ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS AND CHARACTERIZATION OF IONIC GUAR GUM DERIVATIVES

M.Sc. THESIS

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Department of Polymer Science and Technology

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

İYONİK GUAR ZAMKI TÜREVLERİNİN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

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Aslıhan Namlı, an M.Sc. student of İTU Graduate School student ID 515201018, successfully defended the thesis/dissertation entitled "SYNTHESIS AND CHARATERIZATION OF IONIC GUAR GUM DERIVATIVES", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my spouse and family,

FOREWORD

I am indebted to my esteemed advisor, Assoc. Prof. Dr. Cüneyt Hüseyin Ünlü provided unwavering support at every stage during my research efforts and throughout my master's degree education. He provided valuable guidance, not only in laboratory work but in all facets of my academic journey. His support was invaluable and greatly appreciated.

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January 2024

Aslıhan NAMLI
(Chemist)

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ABBREVIATIONS

^{1}H NMR	: Proton Nuclear Magnetic Resonance
CGG	**:** Cationic Guar Gum
CHPTAC	**:** 3-Chloro-2-hydroxypropyltrimethylammonium chloride
FTIR	**:** Fourier-Transform Infrared Spectroscopy
GG	**:** Guar Gum
MCA	**:** Sodium Monochloroacetic acid
PCA	**:** Principal Component Analysis
TGA	**:** Thermogravimetric Analysis

SYMBOLS

A	**:** Area
F	**:** Shear force
h	**:** Distance
L	**:** Length
p	**:** Pressure
r	**:** Radius
v	**:** Velocity
α	**:** Alpha
β	**:** Beta
$\dot{\gamma}$	**:** Shear rate
η	**:** Apparent viscosity
τ	**:** Shear stress

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SYNTHESIS AND CHARACTERIZATION OF IONIC GUAR GUM DERIVATIVES

SUMMARY

Polysaccharides are unique biopolymers with a significant structural diversity. Many organisms, including plants, animals, fungi, algae, and microorganisms, form large amounts of polysaccharides through biosynthesis due to their structure-forming ability as storage polymers and as structure-forming macromolecules. Thanks to their ability to form structures by supramolecular interactions of variable types, polysaccharides are exceptional. Furthermore, polysaccharides are increasingly recognized as essential substances in biotransformation processes, for example, in terms of activity and selectivity. While naturally occurring polysaccharides are already remarkable, chemical modification can improve given properties and can even be used to tailor-engineer advanced materials.

Polysaccharides are used in food and other industries as stabilizers, thickeners, gelling agents and inhibitors of crystal formation. Polysaccharides such as cellulose, xylan and chitosan appear in nature as structural materials. They form the cell walls of plants and the shells of crustaceans and insects. Other polysaccharides such as glycogen, amylose and amylopectin are essential for storing sugar in many animals and plants (Seidi et al., 2018). Gums are also categorized under polysaccharides. Guar gum, cashew gum, xanthan gum, gum arabic, and chitin are some examples of gums.

Guar gum is a galactomannan, a naturally occurring polymer, obtained from the soil endosperm of the plant Cyamopsis tetragonolobus or Cyamopsis psoraloides. Guar gum belongs to the legume family. When dissolved in water, the presence of a large number of hydroxyl groups increases the ability of guar gum to form hydrogen bonds. Thanks to this ability, it increases the viscosity and enhances the gelling properties. Based on these properties, guar gum has a variety of applications in various industries, such as textiles, food, petrochemicals, mining, and paper.

With the increasing supply in the market in recent years, there has been increased work on the development of various compounds of guar gum. Combining guar gum with other substances not only enhances its properties but also increases its versatility for different applications in various fields such as water treatment, drug delivery, pharmaceutical, cosmetic and food industries.

The aim of this study was to investigate the rheological properties of pure guar gum and cationic and anionic modifications of guar gum. Guar gum was preferred in this study due to its water solubility, thickening properties, and industrial use as a stabilizing agent.

3-Chloro-2hydroxypropyltrimethylammonium chloride (CHPTAC) was used as an etherifying agent in different ratios for the cationic modification of guar gum. The reaction medium was determined as water. After the guar gum was completely dissolved in water, CHPTAC was added to the system using a dropping funnel. At the end of the addition, the temperature was adjusted to 50°C and the reaction was carried out at this temperature for 24 hours in a basic environment. The new product obtained

at the end of the reaction was collected by precipitation with ethanol. A freeze-drying system was preferred to remove the water in the medium.

Anionic modification of guar gum was obtained from the reaction of guar gum with different ratios of monochloroacetic acid (MCA) aqueous solutions. The reaction medium was determined as water, and the reaction was carried out at basic pH as in the cationic modification. MCA aqueous solution was added to the system with a dropping funnel of 1 mL/min. After adding the MCA aqueous solution, the reaction was carried out at 50°C for 4 hours. After the reaction time, precipitation and freeze-drying processes were applied, respectively, to collect the synthesized product. Ethanol was used in the precipitation step as in the cationic modification.

FTIR analyses were performed to determine the spectral properties of the modifications obtained from the reactions. The 1642 cm^{-1} peak in the FTIR analyses of the products obtained as a result of cationic modification proves that the reaction was successful.

In the anionic modification, 1600 cm^{-1}, 1391 cm^{-1}, and 1253 cm^{-1} belong to the asymmetric and symmetric stretching vibrations of the added -COO- group, respectively. The presence of these peaks proves that the anionic modification was successful.

^{1}H NMR analysis was performed to understand the difference in modified guar gums. The characteristic signals were observed in the ^{1}H NMR.

TGA analyses were performed to understand how the thermal properties of unmodified guar gum were affected as a result of the modifications. In TGA analyses, 25-600°C and 20 °C/min heating rate were used. According to the TGA results, the thermal stability of anionic and cationic modification decreased compared to guar gum as expected. This shows that the added groups were successfully reacted.

In order to examine the rheological behaviour of the obtained modifications and natural guar gum in water, viscosity-shear rate graphs were plotted.

In order to examine the rheological properties, solutions were formed by dissolving each modification in pure water at the same ratio. The rheological properties of anionic, cationic modifications, and guar gum were investigated under increasing shear rate.

As a result of the measurements, it was observed that aqueous solutions of the cationic modification showed Newtonian flow properties. The initial viscosity values of the modifications are lower than those of natural guar gum.

It was observed that anionic modifications showed shear thinning flow properties like guar gum. The rheological difference of anionic modifications from guar gum is that the viscosity value at each shear rate is higher than guar gum.

In order to examine the rheological effects of anionic and cationic modifications on each other, aqueous solutions of cationic and anionic modifications at the same concentration were mixed 1:1 by weight and viscosity values were measured against increasing shear rate.

In the mixture of the cationic modification containing a low percentage of CHPTAC (AK-6) with the modification of the anionic modification containing a high percentage of MCA (AK-A2), the mixture showed shear thinning flow characteristics as in the

anionic modification. In the mixture of AK-6 with low MCA containing modification (AK-A1), the mixture showed shear thinning flow characteristics.

In the mixture of the modification of the cationic modification (AK-9) with high etherifying agent (CHPTAC) with the anionic modification (AK-A1) containing low MCA, the mixture showed shear thinning flow behaviour at low shear rates and Newtonian flow at high shear rates. The modification of AK-9 with high MCA content (AK-A2) showed Newtonian flow as in the cationic modification.

İYONİK GUAR ZAMKI TÜREVLERİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Polisakkaritler, büyük bir yapısal çeşitliliğe sahip olan benzersiz biyopolimerlerdir. Birçok organizma, bitkiler, hayvanlar, mantarlar, algler ve mikroorganizmalar dahil olmak üzere, depo polimerleri ve yapı oluşturan makromoleküller olarak, yapı oluşturma yetenekleri nedeniyle biyosentez yoluyla büyük miktarlarda polisakkarit oluşturur. Polisakkaritler, değişken tipteki supramoleküler etkileşimlerle yapı oluşturma yetenekleri sayesinde olağanüstüdür. Ayrıca, polisakkaritler, örneğin aktivite ve seçicilik açısından biyotransformasyon süreçlerinde önemli maddeler olarak giderek daha fazla tanınmaktadır. Doğal olarak meydana gelen polisakkaritler zaten olağanüstü olsa da kimyasal modifikasyon verilen özellikleri iyileştirebilir ve hatta gelişmiş malzemeleri özel olarak tasarlamak için kullanılabilir.

Polisakkaritler, gıda ve diğer endüstrilerde stabilizatör, kalınlaştırıcı ve jelleştirici, kristal oluşmasının engelleyen inhibitör amaçları ile kullanılmaktadır. Selüloz gibi polisakkaritler, ksilan ve kitosan doğada yapısal malzeme olarak karşımıza çıkmaktadır. Bitkilerin hücre duvarlarını, kabukluların ve böceklerin kabuklarını oluşturur. Diğer glikojen, amiloz ve amilopektin gibi polisakkaritler çok hayvanlarda ve bitkilerde şeker depolamak için önemlidir (Seidi ve arkadaşları, 2018). Zamklar da polisakkaritler altında yer almaktadır. Guar zamkı, kaju zamkı, ksantan zamkı, arap zamkı ve kitin zamklara örnek verilebilir.

Guar zamkı, baklagiller ailesiden Cyamopsis tetragonolobus veya Cyamopsis psoraloides bitkisinin toprak endospermi ile elde edilen doğada bulunan bir galaktomannandır. Guar zamkının yapısında çok sayıda hidroksil grubunun bulunması hidrojen bağı oluşturma yeteneğinden dolayı sulu çözeltide viskoziteyi ve jelleşme özelliklerini arttırır. Bu özelliklere dayalı olarak guar zamkı; tekstil, gıda, petrokimya, madencilik ve kağıt gibi çeşitli endüstrilerde özellikle viskozite ayarlama amacıyla kullanılır.

Son yıllarda yeşil çözüm arayışlarının artması ile birlikte, zamkların çeşitli şekillerde modifikasyonuna yönelik çalışmalar devam etmektedir. Guar zamkının diğer maddelerle kullanılması, sadece özelliklerini arttırmakla kalmaz, aynı zamanda su arıtma, ilaç dağıtımı, ilaç, kozmetik ve gıda endüstrileri gibi çeşitli alanlarda farklı uygulamalar için kullanımını zenginleştirir.

Bu çalışmada guar zamkı sudaki çözünürlüğünün yüksek olması, kıvamlaştırma özelliği ve endüstride stabilizasyon ajanı olarak sıklıkla kullanılmasından dolayı tercih edilmiştir. Çalışmanın amacı guar zamkının modifikasyonu ile katyonik ve anyonik türevlerini elde etmek ve bu türevlerin reolojik özelliklerini incelemektir.

Guar zamkının katyonik modifikasyonu için bu amaçla sıklıkla kullanılan 3-Klor-2hidroksipropiltrimetilamonyum klorür (CHPTAC) eterleştirme ajanı kullanılmıştır. Farklı guar zamkı/CHPTAC oranları kullanılarak sulu ortamda reaksiyonlar yapılmıştır. Genel olarak önce 2 gr guar zamkı 100 mL suda tamamen çözülmüştür. GG tamamen çözüldükten sonra her bir karışıma 10 mL %50'lik NaOH sulu çözeltisi

eklenmiştir. Daha sonra CHPTAC yavaş bir şekilde damlatma hunisi kullanılarak reaksiyon ortamına eklenmiştir. Ekleme sonunda sıcaklık 50°C'e getirilip reaksiyon bu sıcaklıkta 24 saat bazik ortamda gerçekleşmiştir. Reaksiyon sonunda elde edilen ürün 3 hacim etanol ile çöktürülüp vakum yardımıyla süzülmüştür. Ortamdaki suyu uzaklaştırmak için ise dondurarak kurutma sistemi tercih edilmiştir. 7.5 mL CHPTAC içeren modifikasyon AK-6, 30 mL CHPTAC içeren modifikasyon ise AK-9 olarak kodlanmıştır.

Guar zamkının anyonik modifikasyonu da karboksimetilasyon reaksiyonu kullanılarak gerçekleştirilmiştir. Farklı oranlarda monokloro asetik asit (MCA) ve guar zamkı kullanılmıştır. 2 gr GG 100 mL suda çözülmüştür. Reaksiyon sıcaklığı 50°C'ye ayarlandıktan sonra reaksiyona 15 mL %10 NaOH damlatma hunisi yardımı ile verilmiştir. 15 mL deionize su içerisinde farklı oranlarda MCA çözülmüştür. Hazırlanan MCA sulu çözeltileri damlatma hunisi yardımıyla 1 mL/min olacak şekilde sisteme yavaşça eklenmiştir. MCA sulu çözeltisi eklendikten sonra reaksiyon 50°C'de 4 saatte gerçekleşmiştir. Reaksiyon süresi sonrasında sentezlenen ürünü toplamak amacıyla 2 hacim etanol ile elde edilen ürün çöktürülmüştür. Çöktürülen ürün vakum yardımıyla süzüldükten sonra dondurarak kurutma işlemi yardımıyla ortamdaki su uzaklaştırılmıştır. %26.69 MCA içeren modifikasyon AK-A1, %53.36 MCA içeren modifikasyon ise AK-A2 olarak kodlanmıştır.

Yapılan reaksiyonlardan elde edilen modifiye ürünlerin spektral özelliklerini belirlemek için ilk olarak FTIR analizleri yapılmıştır. GG'ın FTIR analizlerindeki karakteriksel pikleri sırasıyla 3300, 2900 ve 1640 cm^{-1}'da yer almaktadır. 1640 cm^{-1} pikindeki değişim $N^{+}(CH_3)_3$ iyonlarının GG'ın yapısına katıldığını kanıtlar niteliktedir.

Anyonik modifikasyonda ise sırasıyla 1600, 1391 ve 1253 cm^{-1} dalga sayılarından bulunan bantlar, eklenen $-COO^{-}$ grubunun asimetrik ve simetrik gerilme titreşimine aittir. Bu piklerin varlığı anyonik modifikasyonun başarılı bir şekilde yapıldığını kanıtlar niteliktedir.

^{1}H NMR analizleri, guar zamkının modifikasyonlarındaki değişiklikleri anlamak amacıyla yapılmıştır. ^{1}H NMR sonuçlarında karakteristik sinyaller gözlemlenmiştir. Katyonik modifikasyonlar sonucunda elde edilen ürünlerin 1H NMR sonuçlarında 3.08 ve 4.30 ppmde yer alan pikler katyonik modifikasyonların başarılı bir şekilde gerçekleştirildiğini göstermektedir. Anyonik modifikasyonlarda ise 3.79, 3.90 ve 4.22 ppmde yer alan pikler karboksimetilasyon reaksiyonunun başarılı bir şekilde gerçekleştiğini göstermektedir.

