} = \frac{\partial \mathbf{S}_{r\emptyset}}{\partial t} + v_r \frac{\partial \mathbf{S}_{r\emptyset}}{\partial r} + v_\theta \left(\frac{1}{r}\frac{\partial \mathbf{S}_{r\emptyset}}{\partial \theta} - \frac{1}{r}\mathbf{S}_{\theta\emptyset}\right) + v_\emptyset \left(\frac{1}{r\sin\theta}\frac{\partial \mathbf{S}_{r\emptyset}}{\partial \emptyset} + \frac{1}{r}(\mathbf{S}_{rr} - \mathbf{S}_{\emptyset\emptyset}) + \frac{\cot\theta}{r}\mathbf{S}_{r\theta}\right)$$

$$= \frac{\partial \mathbf{S}_{r\emptyset}}{\partial t} + \omega \frac{\partial \mathbf{S}_{r\emptyset}}{\partial \emptyset} + \omega(\mathbf{S}_{rr} - \mathbf{S}_{\emptyset\emptyset}) \tag{40}$$

$$\left(\frac{D\mathbf{S}}{Dt}\right)_{\theta\emptyset} = \frac{\partial \mathbf{S}_{\theta\emptyset}}{\partial t} + v_r \frac{\partial \mathbf{S}_{\theta\emptyset}}{\partial r} + v_\theta \left(\frac{1}{r}\frac{\partial \mathbf{S}_{\theta\emptyset}}{\partial \theta} + \frac{1}{r}\mathbf{S}_{r\emptyset}\right) + v_\emptyset \left(\frac{1}{r\sin\theta}\frac{\partial \mathbf{S}_{\theta\emptyset}}{\partial \emptyset} + \frac{1}{r}\mathbf{S}_{r\theta} + \frac{\cot\theta}{r}(\mathbf{S}_{\theta\theta} - \mathbf{S}_{\emptyset\emptyset})\right)$$

$$= \frac{\partial \mathbf{S}_{\theta\emptyset}}{\partial t} + \omega \frac{\partial \mathbf{S}_{\theta\emptyset}}{\partial \emptyset} + \omega \mathbf{S}_{r\theta} \tag{41}$$

$$\left(\frac{D\mathbf{S}}{Dt}\right)_{\emptyset\emptyset} = \frac{\partial \mathbf{S}_{\emptyset\emptyset}}{\partial t} + v_r \frac{\partial \mathbf{S}_{\emptyset\emptyset}}{\partial r} + v_\theta \frac{1}{r}\frac{\partial \mathbf{S}_{\emptyset\emptyset}}{\partial \theta} + v_\emptyset \left(\frac{1}{r\sin\theta}\frac{\partial \mathbf{S}_{\emptyset\emptyset}}{\partial \emptyset} + \frac{2}{r}\mathbf{S}_{r\emptyset} + \frac{2\cot\theta}{r}\mathbf{S}_{\theta\emptyset}\right)$$

$$= \frac{\partial \mathbf{S}_{\emptyset\emptyset}}{\partial t} + \omega \frac{\partial \mathbf{S}_{\emptyset\emptyset}}{\partial \emptyset} + 2\omega \mathbf{S}_{r\emptyset} \tag{42}$$

Substituting equations (28), (31), (32), (33), (37), (38), (39), (40), (42), (42) in the constitutive equation (35)

Equating S components

$$\mathbf{S_{rr}} = -\lambda_1 \left(\frac{\partial \mathbf{S}_{rr}}{\partial t} + \omega \frac{\partial \mathbf{S}_{rr}}{\partial \emptyset}\right) \tag{43}$$

$$\mathbf{S_{r\theta}} = -\lambda_1 \left(\frac{\partial \mathbf{S}_{r\theta}}{\partial t} + \omega \frac{\partial \mathbf{S}_{r\theta}}{\partial \emptyset}\right) \tag{44}$$

$$\mathbf{S_{r\emptyset}} = -\lambda_1 \left(\frac{\partial \mathbf{S}_{r\emptyset}}{\partial t} + \omega \frac{\partial \mathbf{S}_{r\emptyset}}{\partial \emptyset} - \gamma_m \omega \cos\omega t \mathbf{S}_{r\theta}\right) \tag{45}$$

