

# Water Management within Tragacanth gum-g-polyitaconic Acid Hydrogels

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## Abstract

In our investigation, we have studied the interaction of the water molecules with the hydrophilic sites in itaconic acid grafted Tragacanth gum copolymer. The water existed in two different states within the hydrogel matrix. There is one fraction of water which has close interaction with functional groups and does not undergo freezing during cooling. Besides, this the other type of water undergoes thermal transitions and freezes at  $-50^{\circ}\text{C}$ . The water management within the grafted matrix seems to be strongly governed by hydrophilicity, crosslinked density and functionality. The water uptake by the hydrogel increased significantly as the degree of grafting increased, in spite of the increasing crosslink density of the matrix. Results have been explained in terms of the carboxylic groups and their ionization which has an overriding influencing the hydrogel structure leading to a more amenable structure for the water diffusion. Copyright © VBRI Press.

**Keywords:** Tragacanth gum, itaconic acid, graft copolymer, water management

## Introduction

Hydrogels are hydrophilic polymers and have an inherent feature of water absorption from an aqueous medium. These materials absorb significantly large amount of water by virtue of the strong hydrogen bonding of the functional group with the water molecules, thereby producing a 3D network of polymer chains. The interaction of water with the hydrogels is of significant importance for several important domains in biotechnology where diffusivity and controlled release of a bioactive component becomes important [1-4]. This opens up a beautiful domain of smart biomedical engineering. Water may diffuse into the matrix but their interaction with the ionic sites may be different depending upon the chemical nature of the hydrogel. Most of the hydrophilic functional groups fall as the -OH, -COOH, -SO<sub>3</sub>H, -CONH<sub>2</sub> and NH<sub>3</sub> and hence the water interaction will be determined by the nature of these functional groups along the polymer chain.

Several studies have been reported on the water interaction within the hydrogels [5-8]. It is found that the water exists in three different forms as investigated by differential scanning calorimetry (DSC). The first one is *non-freezing water* which remains tightly bonded to the core of the functional groups and does not show up in DSC investigations as this type of water does not

follow phase transitions. The other type of water does not have direct association with the hydrophilic groups and known as *freezing free water* lying within the amorphous zone. The third type of water remains at the interface *between non-freezing and freezing free water* and is known as *freezing bound water*. It was observed that the *non-freezing water* per ionic site remains almost identical in different types of hydrogels, but the *free water* content increases as the graft levels increase in the hydrogel matrix. An excellent review on states of water has been recently published [9].

Polysaccharides have a very different architecture and chemical composition. The interaction of water with the polysaccharides may alter with the nature of the chemical functionalization. However, the situation becomes a bit complex as both the inherent hydroxyl and the grafted hydrophilic groups show affinity to the water molecules. Therefore, it becomes difficult to investigate the fraction of water being absorbed by each of the functional groups. We have been working on the development of functional hydrogels by graft polymerization of itaconic acid on TG by microwave irradiation and chemical initiation [10, 11]. We have been working on the development of tragacanth gum-g-polyitaconic acid hydrogels which may exhibit pH-sensitive nature in a system. These materials show

smart behaviour by opening up their structure at colon pH, thereby triggering the release of an anticancer drug. Water in such hydrogels plays an important role in defining the diffusion of the drug across its matrix and hence needs a careful look at the interaction of the water with hydrogel matrix. Our interest is to look at the nature of the interaction of water with the hydrophilic groups and the water management pattern within the graft copolymer (Tragacanth gum-g-polyitaconic acid) structure that develops by the grafting process. The DSC has been used to observe the transitions for the water management within the hydrogel matrix.

## Materials and methods

### Materials

Tragacanth gum (TG) was purchased from Loba Chemie, Pvt. Ltd. India and was purified by dissolution in water followed by re-precipitation in acetone to remove the impurity. The monomer itaconic acid was supplied by Sigma Aldrich, India. Potassium persulfate (KPS), heptane and acetone were purchased from Merck, India. Ultra-pure water was used throughout the experimental work.

