



# Viscoelastic and high ion conducting gum tragacanth-based gel polymer electrolytes

VINEY SHARMA<sup>1,2,3</sup>, NARINDER ARORA<sup>1,\*</sup> , RAJIV KUMAR<sup>2</sup>, SUNAINA VERMA<sup>4</sup> and SHUCHI SHARMA<sup>2</sup>

<sup>1</sup>Department of Physics, D.A.V. College, Amritsar 143001, India

<sup>2</sup>Department of Physics, G.G.D.S.D. College, Hoshiarpur 144208, India

<sup>3</sup>Department of Physics, Panjab University, Chandigarh 160014, India

<sup>4</sup>Department of Engineering and Technology, IKG Punjab Technical University, Kapurthala 144603, India

\*Author for correspondence (n\_arora2k@yahoo.com; narora@davcollegear.org)

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**Abstract.** Gum tragacanth (GT) based gel polymer electrolytes (GPEs)/hydrogels have been synthesized using deionized water (DW) and NaOH salt, and characterized through ionic conductivity, Fourier transform infrared (FTIR), pH, thermal and mechanical studies. Ionic conductivity decrement of liquid and GPEs was observed with the increase of temperature that contradicts pre-existing theoretical equation, i.e.,  $\sigma = \sigma_0 \exp(-E_a/kT)$  and maximum ionic conductivity of  $8.75 \times 10^{-2} \text{ S cm}^{-1}$  observed for GPE containing 0.625 M NaOH salt at 30°C. Effect of temperature on pH has been investigated for different GPEs and the results were also supported by FTIR studies by formation of new and disappearance of old peaks. Thermogravimetric analysis studies involved the measurements of  $T_g$  for GPEs with the incorporation of different concentrations of NaOH salt, supported by DTG thermograms. Viscoelastic behaviour of GPEs with and without salt have been described by rheological studies at 30°C. In spite of that, time-dependent high structure recovery ratio pointed out the sol to gel transition in GPEs after the removal of applied shear rate. Due to high ion conducting, thermally and mechanically strengthened GPEs-based materials may make them applicable for their use in different device applications.

**Keywords.** Gel polymer electrolyte; conductivity; thermal studies; thixotropy.

## 1. Introduction

Polymer electrolyte is a polymer salt complex, in which polymer acts like a host that provides rigid backbone and salt provides ions for conduction and creating better network. In order to get high performance in electrochemical devices, a large number of synthesized polymers-based electrolytes have been explored with different compositions containing inorganic salts (LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, NaI, NaCF<sub>3</sub>SO<sub>3</sub>, NaYF<sub>4</sub>, etc.), nano-fillers, copolymerization, cross-linkers, polymer liquid hybrids as well as polymer blending. An electrolyte is an important one that provides ions for conduction as well as act as insulator in the off state of device. Different type of synthetic polymers have been used in different electrolytes, including poly(methyl methacrylate), polyvinylidene fluoride, polyethylene oxide, polyacrylonitrile, poly(vinylidene fluoride-co-hexafluoropropylene), etc. [1,2]. In spite of achieving practical applicability in commercially available portable electronic devices, these polymer electrolytes deal with number of challenging limitations, i.e., safety issues with the use of organic liquids, toxicity, less flexibility, low ionic

conductivity in solid polymer electrolyte, poor electrolyte/electrode interfacial contact and high cost as well [3,4]. To overcome these limitations of synthesized polymer-based electrolytes, the present scenario deals with the probing of some natural polymers, which exhibit remarkable properties like non-toxicity, flexibility, higher ionic conductivity ( $\geq 10^{-3} \text{ S cm}^{-1}$ ), ease of availability, biodegradable in nature, good mechanical, electrical as well as thermal stability. These polymers are attracting huge attention and have been studied as an electrode binders by various researchers in order to replace the conventional polymers. Some of these natural polymers have been reported in the literature, such as xanthan gum, guar gum, carboxymethyl cellulose, gum tragacanth (GT), chitosan, karyya gum, gum Arabic, etc. [5,6]. These natural polymers can form solid as well as semi-solid (gel) matrices that may retain the rigid backbone and high ionic conductivity [7].

