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Synthesis and Rheological Characterisation of the Natural gum Polysaccharide and Acrylic acid based hydrogels

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Abstract:

Gum ghatti and poly (acrylic acid) based hydrogels prepared by free radical polymerization reaction initiated by initiator of potassium per sulphate (KPS) and N, N, MBA used as crosslinker. In this work, we prepared hydrogels by using Gum ghatti as natural gum polysaccharide with a variation of concentration of crosslinker. In rheology characterization, hydrogels systems exhibit the shear thinning flow behavior. Frequency sweep carried out in the linear viscoelastic regime (LVR). Frequency sweep results revealed that the storage modulus increased with angular frequency as compared to loss modulus. Furthermore, the temperature sweep performed at 15 ^{0}C to 95^{0}C. It can be observed that the storage modulus increased as temperature was increasing.

Keywords

Hydrogel, Rheology, Gum ghatti, Degree of Crosslinking, Shear responsive system.

1. Introduction

Hydrogels represent the class of materials which have cross-linked, 3D network and able to absorb the water hundreds times greater than their weight [1]. Another definition of hydrogels, they are three-dimensional crosslinked network, which formed by the homo polymer or copolymer by physical or chemical crosslinking agent and they have ability to absorb the large amount of water and biological fluids [2]. Based on source of polymers, hydrogels may be classified as synthetic, natural, and hybrid hydrogels. Hydrogels prepared by chemical and physical interactions [3]. Compared with other types of biomaterials, hydrogels have the advantages of increase biocompatibility, tunable biodegradability, properly mechanical strength, porous structure, and so on. However, due to the low mechanical strength and fragile nature of the hydrogels, the feasibility of applying hydrogels is still limited [4]. Water absorption ability of hydrogel is key property and hydrogel are able to absorb large quantity of water due to the presence of hydrophilic functional groups in their crosslinked network. Hydrogels have exceptional properties like swelling capacity, soft nature, and elasticity.

Hydrogel can be prepared from various natural polymers such as proteins, DNA, and polysaccharide. Natural gum polysaccharides have number merits over the synthetic polymers like low cost, easy availability, biodegradability, biocompatibility, renewability, and nontoxicity [5-6]. Gum ghatti is a plant gum polysaccharide obtained from the plant Anogeissus latifolia and the backbone of gum ghatti mainly composed of L-arabinose, D-galactose, D-mannose, D-xylose, D-glucoronic acid, and their molar ratio of 48:29:10:5:10 [7]. Past few years, a number of publication published on gum ghatti based hydrogels with different applications like adsorption of saline, drug delivery, dye removal, metal ion removal, conductive hydrogels [8-12].

Crosslinking present in the hydrogel network due to prevent the dissolution of hydrogels. Crosslinking density in hydrogels can be controlled by the concentration of crosslinker. Crosslinkers are hazardous, so it should be removed from hydrogel systems before used in biomedical and tissue engineering. While change in concentration of crosslinker then the crosslinking density in hydrogel network also change and change in the swelling and mechanical property of hydrogels. Thus, crosslinker play crucial role in mechanical properties of hydrogel. Application of polysaccharide based in biomedical and tissue engineering field, requires biodegradable, and proper mechanically strength. Thus, we tried to investigate the influence of crosslinker on gum ghatti and acrylic acid based hydrogels.

The purpose of this work was to assess the formation of less crosslinked hydrogel and investigate the impact of cross-linker on the mechanical properties in terms of rheological characterisation of gum ghatti based hydrogels. To the best of our knowledge, a detailed rheology characterisation of gum ghatti hydrogels not reported before. Gum ghatti and acrylic acid hydrogels prepared by using different

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concentration of MBA as crosslinker and their rheological characterisation discussed here.

2. .Materials and Method:

2.1. Materials and chemicals

Gum ghatti, Acrylic acid used as monomer both purchased from Qualikems (India), Potassium persulphate (KPS) used as initiator purchased from Chemdyes Corporation (India), N.N. Methylene Bis-acrylamide (NMBA) used as crosslinker purchased from Sisco research laboratories (India), Mili-Q water used as solvent.

