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**DEVELOPMENT OF WATER-BASED GELLING SYSTEM FOR
HIGH-TEMPERATURE WELLBORE CLEANOUT OPERATION**



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ABSTRACT

The concerns on finding an excellent gelling fluid for high temperature reservoir have dragged many attentions for the improvement of conventional gelling fluid. In the present study, cationic diutan gum (CDG) was modified to enhance its thermal and viscosity properties by attaching quaternary amine group to hydroxyl group of diutan gum (DG). N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) was used as the source of the quaternary amine group. The effect of differing concentration of CHPTAC with the presence of NaOH upon DG was studied. The efficiency of the modification was studied using Fourier transform infrared (FTIR), Field emission scanning electron microscope (FESEM), thermal analysis and viscosity analysis. The viscosity analysis shows that the viscosity increased as the amount of CHPTAC used increased. Moreover, from the thermal analyses, the data indicate that the cationic gum has much better thermal resistance compare with the unmodified gum. Therefore, the modification of DG by attaching the quaternary amine group on the hydroxyl group of DG has presented a promising alternative for the exploration of high temperature reservoir. In addition, the used of modified biopolymer like DG is a sustainable substitute for environmentally friendly gelling agent for oil and gas industry.

The logo for UIMP (Universitas Islam Malang) is a large, stylized letter 'U' composed of four overlapping triangles in shades of teal and light blue. The letters 'UIMP' are printed in white, bold, sans-serif font across the center of the 'U' shape.

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ABSTRAK

Kebimbangan mengenai penemuan cairan yang terbaik untuk takungan suhu tinggi telah menarik banyak perhatian untuk menambah baik cecair gel konvensional. Dalam kajian ini, kationik diutan gam (CDG) telah diubah suai untuk meningkatkan sifat haba dan kelikatannya dengan melampirkan kumpulan amina kuateren kepada kumpulan hidroksil diutan gam (DG). N-(3-chloro-2-hidroksipropil) trimetil amonium klorida (CHPTAC) digunakan sebagai sumber kumpulan amina kuaterner. Kesan kepekatan CHPTAC yang berlainan dengan kehadiran NaOH pada DG dipelajari. Kecekapan pengubahsuaian dikaji menggunakan Fourier pengubah inframerah (FTIR), mikroskop elektron pengimbasan pelepasan lapangan (FESEM), analisis haba dan analisis kelikatan. Analisis kelikatan menunjukkan bahawa kelikatan meningkat apabila jumlah penggunaan CHPTAC meningkat. Selain itu, dari analisis haba, data menunjukkan bahawa kationik gam mempunyai rintangan haba yang lebih baik berbanding dengan gam yang tidak diubahsuai. Oleh itu, pengubahsuaian DG dengan melampirkan kumpulan amina kuateren pada kumpulan hidroksil DG telah membentangkan alternatif yang menjanjikan untuk penerokaan takungan suhu tinggi. Di samping itu, penggunaan biopolimer yang diubahsuai seperti DG adalah pengganti yang mampan untuk agen gel mesra alam untuk industri minyak dan gas.

The logo of Universiti Malaysia Perlis (UMP) is a large, stylized letter 'V' shape. It is composed of four triangular sections meeting at the center. The top-left and bottom-right sections are light blue, while the top-right and bottom-left sections are light purple. The letters 'UMP' are written in a bold, white, sans-serif font across the center of the 'V' shape.