Yapılan modifikasyonlar sonucunda modifiye edilmiş ve edilmemiş guar zamkının termal özelliklerinin nasıl değişime uğradığını anlamak amacıyla TGA analizlerine bakılmıştır. TGA analizlerinde 25-600°C ve 20 °C/min ısıtma hızı kullanılmıştır. Modifikasyonlar sonucunda eklenen amin (CHPTAC) ve asit (MCA) gruplarının termal özellikleri GG üzerinde yer alan gruplara göre daha düşüktür. Bu sebeple TGA ölçümlerinde modifikasyon sonucu elde edilen ürünlerin daha düşük sıcaklıklarda bozunmaya başlaması beklenmektedir. TGA sonuçlarına göre anyonik modifiye ürünlerin (AK-A1 ve AK-A2) ve katyonik modifiye ürünlerin (AK-6 ve AK-9) termal stabilitesi, guar zamkına kıyasla beklenildiği gibi azalmıştır. Bu da eklenen grupların başarılı bir şekilde gerçekleştiğini göstermektedir.

Elde edilen modifiye ürünlerin ve saf guar zamkının sudaki reolojik davranışlarını incelemek adına viskozite–kesme hızı grafiği çizilmiştir. Artan kesme hızına karşılık o değerdeki viskozite değeri ölçülerek ürünlerin akış özellikleri belirlenmiştir.

Reolojik ölçümler reometre cihazı ile yapılmıştır. Reolojik özelliklerin incelenmesi için her bir modifikasyon sonucu elde edilen ürünler (AK-6, AK-9, AK-A1 ve AK-A2) ve guar zamkının kendisi, aynı oranda saf su ile karıştırılıp çözelti halinde hazırlanmışlardır. Suda hazırlanan AK-6, AK-9, AK-A1 ve AK-A2'nin reolojik özellikleri artan kesme hızı altında incelenmiştir. Kesme hızı 0,1 1/s'den logaritmik olarak artmaya başlayıp 100 1/s'de son bulmuştur. Bu kesme hızlarındaki her bir viskozite değeri kaydedilip grafik halinde verilmiştir. Ölçümlerde silindirik ölçüm başlığı kullanılmıştır.

Yapılan ölçümler sonucunda katyonik modifiye ürünlerin (AK-6 ve AK-9) sulu çözeltilerinin artan kesme kuvveti altında Newtonian akış özelliği gösterdiği görülmüştür. AK-6 ve AK-9'un sulu çözeltilerinin başlangıç viskozite değerleri, saf guar zamkından düşüktür. Saf guar zamkının üzerinde bulunan OH grupları, CHPTAC tarafından değiştirildiği için AK-6 ve AK-9'un H bağı yapma kapasitelerinde azalma meydana gelmiştir. Bu sebeple AK-6 ve AK-9, Newtonian akış özelliği göstermiştir.

Anyonik modifikasyon sonucunda elde edilen ürünler (AK-A1 ve AK-A2) ile hazırlanan sulu çözeltiler ise guar zamkı gibi kayma incelme akış özelliği gösterdiği görülmüştür. AK-A1 ve AK-A2 sulu çözeltisinin guar zamkından reolojik olarak farkı ise her kesme hızında viskozite değeri, guar zamkından yüksek olması yapılan ölçümlerden çıkarılmaktadır. AK-A1 ve AK-A2 üzerine eklenen asidik grupların H bağı yapma özellikleri olduğundan AK-A1 ve AK-A2'nin bütün kesme hızlarında viskozite değeri saf guar zamkinden yüksek olarak ölçülmüştür.

Anyonik ve katyonik modifikasyon sonucu elde edilen ürünlerin, reolojik anlamda birbirlerine etkilerini incelemek adına ise aynı konsantrasyondaki katyonik ve anyonik modifikasyon ürünlerinin sulu çözeltileri 1:1 ağırlıkça olacak şekilde karıştırılıp artan kesme hızına karşılık viskozite değerleri ölçülmüştür.

7.5 mL %60'lık CHPTAC içeren katyonik modifikasyonun (AK-6), anyonik modifikasyonun 8 gram MCA içeren modifikasyonu (AK-A2) ile olan karışımında karışım, anyonik modifikasyon sonucu elde edilen ürünlerin çözeltilerinde olduğu gibi kayma incelme akış özelliği göstermiştir. AK-6'nın, 4 gram MCA içeren modifikasyonu (AK-A1) ile olan karışımında karışım kayma incelme akış özelliği göstermiştir.

30 mL %60'lık CHPTAC içeren katyonik modifikasyonun (AK-9), 8 gram MCA içeren anyonik modifikasyonu (AK-A1) ile olan karışımında ise karışım, düşük kesme kuvvetlerinde kesme incelme akış davranışı gösterirken yüksek kesme kuvvetlerinde Newtonian akış özelliği göstermiştir. AK-9'un 8 gram MCA içeren modifikasyonu (AK-A2), katyonik modifikasyondaki gibi Newtonian akış göstermiştir.

1. INTRODUCTION AND AIM

Polysaccharides comprise extended chains of distinct monosaccharide units and are ecologically safe, renewable, and sustainable polymeric carbohydrate macromolecules (Nasrollahzadeh et al., 2021). These monosaccharides are linked to each other via glucosidic linkage. They consist of three to nine carbon atoms (Yadav & Karthikeyan, 2019).

Some industries use polysaccharides, especially gums, as a rheology additive to modify the flow and viscosity of the product. In many industries, rheology additives have great importance. Rheology additives are used for many reasons, including flow control, adjustment of stability of the product, adjustment of thixotropy, shelf-life control, etc. There are many ways to classify polysaccharides (Figure 2.2). Classification according to plant origin is the one option for the classification of polysaccharides. One of the examples of polysaccharides categorized by plant origin is gums.

Gums are natural, green, and economical materials. Gums are preferred as a rheology modifier in cosmetics, the paint industry, the food industry, and pharmaceuticals. These features make gums an excellent material to be used as a green rheology modifier in many industries. Guar gum is a water-soluble polysaccharide and is extracted from the endosperm plant Cyamopsis tetragonoloba. Because of its superior water absorption, stabilizing, and thickening qualities, guar gum is utilized extensively in the food business (Shen & Li, 2021).

The aim of this study is to modify the guar gum to obtain anionic and cationic derivatives to examine the effect of modifications on rheological properties. For this purpose, anionic modification of guar gum and cationic modification of guar gum will be synthesized. The characterization of synthesized materials will be done by Fourier transform infrared (FTIR), proton nuclear magnetic resonance (^{1}H NMR), and thermogravimetric analysis (TGA). The rheological properties of the samples will also be evaluated via a rheometer.

2. THEORETICAL SECTION AND LITERATURE REVIEW

2.1 Carbohydrates

Carbohydrates present in various microorganisms, plants, and animals can be derived from biodegradable, biocompatible, non-toxic, and renewable sources, making them crucial in the development and utilization of superior biomaterials with exceptional properties (Suner, 2018). The empirical formula of carbohydrates is $C_n(H_2O)_m$.

The term "monosaccharide" denotes a carbohydrate derivative with a singular carbon chain. Monosaccharides are classified as aldoses or ketoses based on whether the carbonyl group in their structure is an aldehyde or a ketone, respectively.

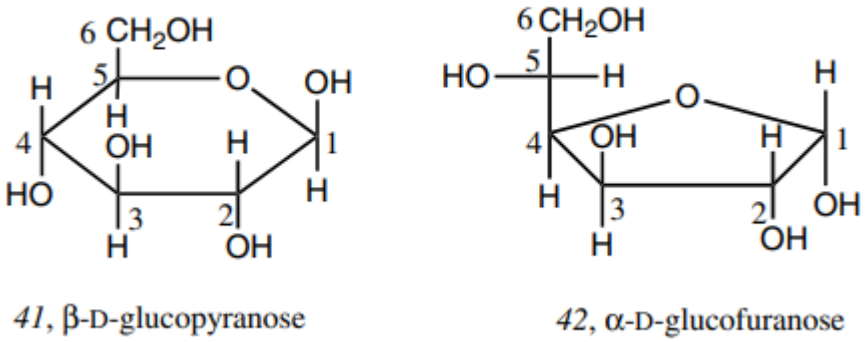
One of the most important monosaccharides is glucose. Its formula is $C_6H_{12}O_6$. The other monosaccharides with the same chemical formula are named as fructose and galactose. The difference among them is the arrangement of -OH groups.

Carbohydrate molecules can be drawn in various ways, with the Fischer projection being one of the most common methods. This approach utilizes a two-dimensional representation to effectively visualize the spatial orientation of atoms within the sugar molecule.

The stereochemistry of monosaccharides was deduced by Emily Fischer in 1981. In a sugar molecule, where the carbon chain is drawn vertically with the most oxidized carbon (usually aldehyde or ketone) at the top and the hydroxyl group (OH) on the lowest asymmetric center points to the right, the sugar has a D configuration.

If the hydroxyl group (OH) on the lowest asymmetric center points to the left, the sugar has a L configuration.Haworth structures also provide the information about the carbohydrate structure. Haworth projections are simplified drawings of ring-shaped sugars. They might not show all the hydrogens. When a sugar forms a ring, it can exist in two forms called alpha (α) and beta (β). These forms switch back and forth as the ring opens and closes. In the α form, the -OH group on the special carbon points down, while in the β form, it points up (Figure 2.1) (Miljković, 2009).

Meanwhile, "disaccharide" and "trisaccharide" describe molecules comprising two or three monosaccharide units that are linked together by acetal or ketal bonds. The terms mono-, di-, and lower oligosaccharides are referred to as "sugar.". Sugars, with their unbranched carbon chains, form different groups based on their number of carbons. These groups include trioses, tetroses, pentoses, hexoses, heptoses, and octoses (Sinnott, 2013).



41, β-D-glucopyranose *42*, α-D-glucofuranose

Figure 2.1: Alpha and beta form of glucose.

2.2 Polysaccharides

Polymers are compound structures consisting of repeating monomer units, forming long-chain and high-molecular-weight entities with linear or branched configurations. Biopolymers, also known as biomacromolecules, can be found in nature as polymeric forms, such as carbohydrates, polynucleotides, proteins, natural elastomers, and polyphenols.

Carbohydrates, which are natural polysaccharides, form the polymeric structure of living organisms and serve as the fundamental building blocks. These natural polysaccharides are generated through various forms of condensation reactions of monosaccharides, such as glucose, galactose, and fructose.

Polysaccharides are environmentally friendly, sustainable polymers made up of various sugar units. They constitute the majority of biomass and exhibit remarkable diversity in nature, with numerous herbal and microbial polysaccharides still remaining undiscovered. These natural polysaccharides serve as integral elements within various living organisms, fulfilling roles as structural components as well as storage molecules for both energy and carbon.

Polysaccharides form through the establishment of α or β-glycosidic linkages between individual monosaccharide units, contributing to the distinct characteristics that differentiate them (Nasrollahzadeh et al., 2021).

Polysaccharides have a wide range of sources, originating from various organisms such as higher photosynthetic plants, fungi, algae, bacteria, and more. At the cellular level, these polysaccharides serve as either storage compounds in the cytoplasm (e.g., starch) or as integral components of cellular membranes or walls (e.g., cellulose).

The isolation, purification, and utilization of polysaccharides are determined by their specific structural characteristics. While the overall structures of natural polysaccharides can be highly complex and diverse, their fundamental backbone chains often consist of carbohydrates like glucan, fructan, xylan, mannan, galactan, or combinations of several monosaccharides (Shi, 2016).

Polysaccharides can be categorized based on whether they are composed of either identical or different monosaccharides, resulting in the distinction between homopolysaccharides and heteropolysaccharides, respectively, as shown in Figure 2.3 (Nasrollahzadeh et al., 2021).

Polysaccharides constitute a diverse group of polymers characterized by a wide range of structures, which can be either linear or branched, and they are connected by various types of linkages joining the individual monomer units (Seidi et al., 2018).

Homopolysaccharides are polysaccharides made up entirely of a single type of monosaccharide. Natural polysaccharides constitute the building blocks of living organisms and are formed through condensation reactions of monosaccharides such as glucose, galactose, and fructose, etc. (Suner, 2018).

The term "heteropolysaccharide" may be used when two or more distinct types of monomeric units are present (Yadav & Karthikeyan, 2019).

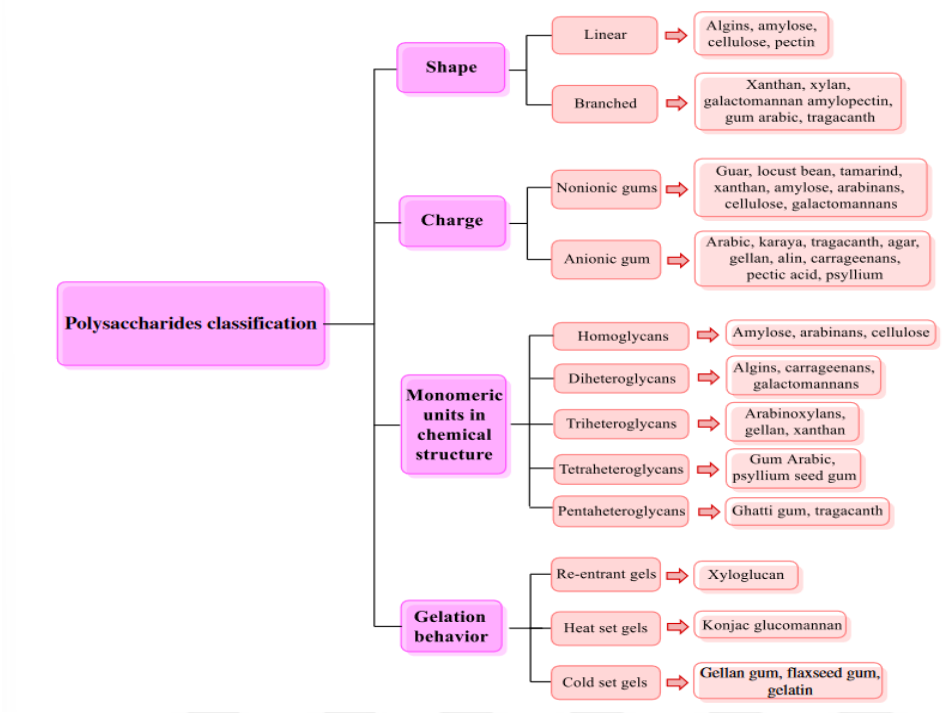


Figure 2.2: Polysaccharide classification.

