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Modification of Xanthan Gum with Methyl Methacrylate and Investigation of Its Rheological Properties

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Abstract. Xanthan gum modification is considered a significant step in improving shearing, thermal degradation performance, and rheological properties. This paper investigates the rheology properties of the grafted copolymer based on xanthan gum and methyl methacrylate (XG-g-MMA), including shear stress and viscosity versus shear rate. The grafted copolymer XG-g-MMA was synthesized with different composition ratios of methyl methacrylate (MMA) (1:1.6, 1:5, and 1:8 wt.%) in the presence of a potassium persulphate initiator. Fourier transform infrared spectroscopy (FTIR) characterized the obtained grafted xanthan gum (XG) to confirm the grafting process. The results of the rheology analysis show that grafted XG exhibited higher shear stress and viscosity than pure XG. However, increasing the MMA ratio increases shear stress and viscosity with increasing shear rate. In addition, the rheology measurement of the grafted copolymer showed non-Newtonian shear thinning behavior for XG and XG-g-MMA. These results can further its application in different fields, such as oil recovery and pharmaceuticals.

Keywords: Copolymer; Grafted; MMA; Rheology; Xanthan gum

1. Introduction

Today, in choosing a material or a raw material, preference is given to multifunctional safe materials that do not harm health and the environment. One of these materials is biopolymer xanthan gum (Mohamed et al., 2018; Kusrini et al., 2021). Xanthan gum, weighing approximately 2.65 x 10^6 Da (Khouryieh et al., 2007), is a valuable polysaccharide, a polymer of biological origin, produced by the bacterium *Xanthomonas campestris*. This polysaccharide has many alkyl groups (Figure 1) that can be replaced by other functional groups, providing different properties. It is composed of a β-1,4 glycosidic bond-linked main chain and a trisacharides side chain, successively containing mannose, glucuronic acid, and mannose (Hu et al., 2019). The scope of xanthan gum application is broad, ranging from the food industry to oil extraction. It is valuable due to its biodegradability, safety for the organisms and the environment, and in-demand qualities, such as thickening,

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moisturizing, wetting, stabilizing properties, and resistance to different environmental conditions (Sworn, 2009; Sofia & Djamel, 2016; Filimon, 2018; Jindal & Khattar, 2018). However, because it is inferior to synthetic polymers in some characteristics, it is sometimes expected to be modified to improve its specific properties, such as its rheological characteristics and solubility. Chain stiffness is known to affect physicochemical properties (Fantou et al., 2017). The xanthan chains cannot associate under ordered conformation, but they associate exhibiting a gel-like behavior under disordered conformation. Therefore, most of the modifications are based on the grafting process, which impacts polymer sight chains. In particular, modification improves the rheology of substances (Alas & Ali, 2019; Mau et al., 2020). Modification implies modifying xanthan gum by applying chemical methods, such as co-polymerization (Wang et al., 2013; Elella et al., 2017), treatment with chemical substances (surfactants, acids, etc.) (Skender et al., 2013; Costa et al., 2014), physical methods, such as cold plasma (Jampala et al., 2015), and biological methods, such as fermentation (Costa et al., 2014), to improve its rheological properties. Moreover, xanthan gum has antibacterial properties (Schnizlein et al., 2020; Munir et al., 2017; Bernice et al., 2018) that are considered essential for pharmaceuticals Bernice et al., 2018).

Modification of xanthan gum can enhance some of its physical and chemical properties. Therefore, the present work aims to prepare grafted xanthan (XG-g-MMA) using methyl methacrylate (MMA). The mechanical and thermal properties, high transparency, and excellent weather ability of MMA make it the most widely used monomer in practical applications (Al-Odayni et al., 2020), such as production of medicine, and adhesives. XG-g-MMA was prepared using an initiator (potassium persulfate, $K_2S_2O_8$) and different composition ratios of MMA to define the better ratio for grafting. The new polymers were then characterized by rheological properties and Fourier transform infrared spectroscopy (FTIR) spectra. Additionally, this work investigates the rheological properties of XG-g-MMA and the effect of different temperatures and composition ratios of MMA on its rheologal properties.

