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Modification of Xanthan Gum with Styrene and Investigation of its Rheological Properties

P.T. Kusherova*[a], El-Sayed Negim[b,c], Khaldun M. Al Azzam[d], Zh. S. Mukatayeva[e], A. K. Baidullayeva[f], Moshera Samy[g]

[a]*School of Chemical Engineering, Kazakh-British Technical University, Almaty, Kazakhstan.*
[b]*School of Materials Science and Green Technologies, Kazakh-British Technical University, St. Tole bi, 59, Almaty 050000, Kazakhstan.*
[c]*School of Petroleum Engineering, Satbayev University, 22 Satpayev Street, Almaty 050013, Kazakhstan*
[d]*Department of Chemistry, School of Science, The University of Jordan, 11942 Amman, Jordan.*
[e]*Institute of Natural Science and Geography of KazNPU named after Abai, Almaty, Kazakhstan*
[f]*Department of Engineering disciplines and good practices, School of Pharmacy, Kazakh National Medical university named after S.D. Asfendiyarov*
[g]*Polymers and Pigments Department, National Research Centre, 33 El Buhouth St., Dokki, Giza 12622, Egypt.*

Abstract

A "green" polymer made by bacteria, xanthan gum has several applications in both the food and drug industries. Because of its harmlessness, xanthan gum is frequently used in other fields after quality improvement through modification. This article describes the grafting process of xanthan gum with styrene and investigates the rheological properties of the modified (grafted) copolymer. For copolymerization, different ratios of xanthan and styrene compositions (XG: St - 1:1.6, 1:5, and 1:8 w/w%) were used. The FTIR spectra of XG-g-St revealed an increase at 1120 cm^{-1}, indicating the formation of additional ether groups due to the St and XG interaction. The rheology properties were investigated at 30, 60, and 80°C. The shear stress of XG dropped from 30 to 80°C, with a maximum shear stress value of 8 Pa at 30°C and a minimum value of 5 Pa at 80°C.According to the findings, grafted with styrene xanthan gum has higher shear stress and better resistance to temperature in comparison with un-modified pure xanthan gum. Due to the grafting new side chains and bonds appear on polymer molecules which affect its viscoelasticity. These findings could be useful in a variety of fields, including oil recovery and construction.

Keywords: Copolymerization, Shear stress, Xanthan gum, Styrene, Rheology

1. Introduction

Multifunctional, safe for the environment, and healthy materials are preferred in every field of work. Xanthan gum, a biopolymer, is one of the safest and most multifunctional materials[1,2]. Xanthan gum is considered a polysaccharide polymer produced from biological origin that weighs approximately 2.65 × 106 Da[3]. Because of its natural origin and safety (Figure 1), xanthan gum is a valuable product[2]. The bacteria Xanthomonas campestris makes this biopolymer[4,5]. It is made up of a 1,4-glycosidic bond-linking the main chain and a trisaccharide side chain including mannose as well as glucuronic acid[6].

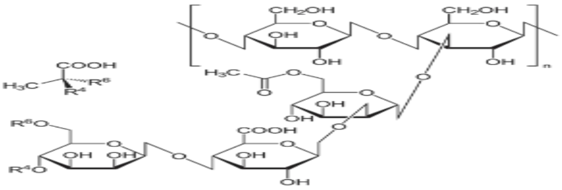

Figure 1. The chemical structure of xanthan gum.

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*Corresponding author e-mail: partykush@mail.ru.; (P.T. Kusherova).
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Xanthan gum has an extensive range of applications, varying starting the food industry to extraction of oil. It is considered one of the valuable materials owing to its biodegradability nature, safety for the environment and organisms, and desired properties such as moisturizing, thickening, stabilizing, and wetting, as well as resistance to various environmental conditions such as pH and temperature[2,5,7].Apart from these benefits, xanthan gum has the following disadvantages: it is susceptible to degradation by bacteria, and the thermal transition temperature of xanthan gum salt-free solution is about 40°C when compared to a salt-containing xanthan gum solution of concentration equal to 0.5% xanthan gum that dissolved in 1% NaCl solution, where the thermal transition occurs at significantly higher temperatures, typically exceeding 90°C. Gums' drawbacks can be improved by changing them including chemical derivatization as well as graft copolymerization. Modification of polysaccharides frequently results in enhanced resistance to degradation, high viscosity, and shear-resistance, and electric and other properties. Additionally, the modified polymers could find extensive use as flocculating agents, drug delivery vehicles, drilling additives, toxic heavy metal and dye adsorbents, sand-binding materials, everyday chemicals, thickeners, macromolecular surfactants, and electrical biomaterials[8,9].