$$\mathbf{S}_{\theta\theta} = -\lambda_1 \left(\frac{\partial \mathbf{S}_{\theta\theta}}{\partial t} + \omega \frac{\partial \mathbf{S}_{\theta\theta}}{\partial \emptyset}\right) \tag{46}$$

$$\mathbf{S}_{\emptyset\theta} = \mu\gamma_m \omega \cos\omega t - \lambda_1 \left(\frac{\partial \mathbf{S}_{\emptyset\theta}}{\partial t} + \omega \frac{\partial \mathbf{S}_{\emptyset\theta}}{\partial \emptyset} - \gamma_m \omega \cos\omega t \mathbf{S}_{\theta\theta}\right) \tag{47}$$

$$\mathbf{S}_{\phi\phi} = -\lambda_1 \left(\frac{\partial \mathbf{S}_{\phi\phi}}{\partial t} + \omega \frac{\partial \mathbf{S}_{\phi\phi}}{\partial \phi} - 2\gamma_m \omega \cos\omega t \mathbf{S}_{\theta\phi} \right) \tag{48}$$

We further assume $S_{\theta\phi}(r,\theta)$- shear stress, $S_{\phi\phi}(r,\theta)$- normal stress.

By comparing the solution for steady shear flow between cone and plate, we set $S_{rr}=S_{r\theta}= S_{r\phi}= S_{\theta\theta}= 0$ for both steady and unsteady flow cases. We thus obtain the relations for shear and normal stress given below.

For Steady State

From equation (47)

$$\mathbf{S}_{\phi\theta} = \mu\gamma_m \omega \cos\omega t \tag{49}$$

From equation (48)

$$\mathbf{S}_{\phi\phi} = 2\mu\lambda_1 (\gamma_m \omega \cos\omega t)^2 \tag{50}$$

For Unsteady State

From equation (47)

$$\mathbf{S}_{\phi\theta} = \mu\gamma_m \omega \cos\omega t - \lambda_1 \frac{\partial \mathbf{S}_{\phi\theta}}{\partial t}$$

$$\frac{\partial \mathbf{S}_{\phi\theta}}{\partial t} = \frac{\mu\gamma_m \omega \cos\omega t - \mathbf{S}_{\phi\theta}}{\lambda_1} \text{ IVP 1} \tag{51}$$

From equation (48)

$$\mathbf{S}_{\phi\phi} = -\lambda_1 \left(\frac{\partial \mathbf{S}_{\phi\phi}}{\partial t} - 2\gamma_m \omega \cos\omega t \mathbf{S}_{\theta\phi} \right)$$

$$\frac{\partial \mathbf{S}_{\phi\phi}}{\partial t} = \left(\frac{2\lambda_1 \gamma_m \omega \cos\omega t \mathbf{S}_{\theta\phi} - \mathbf{S}_{\phi\phi}}{\lambda_1} \right) \text{ IVP 2} \tag{52}$$

Initial Conditions

$$\mathbf{S}_{\phi\theta}(r, \theta, 0) = 0$$

$$\mathbf{S}_{\phi\phi}(r, \theta, 0) = 0$$

The substitution of the assumed flow field results in the two coupled ODEs (equations 51&52) with fixed initial conditions. While such a solution is obtained by standard numerical procedures, we will first check if the assumed flow field satisfies mass and momentum balance before proceeding to calculate the solution.

3.2.4 Mass Balance

$$\frac{1}{r}\frac{\partial(rv_r)}{\partial r}+\frac{1}{r}\frac{\partial(v_\theta)}{\partial\theta}+\frac{v_\theta\cot\theta}{r}+\frac{v_r}{r}+\frac{1}{r\sin\theta}\frac{\partial v_\phi}{\partial\phi}=0 \quad (53)$$

$$v_\phi = r\omega$$

$$v_r = v_\theta = 0$$

LHS=RHS=0

Hence mass balance is satisfied by the assumed flow field

3.2.5 Momentum Balance

Along r-direction

$$\boldsymbol{\rho\left(\frac{\partial v_r}{\partial t}+v_r\frac{\partial v_r}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_r}{\partial\theta}+\frac{v_\phi}{r\sin\theta}\frac{\partial v_r}{\partial\phi}-\frac{{v_\theta}^2+{v_\phi}^2}{r}\right)=\frac{1}{r^2}\frac{\partial}{\partial r}(r^2S_{rr})+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(S_{\theta r}\sin\theta)+\frac{1}{r\sin\theta}\frac{\partial S_{\phi r}}{\partial\phi}-\frac{(S_{\theta\theta}+S_{\phi\phi})}{r}-\frac{1}{r}\frac{\partial p}{\partial r}+\rho g_r} \quad (54)$$

$$0=-\frac{S_{\phi\phi}}{r}-\frac{\partial p}{\partial r}$$

p = p(r,ϕ) (adjusts according to solution)