Gum tragacanth (GT) is one of these natural polymers that is composed of subtle mixture of acidic hetero-polysaccharides containing D-galacturonic acid and produces 6-deoxy-L-galactose, L-arabinose, D-galactose and D-xylose followed by hydrolysis in acid. [8]. Two major components of

GT are water-soluble tragacanthin and insoluble bassorin that are responsible for solubility (formation of colloidal hydro-sol) and swelling of GT in water, respectively. GT has a capacity to form three-dimensional water swollen gel network through the interactions between polymeric chains and can retain a large amount of water within its network [9]. So far, GT has been explored in biomedical/pharmaceutical sciences, especially in food industry (like thickening agent, emulsifier and stabilizer), cosmetics, wound healing and drug delivery systems due to its characteristics like biocompatibility, biodegradable, bio-stable, high water uptake capacity/swelling, economical, abundant, pH responsive, etc. But along with this, GT is an anionic polysaccharide that contains a number of carboxylic groups that can dissociate in the solvent as well as hydroxyl groups present in highly branched structure that may provide active sites for the conduction [10]. The role of GT as an active material for different device applications needs to be explore yet.

The contemporary research deals with an effort to synthesize GT-based gel polymer electrolytes (GPEs), in which GT acts as host polymer doped with NaOH salt and deionized water. The prepared samples have been analysed through various characterizations, such as ionic conductivity, thermal stability, mechanical stability, Fourier transform infrared (FTIR) and pH. These electrolytes may be useful in future as active materials for different solid-state devices, such as batteries, super-capacitors, sensors, separators and other electrochemical devices.

## 2. Experimental

Gum tragacanth powder acquired from Sigma-Aldrich and sodium hydroxide salt (NaOH, 98% purity) in pallet form from LOBA Chemie, India, were used as raw materials. Deionized water (DW) was taken as a solvent with ionic conductivity of  $7 \mu\text{S cm}^{-1}$  at room temperature.

### 2.1 Preparation of GPEs

GT-based GPEs were synthesized by the procedure comprising of two stages. The first stage reports the synthesis of liquid electrolyte by dissolving an appropriate concentration of salt into DW with continuous stirring at room temperature. While at the second stage, GT contents were added gradually to liquid electrolyte in order to maintain homogeneity. The whole mixture was stirred continuously at  $30^\circ\text{C}$  till the achievement of jellification, i.e., the formation of gel polymer electrolyte.

### 2.2 Characterization

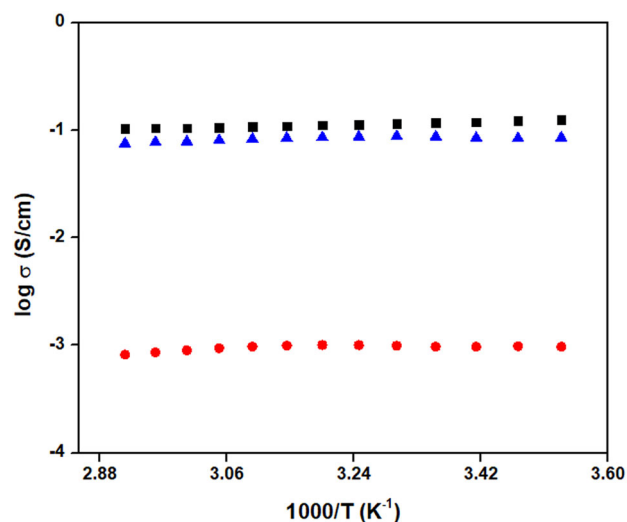
Gum tragacanth and salt were weighted with an accuracy up-to four decimal places using weighing balance ATX 124,