Xanthan exists in water in two different states: a stiff state at low temperatures and a flexible state at high temperatures[10]. Its bulk viscoelasticity decreases after thermal treatment while its interfacial viscoelasticity enhanced, allowing it to act independently. However, after the hydrophobic modification of xanthan, its elasticity improved even after thermal treatment. The high stiffness of xanthan chains prevents hydrophobic fragments from forming associations. In contrast, xanthan in its disordered conformation demonstrated gel-like behavior with no chain relaxation[9].

Solubility[11], rheology[12], stability[13], and other properties are easily changed by affecting chemical methods such as copolymerization[14,15],using chemical substances such as acids and surfactants for treatment[11,15,16], and biological methods as fermentation[17,18,19].All these methods can be used to modify xanthan gum. The current work concentrates on the rheological properties of xanthan grafted with styrene.Styrene (phenylethylene) is a key petrochemical product used to make polymers (polystyrene, synthetic rubber) and copolymers (high-impact polystyrene). Despite its toxicity,styrene is used to manufacture a wide range of materials, including polystyrene plastics, styrene-butadiene rubbers, paints and varnishes, adhesives, ABS plastics, thermoplastic elastomers, and as a solvent for polyesters and polyester resins[20]. In 2010, approximately 25 million tons of styrene were produced, and approximately 35 million tons by 2018[21].

The current study aims to prepare grafted xanthan using styrene. Additionally, to determine the best grafting ratio. XG-g-St was prepared with various ratios of XG and St compositions. An initiator (potassium persulfate) was used to initiate the copolymerization process. For characterization purposes, rheometer and Fourier transform infrared spectroscopy (FTIR) were utilized. Furthermore, the current work examines the rheological properties of XG-g-St as well as the influence of using various temperatures and styrene composition ratios on its rheological properties.

2. Experimental

2.1. Materials

Styrene (St), potassium persulfate($K_2S_2O_8$), and biopolymer xanthan gum (XG) were purchased from Sigma-Aldrich Chemical Co. (USA).

2.2. Grafted xanthan gum synthesis

Grafting was used to make copolymers XG-g-St (1:1.6, 1:5, and 1:8 w/w, %). For a total weight of 0.60 g, the xanthan gum was weighed and then dissolved in 100 mL of distilled water. It was then placed into a 250 mL volumetric flask and mechanically agitated at 350 rpm while 0.5 g of potassium persulfate solution was added. Then, during the stirring at 65°C in the water bath, the required amount of styrene (St) monomer was added dropwise within 25 minutes. The stirring procedure was extended for 3 hours when the formation of new polymer could be seen.

2.3. Measurements

FT-IR Spectrometer, model Nicolet iS10 was used for the study of polymers functional groups. Bohlin rheometer, model Rheolab QC was used for measuring the rheological properties.

Two measurement systems—the Cup Stainless (25 mm) and the Cone Plate (CP440 mm)—were used to test the samples' viscosities by modified XG. The viscometer analysisamended the following measurements: range (linear), 10 secintegration time, 10 sec delay time, proportionality, ramp dir (up), and isothermal temperature mode operated at 25°C. The start shear was changed to 0.08 S^{-1}, while the end shear was changed to 12.75 S^{-1}. The creep analysis was carried out under the following conditions: 1 Pa stress, 100 seconds creep time, 50 seconds recovery time, and isothermal temperature mode at 25°C.

4. Results and Discussion

4.1. FTIR analysis

Figure 2 describes the FTIR spectrums of XG and XG-g-St. There are a few XG peaks attributed to the -OH group (3300 cm^{-1}), the carbonyl group (1630 cm^{-1}), and the ether group (1025 cm^{-1})[22,23]. The grafting polymerization of St onto XG (XG-g-St) caused a reduction in the frequency stretching peak of -OH and C=O in the XG-g-St spectrum. Furthermore, the spectrum of XG-g-St increased at 1120 cm^{-1}, indicating that other ether groups were formed, as a result of the reaction between St and XG.

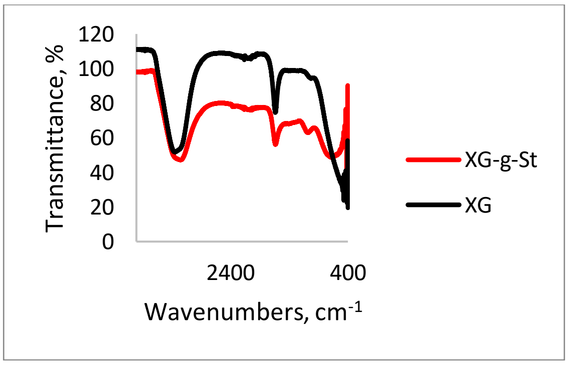


Figure 2. FTIR-spectrums of XG and XG-g-St

4.2. Rheological analysis

Figure 3 describes how XG viscosity and shear stress change with shear rate and temperature. The shear stress increased as the shear rate increased. Because XG operates as a fluid that thins shear in a non-Newtonian manner, curves are rounded to the shear stress axis.