### Graft polymerization

The graft polymerization of itaconic acid (IA) on TG was carried out by using KPS as the initiator. The monomer was added and the system was deaerated by using nitrogen flushing for five minutes. The tube was placed in a constant temperature water bath for a desired period. After the grafting reaction, the content in the tube was precipitated in acetone. The resultant TG-g-PIA (GTG) was dried under vacuum oven at 80°C to a constant weight. The degree of grafting was determined as per the following equation [10].

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100$$

where,  $W_o$  and  $W_g$  are the weight of the virgin TG and the GTG, respectively.

### Gel content determination

The gel content of the samples was measured by dissolving samples in aqueous system at 80°C for 6h. Subsequently, the content in the beaker was filtered, dried and weighed. The gel fraction was obtained as the amount of undissolved content with respect to the original weight of the hydrogel [12].

$$\text{Gel Content (\%)} = \frac{W_o - W_g}{W_o} \times 100$$

where,  $W_o$  and  $W_g$  are the weight of the before and after the dissolution, respectively.

### Swelling measurements

Vacuum dried samples were used for the swelling measurements. Samples were emerged in the deionised

water at ambient temperature of  $25 \pm 2^\circ\text{C}$  for 16 h. Samples were taken out, wiped with a tissue and were weighed. The swelling was calculated as per the following equation [12].

$$\text{Swelling (\%)} = \frac{W_s - W_o}{W_o} \times 100$$

where,  $W_o$  and  $W_s$  the weight of the dry and the swollen samples, respectively.

### Differential Scanning Calorimetry (DSC)

DSC analysis was conducted by using a TA system in the temperature range of  $-50$ – $40^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$  under nitrogen atmosphere. The sample was cooled down to of  $-50^\circ\text{C}$  and kept on hold for 2 minutes at the same temperature. The thermograms was run at a heating rate of  $5^\circ\text{C}/\text{min}$  up to  $40^\circ\text{C}$ . The heat of melting,  $\Delta H_{f(\text{ice})}$  of the sample was obtained from the thermograms. The amount of water in the sample was calculated from the following equation by using  $\Delta H_{f(\text{ice})}$  of  $334 \text{ J/g}$  as the heat of melting of the pure ice [5].

$$\text{Freezing Water (g/g)} = \frac{\Delta F_{f(\text{DSC})}}{\Delta H_{f(\text{ice})}}$$

## Results and discussion

The grafting of IA on TG leads to the development of a functional copolymer which shows high swelling in aqueous system (as shown in Fig. 1). The matrix capacity for water absorption increases from 165 to 320% with the increase in the grafting from 22 to 104%. Looking at the chemical composition of the TG graft copolymer, the absorption of the water may be assigned to the interaction with hydroxyl and carboxyl groups together.

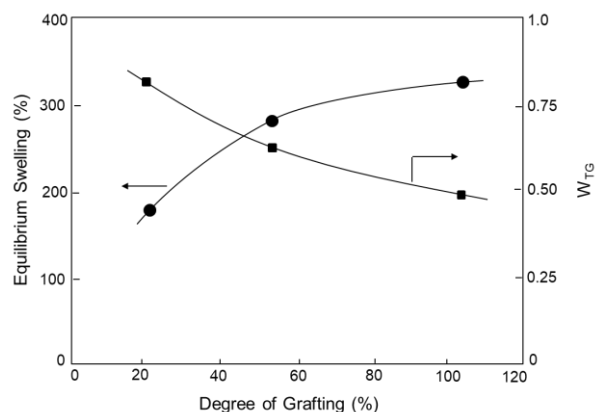
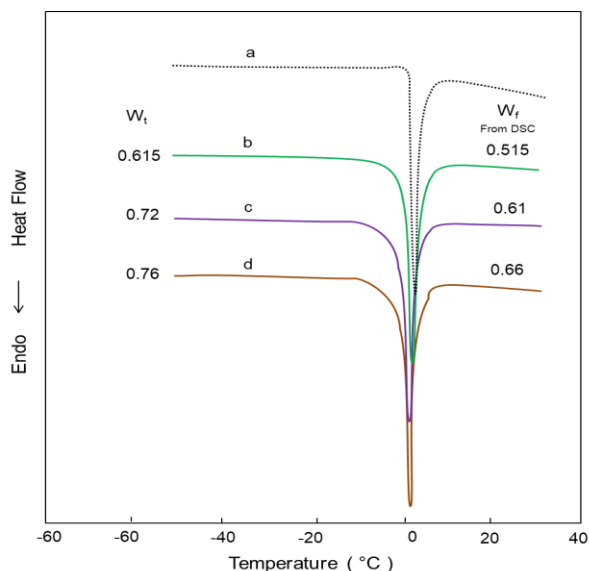