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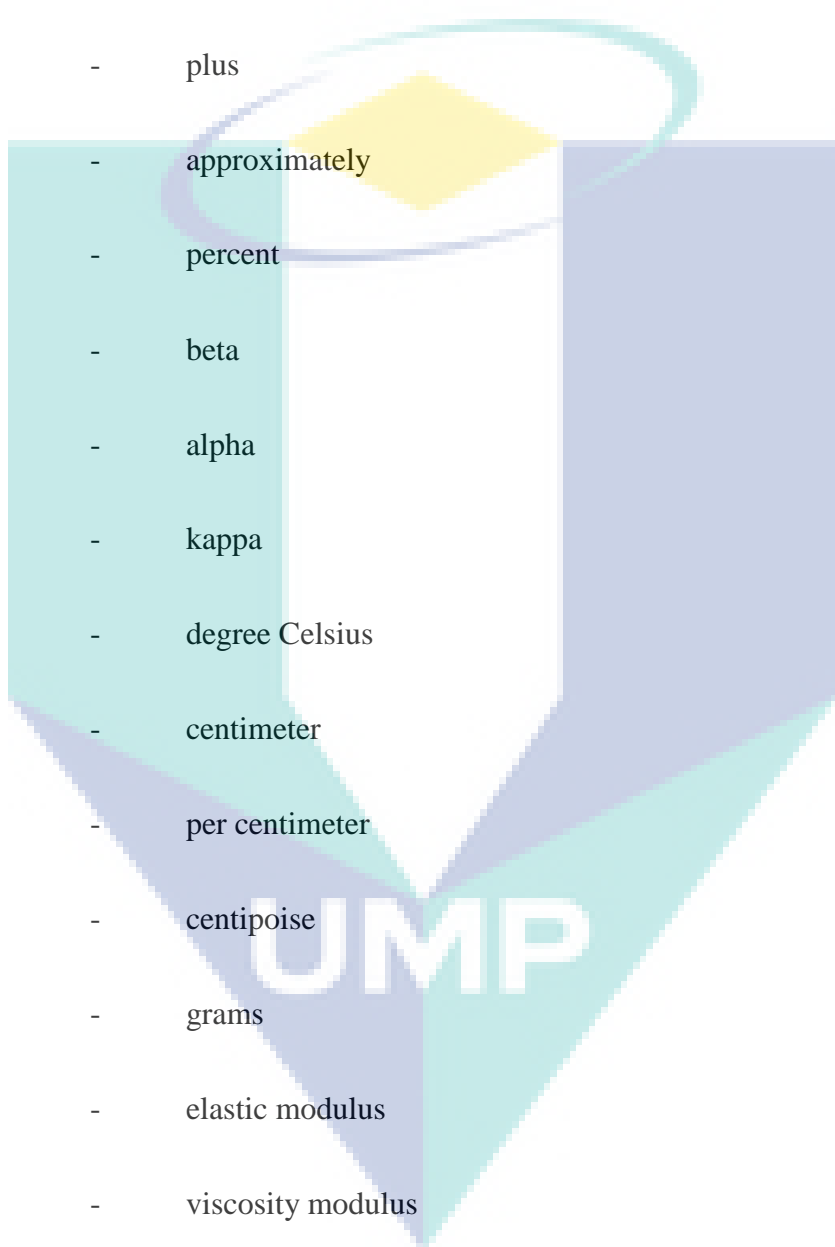