2.2 Method

Hydrogels prepared by using the reported method in literature [13]. To obtain the less crosslinked hydrogels, 0.5 gm. gum ghatti added in 10 ml solvent in 100 ml of beaker and kept overnight for the better dispersion of gum polysaccharide. To this reaction mixture, definite amount the initiator and crosslinker both added. The reaction allowed to proceeds at 50 ^{0}C with continuous stirring. Finally, the acrylic acid added into the reaction mixture and the reaction allowed to take place at 50 ^{0}C with continuous stirring during 180 mints. Detailed of compositions can be obtained in below table 1

Table1. Composition of hydrogels

Code	H-1	H-2	H-3
Solvent (ml)	10	10	10
Gum ghatti (gm.)	0.5	0.5	0.5
Monomer (moll^{-1} x 10^{-3})	0.291	0.291	0.291
Initiator (moll^{-1} x 10^{-1})	0.122	0.122	0.122
Cross linker (moll^{-1} x10^{-2})	0.643	0.713	1.29
pH	7	7	7

3. Rheology Characterisation

Rheological measurements of the hydrogel systems carried out using Anton Paar MCR 102 Rheometer. For hydrogel systems, plate-plate system was used with a diameter of 25 mm. The gap between the upper plate and sample dish was set at 1 mm. The temperature during the measurements was maintained by an inbuilt peltier system with an accuracy of ± 0.01 ^{0}C. The data obtained by using Rheoplus software.

3.1 Shear viscosity

The shear viscosity measurement carried out at constant shear rates ranging from 0.1 to 100 S^{-1} at 25 ^{0}C of temperature. The shear viscosity measured under disciplined scan of shear rate without large gaps.

3.2 Frequency sweep measurement:

Frequency sweep performed on the gum polysaccharide and acrylic acid hydrogel systems in the linear viscoelastic region from 0.01 to 100 rad/s.

3.3 Temperature sweep:

The viscoelastic properties of gum ghatti hydrogels were investigated using dynamic shear deformation experiments. The evolution of the elastic moduli, viscous moduli, and complex moduli as a function of temperature was investigated and temperature range from 15 °C to 95 °C with heating rate of 10 °C at constant angular frequency of 10 Hz.3.3.

4. Result and Discussion:-

Rheology Characterisation

Shear viscosity

Fig.1 shows the result of shear flow experiments of hydrogel system with moderate crosslinking with crosslinker. The viscosity of the hydrogel systems as the function of the shear rate measured. The result of the all hydrogels shows the strong shear thinning behavior. It can be observing from flow curve results that the viscosity of hydrogels increased due to formation of hydrogel of gum ghatti and PAA. At the lower shear rate, the hydrogel systems display the non-viscous flow behavior. At lower shear rate, the non-covalent interaction forces of hydrogels system

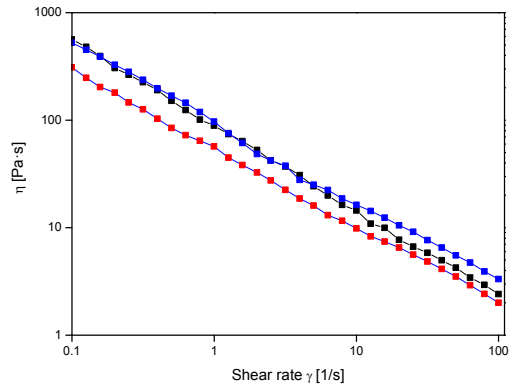

Figure 1, Shear viscosity as function of viscosity. (■) HG-1, (■) HG-2, (■) HG-3

were higher than the shear stress and hydrogel systems were able to retain their structure. At the higher shear rate, the shear stress became the higher than the interaction forces of hydrogels, which repels the interaction forces of hydrogels then hydrogel shows the shear thinning behavior. In flow curve, shear-thinning behavior of hydrogels due to the interaction forces of hydrogels were higher than

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shear stress at the initial stage, while later at higher shear stress, interaction forces became the lower.

Frequency sweep test:

A frequency sweep measurements used to investigate the viscoelastic characteristic of hydrogels. The elastic modulus (G′) is represent the reversibly deformation energy, whereas the viscous modulus (G″) represent the irreversible energy dissipated during flow.