Along θ-direction

$$\rho\left(\frac{\partial v_\theta}{\partial t}+v_r\frac{\partial v_\theta}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_\theta}{\partial\theta}+\frac{v_\phi}{r\sin\theta}\frac{\partial v_\theta}{\partial\phi}+\frac{v_r v_\theta}{r}-\frac{{v_\phi}^2\cot\theta}{r}\right)=\frac{1}{r^3}\frac{\partial}{\partial r}(r^3\mathbf{S}_{r\theta})+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\mathbf{S}_{\theta\theta}\sin\theta)+\frac{1}{r\sin\theta}\frac{\partial\mathbf{S}_{\phi\theta}}{\partial\phi}+\frac{(\mathbf{S}_{\theta r}-\mathbf{S}_{r\theta})-\mathbf{S}_{\phi\phi}\cot\theta}{r}-\frac{1}{r}\frac{\partial p}{\partial r}+\rho g_\theta \quad (55)$$

$$0=-\frac{1}{r}\frac{\partial p}{\partial\theta}$$

p = p(r,ϕ)

Along ∅-direction

$$\rho\left(\frac{\partial v_\phi}{\partial t}+v_r\frac{\partial v_\phi}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_\phi}{\partial\theta}+\frac{v_\phi}{r\sin\theta}\frac{\partial v_\phi}{\partial\phi}+\frac{v_\phi v_r}{r}-\frac{v_\theta v_\phi}{r}\cot\theta\right)=\frac{1}{r^3}\frac{\partial}{\partial r}(r^3\mathbf{S}_{r\phi})+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\mathbf{S}_{\theta\phi}\sin\theta)+\frac{1}{r\sin\theta}\frac{\partial\mathbf{S}_{\phi\phi}}{\partial\phi}+\frac{(\mathbf{S}_{\phi r}-\mathbf{S}_{r\phi})+\mathbf{S}_{\phi\theta}\cot\theta}{r}-\frac{1}{r\sin\theta}\frac{\partial p}{\partial\phi}+\rho g_\phi \quad (56)$$

$$\rho\left(\frac{\partial v_\phi}{\partial t}\right)=-\frac{1}{r}\frac{\partial p}{\partial\phi}$$

p = p(r,ϕ)(adjusts according to solution)

We have now detailed the acquisition of SAOS experimental data for PVA-SB gel, as well as the equations obtained to describe a Maxwell fluid subject to SAOS in a cone and plate Rheometer. Our main objective now is to identify the parameters (λ_1&μ) for the Maxwell fluid model so that the theoretically predicted values of G' and G'' match the experimentally obtained values for PVA-SB gel. The procedure to do this is outlined below.

In order to calculate the theoretically predicted values of G' and G", ordinary differential equations (51) & (52) are solved by ode45 solver (Runge-Kutta, 4^{th} order method in MATLAB R2010ab) subject to the following initial conditions

At t = 0 $S_{\phi\theta} = 0$ and $S_{\phi\phi} = 0$

This yields a set of values for G' and G" for a given choice of λ_1& μ. However, the error between the predicted values of G' and G" and the experimental values has not been minimized at this stage. In order to do this, error minimization is done using the 'fminsearch' function in MATLAB. Fminsearch finds the minimum of a scalar function of several variables starting with an initial estimate. In our case, the function to be minimized is the error between predicted values and experimental values of G' and G". The variables that need to be adjusted to minimize the error are λ_1& μ. The results of this error minimization are given next.