Both the composition of the liquid and the temperature have an impact on the flow behavior of non-Newtonian fluids[24].

From 30 till 80°C, the shear stress of XG decreased, reaching a highest shear stress value of 8 Pa at 30°Cand a lowest shear stress value of 5 Pa at 80°C.

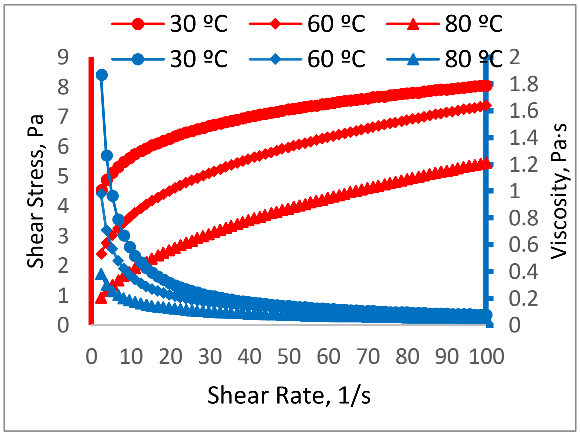


Figure 3. Viscosity and shear are dependent on the shear rate for XG at different values of temperatures.

The viscosity of XG decreased as the shear rate increased (Figure 4). The decrease in viscosity is caused by a variety of factors, including particle deformation, non-spherical particle orientation, polymer chain orientation in the flow direction, and chain deformation[25].

Figure 5 shows the impact of temperature on the shear stress and viscosity of XG-g-St (1:5 w/w %) when the shear rate is varied. Shear stress rose as shear rate increased, but viscosity dropped. When the temperature dropped from 80 to 30°C, the grafted copolymer also showed an increase in shear stress. The grafted copolymer's maximum shear stress (13 Pa) was reached at 30 °C, while at 80°C it had the lowest shear stress (8 Pa).

As a result, XG-g-St possesses greater shear stress and viscosity than un-grafted xanthan (XG). This is because the XG-g-St network structure is branched, cross-linked, and three-dimensional[26]. Theviscosity of polymers changed slightly, it reached about 0.1 Pa·s.

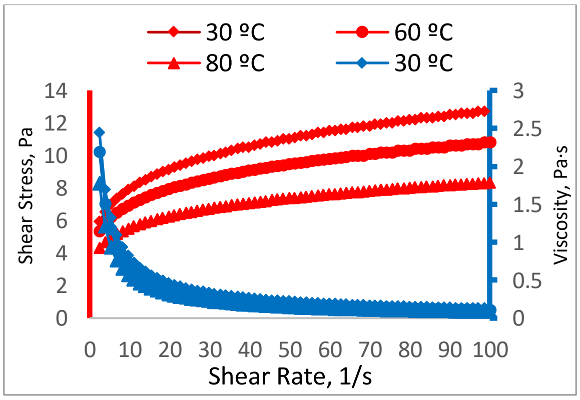


Figure 4. Viscosity and shear stress dependence on the shear rate for XG-g-St at different values of temperatures

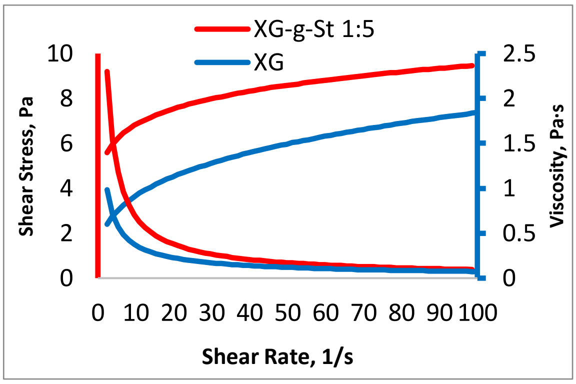


Figure 5. Viscosity and shear stress dependence on the shear rate for XG-g-St and XGin comparison (at 25 ºC).

A variety of factors influence the rheological properties of polymer solutions, including copolymer type, composition ratios, and concentration of polymer. Figure 6 describes the rheological properties of XG-g-St in various ratios at 60ºC. The grafted copolymer's XG-g-St viscosity and shear stress increased as the St ratio did. The XG-g-St 1:8 w/w% showed the maximum shear stress (11 Pa), while the XG-g-St 1:1.6 w/w% showed the lowest shear stress (8 Pa), at 60 ºC.