Shimadzu. WTW 3210 conductivity metre was used to compute ionic conductivity (with an accuracy of  $\pm 1\%$ ) of liquid and GPEs. This instrument is based upon four-probe set up having inbuilt temperature sensors with an accuracy of  $\pm 1^\circ\text{C}$ , and the conductivity measurement of prepared samples was performed in closed system. Cary 630 FTIR spectrometer (Agilent Technologies, America) was used to obtain Fourier transform infrared spectra of synthesized analytes within  $4000\text{--}400 \text{ cm}^{-1}$  wavenumber range. Acidic and basic character of prepared samples was investigated using Mettler Toledo pH meter (Model: S-210) linked within lab viscous electrode. Rheological studies of prepared GPEs were obtained using Rheolab QC (Anton paar, Germany) at room temperature that provide the material viscosity with time under applied shear rate. Also, thermal analysis was performed within the temperature range of  $0\text{--}400^\circ\text{C}$  using Thermo gravimetric Analyzer STA7000 (HITACHI from Japan) at the heating rate of  $10^\circ\text{C min}^{-1}$ . The platinum crucible was used for loading the samples, and nitrogen atmosphere was maintained during the whole thermal analysis.

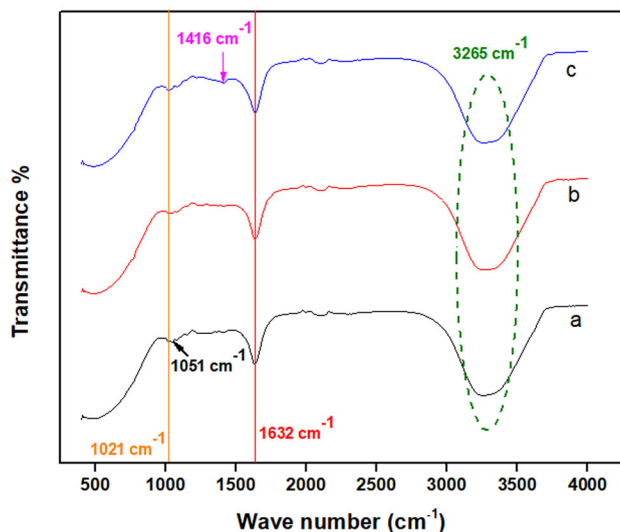
## 3. Results and discussion

### 3.1 Ionic conductivity

Ionic conductivity is an important parameter that plays a major role in the practical applicability of gel electrolytes. Figure 1 represents the temperature variation of ionic conductivity for liquid electrolyte, containing NaOH in deionized water as well as GT-based GPEs with and without incorporation of NaOH salt within the temperature range of  $10\text{--}70^\circ\text{C}$ . From figure 1, it is observed that the conductivity of liquid and GPEs decreases with an increase in



**Figure 1.** Temperature-dependent conductivity comparisons of different GPEs compositions as: DW-0.625 M NaOH (■); DW-GT (●); DW-0.625 M NaOH-GT (▲).



**Figure 2.** FTIR spectra of GT-based systems: (a) DW–10 wt% GT; (b) DW–0.01 M NaOH–10 wt% GT; (c) DW–0.625 M NaOH–10 wt% GT.

temperature but a factor wise only. However, this result is in contradiction with  $\sigma = \sigma_0 \exp(-E_a/kT)$ , where  $\sigma_0$  is pre-exponential factor,  $E_a$  is the activation energy,  $k$  the Boltzmann constant and  $T$  the absolute temperature. The observed conductivity decrement may be due to the water evaporation from gel matrix with an increase in temperature that results in reduced volume for the transportation of ions and hence lowering conductivity [11,12].

However, the observed ionic conductivity for liquid electrolyte exhibit higher values than GPEs at all temperature regions. The addition of GT leads to the viscosity enhancement, which may be due to the increase in viscosity according to the following relation:

$$\mu = q/6\pi\eta r,$$

where  $\mu$  is the ionic mobility,  $\eta$  the gel viscosity and  $r$  the ionic radius of mobile ion [13].

Along with this, the presence of NaOH salt in gel matrix lead to increase in the ionic charge density (as more ions provided by NaOH salt on dissociation), which may reflect in the conductivity enhancement for GPE with salt as compared to GPE without salt.