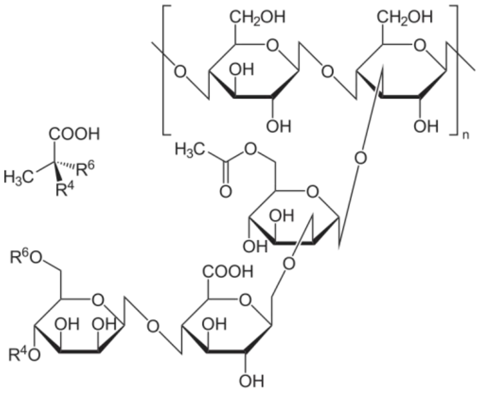


Figure 1 Chemical structure of xanthan gum

2. Methods

2.1. Materials

Biopolymer xanthan gum (XG), methylmethacrylate (MMA), and potassium persulfate (KPS) were supplied by Sigma-Aldrich Chemical Co. (USA).

2.2. Synthesis of grafted xanthan gum

Copolymerization of XG with different feed compositions of MMA (1:1.6, 1:5, and 1:8 wt.%) were prepared by the method of grafting. The MMA ratio has a direct effect on the rheological and physicochemical properties and has practical significance in the production of various polymers. First, 0.6 g of XG was dissolved in 100 mL of distilled water and charged into 250 mL. Then, the free radical initiator potassium persulfate (KPS) (0.5 g) was added to the flask during mechanical stirring at 350 rpm. Finally, a required amount of MMA monomer was added drop by drop for 25 minutes during the stirring process at 65°C, using an automatically controlled water bath for a period of 3 hours.

2.3. *Measurements*

Infrared spectra were recorded on an FT-IR Spectrometer Nicolet iS10 4000.0–400.0 cm^{-1}. The rheological properties were measured using a Bohlin rheometer, model Rheolab QC, UK. The samples were measured using two measuring systems, Cup Stainless (25 mm) and Cone Plate (CP4 40 mm), according to the modified XG viscosity. The FT-IR instrument had PC software installed. After adjusting the measurement conditions, the resultant data were automatically obtained as a table, graph, and/or absolute values. In the viscometry analysis, the requirements of measurement were adjusted as follows: start shear (0.08 S^{-1}), end shear (12.75 S^{-1}), range (linear), delay time (10 sec), integration time (10 sec), proportionality (constant), ramp dir (up), and temperature mode (isothermal 25°C). The selected measurement conditions adjusted for the creep analysis were as follows: stress (1 Pa), creep time (100 sec), recovery time (50 sec), and temperature mode (isothermal 25°C). The particle size and distribution for non-grafted XG and grafted XG-g-MMA were analyzed by Malvern Zetasizer NanoZS 90.

3. Results and Discussion

3.1. *FTIR analysis*

The FTIR spectra of xanthan gum (XG) and grafted xanthan gum with MMA (XG-g-MMA) are displayed in Figure 2. The FTIR spectrum of the XG showed peaks at 3300 cm^{-1} (OH stretching), which coincides with the published data in the work done by Sinha (2012); 1675 cm^{-1} (carbonyl group stretching), which coincides with the findings reported by Sahoo et al. (2012); 1385 cm^{-1} (COO– group); and 1050 cm^{-1} (ether group). The XG-g-MMA spectrum showed a decrease in the frequency stretching peak of –OH at 3300 cm^{-1}, which is attributed to grafting polymerization of MMA onto XG—the same finding was made by Jalal and Al-Lami (2014). In addition, there was a new peak at 2948 cm^{-1} due to the stretching band of the C–H groups and strong peaks at 1724 cm^{-1} (–C=O group) and at 1141 cm^{-1} (ether group). Furthermore, there were peaks at 1605 and 1433 cm^{-1} attributed to the COO– group.