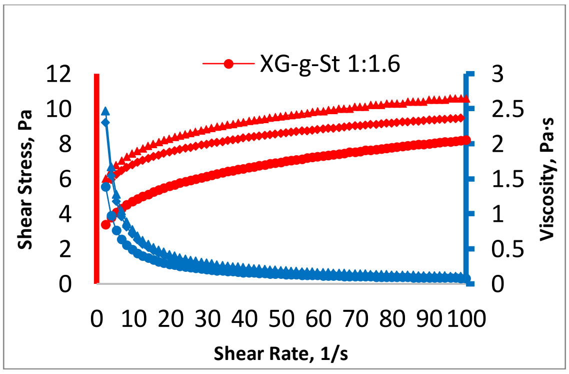
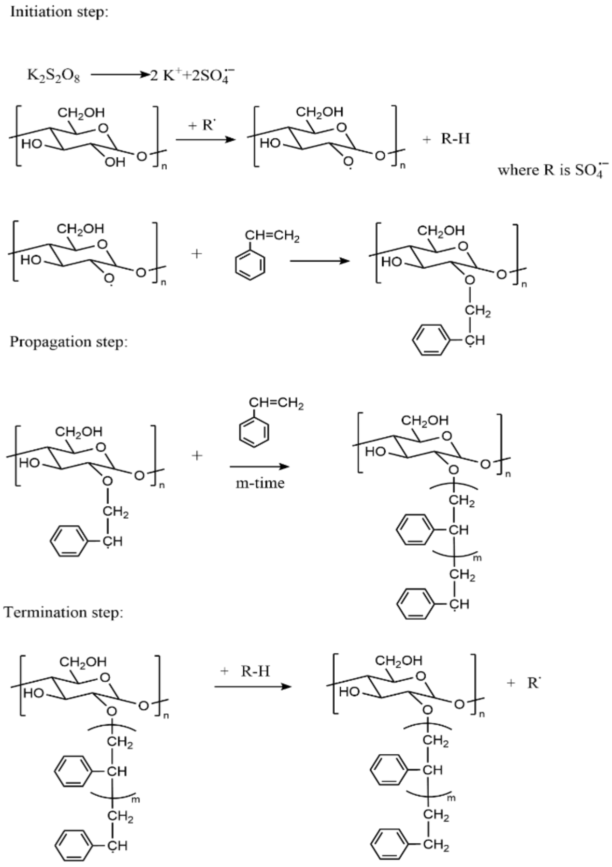


Figure 6. Viscosity and shear stress dependence on shear rate for various composition ratios of XG-g-St at temperature 60°C.

Following the grafting process, differences in molecular weight, chemical structure, and chain branching cause an increase in the XG-g-St rheological properties[25].

Some polymeric species have short-chain branches which added to them have a small impact on rheological performance but are positive for specific end-use properties[27].Scheme 1 shows the grafting process's reaction mechanisms.



Scheme 1. Illustration of the proposed mechanism for the grafting of styrene (St.) onto XG."

5. Conclusions

To investigate how temperature and St's composition ratio affect rheological qualities, copolymers (grafted) were synthesized using different ratios of St in the presence of the initiator. All XG and XG-g-St solutions had non-Newtonian pseudoplastic characteristics. The quantity of St makes a difference in the viscosity and shear stress of XG-g-St vs. the shear rate. The shear stress of XG and XG-g-St decreased when the temperature was increased from 30 to 80°C. XG-g-St had better shear stress as well as viscosity in comparison with XG owing to the interaction of the side chains. XG-g-St can be used in the field of construction or enhanced oil recovery owing to its high resistance to temperature as well as shear rate. The XG-g-St FTIR spectra showed an increase at 1120 cm^{-1}, which suggested that the St and XG interaction was responsible for the production of extra ether groups. At 30, 60, and 80°C, the rheological characteristics were examined. With a minimum value of 5 Pa at 80°C and a maximum value of 8 Pa at 30°C, the shear stress of XG decreased from 30 to 80°C. Furthermore, XG-g-St can be used in the pharmaceutical industry, such as in drug delivery systems that employ a variety of grafted natural polysaccharides; in the plastic industry, polymers have largely replaced conventional methods, including those involving metal, wood, ceramic, and glass in the majority of earlier applications. Furthermore, when employed at the ideal dosage, the grafted polymer's flocculation effectiveness was initiated to the greatest at pH 4.0 for the removal of suspended solids (SS) and pH 7.0 for the removal of total dissolved solids (TDS) in the textile sector [28].

Acknowledgments

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Conflicts of interests

There are no conflicts to declare.

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