### 3.2 FTIR studies

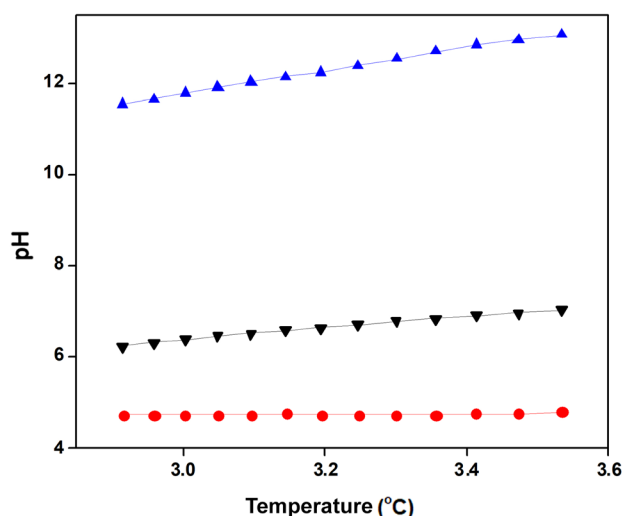
FTIR analysis of GT-based GPEs have been carried out to check the interaction among different components of the gel polymer matrix, i.e., gum, salt and DW. FTIR spectra of GT-based GPEs have been analysed for different gel samples: (a) DW–GT, (b) DW–0.01 M NaOH–GT, (c) DW–0.625 M NaOH–GT. The results are shown in figure 2. The characteristic peaks for DW–GT system are 1021  $\text{cm}^{-1}$  (C–O and C–O–C stretching vibrations), 1051  $\text{cm}^{-1}$  (due to C–O and C–C stretching vibrations of pyranose rings of polysaccharide), 1632  $\text{cm}^{-1}$  (corresponds to C=O and  $-\text{COO}^-$  vibrations that may be due to carboxylic acid groups present in GT) and 3265  $\text{cm}^{-1}$  (OH stretching vibrations of polysaccharide) [9,14–16]. The wavenumber assignments corresponding to different peaks are represented in table 1.

With the addition of NaOH salt in GPEs leads to the appearance of a new peak at 1416  $\text{cm}^{-1}$ , which may be attributed to OH bending vibrations [16,17]. The intensity of the peak increases with the addition of more salt concentration (0.625 M) that may be due to enhancement of free  $\text{OH}^-$  ions provided by the dissociation of NaOH salt, as discussed in the conductivity results. The appearance of new peaks suggests the presence of free ions provided by dissociation of salt due to interaction among the components of gel polymer matrix, i.e., salt (NaOH), solvent (DW) and natural gum (GT).

pH variation of GT-based gel electrolytes has also been studied as a function of temperature in the range of 10–70°C and the results obtained are illustrated in figure 3. Figure 3 reveals that the pH values for DW–GT hydrogel show a

**Table 1.** Some peaks and their assignments of FTIR spectra for DW–NaOH–GT-based gel systems.

DW–GT	DW–0.01 M NaOH–GT	DW–0.625 M NaOH–GT	Assignments	References
1021 $\text{cm}^{-1}$	1021 $\text{cm}^{-1}$	1021 $\text{cm}^{-1}$	C–O stretching (carboxylic acid) resulting from C–O and C–O–C stretching vibrations	[15,16]
1051 $\text{cm}^{-1}$			C–O and C–C stretching vibrations of pyranose rings of polysaccharide	[14]
		1416 $\text{cm}^{-1}$	OH bending	[17]
	1453 $\text{cm}^{-1}$	1453 $\text{cm}^{-1}$	CH, $\text{CH}_2$ and OH in-plane bending in carbohydrate	[16]
1632 $\text{cm}^{-1}$	1632 $\text{cm}^{-1}$	1632 $\text{cm}^{-1}$	Vibrations due to C=O, $-\text{COO}^-$ may be due to carboxylic acid or carboxylate anion form of d-galacturonic acid present in gum tragacanth	[14]
3265 $\text{cm}^{-1}$	3265 $\text{cm}^{-1}$	3265 $\text{cm}^{-1}$	OH stretching vibrations	[9,14,15]