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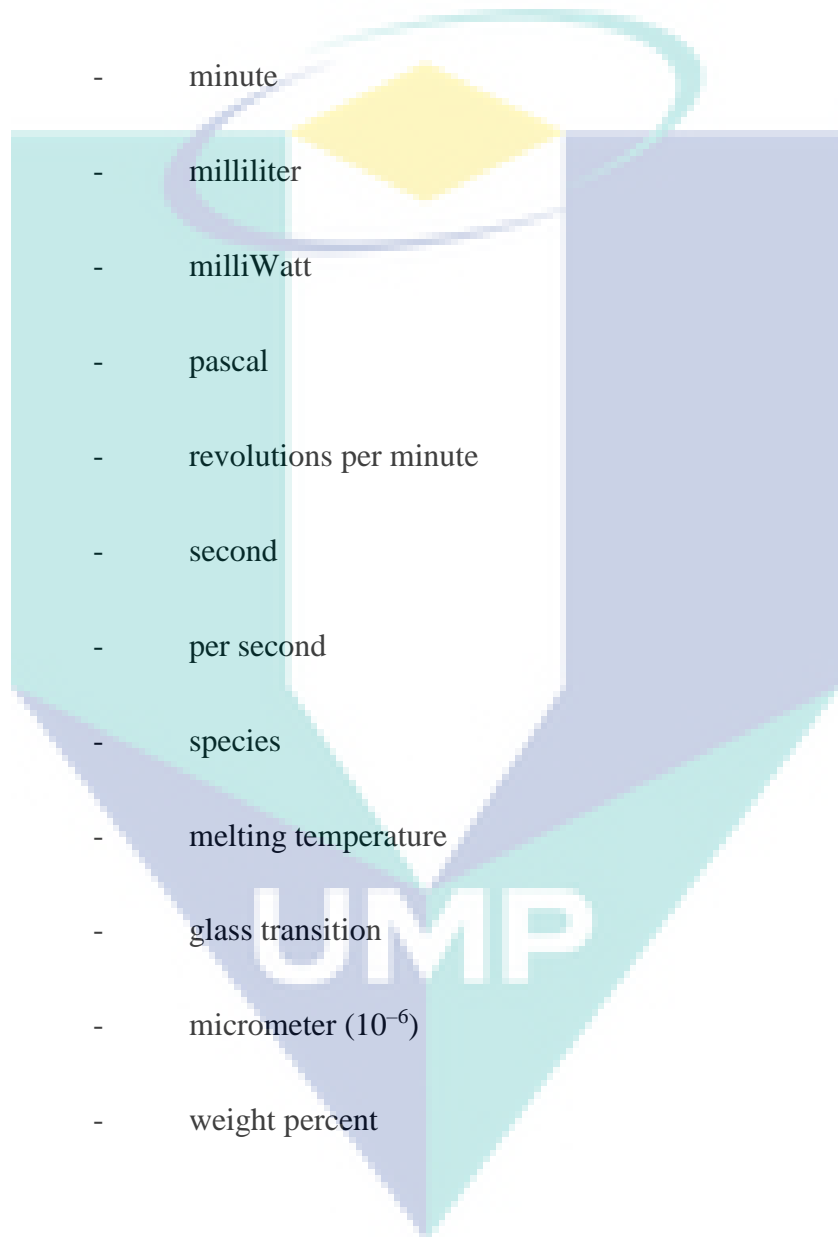
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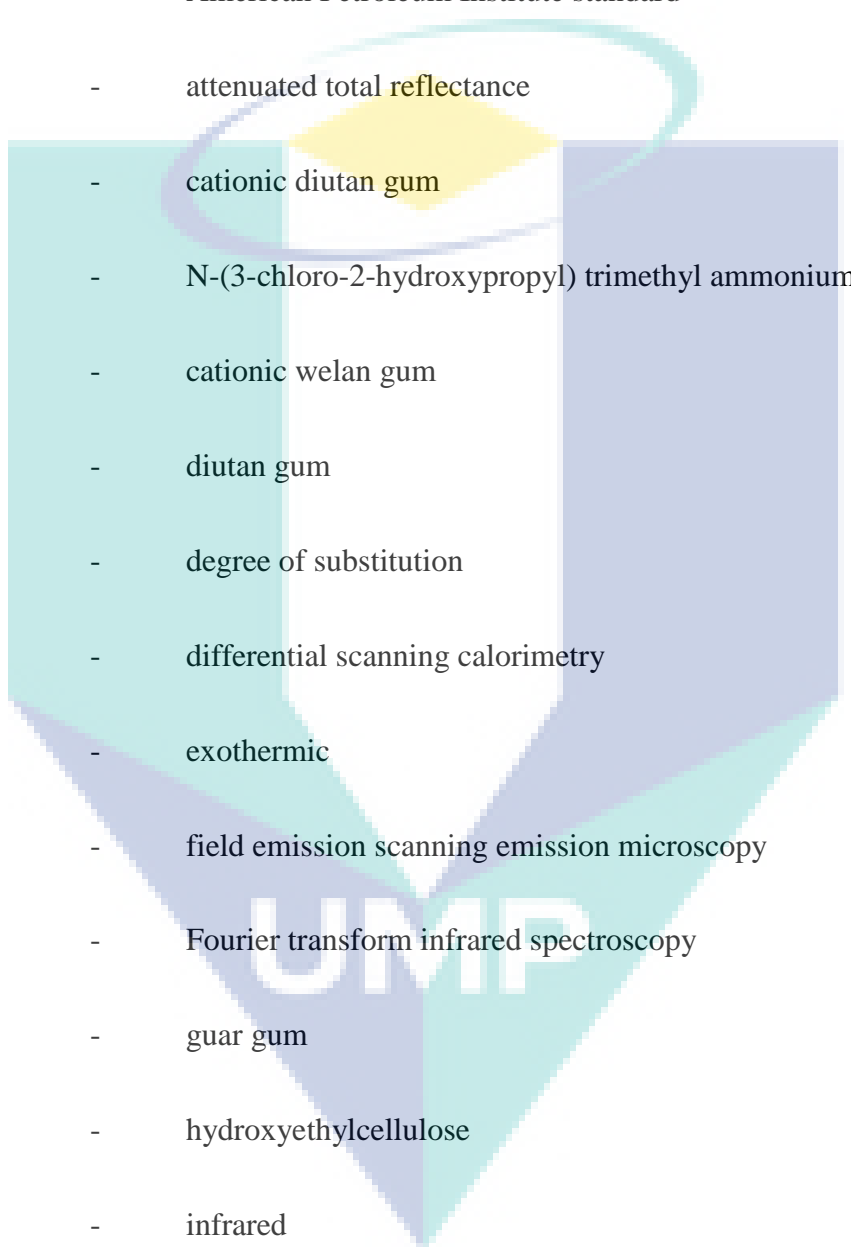


<	-	less than
+	-	plus
~	-	approximately
%	-	percent
β	-	beta
α	-	alpha
κ	-	kappa
$^{\circ}\text{C}$	-	degree Celsius
cm	-	centimeter
cm^{-1}	-	per centimeter
cP	-	centipoise
g	-	grams
G'	-	elastic modulus
G''	-	viscosity modulus
h	-	hour
Hz	-	hertz

kV	-	kilo volt
L	-	liter
mg	-	milligram
min	-	minute
ml	-	milliliter
mW	-	milliWatt
Pa	-	pascal
rpm	-	revolutions per minute
s	-	second
s ⁻¹	-	per second
sp.	-	species
T _m	-	melting temperature
T _g	-	glass transition
μm	-	micrometer (10 ⁻⁶)
wt. %	-	weight percent