Polysaccharides might be classified according to their origin, as given below (Yadav & Karthikeyan, 2019).

- Algal origin: alginates, galactans
- Animal origin: chitin, hyaluronic acid, glycosaminoglycans
- Microbial origin: pullulan, dextran, gellan, xantham gum
- Plant origin: exudate gums, cellulose, starch, guar gum, gum arabic, locust bean gum

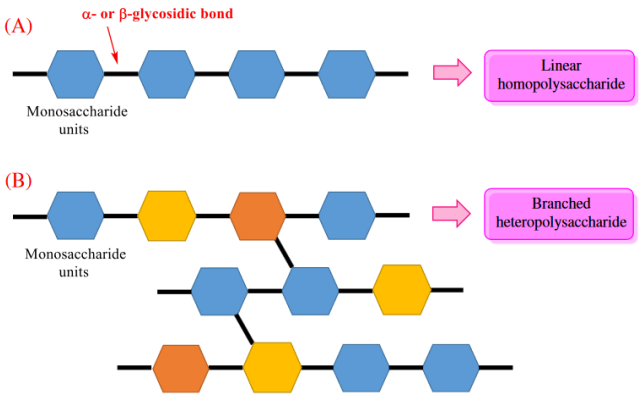


Figure 2.3 : A) Homopolysaccharide structure and B) Heteropolysaccharide structure.

2.2.1 Gums

Generally, they have a heteropolysaccharide structure formed by the bonding of various sugar units, and as the molecular structure changes, the physicochemical properties of the materials also vary (Suner, 2018). Some of the gums have bacterial origins, such as xanthan gum, guar gum, arabic gum, and etc. They are obtained through fermentation from bacteria such as Xanthomonas campestris. However, some gums are obtained from various plants like Caratonia silique, Cyamopsis tetragonalobus, Cyamopsis psoraloides, Acacia seyal, and Acacia Senegal.

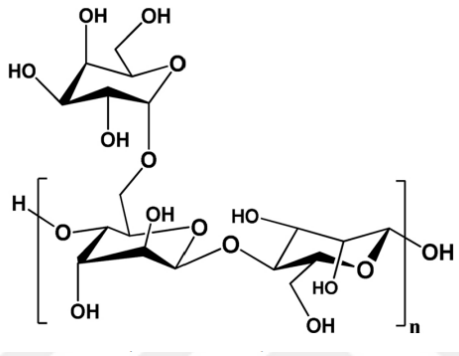


Figure 2.4: Chemical structure of guar gum.

Guar gum (GG) is a plant-based natural polysaccharide with a hydrophilic and non-ionic structure, consisting of 1→4-β-D-mannopyranose units with 1→6-β-D-galactopyranose groups attached to the main chain (Mudgil et al., 2012). One of the cheapest ways to obtain galactomannan is guar gum. The color of the guar gum is white to yellowish white. It is categorized as a high-molecular-weight polysaccharide. The chemical composition of guar gum is represented in Table 2.1 (Sharma et al.,2018).

Table 2.1 : Chemical composition of guar gum.

Components	Percentage
Polysaccharides, which are water-soluble	88.50
Polysaccharides which are not water-soluble	7.75
Protein	3.5-4.0
Fractions which are alcohol soluble	1.50
Ash	1.07
Nitrogen	0.67
Phosphorus	0.06

Guar galactomannan is formed from galactose and mannose units, with a ratio of 1:2 between them (Mudgil et al., 2012). Guar gums consist of a rod-like polymeric structures. Figure 2.4 and Figure 2.5 illustrate the different representations of guar gum (Mudgil et al., 2012, Sharma et al., 2018). The hydroxyl groups make the guar gum one of the best options for industrial applications (Sharma et al., 2018). It is widely used in industry due to its renewable source, biodegradable, and biocompatible properties, often obtained from sources like the Cyamopsis tetragonalobus plant. Its thickening properties make it particularly common in cosmetics and as a food additive in the food industry (Barbucci et al., 2008).

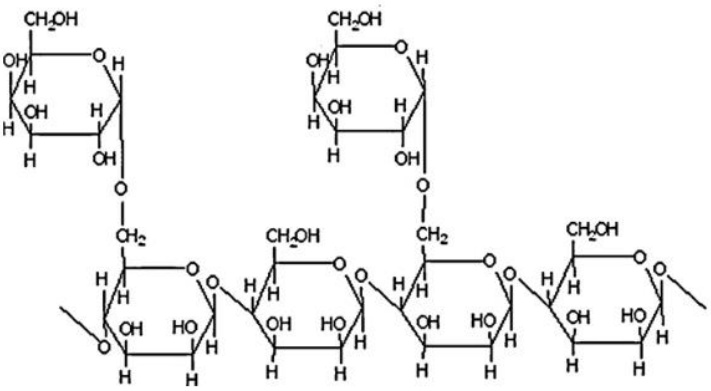


Figure 2.5: Guar galactomannan chemical structure.

In the literature, there are various potential applications for guar gum, such as the preparation of polymeric structures in nano, micro, and macro sizes, either alone or in conjunction with various biopolymers like xanthan gum, alginate, collagen, or synthetic monomers like acrylamide. These structures, including their cross-linked forms, have potential applications in a wide range of fields, including the purification and separation of biomacromolecules such as proteins and enzymes, immobilization, and drug delivery (Ahmed & Thomas, 2018; Suner, 2018; Valetti & Pico, 2016).

The elevated viscosity of guar gum solutions results from both the substantial molecular size of guar gum and the existence of extensive intermolecular connections (entanglement) facilitated by hydrogen bonding (Gong et al., 2012).

2.2.2 Gum production

Guar gum is industrially extracted from guar seeds. During the production process, mechanical processes such as roasting, dehulling, screening, and polishing are applied.

The protein-rich hull is utilized as animal feed. Refined guar is converted into a fine powder form depending on the desired final product structure. High-purity GG is produced in various viscosities, hydration capacities, and particle sizes for use in the food, feed, and pharmaceutical industries. One of the most significant characteristics of GG is its rapid hydration ability in cold or hot water to achieve homogeneous and very high viscosity even at relatively low concentrations. Another feature associated with GG is its ability to provide full viscosity even in cold water (Agkus, 2019).

2.3 Rheology

A branch of physics which concerns itself with the mechanism of deformable bodies is the definition of rheology (Lenk, 1978). Rheology, derived from the Greek word "rhein," meaning flow or stream, is a scientific discipline focused on the examination of how materials flow and deform. Instruments employed to assess these material characteristics are referred to as rheometers, and the associated measurement methodology is termed rheometry (Barnes et al.,2005).

In 1922, the American Rheological Society formally defined "rheology" as the scientific field dedicated to exploring the properties of matter related to deformation and flow. The term itself was coined by Professor Dr. Eugene C. Bingham, who was associated with Lafayette University in India in 1928 (Barnes et al.,2005).

The Two-Plates Model is a fundamental tool used to measure the flow behavior of materials, also known as their rheology. Imagine two flat plates with a gap (h) between them (Figure 2.6) (Mezger, 2014). The top plate is moved with a velocity v, causing the material within the gap to shear (slide past itself). By measuring the force F needed to move the plate and the resulting speed of the material, scientists can calculate important properties like viscosity.

Two key assumptions are made when using this model:

- No wall slip: The material sticks perfectly to both plates, meaning there's no slipping at the interface.
- Laminar flow: The material flows in smooth, parallel layers without turbulence or swirling eddies.

These assumptions are crucial for accurate measurements. If the material slips at the walls or experiences turbulent flow, the calculated rheological parameters will be inaccurate (Mezger, 2014).

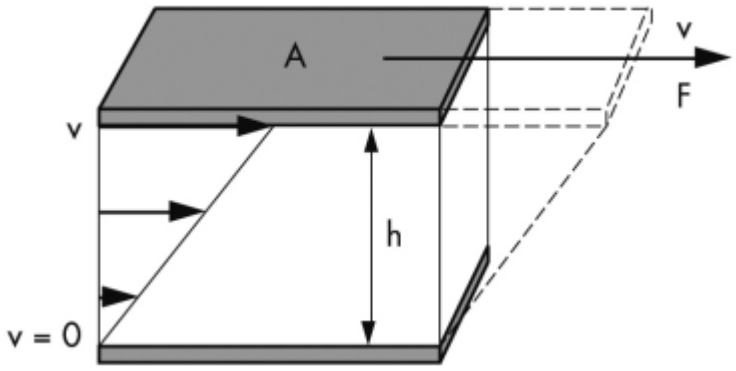


Figure 2.6: The Two-Plates Model is used in shear tests to show how a fluid's velocity distribution changes as it flows across a shear gap.

The shear stress (τ) is calculated by dividing force F by area A. The unit of shear stress is N/m^2 or Pa. Shear stress refers to the force component required to induce a specific deformation in a material. It results in the successive movement of adjacent parallel layers within a material body relative to one another.

The shear rate is a measure of the ratio between the velocity change (dv) and the distance (dh). It quantifies the rate of shear strain, which represents the relative deformation in shear per unit of time. The unit of shear rate is s^{-1}.

The ratio of shear stress (τ) and corresponding shear rate ($\dot{\gamma}$) is the apparent viscosity. The unit of apparent viscosity is Pascal-seconds, Pas (Mezger, 2014).

A substance that experiences continuous deformation under anisotropic stress conditions is called a fluid (Irgens, 2013). When fluids are in motion, their molecules move relative to each other, and this motion comes with internal frictional forces. As a result, any fluid in motion encounters resistance to its flow, which can be measured as viscosity. Substances that display noticeable flow properties are typically classified as fluids (Mezger, 2014). Basically, there are two different modes of rheological behavior: Newtonian and non-Newtonian (Zengin, 2019).

Newtonian fluids are independent of shear load, but they are dependent on pressure and temperature, as shown in Figure 2.7 (Acikgoz, 2014, Mezger, 2014). They can be expressed via Newton's law, see Equation 2.1 (Ionescu et al., 2020).

$$\tau_{yx} = -\eta\, \dot{\gamma}_{yx} \tag{2.1}$$

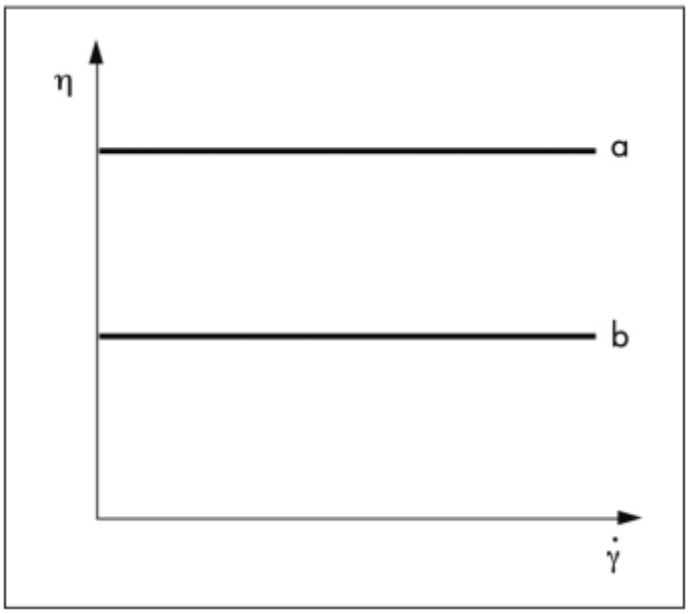


Figure 2.7: Two ideally viscous fluids' viscosity curves.

Within the realm of shear rates, two distinct regions are observed in the behavior of fluids. At low shear rates and very high shear rates, there exists a Newtonian region where viscosity remains constant, unaffected by changes in shear rate, as shown in Figure 2.8 (Ionescu et al., 2020). However, it is worth noting that the Newtonian plateau at extremely high shear rates is rarely observable due to limitations in measurement capabilities.

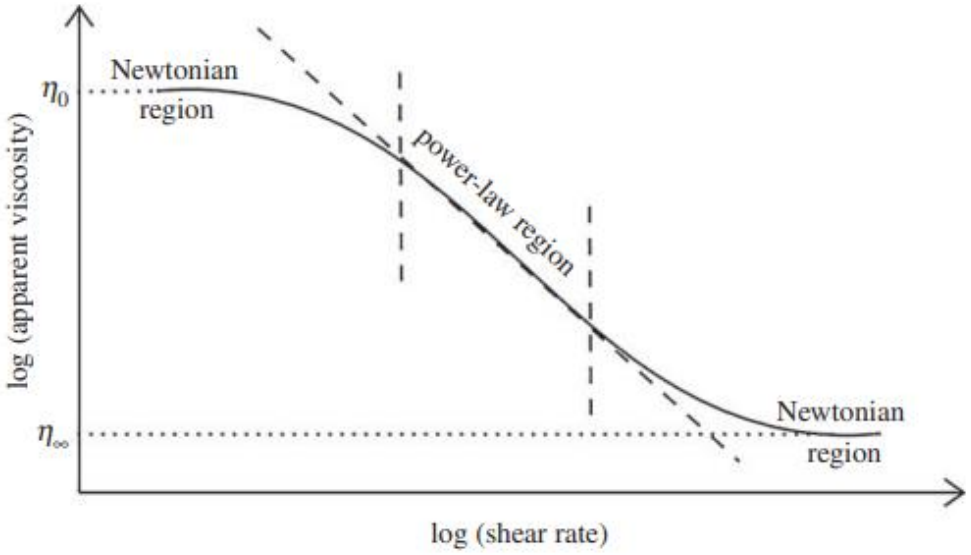


Figure 2.8: Apparent viscosity behavior for a pseudoplastic fluid.

Non-Newtonian fluids deviate from Newton's law, meaning that the relationship between shear stress and shear rate is not linear. In other words, their viscosity can change over time and depends on various factors such as flow conditions (like flow geometry), the applied shear stress, the developed shear rate, the duration of applied shear stress, and the past behavior of the sample. These fluids can be further categorized into three types: (i) shear-thinning or pseudoplastic, (ii) viscoplastics, including Bingham plastics, and (iii) shear-thickening or dilatant (Figure 2.9) (Ionescu et al., 2020, Elkington, 2023). The viscosity of shear-thinning fluids decreases with increasing shear rate. On the other hand, the viscosity of shear-thickening fluids increases under increasing shear rate.