Chapter 4

Results and Discussions

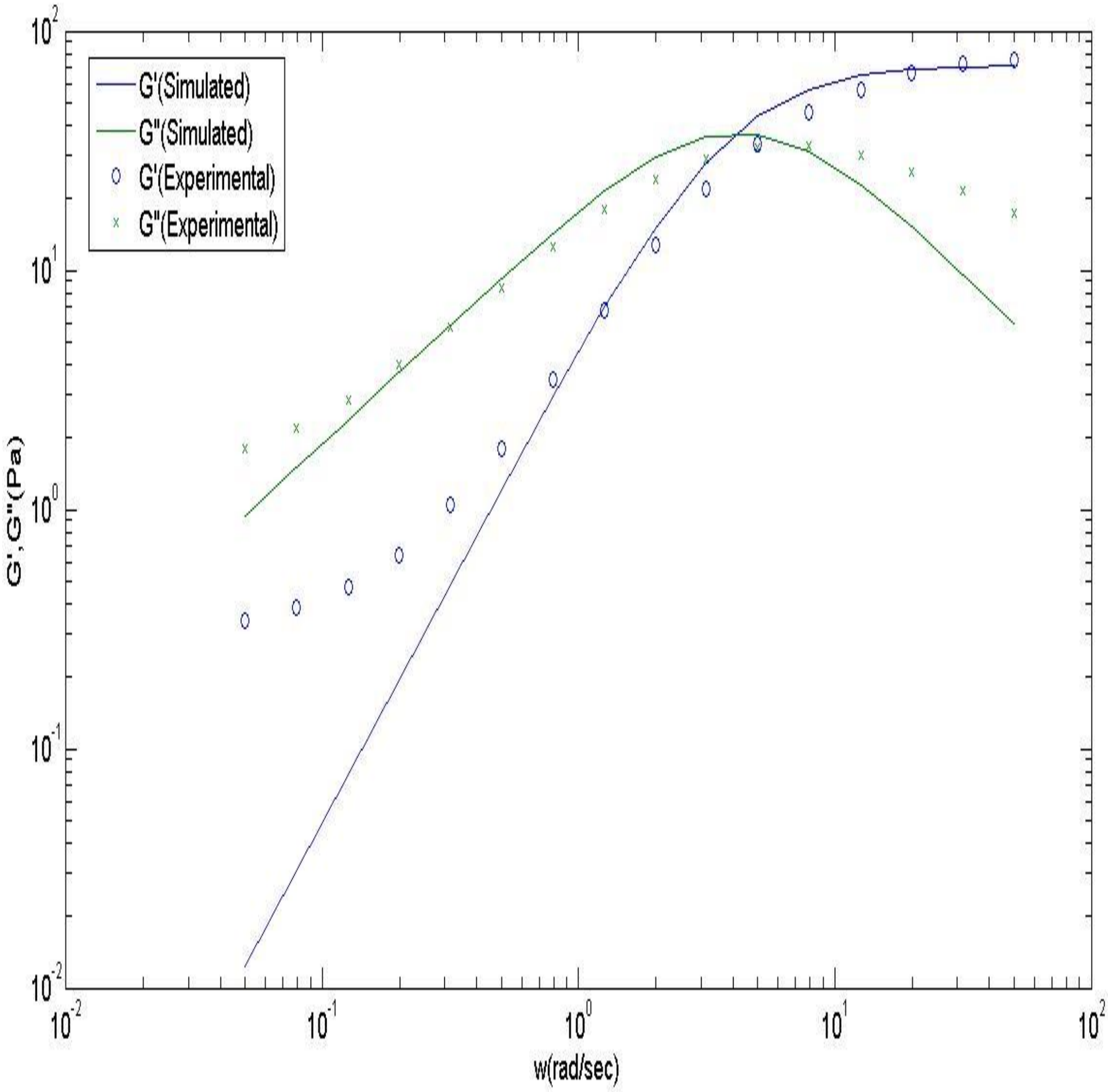
The table below lists the parameter combinations (λ_1& μ) that minimize the error between predicted and experimental values of G' and G". The values are reported for each PVA-SB gel (ie. for varying concentrations of SB).