LIST OF ABBREVIATIONS



API	-	American Petroleum Institute standard
ATR	-	attenuated total reflectance
CDG	-	cationic diutan gum
CHPTAC	-	N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride
CWG	-	cationic welan gum
DG	-	diutan gum
DS	-	degree of substitution
DSC	-	differential scanning calorimetry
EXO	-	exothermic
FESEM	-	field emission scanning emission microscopy
FTIR	-	Fourier transform infrared spectroscopy
GG	-	guar gum
HEC	-	hydroxyethylcellulose
IR	-	infrared
KBr	-	potassium bromide
LVER	-	linear viscoelastic region

MDG - modified-diutan gums

NaCl - sodium chloride

NaOH - sodium hydroxide

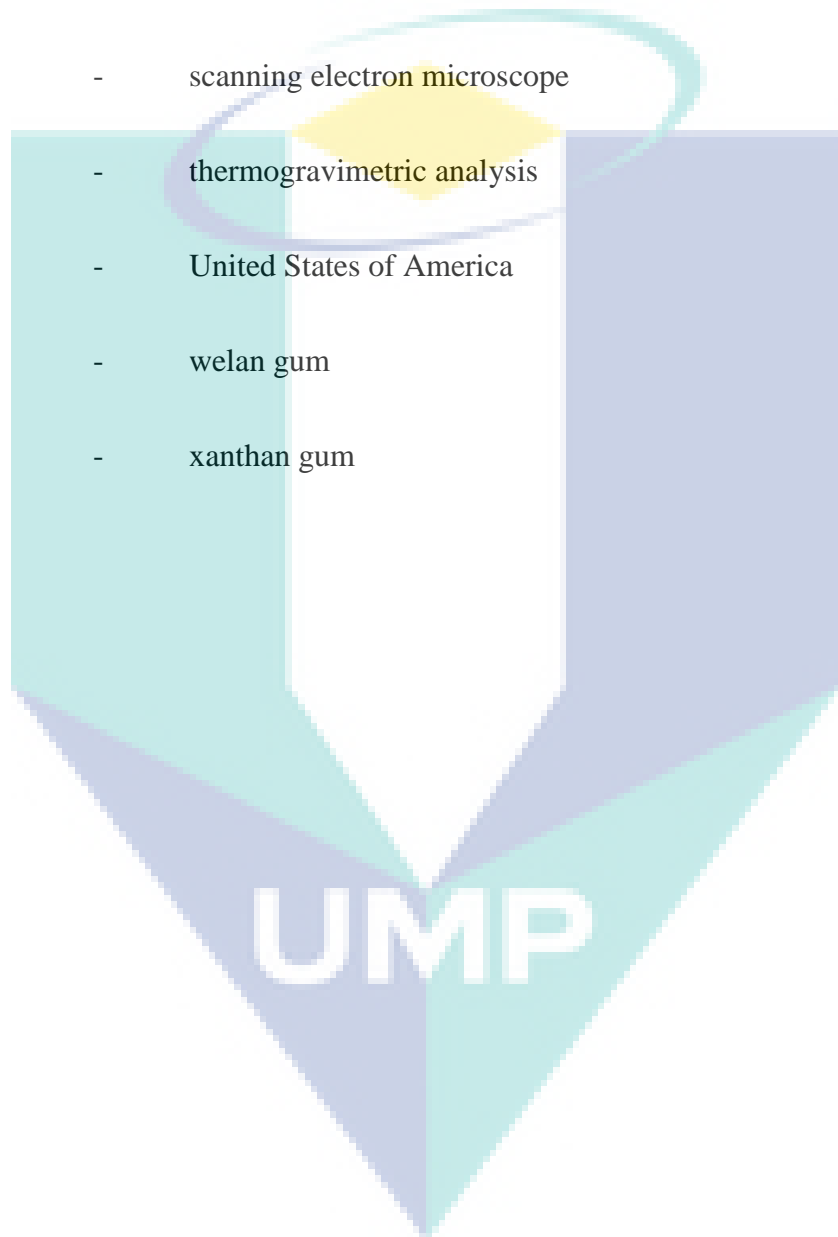
SEM - scanning electron microscope

TGA - thermogravimetric analysis

USA - United States of America

WG - welan gum

XG - xanthan gum



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CHAPTER 1

1. Introduction

Application of a viscous fracturing fluid in a wellbore has been a common practice to enhance the production of oil and gas hydrocarbons (Barati & Liang, 2014). Fracturing fluid is normally used to carry sand or proppant into subterranean formations to hold the fracture after the pressure is relieved, which in turn, increases the production of oil and gas from the well (Zhao et al., 2015). During the hydraulic fracturing process, fluids which consist of water, sand, and chemical are released at high pressure into the underground rock formation to create millimetre-sized cracks. This process will allow the natural gas trapped in the shale to flow from the fissures into the oil well. In order to produce the viscous fluid, a thickening or gelling agent such as polymer was added into water or an aqueous solution. Various polymers were known for this purpose, including a number of polysaccharides such as guar gum, guar gum derivatives (Wang, He, Guo, Zhao, & Tang, 2015), xanthan gum (Tian et al., 2015), carboxymethyl cellulose (Esmailirad, Terry, & Carlson, 2016) and hydroxyethylcellulose (HEC) (Abbas, Sanders, & Donovan, 2013). Usually, water-based fracturing fluids were preferable compared with oil-based fracturing fluid because they are environmental friendly, biodegradable, and derived from renewable resources.