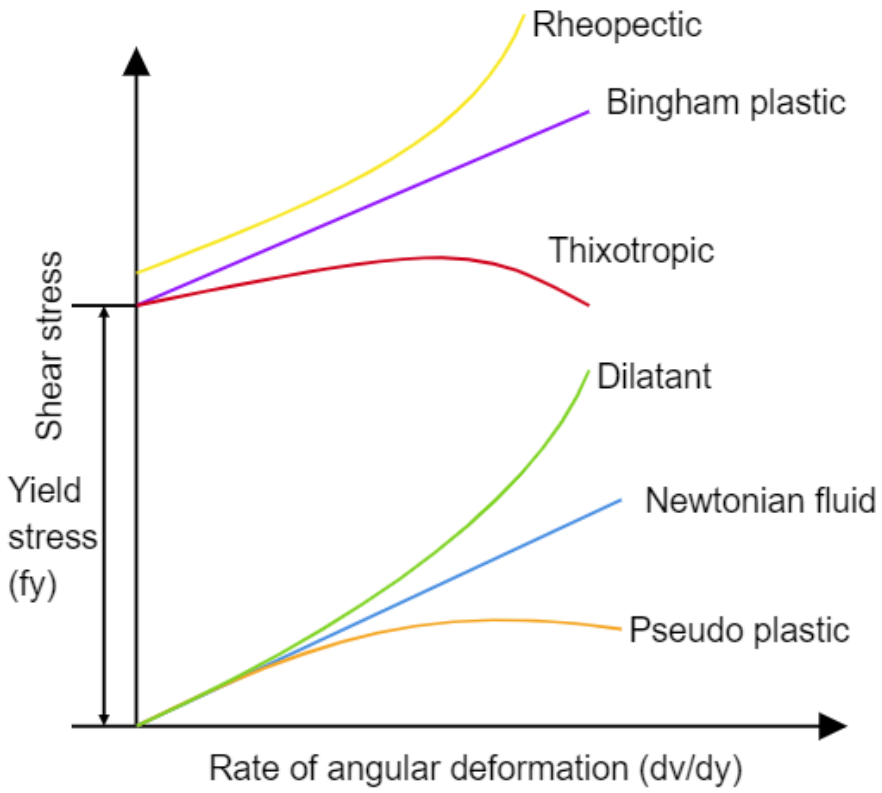


Figure 2.9: Viscosity curve of rheopectic, Bingham plastic, thixotropic, dilatant, Newtonian fluid, and pseudoplastic fluids.

The shear stress of thixotropic fluids at a constant shear rate decreases as a monotonic function. In addition to this, the shear stress of rheopectic fluids at a constant shear rate increases monotonically. These kinds of fluids are named thixotropic fluids.

The simplest viscoplastic fluid model, known as the Bingham fluid and named after Professor Bingham, who coined the term Rheology, exhibits Newtonian fluid behavior while in motion. There are various examples of fluids that display a yield shear stress, including drilling fluids, sand suspended in water, granular substances, margarine, toothpaste, certain types of paint, some polymer melts, and freshly mixed concrete. Figure 2.10 illustrates the velocity profile of a viscoplastic fluid flowing through a tube under the influence of a pressure gradient. In this flow, the central portion of the fluid moves uniformly, resembling a plug-like flow. An observable example of this behavior is the way toothpaste flows when squeezed from a toothpaste tube (Irgens, 2013).

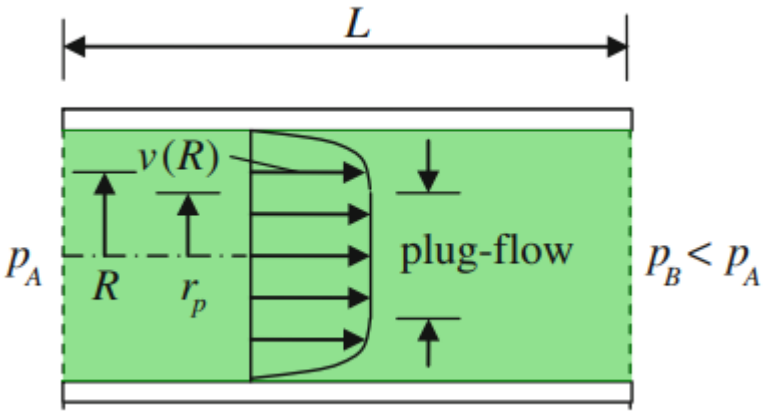


Figure 2.10: Plug-flow representation in a tube.

A purely viscous fluid is considered shear-thinning or pseudoplastic when its viscosity, as denoted by the viscosity function, decreases as the shear rate rises. (Equation 2.2)

$$\eta(\dot{\gamma}) = \frac{\tau}{\dot{\gamma}} \tag{2.2}$$

The majority of actual non-Newtonian fluids exhibit shear-thinning behavior. This includes nearly all polymer melts, polymer solutions, biological fluids, and substances like mayonnaise. The term "pseudoplastic" is used because the viscosity function of a shear-thinning fluid shares certain characteristics with the viscosity models of viscoplastic fluids.

In a relatively limited category of actual liquids, there's a phenomenon where the "apparent viscosity" (denoted as $\tau/\dot{\gamma}$) rises as the shear rate increases. These fluids are known as shear-thickening fluids or dilatant fluids, with the latter term emphasizing their tendency to increase in volume when exposed to shear stresses. Although these two effects may seem distinct from a phenomenological standpoint, fluids exhibiting one of these effects tend to display the other as well (Irgens, 2013).

3. EXPERIMENTAL WORK

3.1 Materials Used

Alfasol guar gum (GG) was supplied from Kimbiotek Kimyevi Maddeler San ve Tic. A.Ş. (3-Chloro-2-hydroxypropyl)trimethyl-ammonium chloride, 60% wt solution in water (CHPTAC) is purchased from Aldrich Chemical Co., and it was used as an etherifying agent. Sodium monocholoroacetic acid (MCA) was purchased from Riedel-De Haën. All reagents were used as received. During the preparation of the solutions used in the reactions, distilled water was used as a solvent.

3.2 Synthesis of Cationic Guar Gum

In the synthesis procedure of cationic guar gum, the slightly changed method of Huang et al. was used (Huang et al., 2007). Deionized water was used to dissolve 2 g of GG to prepare a 2% wt. concentration solution in water with the help of a mechanical stirrer. 10 ml 50 wt% aqueous NaOH was added into the reaction medium. A dropping funnel was used to add different amounts of a 60% wt CHPTAC aqueous solution to the alkali-GG solution after the GG had completely dispersed. The solution was then neutralized with 10% wt hydrochloric acid after being stirred continuously for 24 hours at 50 °C. Ethanol was used to precipitate the reaction product CGG, which was then washed twice with 75% ethanol. The product was put into distilled water and frozen. Cationic guar gum was obtained as a white powder after freeze-drying. The reaction details are mentioned in Figure 3.1.

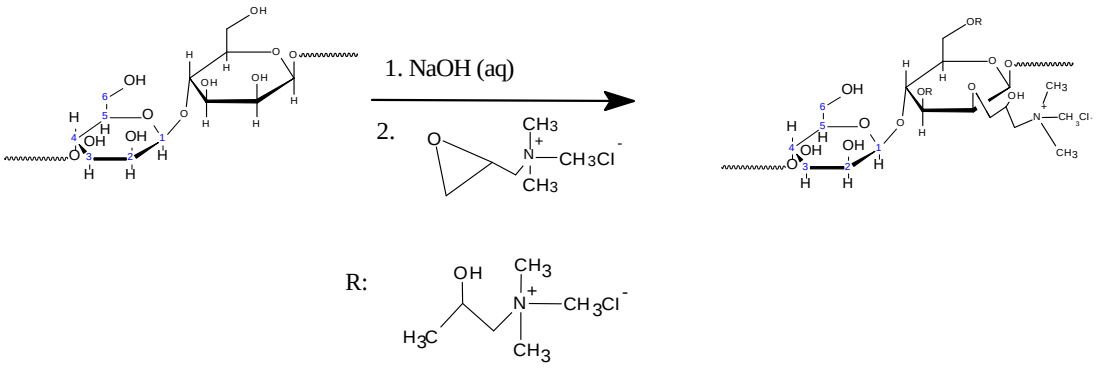


Figure 3.1 : Reaction scheme for cationic modification.

3.3 Synthesis of Anionic Guar Gum

The following method of Iqbal et al. was modified slightly to perform carboxymethylation from guar gum and monochloroacetic acid in a heterogeneous reaction environment (Iqbal et al., 2020). 2 gr GG was dissolved to prepare 2% wt. GG solution in water in mechanical stirrer. After GG was fully dissolved, nitrogen gas was purged into the reaction medium. 15 mL 10% wt. solution NaOH was added to the system by dropping funnel with a feeding rate of 1mL/min. Reaction was proceeded for 1h at 50˚C. Different concentrations of MCA were prepared separately. Sodium monochloroacetic acid solution (MCA) with different concentrations in distilled water was added to the system with a feeding rate of 1 mL/min at the same temperature. The reaction was proceeded for 3h at 50˚C. The reaction mixture was cooled to room temperature. The anionic guar gum was precipitated with ethanol. The product was mixed with distilled water. The prepared solution was frozen and freeze-dried. Anionic guar gum was obtained as a white powder after freeze-drying. The reaction details were mentioned in Figure 3.2.

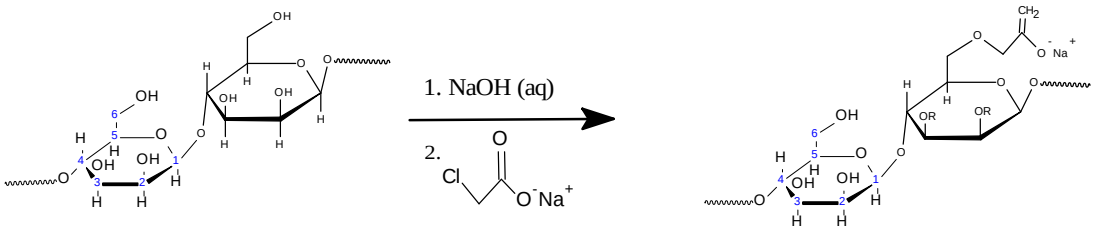


Figure 3.2 : Reaction scheme for anionic modification.

3.4 Characterization of Modified Guar Gums

3.4.1 FTIR-ATR spectroscopy

Fourier transform infrared (FTIR) analysis was carried out by Pelkin Elmer Spectrum Two, and attenuated total reflectance (ATR) accessory was used for the measurements. FTIR was used to determine the fingerprint of natural GG, synthesized cationic GGs, and synthesized anionic GGs. The products were measured using 4 scans, and the resolution was 4 cm^{-1}. The frequency range of the equipment was 4000-450 cm^{-1}.

3.4.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was measured by Mettler Toledo TGA 2 to examine the degradation mechanism of samples with respect to different temperatures. 4-8 mg samples were taken into the furnace. The sample was heated from 25°C to 600°C with a heating rate of 20 °C/min.

3.4.3 Proton nuclear magnetic resonance (^{1}H NMR)

Varian 500 MHz ^{1}H NMR was used for measurements. D_2O was selected for the solution.

3.5 Rheological Behavior

The rheological behaviour of each sample was determined by Anton Paar MCR 302 with a cylindrical head. The viscosity curve was drawn using RheoCompass software at 23°C. Viscosity was measured with respect to increasing the shear rate from 0.1 1/s to 100 1/s.

4. RESULTS AND DISCUSSION

4.1 Characterization of Synthesized Guar Gums

In this section, the differences among guar gum, cationic modification of guar gum, and anionic modification of guar gum are discussed by using FTIR, ^{1}H NMR, TGA, and rheological properties.

At the beginning of the laboratory studies, GG was tried to modified by using oleic acid. This reaction was not successful. The reaction product was not precipitated and collected. The first 5 experiments were based on the modification by oleic acid.

The cationic modification was the slightly changed version of the study of Huang et al. The quaternization of GG using CHPTAC as the etherifying agent underwent a series of sequential reactions facilitated by the catalytic influence of NaOH.

CHPTAC amount regarding reaction codes and yield percentage for cationic modification can be seen in Table 4.1.

The physical appearance of synthesized guar gums was fluffy white powders. The form of powder was changed in the addition rate of CHPTAC. When CHPTAC was added to the reaction medium quickly, the powder particles became denser than the reaction in which CHPTAC was added slowly.

The particle form of the product after cationic modification of GG can be seen in Figure 4.1. The form of the particle became fluffy after the treatment.

Table 4.1 : Cationic modification.

Sample Name	CHPTAC 60% amount, ml
AK-6	7.5
AK-9	30

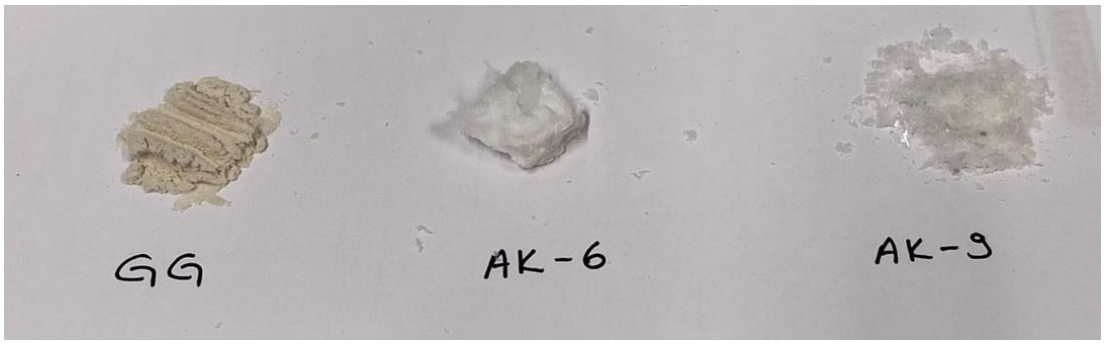


Figure 4.1: GG and different cationic modification of guar gums.

The anionic modification recipe was a slightly changed version of the study of Iqbal et al. Carboxymethylation of guar gum was done under heterogeneous reaction conditions.

MCA amount regarding reaction codes and yield percentage can be seen in Table 4.2.

Table 4.2: Anionic modification.