Sample	λ_1(s)	μ(Pa.s)
4%PVA-1%SB	0.2608	18.7771
4%PVA-2%SB	0.2507	20.773
4%PVA-3%SB	0.2559	27.0915
4%PVA-4%SB	0.2163	23.5109

Table 1: Parameters (λ_1& μ) for PVA-SB gel

The match with data is shown in figures 10 through 13

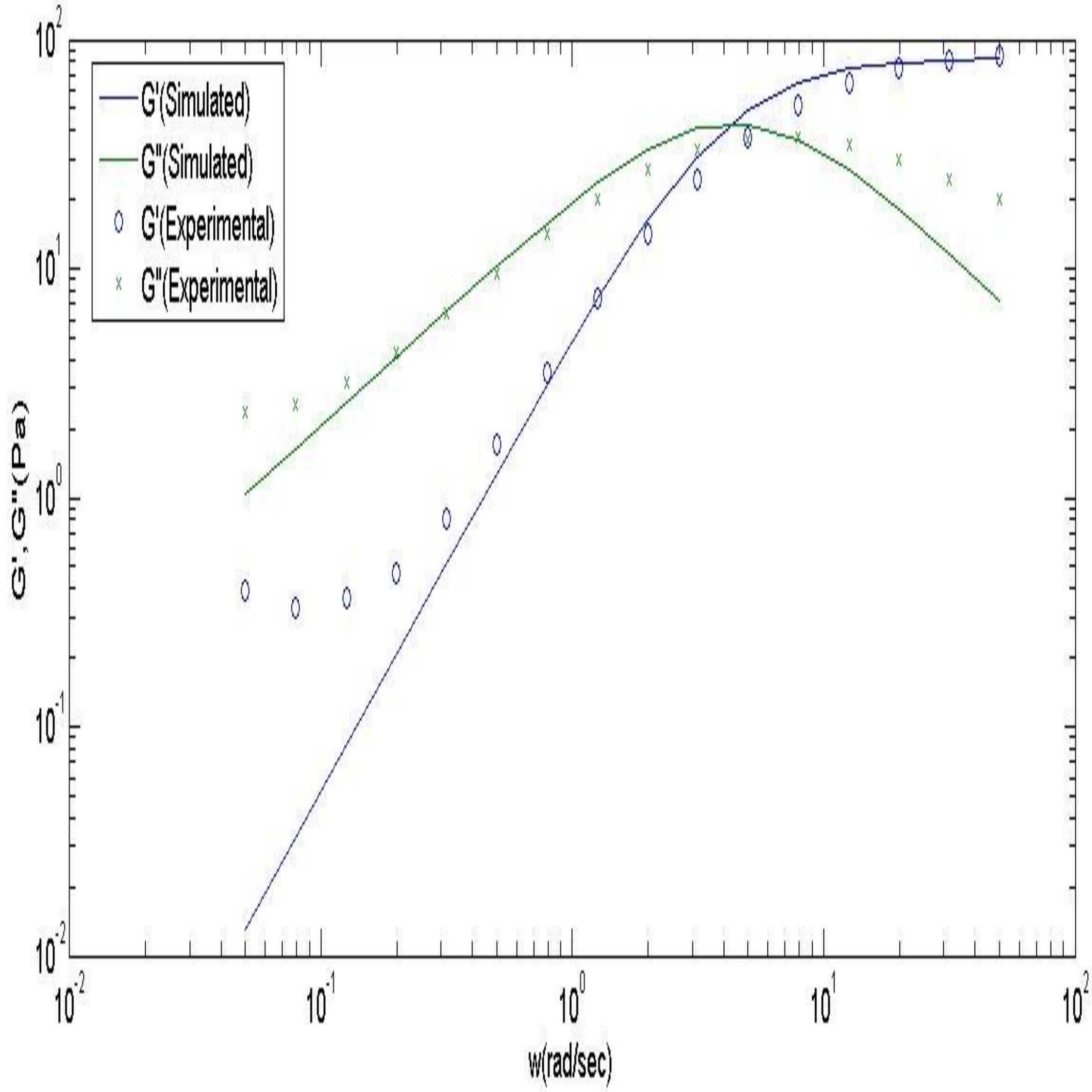
4.1 Frequency Sweep: 4%PVA-1%SB



λ_1=0.2608 Sec μ=18.7771 Pa.S

Fig 10: Comparison between simulation and experimental data for frequency sweep of 4%PVA-1%SB