However, because of the shift in oil exploration toward higher-temperature reservoirs, the application of conventional gelling agents was limited. When biopolymers are exposed to temperatures above 148 °C, they experience thermal degradation and lose their viscosity (Zha et al., 2015). Therefore, numerous researches were conducted to enhance the thermal properties of the

fracturing fluid which can be concluded into three; (1) modification with crosslinker, fluid loss additives and antioxidant (Dobson et al., 1998; Harris, 1993), (2) modification on the gelling agent structure (Dai et al., 2017; Shi et al., 2017; Yang et al., 2017), and (3) using double helical biopolymer (i.e. xanthan, diutan and welan gum) which believed suitable for high temperature and high salinity reservoir (Zhang et al., 2016; Li et al., 2017).

Out of all three methods used to enhance the thermal properties of the fracturing fluid, utilization of double helical biopolymers such as diutan gum (DG) and welan gum (WG) is much more promising and cost efficient. DG and WG is a natural high molecular weight microbial polysaccharide obtained from *Sphingomonas sp.* At present, DG and WG has been mainly used in cement and concrete industry where it can effectively improve the performance of the cement paste in term of viscosity (Zhang et al., 2010). Between those two, DG is reported more superior compared with WG. Moreover, it has been reported that DG is not sensitive to temperature and almost independent to the salinity producing steady apparent viscosity and dynamic modulus which can retained it viscosity at temperature up to 75 °C (Xu et al., 2015). DG was also claimed to be able to retain 90% of it viscosity at 90 °C (Li et al., 2017).

As the double helical biopolymers possess interesting rheological characteristics for high temperature and high salinity, it will be used as a control gelling agent for this study. The thermal stability of the DG will be further increased by modifying the DG structure via substituting some of the hydroxyl groups with quaternary amine groups to produce cationic-diutan gum (CDG). The properties of the DG and the CDG will be characterized using fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC),

thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM). After that, fracturing fluid will be prepared by hydrating the DG and CDG in brine using high speed mixer. Thermal stability of the DG and CDG fracturing fluid will be investigated using hot rolling oven in accordance to American Petroleum Institute standard (API RP 13I) while the rheological properties and suspension capability will be tested using rheometer in oscillation mode.

2. Problem Statement

Nowadays, as the oil exploration has shifted toward higher-temperature reservoir, various modifications have been done on several types of biopolymers. For instance, modifications on guar gum with borate as crosslinker have extended the thermal stability up to 148 °C (Harris, 1993). Crosslinked-guar will produce high viscosity gelling fluid. However, high viscosity requires high pressure to pump the gel which unfavorable during operation.

To overcome the limitation of the crosslinked-guar, xanthan gum is available and widely used as a water-soluble polymer. However, xanthan can only be used at moderate temperature and still could not solve the current problem associated to the high temperature well. Recently, modification on xanthan gum by substituting a quaternary amine groups on xanthan structure is reported have increased the thermal stability (Shi, Wei, Luo, Tan, & Cao, 2017). Hence, it is expected that by applying same modification on DG structure with quaternary amine groups, the thermal stability could be further increases as the quaternary amine group will provide a stronger electrostatic interaction among the chain thus enhances the gel-like structure.

3. Objectives

Broad objective of this research is to study the effect of substituting a quaternary amine on diutan gum to enhance its properties. To achieve this, following specific objective have been conceived.

- 1) To synthesis cationic-diutan gum with quaternary amine groups for fracturing fluid application.
- 2) To investigate the effect of cationic modification on thermal stability of cationic diutan gum.
- 3) To investigate cationic diutan gum viscosity and suspension capabilities via elastic modulus (G') and viscosity modulus (G'').

4. Scope of study

This study has divided into three phases as elaborated below:

Phase 1

In order to achieve objective number 1, the synthesis of CDG has conducted by substituting the hydroxyl group of DG with quaternary amine groups from N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC). The syntheses were performed by adding 0.5, 1.0, 1.5, 2.0 and 2.5 ml of CHPTAC into 30 g of DG to study the effect of different

concentrations of CHPTAC on DG structure. To confirm the modification, the DG and CDG were characterized using FTIR to investigate the presence of amine functional group on CDG.

Phase 2

To achieve objective no 2, TGA were performed to investigate the weight loss and decomposition temperature, while DSC were used to study the glass transition (T_g), and melting temperature (T_m) for DG and CDG. FESEM were used to monitor the morphology of the DG and CDG. The DG and CDG fracturing fluid were tested using autoclaves to determine the thermal stability of the fluid at high temperature up to 200 °C.