Sample Name	MCA amount in 15 mL dH_2O, g
AK-A1	4.0034
AK-A2	8.0038

The particle form of anionic modifications of GG can be seen in Figure 4.2: The form of the particle became fluffy after treatment. However, when they were compared to cationic derivatives of GG, cationic modifications had a more fluffy form than anionic modifications of GG.

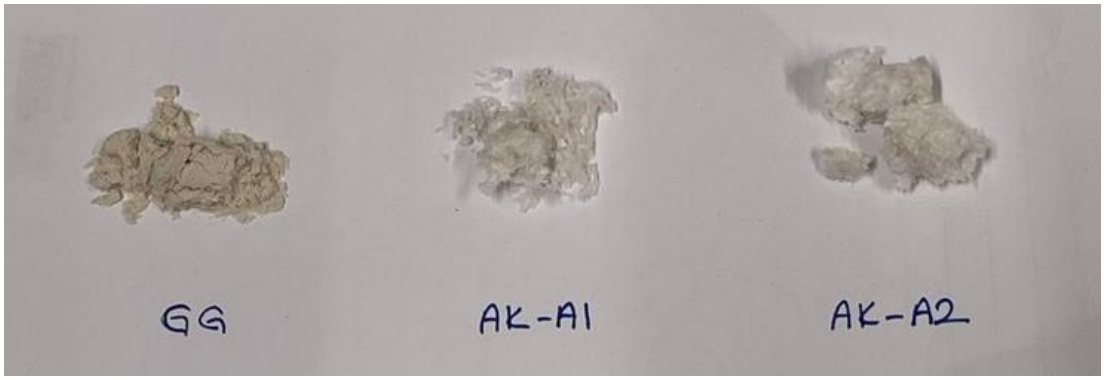


Figure 4.2: GG and different anionic modification of guar gums.

4.1.1 FTIR analysis

Each product resulting from the experiments has undergone FTIR analyses, and the characteristic peaks of guar gum have been identified. FTIR analyses of AK-6, AK-9, AK-A1, and AK-A2 have been examined to identify differences. The characteristic peaks of GG were mentioned in Table 4.3 (Mudgil et al., 2012).

FTIR analysis allows us to observe how intermolecular interactions impact the vibrations of groups within polymer segments. The provided figure displays the FTIR spectra of GG, AK-6, and AK-9, providing insights into these interactions (Huang et al., 2007).

The FTIR spectra of GG, AK-6, and AK-9 was mentioned in Figure 4.3.

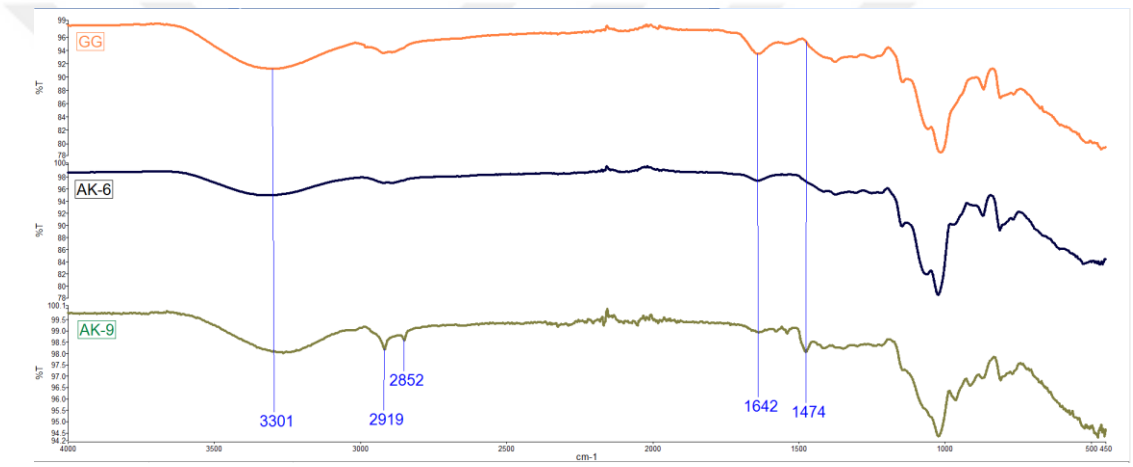


Figure 4.3: FTIR spectra of the GG, AK-6, and AK-9.

The peak that appeared at about 3300 cm^{-1} was the stretching frequency of the O-H groups. 2919 and 2852 cm^{-1} indicate -CH_2- symmetrical stretching vibrations. The absorption band at about 1642 cm^{-1} in guar gum was attributed to the scissoring motion of two O-H bonds in absorbed water. The intensity of the band at 1642 cm^{-1} decreased in AK-6 and AK-9. This result indicated that $–N^+(CH_3)_3$ ions were present(Kaur & Kaur, 2018). The presence of a band at 1474 cm^{-1} in the spectrum was an indication that the methyl groups of ammonium were present, suggesting that the synthesis of CGG has been successful (Huang et al., 2007).

The FTIR spectra of GG, AK-A1, and AK-A2 was mentioned in Figure 4.4.

Table 4.3 : Wave numbers of guar gum.

Characteristic group	Wave number (GG)
-OH stretching vibration	3300 cm^{-1}
-CH stretching of $-CH_2$ group	2900 cm^{-1}
-OH scissoring motion in absorbed water	1640 cm^{-1}

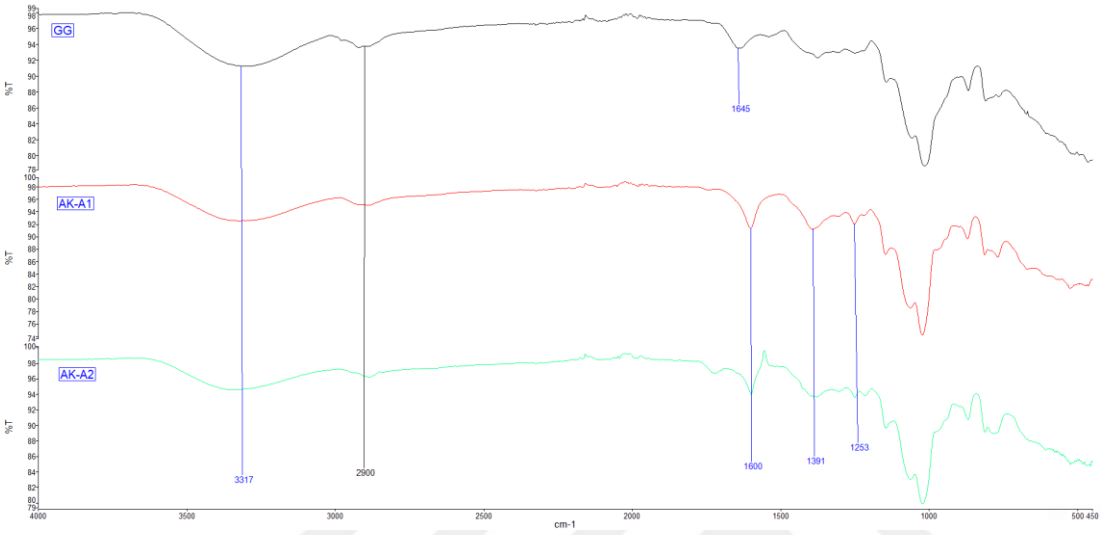


Figure 4.4: FTIR spectra of the GG, AK-A1, and AK-A2.

The FTIR results of anionic guar gums had a relatively weaker band at about 3317 cm^{-1}. This indicated that OH stretching of substituted OH groups (Iqbal et al., 2020). The band at about 2900 cm^{-1} was the indication of CH group stretching, and this peak had a relatively lower intensity compared to native guar gum. This showed that CH groups in the native guar gum reacted with MCA to form anionic guar gums (Dodi et al., 2011). The band at 1645 cm^{-1} in unmodified guar gum is attributed to the scissoring of two OH bonds of absorbed water molecules. The carboxymethylated guar gums had a new peak at about 1600 cm^{-1}, which indicates the $-COO^-$ asymmetric stretching vibrations. 1391 and 1253 cm^{-1} belonged to $-COO^-$ symmetric stretching vibration (Gong et al., 2012).

4.1.2 PCA method

Due to the minimal variations among the samples that were not easily discernible by the naked eye, a statistical approach was employed for differentiation. This study focused on examining the spectra of the obtained polymers, revealing the

concentration of specific regions in the results. To identify these subtle differences, a simplification process was applied using the Principal Component Analysis (PCA) methodology.

The main goal of employing the Principal Component Analysis (PCA) technique is to retain the dataset's highest variance in high-dimensional data while simultaneously reducing its dimensionality. To address potential variations arising from signal magnitudes and enable classification based solely on wave numbers in handling Fourier Transform Infrared (FTIR) data, pre-processing steps were implemented. Initially, the data spanning the spectral range of 2000 to 650 cm-1, where differentiation occurs, underwent transformation into the Fourier Transform Infrared (FTIR) absorption mode. Subsequently, normalization within the 0 to 1 range was applied to the dataset, followed by the computation of the second derivative. The processed data was then analyzed using R software, where PCA results were segregated into scores based on classes and loadings based on differences.

The analysis shows that the PC1 and PC2 charts provide the most substantial outcomes (Figure 4.5).

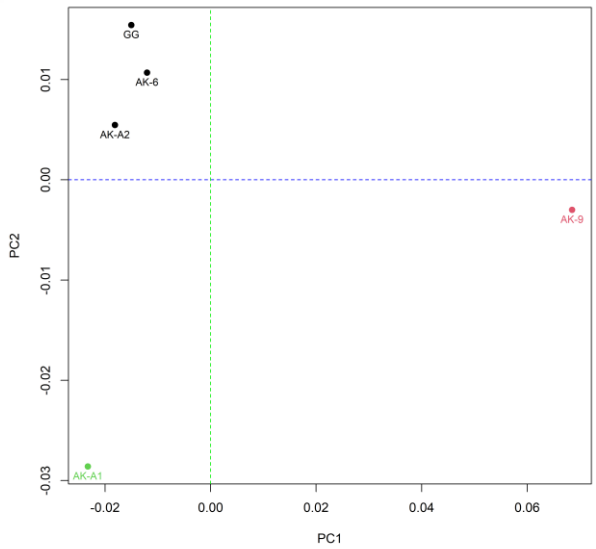


Figure 4.5: PCA scores plot.

The grouping of samples across distinct regions of PCA revealed variations linked to component proportions. A group of samples, predicted to have certain characteristics, were collected, as shown in the diagram. The findings of PCA pinpoint the precise spectral variation apparent in these polymers. The PCA scores plot grouping, loadings

plot differences, help to observe the positioning of the polymers in relation to GG, thus revealing the effect of the modifications. These polymer coordinates on the PCA graph reflect structural differences from the modifications.

The PCA scores plot demonstrated the degree of modification and deviation from the starting material by showing the distance between GG and other derivatives. The loadings plot revealed that PC1 was associated with the amine group at the 1450 cm-1 range, while PC2 corresponded to changes around the 1250 cm-1 range related to the skeletal and C-O-C groups of the structure. The successful modification was clearly indicated by the movement in the axes upon the introduction of the quarternized group and carboxyl group. The degree of modification is characterized by the colors. The different colors mean the high degree of modification, the same colors do not demonstrate huge degree of modification.

4.1.3 ^{1}H NMR analysis

The characteristic ^{1}H NMR peaks of guar gum in literature were located at 5.26 ppm and at 4.06 ppm (Radziej et al., 2022).

In the ^{1}H NMR spectrum of GG and AK-6 was shown in Figure 4.6. The peak arose at 4.67 ppm and was present in both GG and AK-6. This peak came from solvent. The presence of a peak at 3.08 ppm was observed in AK-6. This indicated that the proton of the alkyl group is present in the cationic modification of guar gum (Tyagi et al., 2020). The peaks between 3.17-5.26 ppm belonged to -R-C**H**(R')-OH in the polysaccharide structure in the ^{1}H NMR of GG. The modification changed the intensities and location of peaks in 1H-NMR spectrum. (Wang & Ye, 2023).

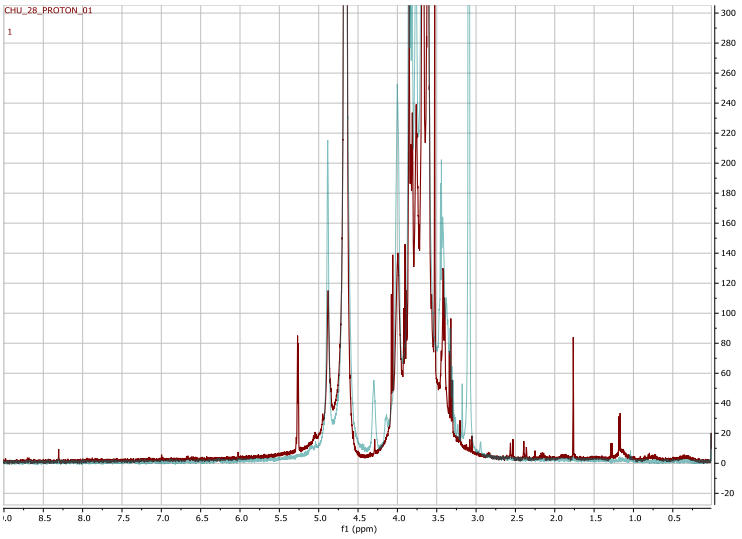


Figure 4.6: ^{1}H NMR spectra comparison of GG in red and AK-6 in blue.

The peaks between 3.29 and 4.07 ppm in the ^{1}H NMR spectrum of GG were due to H2-H6 on guar gum (Figure 4.7) (Dodi et al., 2011). In the ^{1}H NMR spectrum of GG and AK-9, the peaks, which were seen in the GG between 3.29 and 4.27, were shifted to 2.97 and 4.08 ppm in AK-9. There was a distinct peak at 4.30. This indicated that the proton of the alkyl group is present in the cationic modification of guar gum (Tyagi et al., 2020).