Fig. 1. Variation of the equilibrium swelling and the TG weight fraction with the degree of grafting in GTG.

An interesting scenario originated from the DSC studies of hydrogels with different degrees of grafting. The samples were analyzed by freezing the water within the matrix at  $-50^\circ\text{C}$  and subsequently running the thermograms up to  $40^\circ\text{C}$  to observe melting of the frozen ice. A DSC run for deionized water was carried out to have a comparative view of the thermograms for

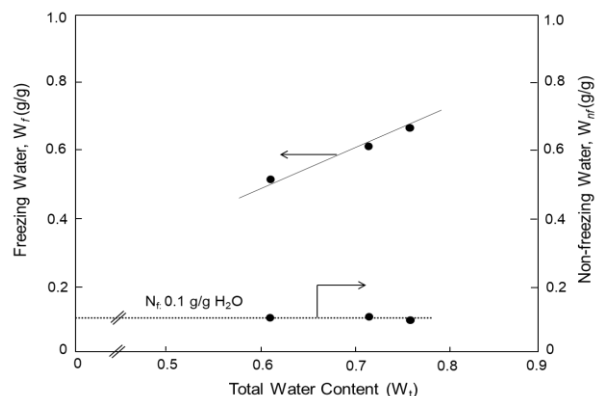
water within the hydrogel (**Fig. 2**). All thermograms show the melting  $\sim 0.8$ - $1.4$  °C irrespective of the degree of grafting. The heat of melting from the thermograms led to the water content of 0.515, 0.61 and 0.66 g/g for the hydrogels with degree of grafting of 22, 52 and 104%, respectively. However, the total water within the hydrogel, as observed by gravimetric was 0.615, 0.72, 0.76 g/g, respectively.



**Fig. 2.** DSC thermograms of (a) pure water; (b) GTG<sub>22</sub>; (c) GTG<sub>52</sub>; (d) GTG<sub>104</sub>

This suggests that the hydrogels have a fraction of water that does not undergo freezing during the cooling of the matrix up to  $-50$ °C and hence is not reflected during the melting of the frozen water within the hydrogel. This indicates that the hydrogels have two types of water molecules; i.e., the first type is confined to the core of the hydrophilic groups along the chain and does not freeze at all and may be termed as non-freezing water. The other type of water forms secondary layer as the free water domains and is mobile. This undergoes freezing as well as melting during the DSC run and may be termed as the freezing water.

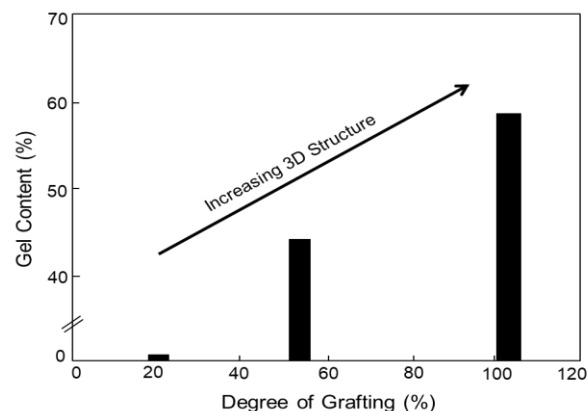
Some of the studies have observed that the freezing water has two different types of states, freezing free and freezing bound water, as evident from the dual peak in the melting reason. Interestingly, we observed only one peak during the melting process and hence may state that the hydrogels in our system do not have such a division of the freezing water. Water with dual states has also been observed by several authors in different hydrogels [13, 14]. The variation of the freezing and nonfreezing water with the total water content is presented in **Fig. 3**. The freezing water varies with the graft levels, but the non-freezing water remains the same for all the hydrogels with different degrees of grafting [15]. This water amounts to be 0.1 g/g for all the hydrogel samples. This suggests that the core water which is bonded to the hydrophilic sites is not affected by the graft levels and only free water varies in the system.