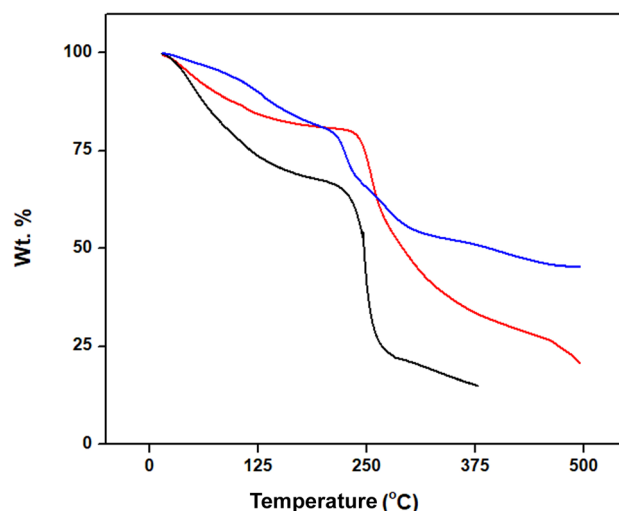
**Figure 3.** Effect of temperature on pH for DW-10 wt% GT (●); DW-0.01 M NaOH-10 wt% GT (▼); DW-0.625 M NaOH-10 wt% GT (▲) based gel electrolytes.

very small decrement (0.06) over the entire mentioned temperature range. Hydrogel containing lower concentration (0.01 M NaOH) of salt show further decrement in pH with the rise in temperature. This pH decrement may be due to the fact that the inclusion of NaOH in gel matrix provides  $\text{OH}^-$  ions, which neutralize the  $\text{H}^+$  ions. Along with this, increase in temperature yields in lowered ionization constant of water, which in turn leads to deprotonation of water [18,19]. However, the prominent decrease in pH with temperature has been observed for higher concentration (0.625 M) of NaOH that may be due to the liberation of more number of hydroxyl ions, which get neutralized with more number of  $\text{H}^+$  ions in gel matrix as discussed earlier. As a result, decrease in pH and conductivity of GPEs/hydrogels are interrelated and show good agreement with temperature.

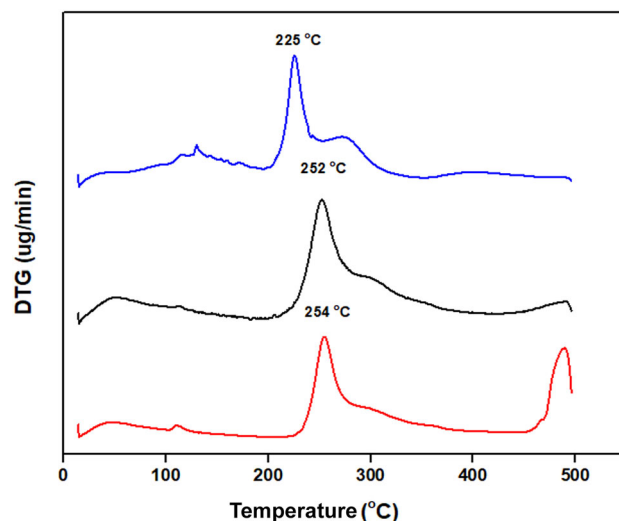
### 3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) studies of prepared samples were performed in order to determine thermal stability as well as to study thermal decomposition of hydrogels. TGA thermograms for the samples have been recorded for different compositions: DW-10 wt% GT; DW-0.01 M NaOH-10 wt% GT; DW-0.625 M NaOH-10 wt% GT and the results are represented in figures 4 and 5. Figure 4 explains the  $T_g$  thermograms/weight loss curves of samples, according to which GT-based gel electrolytes exhibit two decomposition process.

The first stage includes the loss of excess water present in gel matrix as well as the moisture absorbed by natural gum in the temperature range 40–140°C [20,21], as mentioned in table 2. Second stage of thermal decomposition of gel occurs and ends up with a weight loss of 48% in the



**Figure 4.** Weight loss curve of DW-10 wt% GT (red); DW-0.01 M NaOH-10 wt% GT (black) and DW-0.625 M NaOH-10 wt% GT (blue).