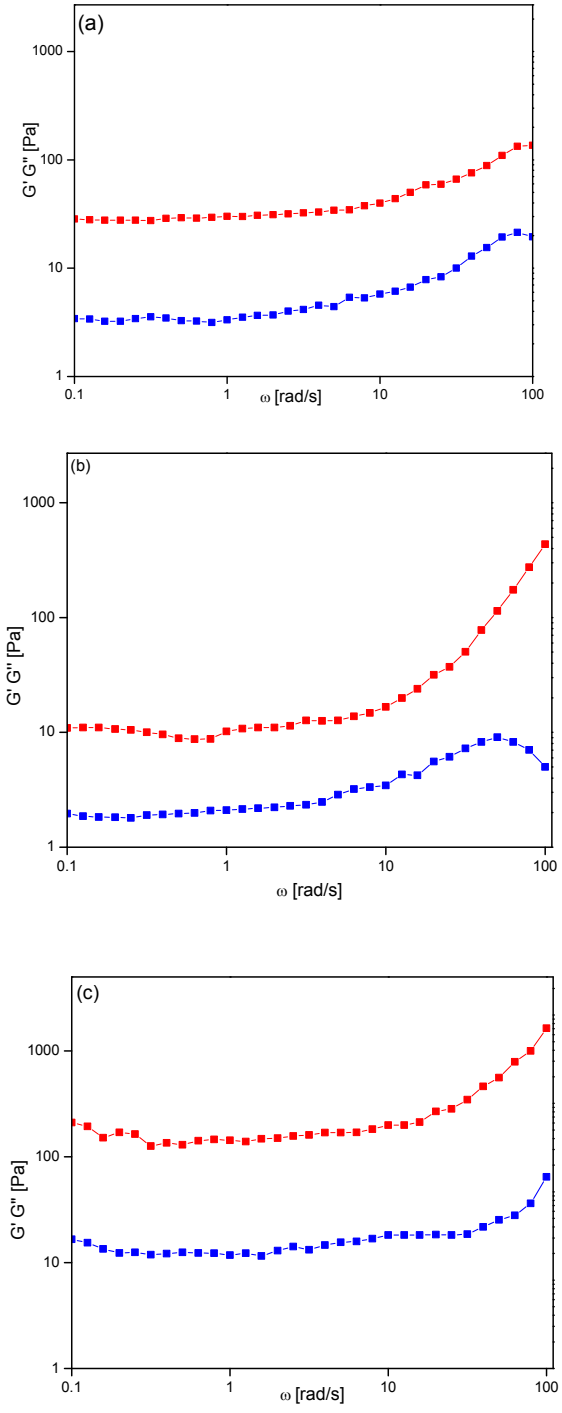

Figure 2 Frequency sweep studies, (a) HG-1, (b) HG-2, (c) HG-3, (■) Storage modulus, (■) Loss modulus

In Fig. 2 ((a) to (c)), shows reliability of elastic and viscous modulus with angular frequency for gum polysaccharide based hydrogels. We investigated the effect of concentration of crosslinker on the viscoelastic properties of gum polysaccharide based hydrogels

The data of results reveals that the values of G′ and G″ increased with increase the frequency. For all hydrogel systems, the storage modulus (G′) was higher than the loss modulus (G″) that means the elastic component dominant over the viscous component. Therefore, samples displayed the strong gel like behaviour [14]. It can be also observed that from the entire range of frequency G′>G″ thus, the systems displayed the polymer like viscoelasticity properties [15]. In fig. 2, Frequency sweep results indicated that as concentration of cross linker with particular limit increase, the value of storage modulus became higher at higher frequency because of at higher concentration of crosslinker in the hydrogel systems, which enhance the mechanical properties.

This type of behaviour of gum polysaccharide based hydrogel system expected. The length of polymeric chain and nature of imposed motion impact on the extent of viscoelastic response of polymeric chains [16]. Hydrogels with the lower crosslinked network have a long polymeric chain, but hydrogels with highly crosslinked having a short polymeric chain. When less crosslinked hydrogels subjected to higher frequency ranges, long polymeric chains fail to readjust themselves in the time scale of the imposed motion, and therefore stiffen up, which characterized by an increase in G′ and G″ [17-18].

Complex viscosity:

In Fig.3, Shows the complex viscosity versus angular frequency for gum polysaccharide based hydrogels. Complex viscosity measurement carried out to understand the viscoelastic nature of hydrogel systems. It can be observed that the complex viscosity of all gum polysaccharide based hydrogel systems exhibit deterioration with the frequency. The complex viscosity decreases with increase of angular frequency denote the gel-like behaviour of hydrogel systems [19]. The deterioration in complex viscosity investigated with increasing the concentration of crosslinker. The deterioration in complex viscosity can be explained by on the bias of entanglements in polymer chains. At low distortion rate, polymeric

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chains require more time to relax but it can be decreased by approaching the sweeping frequency. Thus, decrease in the complex viscosity [20].