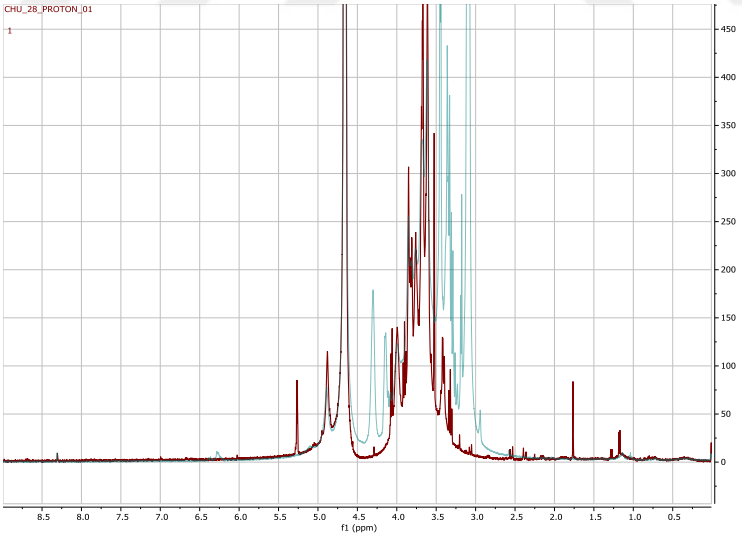


Figure 4.7: ^{1}H NMR spectra comparison of GG in red and AK-9 in blue.

The ^{1}H NMR comparison of GG and the reaction product after anionic modification (AK-A1) can be seen in Figure 4.8. The peaks at 3.79, 3.9, and 4.22 ppm arose from the methylene protons in the carboxymethyloxy substituents (Dodi et al., 2011). The

peaks between 3.20-4.10 ppm belonged to -R-C**H**(R')-OH in the polysaccharide structure in the ^{1}H NMR (Wang & Ye, 2023).

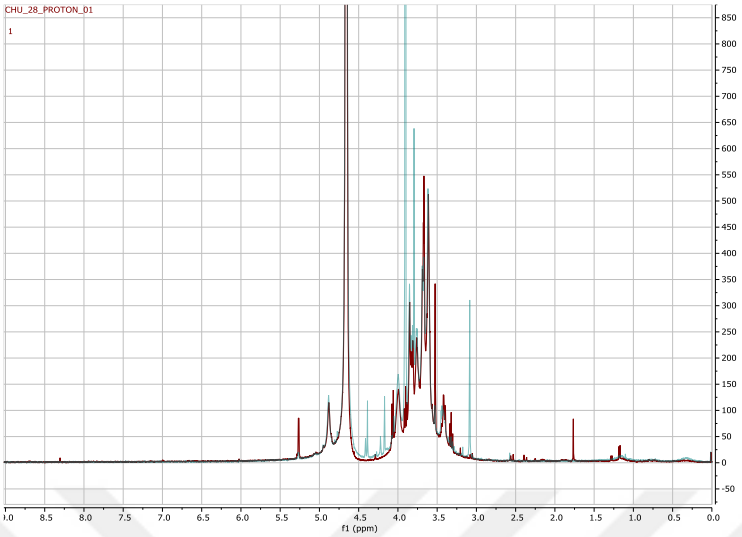


Figure 4.8: ^{1}H NMR spectra comparison of GG in red and AK-A1 in blue**.**

The ^{1}H NMR comparison of GG and the reaction product after anionic modification (AK-A2) can be seen in Figure 4.9. ^{1}H NMR spectrum showed peaks at 3.89, 3.90 and 4.22 ppm. These peaks belonged to the methylene protons coming from the carboxymethylation process (Dodi et al., 2016).

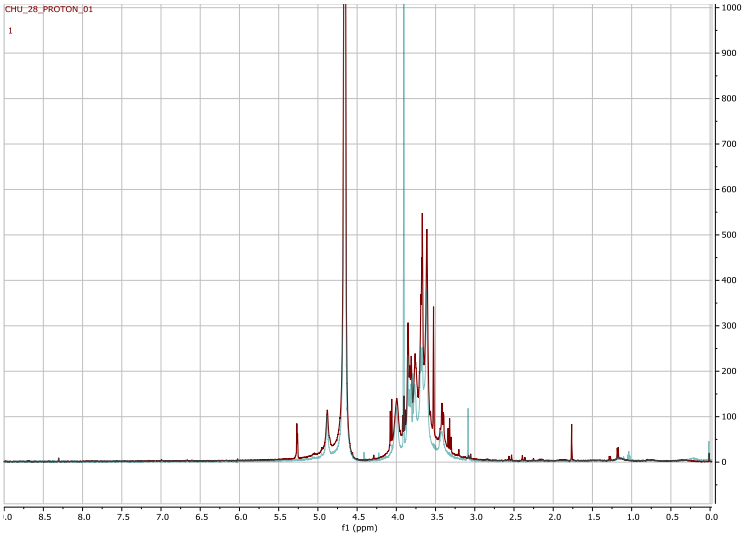


Figure 4.9: ^{1}H NMR spectra comparison of GG in red and AK-A2 in blue.

4.1.4 TGA measurements

The onset temperature is the point in the TGA curve where an initial deviation is noticed from the established baseline before the occurrence of a thermal event.

Activation energies of each reaction product and GG were calculated while using the Broido's method. When a product undergoes degradation upon heating, and it is assumed that the degradation products are volatile, the advancement of the degradation process can be monitored by continuously weighing the sample. Broido demonstrated that the weight of the sample (Wt) under thermal analysis at any given time (t) is connected to the fraction of the initial molecules that have not yet decomposed (y) through an equation (Broido, 1969):

$$y = \frac{Wt - W\infty}{W0 - W\infty} \tag{4.1}$$

The first-order kinetics of the equation becomes:

$$lnln\ \frac{1}{y} = \frac{-Ea}{R}\left(\frac{1}{T}\right) + const. \tag{4.2}$$

The onset temperatures regarding the initial and second weight loss of GG, AK-6, and AK-9 samples were mentioned in Table 4.4. TGA curves of AK-6 and AK-9 were shown in Figure 4.10.

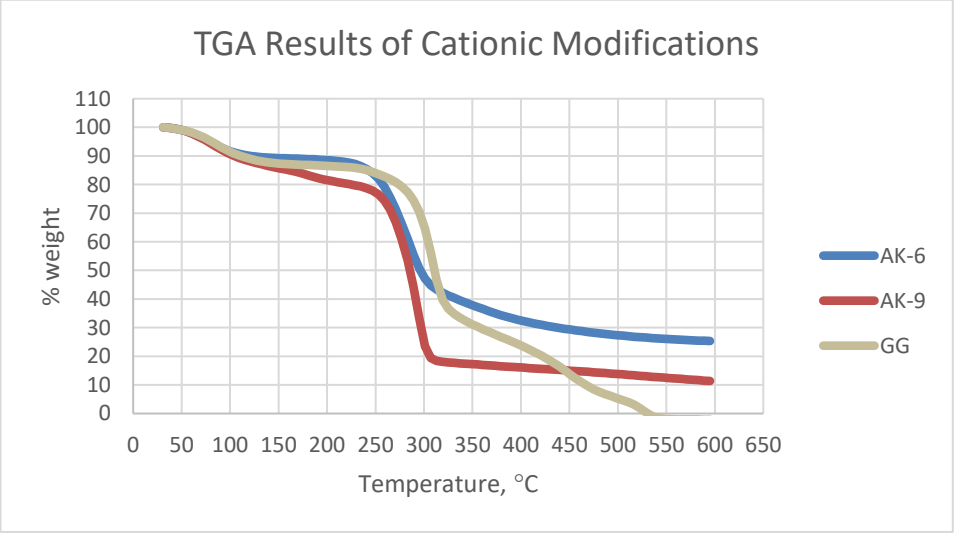


Figure 4.10: TGA spectra of GG, AK-6 and AK-9 with respect to temperature.

The thermal event occurred at around 280°C in GG. This degradation was due to the degradation of the glycosidic bond of the main chain with D-galactose. T_{50} value for GG is at 311°C (Motta et al., 2019). This peak resulted from to the decomposition of of (D)-galactose and (D)-mannose units of the guar gum molecule (Motta et al., 2019). The first weight loss was due to the evaporation of humidity in the samples. The second

weight loss temperature results of cationic derivatives are lower than natural GG, which showed that cationic modification was successful. The amine groups in the new modifications had lower thermal stability. The onset temperature of AK-9 was higher than that of AK-6 (Table 4.4). In AK-9, the added sides on the chain might attract each other, which increased the thermal properties. The T_{50} value indicates the temperature where the 50% weight is lost. The same trend was observed in the T_{50} values. GG has the highest T_{50} value.

Table 4.4 : TGA results of cationically modified guar gums.

Sample Name	Onset temperature for first weight loss	Onset temperature for second weight loss	T_{50} Values
GG	54.05˚C	289.22˚C	311°C
AK-6	47.70˚C	249.07˚C	297°C
AK-9	56.92˚C	258.20˚C	285°C

Broido's method was used to calculate the activation energies of reaction products after cationic modifications (AK-6 and AK-9) and guar gum (Figure 4.11). Different slopes indicated different degradation energies and different degradation steps. GG and AK-6 showed a degradation in 2 steps between 200°C and 400°C, whereas AK-9 showed a degradation in 3 steps. According to calculations, the activation energies regarding degradation steps were mentioned in Table 4.5. The activation energy of AK-9 is the highest in Table 4.5, which showed that AK-9 has stronger bonds than GG and AK-6.

Table 4.5: Activation energies of GG, AK-6, and AK-9

Reaction Code	Range, °C	Ea, kJ/mol
GG-1st degradation	235-325	138.40
GG-2nd degradation	325-391	37.06
AK-6-1st degradation	211-301	153.11
AK-6-2nd degradation	301-343	49.14
AK-9-1st degradation	205-253	77.61
AK-9-2nd degradation	253-313	172.17
AK-9-3rd degradation	313-343	28.82

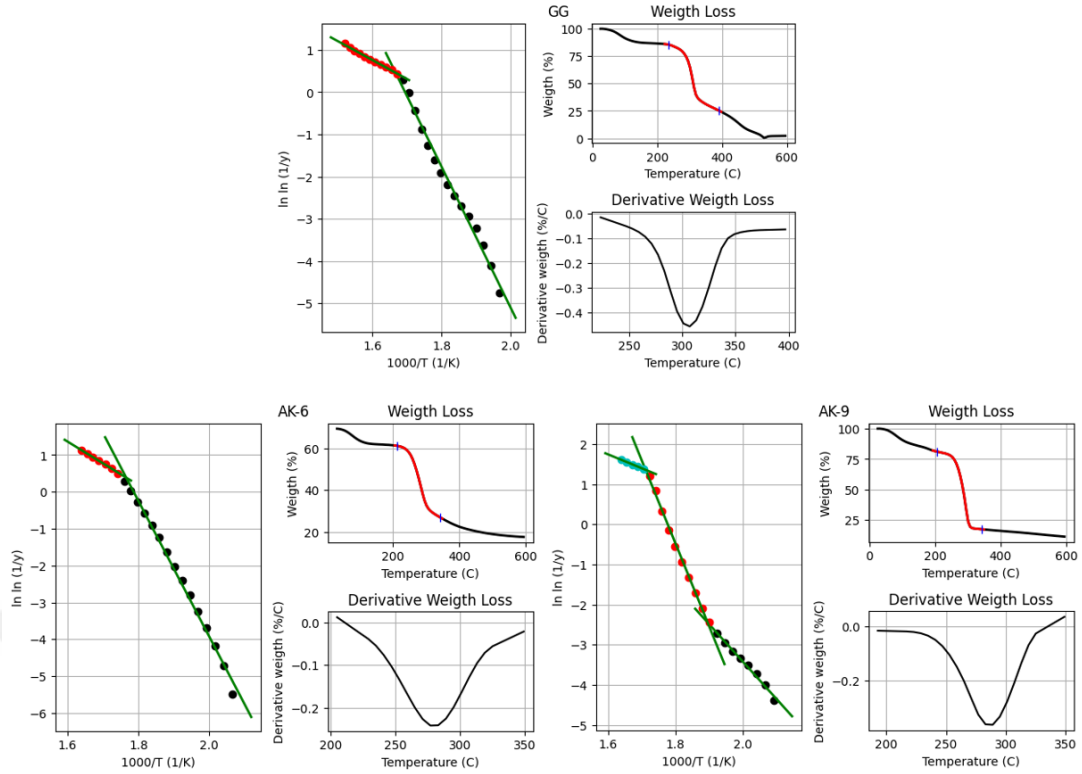


Figure 4.11: The activation energy graphs of GG, AK-6 and AK-9.

The onset temperatures regarding the initial and second weight loss of GG, AK-A1, and AK-A2 samples were mentioned in Table 4.6. The same situation with cationically modified was observed for anionically modified GGs. TGA curves of AK-A1 and AK-A2 were shown in Figure 4.12. The first weight loss was due to the evaporation of humidity in the sample. The second weight loss temperature results of anionic modifications are lower than natural GG, which showed that the carboxymethylation process was done successfully. The groups in the new modifications had lower thermal stability. The same trend was observed in the T_{50} values for anionic derivatives. GG has the highest T_{50} value.

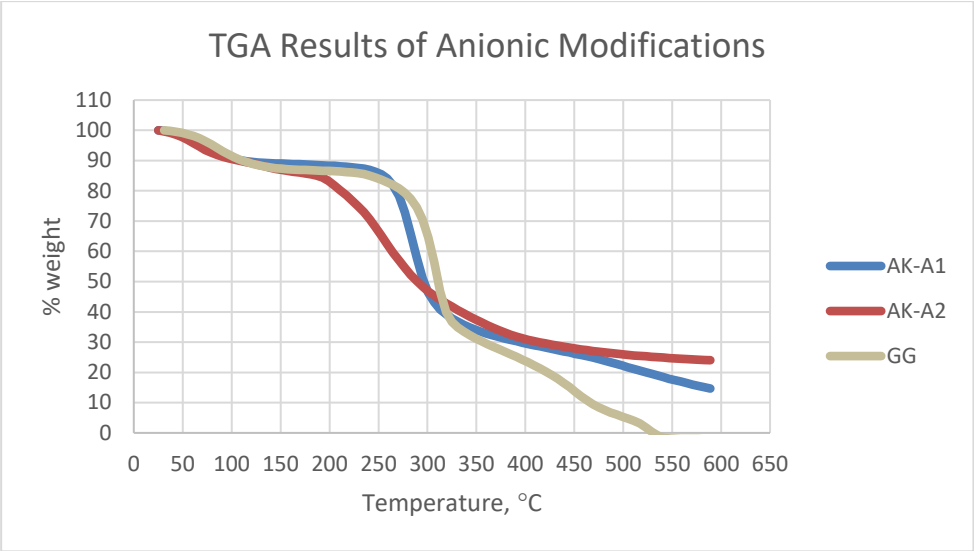


Figure 4.12: TGA spectra of GG, AK-A1 and AK-A2 with respect to temperature.