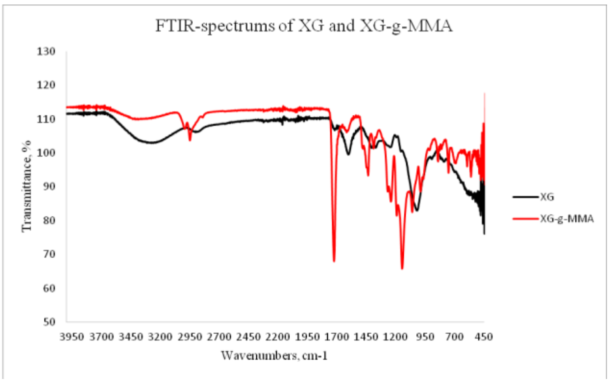


Figure 2 FTIR spectra of XG and XG-g-MMA

3.2. *Rheology analysis*

The effect of the shear rate on the shear stress and viscosity of XG at different temperatures is presented in Figure 3. The flow curves revealed that the shear stress increases as the shear rate increased. These curves are rounded to the shear stress axis, and XG behaves as a non-Newtonian shear-thinning fluid. In non-Newtonian fluids, the flow behavior is dependent on both the temperature and the composition of the liquids (Chhabra & Richardson, 2008). As the temperature increased from 30 to 80°C, the shear stress of XG decreased: the highest shear stress (8 Pa) was at 30°C, and the lowest (4 Pa) at 80°.

On the other hand, the viscosity of XG decreased by increasing the shear rate, as shown in Figure 3. The decrease in viscosity is due to different factors, including deformation of particles (changing their shape from spherical to elliptical), the orientation of non-spherical particles, and orientation of polymer chains in the flow direction and deformation of chains (Ayoub et al., 2003). As the temperature increased from 30 to 80°C, the viscosity of XG decreased due to the increase in intermolecular distances (Yaseen et al., 2005; Pereira et al., 2007). The highest viscosity (0.4 Pa) was at 30°C, and the lowest viscosity (0.07 Pa) at 80°C.

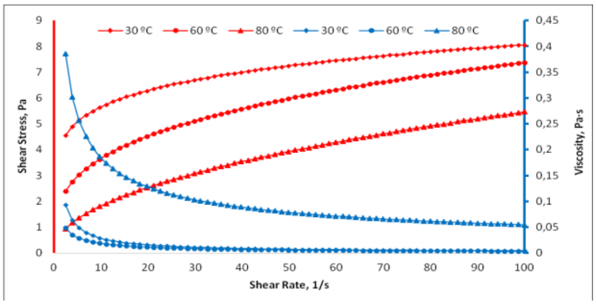


Figure 3 Shear stress and viscosity vs shear rate for XG at different temperatures

Figure 4 shows the effect of the shear rate on the shear stress and viscosity of XG-g-MMA at different temperatures. It can be seen from Figure 4 that shear stress increased and the viscosity of the grafted copolymer decreased with the increasing shear rate. In addition, the shear stress and viscosity of the grafted copolymer increased with decreasing temperature (from 80 to 30°C). The highest shear stress (35 Pa) and viscosity (4.5 Pa) were at 30°C, while the lowest shear stress (18 Pa) and viscosity (0.3 Pa) of the grafted copolymer were at 80°C. However, the value of the shear stress and viscosity of XG-g-MMA is much higher than that of pure xanthan (XG). This is attributed to the branched, crosslinking and three-dimensional network structure in XG-g-MMA (Patel et al., 2020).

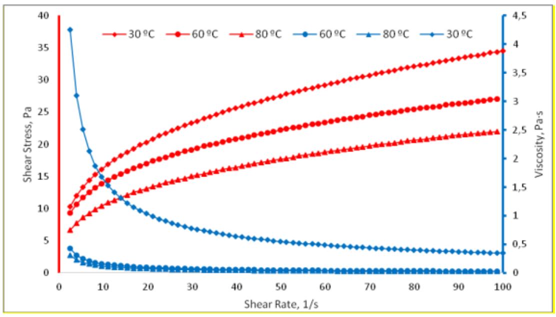


Figure 4 Shear stress and viscosity vs shear rate for XG-g-MMA at different temperatures

The rheological properties of polymer solutions depend on different factors, including the type of copolymer, composition ratios, and concentrations of polymers. Figure 5 shows that the shear stress and viscosity of XG-g-MMA increase with increasing the ratio of MMA in the grafted copolymer, compared to pure xanthan (XG) at 60°C. However, XG-g-MMA (1:8 wt.%) resulted in the highest shear stress (27.5 Pa) and viscosity (8.5 Pa), while XG-g-MMA (1:1.6 wt.%) resulted in the lowest shear stress (12.5 Pa) and viscosity (3.5 Pa), compared to XG (7.2 and 0.7 Pa, respectively). The increase in the rheological properties of XG-g-MMA is due to changes in the chemical structure, molecular weight, and chain branching after the grafting process (Ayoub et al., 2003; Uhlherr et al., 2005), as shown in Scheme 1. It has been reported that long-chain branches are defined by molar masses greater than the molar mass between molecule entanglements, implying that rheological characteristics are affected. Short-chain branches are added to some polymeric species which have little effect on rheological behavior but are advantageous for certain end-use characteristics (Münstedt, 2021). High resistance to temperature and shear rate makes XG-g-MMA one of the green polymers which can be used in enhanced oil recovery (EOR) (Darmayanti et al., 2016).