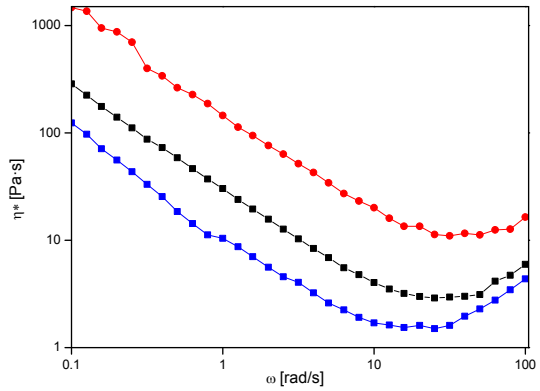

Figure 3, Complex viscosity as a function of viscosity. (■) HG-1, (■) HG-2, (■) HG-3

Temperature Scan:-

In fig. 4, shows the thermal scanning rheological measurements of gum polysaccharide based hydrogels. The storage moduli (G') and loss moduli (G'') were determined as a function of temperature for hydrogel with different concentration of crosslinker. In temperature scanning, the sigmoid graph obtained. At lower temperature, both storage and loss modulus are slightly dependent on the temperature. When the temperature starts to increase above 50 ^{0}C, both storage and loss modulus started slightly decrease and sudden start to increase at higher temperature. While transition temperature for hydrogel samples are not in same but not too much difference in them, so the concentration of crosslinking slight affect the transition temperature but not too much. The results show that elastic modulus was (G′) higher than viscous modulus and above transition temperature that indicating the the elastic nature of hydrogels. The results of graph revealed that the hydrogels with higher crosslinker concentration displayed highly elastic behavior at higher temperature.

5. Conclusion

The present work investigated the influence of crosslinker on the rheological properties of gum ghatti and acrylic acid hydrogels. Flow behaviour experimental data indicated that hydrogels displayed the shear thinning behaviour as increasing the shear rate. From frequency sweep results revealed that the hydrogels having an elastic nature and elastic of nature of hydrogels improved by increasing the concentration of crosslinker. The Complex viscosity also decreased with increased the concentration of crosslinker under measured condition. The temperature-scanning shear rheological showed that

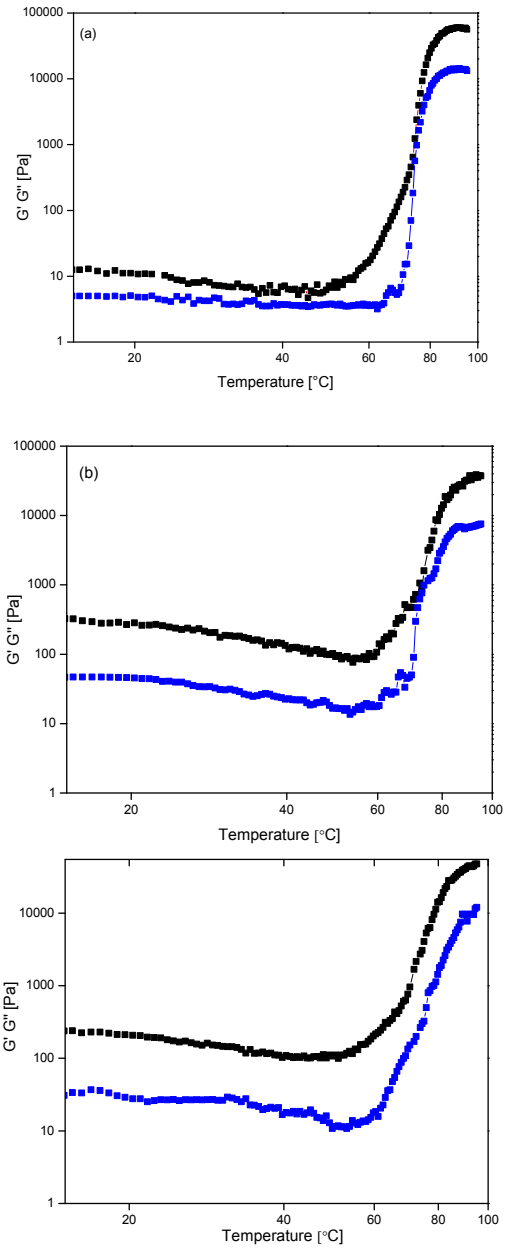

Figure 4, Temperature sweep studies. (a)HG-1, (b) HG-2, (c) HG-3, (■) Storage modulus, (■) Loss modulus

the hydrogels have excellent elastic response at higher temperature. According to the rheological data, such hydrogels should be good candidate for the application in the tissue engineering and biomedical field. After the evolution of biological property, conclusion can be drawn.

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