Table 4.6 : TGA results of anionically modified guar gums.

Sample Name	Onset temperature for first weight loss	Onset temperature for second weight loss	T_{50} Values
GG	54.05˚C	289.22˚C	311°C
AK-A1	55.08˚C	272.75°C	296°C
AK-A2	43.25°C	209.63°C	290°C

The same calculation method was used to calculate activation energies of reaction products AK-A1 and AK-A2 was used (Figure 4.13). GG showed a degradation in 2 steps between 200°C and 400°C, whereas AK-A1 and AK-A2 showed a degradation in 3 steps. According to calculations, the activation energies regarding degradation steps were mentioned in the Table 4.7. The activation energy of AK-A1 is the highest in Table 4.7, which showed that AK-A1 has stronger bonds than GG and AK-A2.

Table 4.7: Activation energies of GG, AK-A1, and AK-A2

Reaction Code	Range, °C	Ea, kJ/mol
GG-1st degradation	235-325	138.40
GG-2nd degradation	325-391	37.06
AK-A1-1st degradation	193-247	79.33
AK-A1-2nd degradation	247-307	170.22
AK-A1-3rd degradation	307-343	67.57
AK-A2-1st degradation	175-217	109.18
AK-A2-2nd degradation	217-283	66.59
AK-A2- 3rd degradation	283-541	25.78

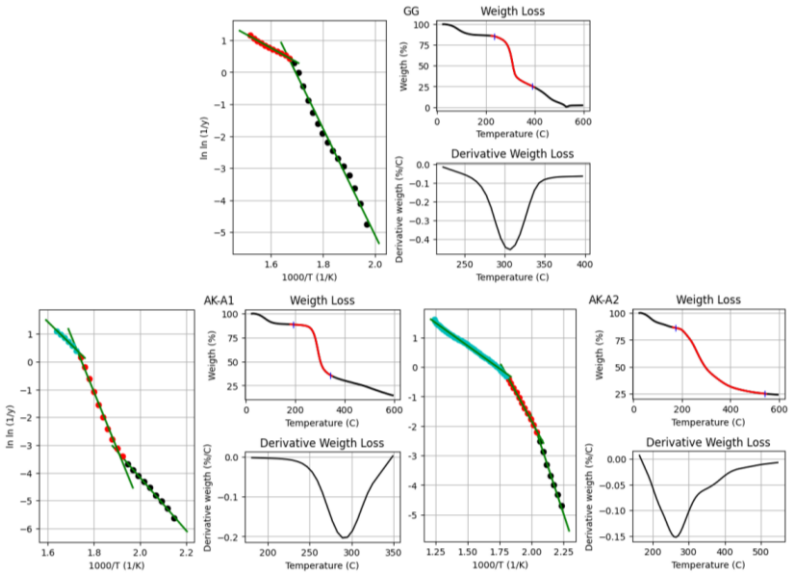


Figure 4.13: The activation energy graphs of GG, AK-A1 and AK-A2.

4.2 Rheological Analysis

The samples were evaluated under increasing shear rate. A viscosity flow curve test was done for the reaction products (AK-6 and AK-9) after cationic modification of GGs, the reaction products after anionic modification (AK-A1 and AK-A2) of GGs, and native GG in water media. The combination of cationic GG and anionic GG was also evaluated to understand the interaction between the molecules in water media.

4.2.1 Cationic GG

The viscosity of AK-6, AK-9 and native GG was evaluated under increasing shear at the same concentration in water. Native guar gum showed shear-thinning or pseudoplastic behavior. When GG was dissolved in water, the viscosity of the solution increased. The GG-water mixture became a gel-like material because there were OH groups on GG. These OH groups made a connection with water via H bonding. When the shear rate was applied, these H bonds were broken, which caused a decrease in viscosity. When native GG reacted with CHPTAC, OH groups on native GG were modified. -OH groups were interchanged by the amines group in CHPTAC. After that modification, the molecules showed Newtonian behavior in the water environment (Figure 4.14). The viscosity of AK-6 was higher than AK-9. In AK-6, there were more free-OH groups compared to AK-9, which caused AK-6 to have more viscosity.

4.2.2 Anionic GG

The viscosity of AK-A1, AK-A2 and native GG was evaluated under increasing shear rate at the same concentration in water. The native GG showed shear thinning flow behavior thanks to -OH groups on the chemical structure. The carboxymethylation process interchanged some of the -OH groups on the chemical structure to acidic groups. These acidic groups were also capable of making H bonding with water.

The modified GG by MCA showed pseudoplastic behavior. The anionic modification of GGs showed the same rheologic properties as the natural GG. The viscosity of modified GGs was higher than the natural GGs in all shear rates. The acidic group in modification enabled the molecule to make more H bonding with water, which caused it to have higher viscosity in water (Figure 4.15). The viscosity of AK-A1 was higher than AK-A2. In AK-A2, the side groups are sterically hindered by another chain. This caused the groups making H bonding to be preserved.

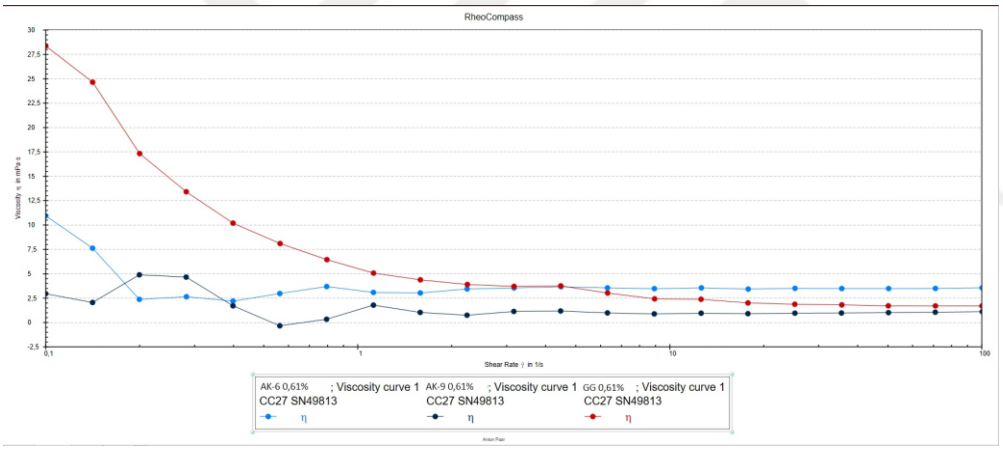


Figure 4.14: Viscosity vs shear rate curve of AK-6, AK-9, and GG.

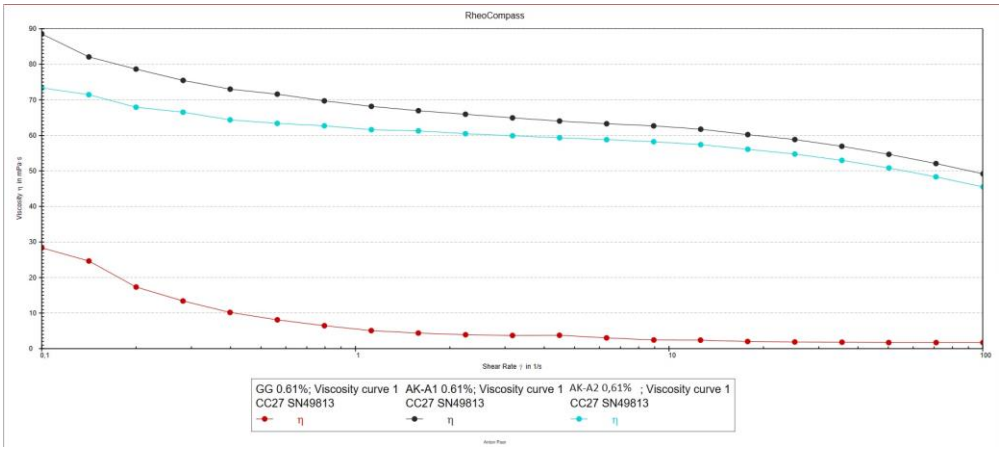


Figure 4.15: Viscosity vs shear rate curve of AK-A1, AK-A2, and GG.

4.2.3 Combinations of anionic GG and cationic GG

The solution of anionic and cationic modifications of GG, which were the same concentration in water, were mixed 1:1 to examine the rheological properties. When AK-6 and AK-A2 were mixed at the same amount, the mixture showed almost shear thinning flow behavior, whereas AK-6 showed Newtonian flow behavior (Figure 4.16). AK-A2 had more reactive side groups compared to AK-6. That's why the solution of AK-6 and AK-A2 showed shear thinning flow behavior as AK-A2. The acid groups on AK-A2 made H bonding with water. These bonds were weak. Under increasing shear rate, they were broken.

When AK-9 and AK-A2 were mixed 1:1 by weight, the mixture behaved like Newtonian fluid (Figure 4.17). Both modification products were dominant in the solution media. The salt formation led the solution of AK-9 and AK-A2 to show Newtonian flow behavior.

The AK-A1 was mixed with the cationic modifications with different CHPTAC amounts equally by weight. The blend of AK-A1 and AK-6 showed shear-thinning flow behavior like AK-A1 (Figure 4.18). AK-A1 had more reactive side groups compared to AK-6. That's why, the solution of AK-6 and AK-A1 showed shear thinning flow behavior as AK-A1. The acid groups on AK-A1 made H bonding with water. These bonds were weak. Under increasing shear rate, they were broken.

The mixture of AK-A1 and AK-9 showed pseudoplastic at low shear rates, whereas it behaved as Newtonian fluid at high shear rates (Figure 4.19). AK-9 was dominant in the solution. AK-A1 made H bonding via water molecules. These bonds were not strong. They were broken at low shear rates. After these bonds were broken, the solution showed Newtonian flow behavior because of the salt formation.

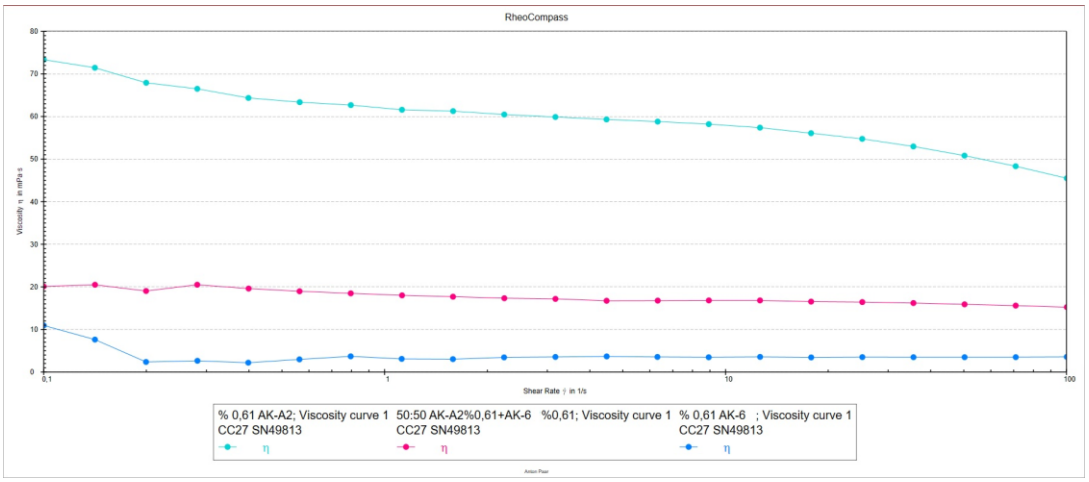


Figure 4.16: Viscosity vs shear rate curve of AK-6 and AK-A2 mixture.

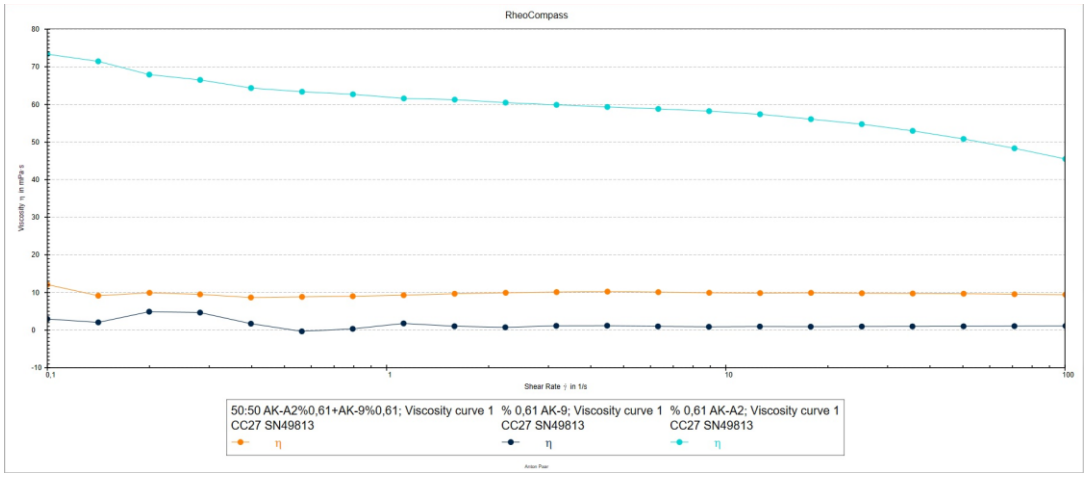


Figure 4.17: Viscosity vs shear rate curve of AK-9 and AK-A2 mixture.

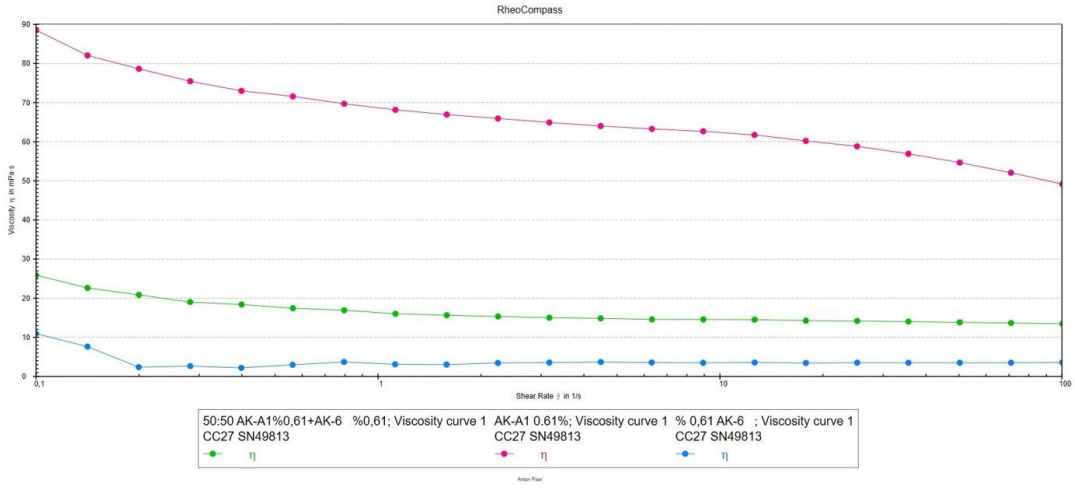


Figure 4.18: Viscosity vs shear rate curve of AK-6 and AK-A1 mixture.