**Fig. 3.** Variation of freezing water and non-freezing water with the total water content in hydrogel.

The water uptake behavior of the samples seems to be fallout of the cumulative effect of the three independent factors, but contributing independently to the interaction of water molecules with the polymer chains. These are *chain hydrophilicity*, *crosslink density* and *functionality*. Interestingly, an increase in the grafting is accompanied by the decrease in the weight fraction of TG in the hydrogel (**Fig. 1**). It may therefore be proposed that the water content increase is largely influenced by the increase in the polyitaconic acid (PIA) in the hydrogel matrix. This affirms that even if the inherent hydroxyl fraction in the copolymer is reduced, the water management within the matrix is favorably influenced by the presence of the PIA.

The crosslinked density of the grafted hydrogel increases as the degree of grafting increases. The gel content increases from 4% to 58% for graft level of 104% (**Fig. 4**). Crosslink density is an unfavorable factor for water absorption within a hydrogel. The presence of such structures reduces chain mobility significantly and hence water diffusivity may be slightly affected. At low graft level, less number of chain are crosslinked and hence the molecular chain mobility may be affected very little as the structure still has interconnectivity for water penetration. The high level of gel formation (for 104% grafting) would certainly lead to a matrix where the water penetration will be difficult due to the reduced chain mobility within the matrix.



**Fig. 4.** Variation in gel content with the degree of grafting.

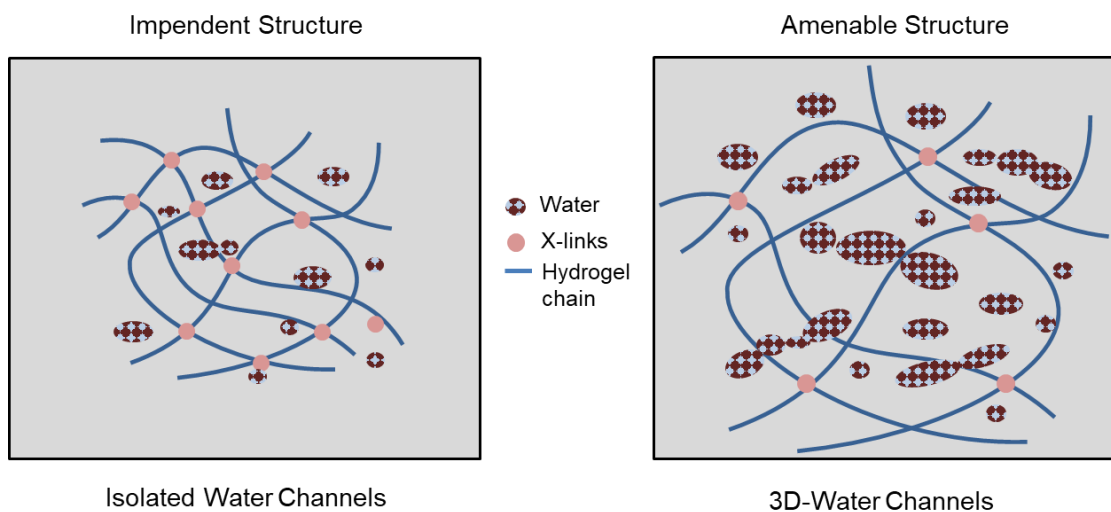


Fig. 5. Schematic representation of the water channel formation in TG and GTG matrix.

It may therefore be understood that with the TG fraction decrease to a level of 49% (at 104% grafting), the hydroxyl functionality also diminishes, significantly. If we look at the combined influence of the hydroxyl group reduction and the enhanced crosslink density, the water penetration within the hydrogel matrix will be expected to decrease significantly. However, the scenario is different where the water uptake instead is significantly enhanced. This shows the role of the carboxyl functionality of PIA grafts which overpowers the negative impact of these two factors and influences the water penetration in a favourable manner (Fig. 5).