Phase 3

In order to achieve objective number 3, viscosity of the DG and CDG fracturing fluid were measured using Malven Kinexus Lab+ rheometer. Cup and bob geometry were used for the measurement with shear rate of 170 s^{-1} at ambient temperature and under non-isothermal heating from ambient to 140 °C. To determine the flow curve, samples were sheared from 0.01 to 1000 s^{-1} . Besides that, the suspension capabilities of the DG and CDG fracturing fluid were determined using rheometer with plate and plate geometry. The linear viscoelastic region (LVER) is determined by conducting the strain sweep from 0.1% to 1000% at frequency 1 Hz and the frequency sweep from 0.01 to 100 Hz. The elastic modulus (G') and viscosity modulus (G'') obtain from the testing were study to determine the suspension capabilities.

CHAPTER 2

Modification of Diutan Gum to Enhance Rheological Properties for Oil and Gas Application

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Abstract. A favorable gelling fluid for oil and gas industry is the one that have good rheological, thermally stable properties and environmental friendly. In the present study, a gelling agent, diutan gum (DG) was modified with N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) to enhance the rheological properties. The modified-diutan gums (MDG) were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and rheometer. FTIR result shows a significant decreasing of hydroxyl group intensity and the appearance of new peak at 1250 cm^{-1} attributed to the substitution of CHPTAC on the DG backbone. In addition, the rheological properties of the MDG fluid showed remarkable increases in apparent viscosity. The elastic modulus (G') and viscous modulus (G'') also increases showing that the MDG have good viscoelastic properties which due to the strong electrostatic interaction between the chains after the modification. This finding showed that, with simple modification using CHPTAC, the rheological properties of MDG gelling agent can be tailored and expected to increase the thermal properties.

Keywords: Diutan gum, elastic modulus (G'), viscous modulus (G''), quaternary amine group, polysaccharide gelling agent.

INTRODUCTION

Utilization of a viscous fluid in a wellbore have been a common practiced to enhance the production of oil and gas hydrocarbons [1]. In order to produce the viscous fluid, a thickening or gelling agent such as polymer was added into water or an aqueous solution. Various polymers were known for this purpose including a number of polysaccharides such as guar gum, guar gum derivatives [2], xanthan gum [3], carboxymethyl cellulose [4] and hydroxyethyl cellulose [5]. Usually, water-based fluids were preferable compared with oil-based fluid because it is environmental friendly, biodegradable and derived from renewable resources. Though the shifted in oil exploration toward higher-temperature reservoir, the application of conventional gelling agents was limited. When biopolymers exposed to the temperature above $148\text{ }^{\circ}\text{C}$, they experienced thermal degradation and lost their viscosity [6].

Numerous research was conducted to enhance the thermal properties including using a double helical biopolymer (i.e. xanthan, diutan and welan gum) which are believed suitable for high temperature and high salinity reservoir [7, 8]. However, in comparison of xanthan and welan gum, Hodder and co-worker [9] found that diutan gum (DG) had better carrying capacity for a given viscosity, alkaline degradation and better temperature resistance. DG is a natural high molecular weight microbial polysaccharide obtained from *Sphingomonas* sp. At present, DG has been mainly used in cement and concrete industry where it can effectively improve the performance of the cement paste in term of viscosity [10]. As the DG possesses interesting rheological characteristics for high temperature and high salinity, it will be used as a control gelling agent for this study.

Recently, xanthan gum have been modified with CHPTAC and shown a good heat resistance [11]. CHPTAC which is the source of the quaternary amine group have been widely used to improve the properties of many polysaccharides because of the stability and not a toxic reagent [12, 13]. Both DG and xanthan gum molecule exist as double helical polymer. However, xanthan structure will be converted to random coil at high temperature while DG will remain in double helix [14]. Therefore, DG modification with CHPTAC is expected to improve the thermal properties and believed a better result compare with modified xanthan. The modification is performed by substituting some of the hydroxyl groups of DG with quaternary amine groups to produce modified-diutan gum (MDG). The MDG powders were characterized and the gel from MDG powder is prepared to study the rheological properties under high temperature conditions.

MATERIALS AND METHODS

Materials

The DG is purchased from Permula Chemicals Sdn Bhd, Malaysia. N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) as an aqueous solution with a concentration of 60 wt%, absolute ethanol, sodium hydroxide (NaOH) and sodium chloride (NaCl) are purchased from Sigma Aldrich.

Preparation of MDG powder and MDG fluid

The DG (40g) was dispersed in 150 ml of ethanol-water solution (the mass fraction of ethanol is 85%). The DG ethanol-water solution was mixed with 3 ml of sodium hydroxide aqueous solution (40 wt%). The mixture was stirred at ambient temperature for 40 minutes. After that, CHPTAC was added and stirred at 70 °C for 3 hours for cationic modification. The mixture was washed thoroughly with absolute ethanol and followed by drying at 80 °C until constant weight achieved.