**Figure 5.** DTG thermograms of DW-10 wt% GT (red); DW-0.01 M NaOH-10 wt% GT (black) and DW-0.625 M NaOH-10 wt% GT (blue).

temperature range 236–397°C. This decomposition may be due to highly branched heterogeneous structure of GT that possesses the dissipation of side chain groups, such as acidic or ester group [22,23].

Hence it has been observed that DW-GT system is thermally stable only upto 236°C. Further, the incorporation of NaOH salt in gel matrix affects the thermal transition, which lowers  $T_g$  of hydrogel to 223°C at 0.01 M NaOH and 210°C at 0.625 M NaOH. This small decrement in  $T_g$  of gel electrolytes may be due to the complexation of salt with natural gum/polysaccharide that facilitates flexibility of gel network. Along with the above-mentioned fact, the

**Table 2.** Glass transition temperature ( $T_g$ ) and DTG analysis for DW–NaOH–GT system.

Sample	DTG maxima (°C)	$T_g$ (°C)	Temperature range (°C)	Weight loss (%)
DW–10 wt% GT	254	236	40–120	13
			236–397	48
DW–0.01 M NaOH–10 wt% GT	252	223	40–130	27
			223–305	60
DW–0.625 M NaOH–10 wt% GT	225	210	40–140	14
			210–300	24

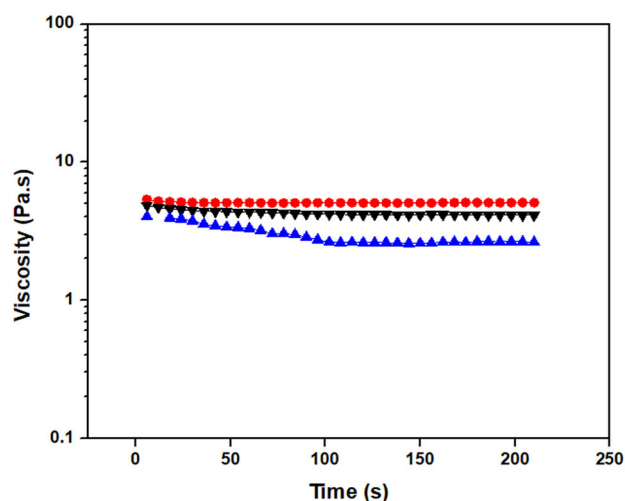
incorporation of NaOH hinders the polysaccharide chain interactions; thus defines the role of salt in gel matrix [24,25].

Figure 5 shows the DTG thermograms corresponding to  $T_g$  for above-mentioned hydrogel systems. DTG maxima has been observed around 254°C for DW–GT system, which is corresponding to the thermal decomposition or  $T_g$  of the gel, as mentioned in TGA studies. This maxima is shifted to 252°C with the incorporation of 0.01 M of NaOH in gel matrix. The increase in salt concentration (i.e., 0.625 M) leads to further decrease in decomposition temperature (or  $T_g$ ) and the DTG maxima shifted to 225°C. Thus, DTG thermograms are in good agreement with  $T_g$  thermograms as well as conductivity results.

### 3.4 Rheological studies

Gel rheology was conducted to investigate the flow behaviour of hydrogels by viscosity measurements under different mechanisms of applied stress. The viscosity of different compositions has been analysed under the application of constant shear rate ( $40 \text{ s}^{-1}$ ) and the results are illustrated in figure 6.