It is important to mention that our earlier studies have revealed amorphous nature of these grafted hydrogels. The presence of PIA introduces carboxyl functional groups which exhibit high hydrophilicity and have a tendency to ionize at a pH higher than 4.6, leading to the pH sensitivity of the copolymer. The carboxyl groups in the hydrogel would therefore form  $\text{COO}^-$  and hence would exert strong repulsive action among the chains. This would allow chains to move away from each other and would create space for the water to diffuse in. This, as a result, would enhance the swelling capacity of the GTG hydrogels, significantly. These materials exhibit interesting feature of smartness in terms of controlled drug delivery at the required site depending on the pH of the system. These materials in nanoform may provide excellent route to the oral administration of the anticancer drugs such as cisplatin at the colon site.

## Conclusion

The water management within the hydrogel matrix is governed by a cumulative effect of physical and chemical parameters. The association of the water and its interaction with the hydrogel chains is very important. The nature of the functional groups has a profound influence on the hydrogel capacity towards water absorption. It was observed that the hydrogels

have an inherent fraction of water which behaves differently than the rest. This water does not freeze even at  $-50^\circ\text{C}$  and hence cannot be identified by DSC melting thermogram. Rest of the water behaves almost identical to the free water and undergoes thermal transitions of freezing and melting process. It is a cumulative effect of the *chain hydrophilicity, crosslink density and functionality* that play a significant role in the water management depending on the impact of the individual factor. It seems that the carboxyl functionality overpowers the negative impact of the loss of hydroxyl and crosslinking of chains by providing a very receptive structure due to ionization in neutral pH. Water channelization may be the reason that the hydrogels show higher absorption in PIA grafted TG matrix.

## References

- Chandrika, K.S.V.P.; Singh, A.; Rathore, A.; Kumar, A.; *Carbohydr Polym.*, **2016**, *149*, 175.
- Kuang, J.; Yuk, K.Y.; Huh, K.M.; *Carbohydr Polym.*, **2011**, *83*, 284.
- Varnier, K.; Vieira, T.; Wolf, M.; Belfiore, L.A.; Tambourgi, E.B.; Paulino, A.T. *Int. J. Biol. Macromol.*, **2018**, *120*, 522.
- Saruchi; Kaith, B.S.; Jindal, R.; Kapur, G.S.; Kumar, V.; *J. Chin. Adv. Mater. Soc.*, **2014**, *2*, 40.
- Gupta, B.; Haas, O.; Scherer, G.G.; *J. Appl. Polym. Sci.*, **1995**, *57*, 855.
- Guan, L.; Xu, H.; Huang, D.; *J. Polym. Res.*, **2011**, *18*, 681.
- Li, W.; Xue, F.; Cheng, R.; *Polymer*, **2005**, *46*, 12026.
- Ping, Z.H.; Nguyen, Q.T.; Chen, S.M.; Zhou, J.Q.; Ding, Y.D.; *Polymer* **2001**, *42*, 8461.
- Gun'ko, V.M.; Savina, I.N.; Mikhalovsky, S.V.; *Gels* **2017**, *3*, 37.
- Verma, C.; Negi, P.; Pathania, D.; Sethi, V.; Gupta, B.; *Polym Int* **2019**, *68*, 344.
- Pathania, D.; Verma, C.; Negi, P.; Tyagi, I.; Asif, M.; Kumar, N.S.; Al-Ghurabi, E.H.; Agarwal, S.; Gupta, V.K.; *Carbohydr. Polym.* **2018**, *196*, 262.
- Anjum, S.; Arora, A.; Alam, M.S.; Gupta, B.; *Int. J. Pharmaceut.*, **2016**, *508*, 92.
- Wang, Y.; Tan, G.; Zhang, S.; Guang, Y.; *Appl. Surf. Sci.* **2008**, *255*, 604.
- Müller-Plathe, F.; *Macromolecules*. **1998**, *31*, 6721.
- Khurma, J.R.; Rohindra, D.R.; Nand, A.V.; *J. Macromol. Sci. A: Pure Appl. Chem.* **2006**, *43*, 749.