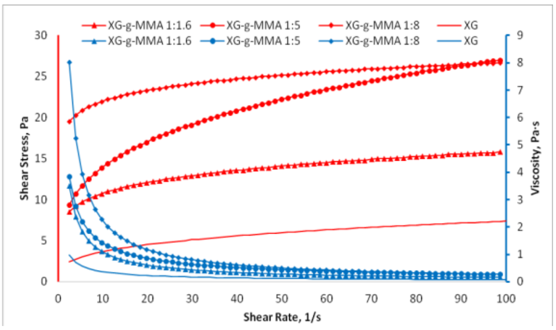
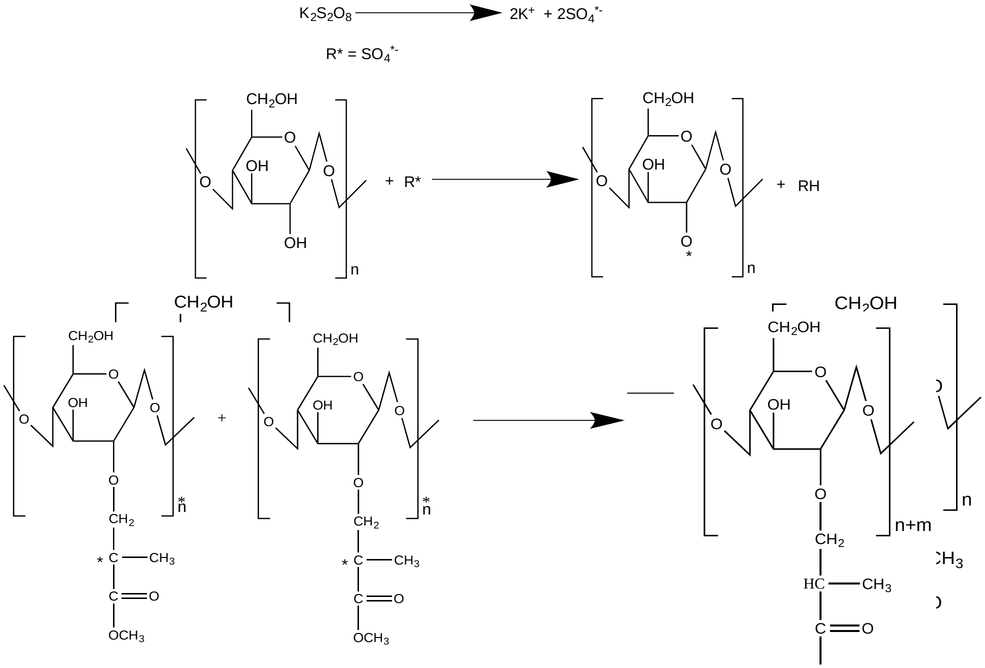


Figure 5 Shear stress and viscosity vs. shear rate for XG and XG-g-MMA with different composition ratios at 60°C

The mechanism of the reaction is supposed to occur as follows:

1. Initiation: The initiation phase describes the step that initially creates a radical species (SO4^{*-}). Once a reactive free radical is generated, it can react with stable molecules to form a new free radical.
2. Propagation: During polymerization, a polymer spends most of its time increasing its chain length, or propagating. After the radical initiator is formed, it attacks a monomer.
3. Termination: Chain termination is a chemical reaction that ceases the formation of reactive intermediates in a chain propagation step in the course of polymerization.



Scheme 1 Mechanism of grafting of MMA onto XG

3.3. Particle size and distribution analysis

The particle size distribution of a particular material is a vital analysis parameter in quality control processes and research applications as many other product properties are directly related to it: particle size distribution affects material properties, such as flow and conveying behavior (for bulk materials), reactivity, solubility, extraction and reaction behavior, taste, and compressibility (Microtrac, 2021).