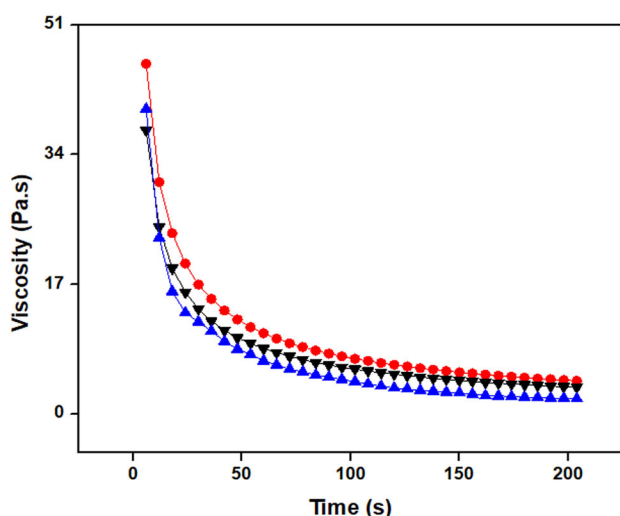
Figure 6 displays the higher viscosity value (5.37 Pa.s) of DW–GT system, as compared to DW–0.01 M NaOH–GT (4.87 Pa.s) and DW–0.625 M NaOH–GT (i.e., 4.03 Pa.s) at constant shear rate of  $40 \text{ s}^{-1}$  after 6 s. Along with this, the hydrogel containing high salt concentration (0.625 M NaOH) shows the maximum viscosity variation with time and least variation is exhibited by DW–GT system. The decrease in viscosity with the addition of NaOH indicates the role of salt, which affects polysaccharide chains interactions and increase its flexibility of gel matrix as mentioned in TGA studies. Polysaccharide chains of GT gets negative charge in DW due to the presence of carboxylate groups that cause the molecular expansion of gum in salt-free solution and thus leading to higher viscosity of the gel electrolyte. But, the presence of positive charged ions (i.e.,  $\text{Na}^+$  ions) provided by the dissociation of NaOH in DW reduces the repulsion among negatively charged gum chains and decreased viscosity values. Also, with an



**Figure 6.** Time varying viscosity (in log scale) at constant shear rate ( $40 \text{ s}^{-1}$ ) for GPEs containing DW–5 wt% GT (●); DW–0.01 M NaOH–5 wt% GT (▼) and DW–0.625 M NaOH–5 wt% GT (▲).

increase in salt concentration (0.625 M NaOH) liberates more number of  $\text{Na}^+$  ions and comes up with further decrease in viscosity values of hydrogel consisting 0.625 M NaOH [26]. Figure 7 represents the viscosity measurements under the varying shear rate ( $0\text{--}50 \text{ s}^{-1}$ ) with the passage of time that shows the reduction in viscosity values of hydrogels with increase in shear rate and thus confirm the shear thinning of hydrogels under the application of increasing stress. The lower viscosity values of different gels under the effect of increasing shear rate may be due to the alignment of random gum chains towards the direction of flow, resulting in less interaction among adjacent gum chains [27].

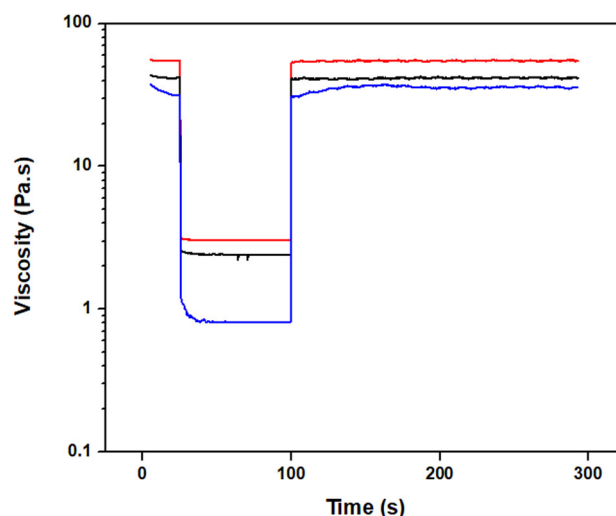
Again, DW–GT system was found to possess larger value of viscosity as compared to other composition that has been already explained to be due to the decrement in gum chains expansion with the incorporation of NaOH. The viscosity values for different gel compositions have been mentioned in table 3. Thus, decreased viscosity of gel samples with the incorporation of NaOH has been reported, which facilitates the ionic mobility and thus supports increase in ionic conductivity of GPEs.