Next, MDG fluid was prepared by mixing 4.8 g of MDG powder with 2% of NaCl brine solution. The mixture was mixed in 1L beaker using Silverson mixer at 6000 rpm for 45 minutes at ambient temperature. The MDG fluid was kept stationary for overnight to remove the bubbles.

Characterizations

The IR spectra of the DG and MDG powder was collected on a Spectrum One (Perkin Elmer, USA) spectrometer using ATR method. The DG and MDG was scanned in the region of 400 to 4000 cm^{-1} and the signal is detected in transmittance mode (% T). The morphologies of DG and MDG powder were examined by scanning electron microscope (SEM) at 2000-fold magnification at an accelerating potential of 5 kV.

The viscosity and viscoelastic properties of the MDG fluid was measured by Malven Kinexus Lab+ rheometer using cone and plate geometry. The apparent viscosity was measured at constant shear rate (170 s^{-1}) at ambient temperature. For viscoelastic testing, linear viscoelastic region (LVER) need to be identified first by performing strain sweep from 0.1% to 1000% at frequency 1 Hz. After that, frequency sweep was performed from 0.01 to 100 Hz. All measurement was conducted within the LVER region.

RESULT AND DISCUSSIONS

Characterizations of MDG powder

The FTIR result of DG and MDG was illustrated in Figure 1. The broad transmittance peak between 3000 and 3600 cm^{-1} are due to the stretching vibration of O-H. The peak between 2980 and 3000 cm^{-1} is due to symmetric and asymmetric stretching vibration of C-H. The O-H (3000 – 3600 cm^{-1}), C=O (1726 cm^{-1}) and C=C (1600 cm^{-1}) peaks for DG have decreased due to the modification of quaternary amine group. The spectrum of MDG presents at peak 1400 cm^{-1} is due to C-H bending vibrations of methyl from the quaternary amine groups. Furthermore, a new peak appeared at 1250 cm^{-1} which is attributed to C-N stretching indicated that quaternary amine groups were

successfully implanted on DG. The assigned bands for the substitution are consistent with those reported for the reaction of xanthan [11], agarose [13], starch [15] and guar gum [16].

Figure 2 shows the surface morphology of DG and MDG powder by SEM photograph. Significant differences can be observed between DG and MDG morphology. The DG surface is smooth and no crack is observed. After the modification, the surface of MDG became slightly rough and cracks were observed. This differences might probably due to the result from grafting reaction between hydroxyl group and quaternary amine group [11].