Based on the results of the particle size distribution of the samples, it can be concluded that after grafting, the size of the macromolecules became larger. The particles of XG are about 500–900 r.nm., while the particle size of XG-g-MMA ranges between 10–14000 r.nm. The influence of particle size on the properties of substances can vary (Basaria & Priadi 2016). Increasing the size of macromolecules can provide the growth of side chains that occurs by attaching MMA to the XG, replacing –OH groups. The particle size and distribution are shown in Figure 6 (A and B).

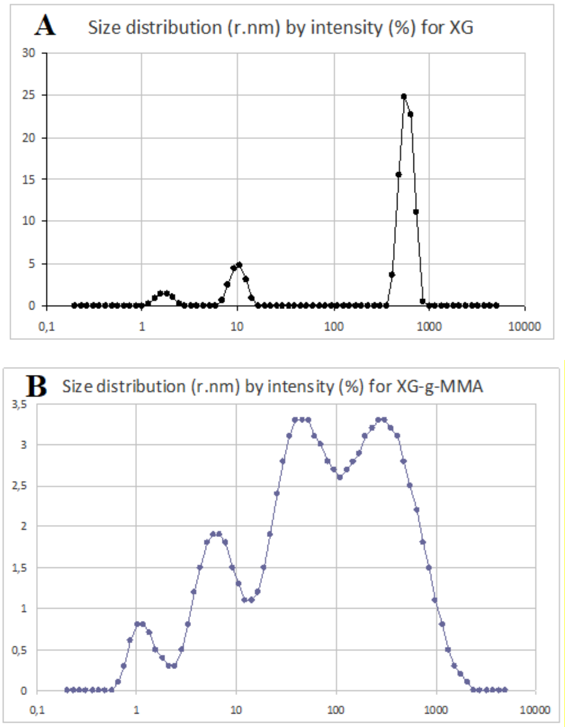


Figure 6 Particle size distribution (r.nm) by intensity (%) for XG (A) and for XG-g-MMA (B)

It is well known that the average particle size, as well as the particle size distribution, has a significant impact on the mechanical and rheological characteristics of a particulate-loaded polymer system (Huber et al., 2015). Smaller particles have a large surface area and tend to agglomerate, resulting in higher viscosities and viscoelastic moduli, whereas larger particles have lower viscosities and viscoelastic moduli. The effect of particle size is also closely related to powder loading (Bek et al., 2020).

Because the particle form, sizes, and size distributions were almost close for the grafted XG-g-MMA (Figure 6, B), which ranged from 10 to 14000 r.nm., the surface area of the particles was also comparable, implying that the surface area of the particles had a similar influence on the rheological behavior of the examined polymer. It has also been reported that the rheological nature of the material changed when filler loading was increased and thus exhibited solid-like behavior at a constant frequency, and the small shear strains and additives mixed with the polymer and fillers significantly affected the rheological properties of composite materials (Bek et al., 2020). In conclusion, the rheological behavior of densely loaded materials is complicated, and various aspects impacting rheological behavior of grafted XG-g-MMA are interconnected, as stated previously.

4. Conclusions

The grafted copolymers were synthesized using XG and MMA with different MMA ratios in the presence of potassium persulphate as the initiator to investigate the effect of the temperature and composition ratio of MMA on the rheological properties. All solutions of XG and XG-g-MMA exhibited non-Newtonian pseudoplastic properties. XG-g-MMA shear stress and viscosity versus shear rate vary proportionately as the quantity of MMA increases. The shear stress and viscosity of XG and XG-g-MMA increase as the temperature was decreased from 60 to 30°C. XG-g-MMA demonstrated much higher shear stress and viscosity than XG due to the interaction of the side chains. These properties of XG-g-MMA provide good prospects for this copolymer to be as a safe thickener in cosmetology or the oil industry. These results are primary data; further investigations should be carried out to research XG-g-MMA applicability.