**Figure 7.** Variation of viscosity as a function of time at variable shear rate ( $0\text{--}50\text{ s}^{-1}$ ) for GPEs containing DW-5 wt% GT (●); DW-0.01 M NaOH-5 wt% GT (▼) and DW-0.625 M NaOH-5 wt% GT (▲).

Thixotropic study is an important aspect of gel rheology in order to depict the viscoelastic behaviour of the gel systems that comprised of viscosity measurements by changing shear rate. Variation in viscosity for GT-based GPEs/hydrogels with gel compositions: DW-GT (red), DW-0.01 M NaOH-GT (black) and DW-0.625 M NaOH-GT (Blue) have been measured and the results are shown in figure 8.

A three stage procedure has been pursued including the implementation of shear rate of  $1\text{ s}^{-1}$  at first stage for 25 s followed with the rise in shear rate to  $80\text{ s}^{-1}$  and kept for 74 s during the second stage. Finally, the shear rate was again shifted to  $1\text{ s}^{-1}$  and held for 194 s. It has been observed that the escalation of shear rate to  $80\text{ s}^{-1}$  with the application of shear stress provides



**Figure 8.** Thixotropic analysis of GPEs composed of DW-5 wt% GT (red); DW-0.01 M NaOH-5 wt% GT (black); DW-0.625 M NaOH-5 wt% GT (blue).

depletion in viscosity that is already explained to be due to alignment of gum chains in the direction of flow. Along with this fact, high shear rate provides disintegration of secondary bonds interactions due to the segmental motion of gum chains; thus reduction in viscosity values and gel to sol transition takes place [14,27]. Finally, decrease in shear rate to  $1\text{ s}^{-1}$  yields time-dependent structure recovery of gel matrix, as shown in table 3.

The slower structure recovery ratio at small time interval after shifting shear rate from  $80$  to  $1\text{ s}^{-1}$  (after 10 s) has been reported to be due to the excess time taken by the molecules in motion during reconstruction [28,29]. Overall, GT-based hydrogels have been observed with high structure recovery after 60 s of removing stress, possessing values as 98.92% for DW-GT, 96.87% for DW-0.01 M NaOH-GT

**Table 3.** Viscosity measurements under constant and varying shear rate for DW-NaOH-GT systems.

Composition	Viscosity (Pa.s) after 6 s at constant shear rate ( $40\text{ s}^{-1}$ )	Viscosity (Pa.s) with varying shear rate ( $0\text{--}50\text{ s}^{-1}$ ) at $50\text{ s}^{-1}$	Structure recovery ratio (%) after 10 s	Structure recovery ratio (%) after 60 s	Viscosity (Pa.s) under applied stress (shear rate $80\text{ s}^{-1}$ ) after 5 s	Viscosity (Pa.s) under applied stress (shear rate $1\text{ s}^{-1}$ ) after 5 s
DW-5 wt% GT	5.37	4.35	94.67	98.92	3.2	55.7
DW-0.01 M NaOH-5 wt% GT	4.87	3.5	89.75	96.87	2.6	43.4
DW-0.625 M NaOH-5 wt% GT	4.03	2	64.71	97.97	1.22	37.6

and 97.97% for DW–0.625 M NaOH–GT. This high structure recovery indicates sol to gel transition in gel samples after the removal of applied strain that define the viscoelastic nature of GT-based hydrogels.

#### 4. Conclusions

Ionic conductivity of GPEs has found to be decreased factor-wise with an increase in temperature from 10 to 70°C. pH decrement was obtained with rise in temperature that may be due to the neutralization of hydroxyl ions in gel network. FTIR studies of prepared samples show the complexation of different components of gel matrix by the formation of new peak (1416 cm<sup>-1</sup>) and disappearance of old peak (1051 cm<sup>-1</sup>) after the incorporation of NaOH salt in GT-based GPEs. Thermogravimetric analysis showed that DW–GT–NaOH system is thermally stable upto 225°C at 0.625 M concentration of NaOH. Rheological studies support the ionic conductivity enhancement of gel samples, as it shows decrement in viscosity values with the addition as well as increase in concentration of NaOH salt. Also, high structure recovery of these gel samples and sol ↔ gel transitions indicate their thixotropic in nature.

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