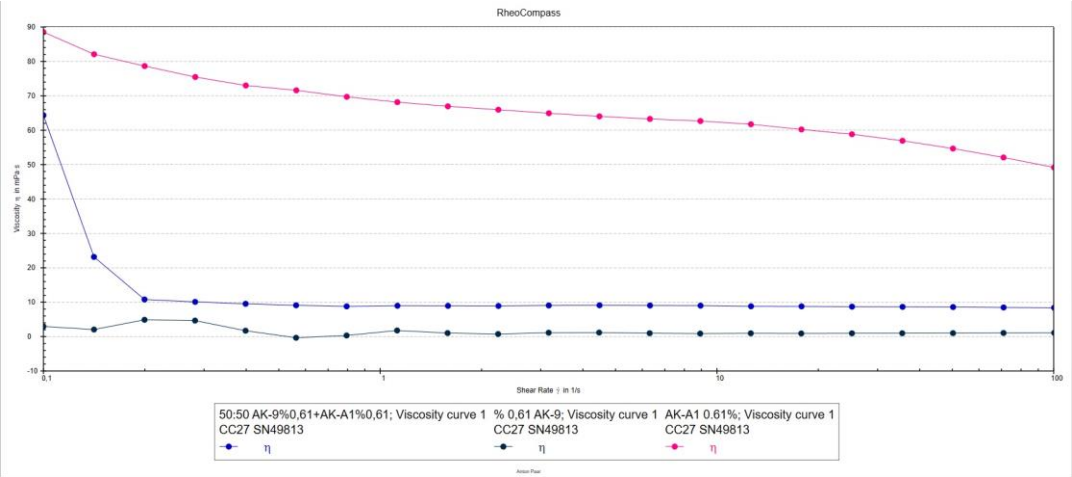


Figure 4.19: Viscosity vs shear rate curve of AK-9 and AK-A1 mixture.

5. CONCLUSIONS AND RECOMMENDATIONS

Having multiple OH groups, guar gum is a good thickener agent for aqueous systems, which makes guar gum an excellent rheology modifier for the textile, cosmetics, pharmaceutical, and paint industries. After the modification of guar gum, the rheological properties of natural guar gum were studied.

The identification of the modification was done by FTIR. In the cationic modification, the band at 1642 cm^{-1} showed that the reaction proceeded in a successful way.

The bands at 1600 cm^{-1}, 1391 cm^{-1}, and 1253 cm^{-1} indicated that anionic modification of guar gum was done successfully. These peaks belonged to the asymmetric and symmetric stretching of $-COO^-$ group.

Thermal properties of the modification and native guar gum were evaluated by TGA: The results showed that the modifications decreased the heat resistance of unmodified guar gum.

The rheological properties of guar gum, cationic modifications, and anionic modifications were evaluated by a rheometer using a flow curve. The cationic modifications of guar gum showed Newtonian flow behavior, whereas natural GG showed shear-thinning flow behavior. As the shear rate increases logarithmically, H bonds are broken, which caused a decrease in viscosity.

Anionic modification of GG behaved differently under increasing shear rate. The viscosity of both anionic modifications drops like native GG. However, the viscosity of the anionic modifications is much higher than the native GG at all different shear rates. The acidic group on the modifications was the reason for an increase in viscosity because of the H-bonding formation. Acidic groups on the modified GGs made H-bonding with water.

In the combination of anionic and cationic modifications, the mixture behaved differently. The solution of AK-6 showed Newtonian flow behavior, whereas AK-A2 showed shear-thinning flow behavior. The mixture of these two solutions had shear-thinning flow behavior.

The solution of AK-9 had Newtonian flow. However, AK-A1 displayed shear-thinning. The mixture of the solution of AK-9 and AK-A1 has a tendency to flow shear-thinning under low shear rates and Newtonian under high shear rates.

The mixture of the AK-9 and AK-A2 in water showed Newtonian flow, whereas the mixture of the AK-6 and AK-A1 had pseudoplastic flow behavior.

For further studies, the modified GGs would be mixed in different amounts to study the rheological properties of interactions, and the modifications would be tried in the paint as a rheology modifier.

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APPENDICES

APPENDIX A: Shear stress vs shear rate curves

APPENDIX A

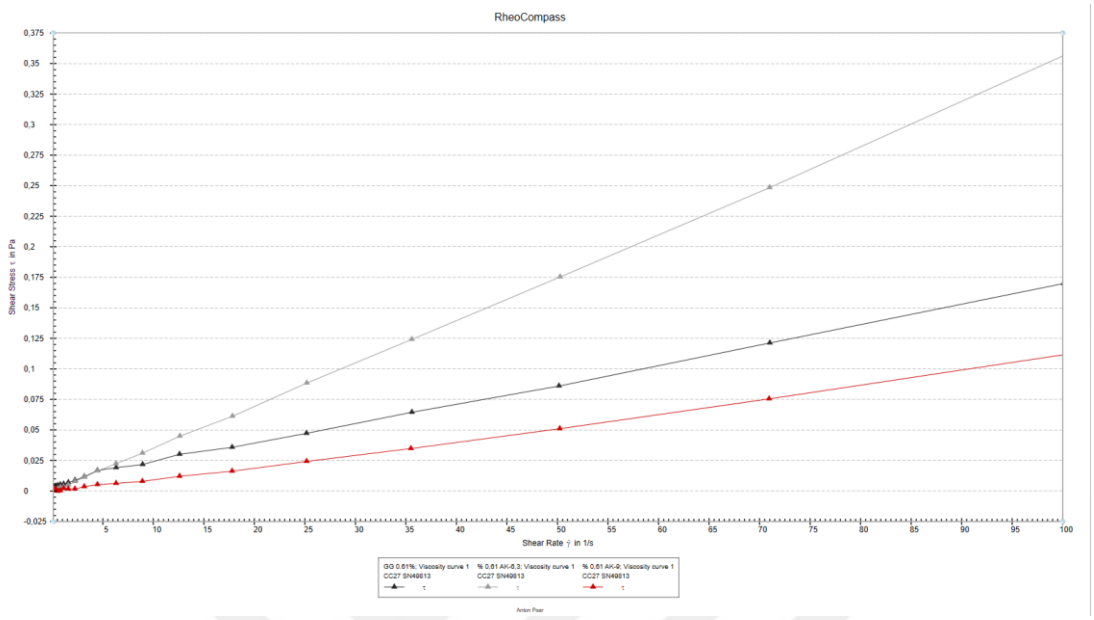

Figure A.1 : Shear stress vs shear rate curves of GG in black, AK-6 in grey and AK-9 in red.

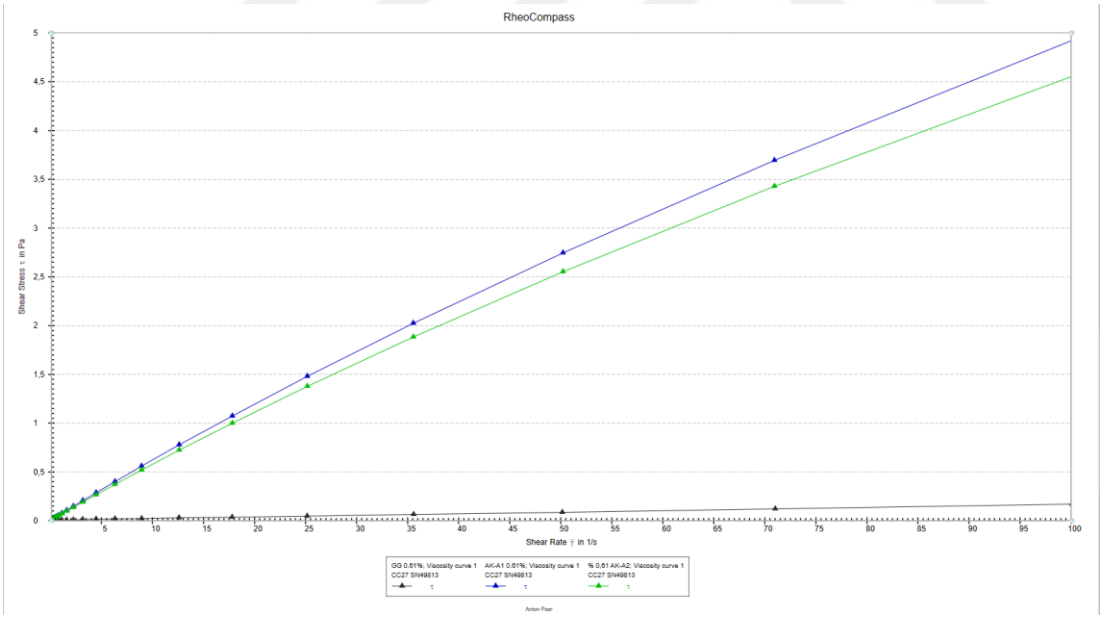

Figure A.2 : Shear stress vs shear rate curves of GG in black, AK-A1 in blue and AK-A2 in green.

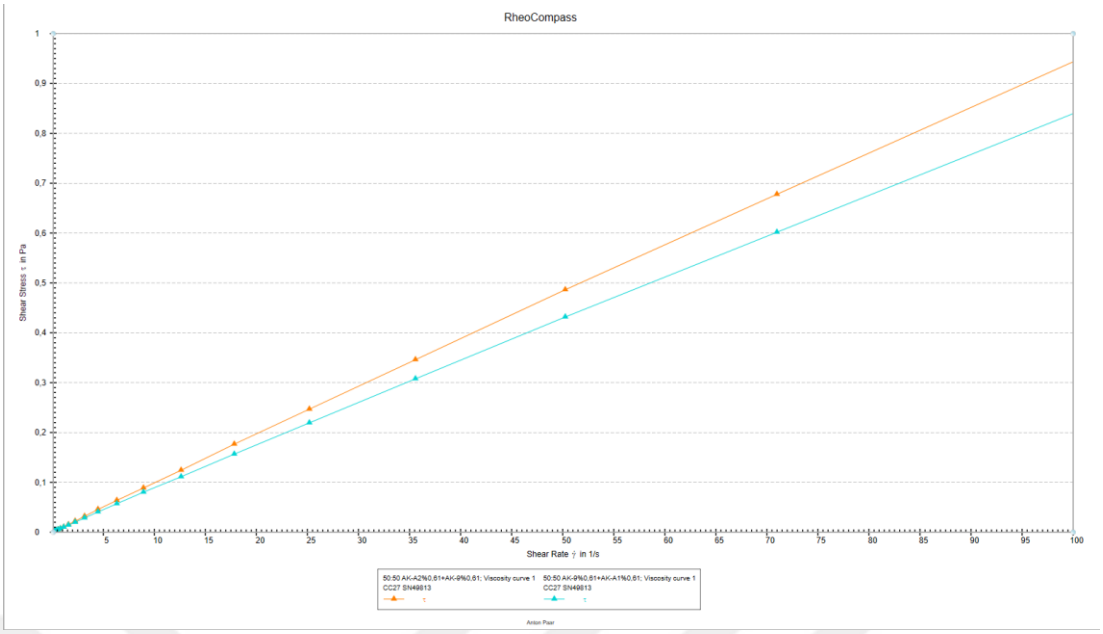

Figure A.3 : Shear stress vs shear rate curves of the mixture of AK-9 and AK-A1 in turquois, and AK-9 and AK-A2 in orange.

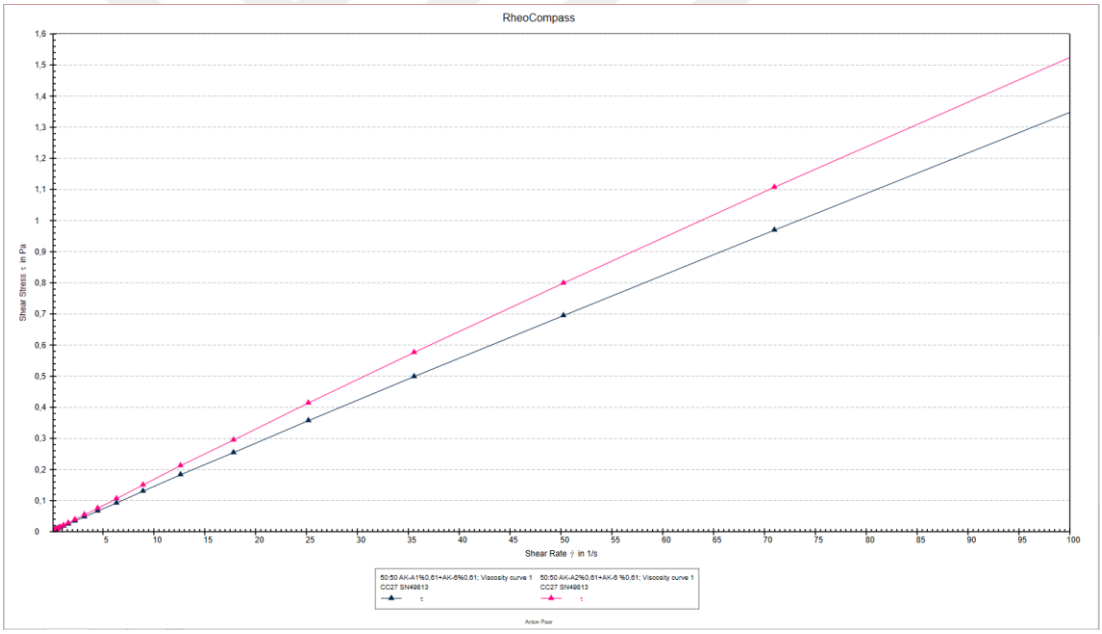

Figure A.4 : Shear stress vs shear rate curves of the mixture of AK-6 and AK-A1 in black, and AK-6 and AK-A2 in pink.

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