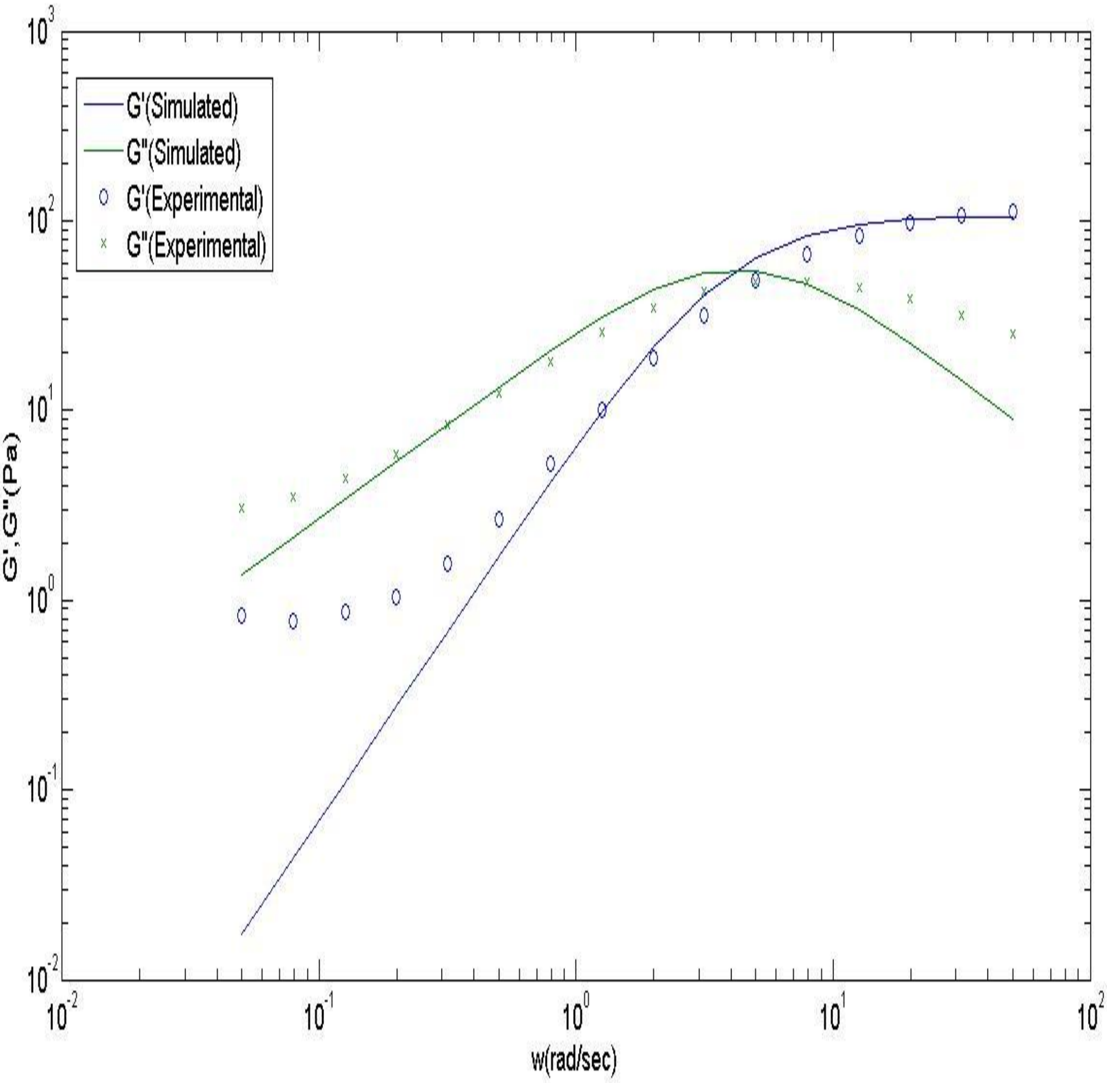
4.2 Frequency Sweep: 4%PVA-2%SB



λ_1=0.2507 Sec μ=20.7730 Pa.S

Fig 11: Comparison between simulation and experimental data for frequency sweep of 4%PVA-2%SB