References

Al-Odayni, A.B., Saeed, W.S., Ahmed, A.Y.B.H., Alrahlah, A., Al-Kahtani, A., Aouak, T., 2020. New Monomer Based on Eugenol Methacrylate, Synthesis, Polymerization and Copolymerization with Methyl Methacrylate–Characterization and Thermal Properties. *Polymers*, Volume 12(1), pp. 160–188

Alas, M., Ali, S.I.A., 2019. Prediction of the High-Temperature Performance of a Geopolymer Modified Asphalt Binder using Artificial Neural Networks. *International Journal of Technology*, Volume 10(2), pp. 417–427

Ayoub, M.M.H., El-Awady, M.M., Nasr, H.E., Negim, S.M., 2003. Synthesis and Rheological Properties of Some Styrene/Methacrylate Copolymer Latices. *Polymer-Plastics Technology and Engineering*, Volume 42(5), pp. 863–880

Basaria, P., Priadi, C.R., 2016. Influence of Organic Fraction of Municipal Solid Waste Particle Size on Biogas Production. *International Journal of Technology*, Volume 7(8), pp. 1431–1437

Bek, M., Gonzalez-Gutierrez, J., Kukla, C., Črešnar, K.P., Maroh, B., Perše, L.S., 2020. Rheological Behaviour of Highly Filled Materials for Injection Moulding and Additive Manufacturing: Effect of Particle Material and Loading. *Applied Sciences*, Volume 10(22), pp. 7993–8016

Bernice, K.-S., Sarah, A.-F., Mulumebet, W., Leonard, W., 2018. Synergetic Effect of Polysaccharide Gums and Antimicrobial Agents on Susceptibility and Protein Expression of Select Pathogenic Microorganisms in Milk. *Journal of Food Research*, Volume 7(2), pp. 35–53

Chhabra, R.P., Richardson, J.F., 2008. *Non-Newtonian Flow and Applied Rheology*. 2nd Edition. Butterworth-Heinemann, Oxford

Darmayanti, M.G., Radiman, C.L., Sudarma, I.M., 2016. Kappa-Carrageenan as an Attractive Green Substitute for Polyacrylamide in Enhanced Oil Recovery Applications. *International Journal of Technology*, Volume 7(3), pp. 431–437

Costa, L.A.De., Campos, M.I., Druzian, J.I., de Oliveira, A.M., de Oliveira Junior, E.N., 2014. Biosynthesis of Xanthan Gum from Fermenting Shrimp Shell: Yield and Apparent Viscosity. *International Journal of Polymer Science*, Volume 2014, pp. 1–8

Elella, M.H.A., Mohamed, R.R., Abd ElHafeez, E., Sabaa, M.W., 2017. Synthesis of Novel Biodegradable Antibacterial Grafted Xanthan Gum. *Carbohydrate Polymers*, Volume 173, pp. 305–311

Fantou, C., Roy, A.N., Dé, E., Comesse, S., Grisel, M., Renou, F., 2017. Chemical Modification of Xanthan in the Ordered and Disordered States: An Open Route for Tuning the Physic-Chemical Properties. *Carbohydrate Polymers*, Volume 178, pp. 115–122

Filimon, A., 2018. *Smart Materials: Integrated Design, Engineering Approaches, and Potential Applications.* 1st Edition. Apple Academic Press, USA

Huber, T., Misra, M., Mohanty, A.K., 2015. The Effect of Particle Size on the Rheological Properties of Polyamide 6/Biochar Composites. *In:* AIP Conference Proceedings 1664, 150004

Hu, X., Wang, K., Yu, M., He, P., Qiao, H., Zhang, H., 2019. Characterization and Antioxidant Activity of a Low-Molecular-Weight Xanthan Gum. *Biomolecules*, *Volume* 9(11), pp. 730–742

Jalal, M.A., Al-Lami, H.S., 2014. New Limited Molecular Weight Polymeric Dispersants Prepared by Melt Condensation Polymerization. *Chemistry and Materials Research*, Volume 6(2), pp. 12–18

Jampala, S.N., Manolache, S., Gunasekaran, S., Denes, F.S., 2015. Plasma-Enhanced Modification of Xanthan Gum and Its Effect on Rheological Properties. *Journal of Agricultural and Food Chemistry*, Volume 53(9), pp. 3618–3625

Jindal, N., Khattar, J.S., 2018. *Microbial Polysaccharide in Food Industry*. In: *Biopolymers for Food Design*, pp. 95–123