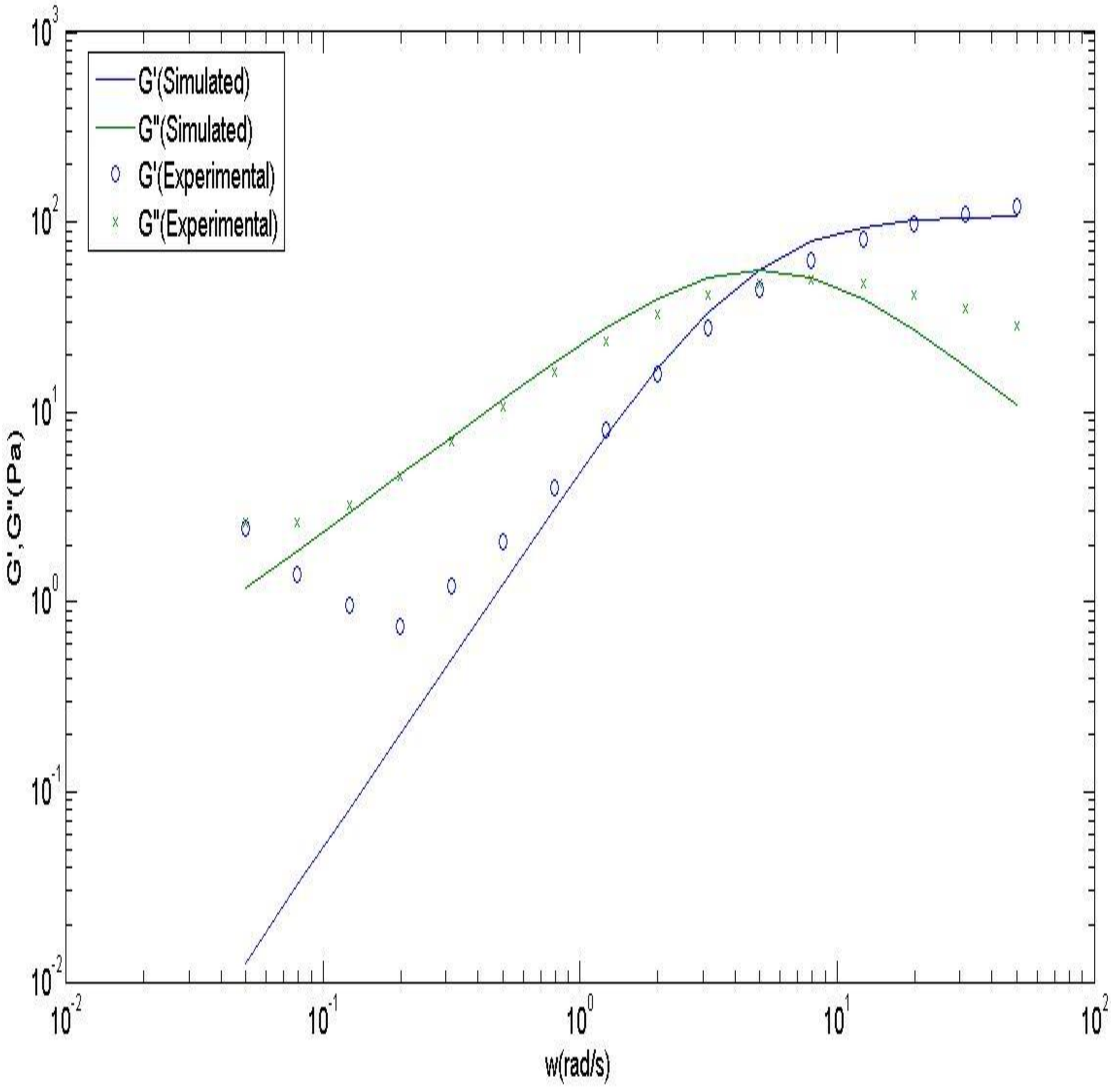
4.3 Frequency Sweep: 4%PVA-3%SB



λ_1=0.2559 Sec μ=18.7771 Pa.S

Fig 12: Comparison between simulation and experimental data for frequency sweep of 4%PVA-3%SB

4.4 Frequency Sweep: 4%PVA4%SB



λ_1=0.2163 Sec μ=23.5109 Pa.S

Fig 13: Comparison between simulation and experimental data for frequency sweep of 4%PVA-4%SB

4.5 Conclusions

We have shown that the Maxwell fluid model matches the experimentally measured values of G’ & G” well, for each PVA-SB gel that was tested. This is so provided the parameters λ_1& μ are selected so as to minimize the error between predicted values of G’ and G”, and experimentally measured values.

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