Khouryieh, H.A., Herald, T.J., Aramouni, F., Bean, S., Alavi, S., 2007. Influence of Deacetylation on the Rheological Properties of Xanthan–Guar Interactions in Dilute Aqueous Solutions. *Journal of Food Science*, Volume 72(3), pp. 173–181

Kusrini, E., Ayuningtyas, K., Mawarni, D.P., Wilson, L.D., Sufyan, M., Rahman, A., Prasetyanto, Y.E.A., Usman, A., 2021. Micro-structured Materials for the Removal of Heavy Metals using a Natural Polymer Composite. *International Journal of Technology, Volume* 12(2), pp. 275–286

Mau, S., Yanuar, Pamitran, A.S., 2020. Rheology Characteristics and Critical Velocity of Particle-laden Flow Affected by Three-lobed Spiral Pipe. *International Journal of Technology*, Volume 11(2), pp. 248–258

Microtrac, MRB, 2021. Analysis of particle size distribution. Available online at: https://www.microtrac.com/knowledge/particle-size-distribution/, Accessed on October 22, 2021

Munir, M., Shahid, M., Munir, H., Javaid, S., Sharif, S., El-Ghorab, A., Misbah, M., Muhammad, S., Hira, M., Fozia, A., Sabah, J., El-Ghorab, A., 2017. Xanthan Gum Biochemical Profiling, Antioxidant, Antibacterial, Biofilm Inhibition and Mutagenic Potential. *Current Science*, Volume 114, pp. 1903–1913

Münstedt, H., 2021. Rheological Measurements and Structural Analysis of Polymeric Materials. *Polymers*, Volume 13(7), pp. 1123–1143

Patel, J., Maji, B., Moorthy, N.S.H.N., Maiti, S., 2020. Xanthan Gum Derivatives: Review of Synthesis, Properties and Diverse Applications. *RSC Advances*, Volume10(45), pp. 27103–27136

Pereira, E.A., Brandáo, E.M., Borges, S.V., Maia, M.C.A., 2007. Effect Of Xanthan Gum Addition on the Rheological Properties of Umbu Fruit Pulb. *B.CEPPA. Curitiba*, Volume 25(2), pp. 285–294

Sahoo, S., Chakraborti, C.K., Behera, P.K., Mishra, S.C., 2012. FTIR and Raman Spectroscopic Investigations of a Norfloxacin/Carbopol 934 Polymeric Suspension. *Journal of Young Pharmacists*. Volume 4(3), pp. 138–145

Schnizlein, M.K., Vendrov, K.C., Edwards, S.J., Martens, E.C., Young, V.B., 2020. Dietary Xanthan Gum Alters Antibiotic Efficacy against the Murine Gut Microbiota and Attenuates *Clostridioides Difficile* Colonization. *mSphere*, Volume 5(1), pp. 1–10

Sinha, D., 2012. Structural Modifications of Gamma Irradiated Polymers: An FT-IR Study. *Advances in Applied Science Research*, Volume 3(3), pp. 1365–1371

Skender, A., Zafour, A.H.Z., Flahaut, E., 2013. Chemical Functionalization of Xanthan Gum for the Dispersion of Double-Walled Carbon Nanotubes in Water. *Carbon*, Volume 62, pp. 149–156

Sofia, G.B., Djamel, A., 2016. A Rheological Study of Xanthan Polymer for Enhanced Oil Recovery. *Journal of Macromolecular Science*, Part B, Volume 55(8), pp. 793–809

Sworn, G., 2009. *Xanthan gum. Handbook of hydrocolloids*. 2nd Edition. pp.186–203

Uhlherr, P.H.T., Guo, J., Tiu, C., Zhang, X.M., Zhou, J.Z.Q., Fang, T.N., 2005. The Shear-Induced Solid-Liquid Transition in Yield Stress Materials with Chemically Different Structures. *Journal of Non-Newtonian Fluid Mechanics*, Volume 125(2-3), 101–119

Wang, A., Wang, W., 2013. Gum-g-Copolymers: Synthesis, Properties, and Applications. In: Kalia S., Sabaa M. (eds) *Polysaccharide Based Graft Copolymers*. Springer-Verlag Berlin, Heidelberg, pp. 149–203

Yaseen, E.I., Herald, T.J., Aramouni, F.M., Alavi, S., 2005. Rheological Properties of Selected Gum Solutions. *Food Research International*, Volume 38(2), pp. 111–119