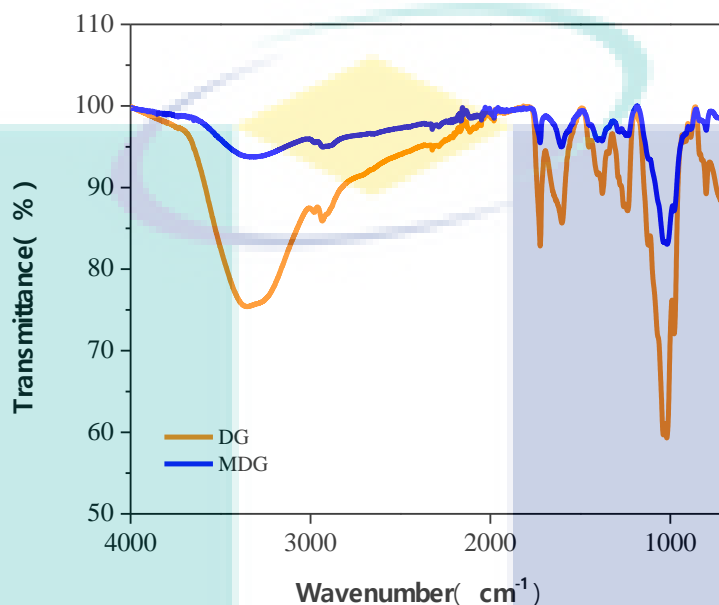


FIGURE 1. FTIR spectra of DG and MDG

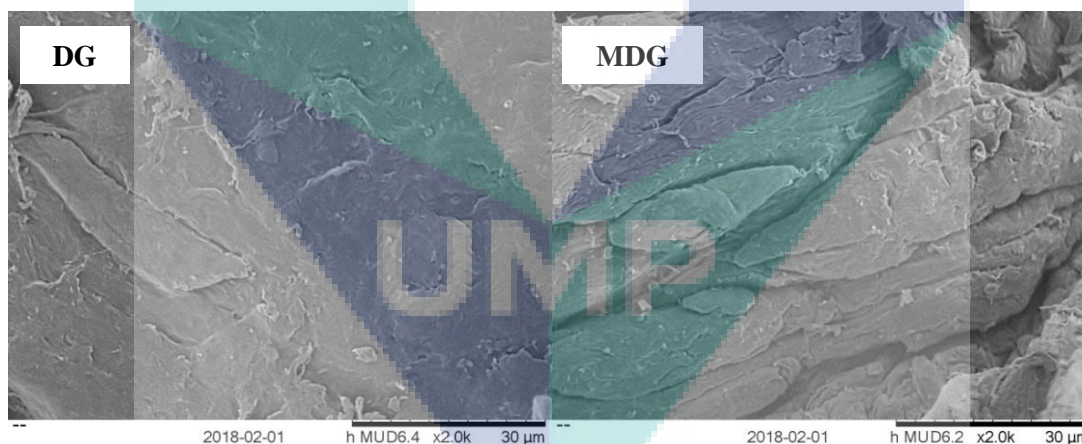


FIGURE 2. Surface morphology of DG and MDG

Rheological properties

The modification of DG has showed a good result in term of apparent viscosity. As shown in Figure 3, with the same concentration, the apparent viscosity of the MDG is higher compare to the DG. The viscosity of MDG is 117 cP while the viscosity for DG 98 cP. This is because of the substitution of quaternary amine group on the hydroxyl group had provided a strong electrostatic interaction among the chains and this increased intertwining segment between the chains [11]. The enhancement has increased the internal flow resistance, therefore increased the apparent viscosity.

The viscoelastic testing was conducted to determine the viscous and elastic characteristic of the DG and MDG gel when they undergo deformations. The deformation involved the macromolecular motion which contains difference microscopic motion hierarchies and forms. Therefore, frequency scanning is important to characterize the feature of the motion unit and the variety of difference chain segment, coils and molecules within the specimen system [14, 17]. To perform this testing, the LVER region needs to be identified first to accurately evaluate the relationships between molecular structure and viscoelastic behavior. The rheological properties under alternating external strain was study by frequency scanning on the DG and MDG gel. As shown in Figure 4, it is showed that the rheological behavior of the MDG is improved after modification. For both samples, the elastic modulus (G') is higher than the viscous modulus (G'') and there is no cross-over displayed by G' and G'' in Figure 4 indicating that the sample have the gel-like structure [18]. Moreover, the G' and G'' of MDG is higher compared to the G' and G'' of DG. Similarly, this is the effect of the stronger electrostatic interaction among the chains after substituting the quaternary amine group on the hydroxyl group of DG. This result indicate that the MDG have a stronger gel strength compare with DG. Therefore, MDG would be more stable in a harsh condition.

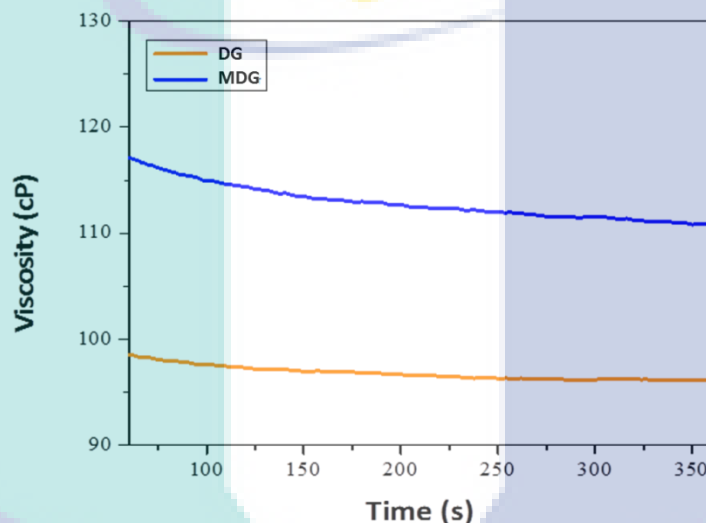


FIGURE 3. Apparent viscosity of same concentration of DG and MDG

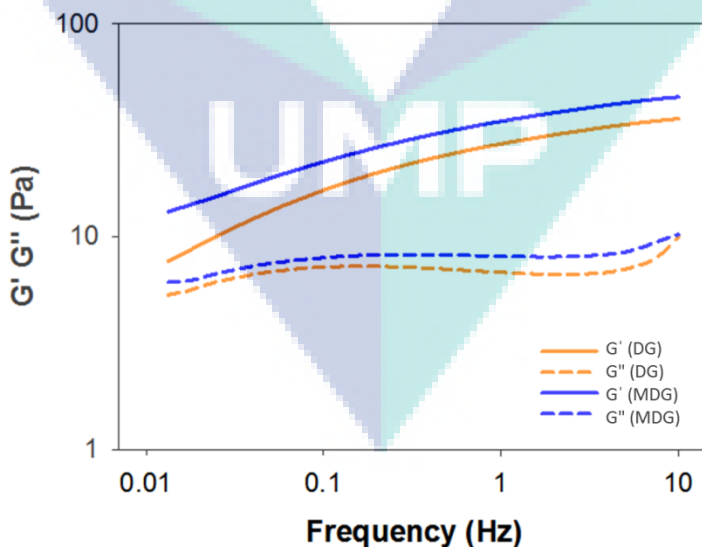
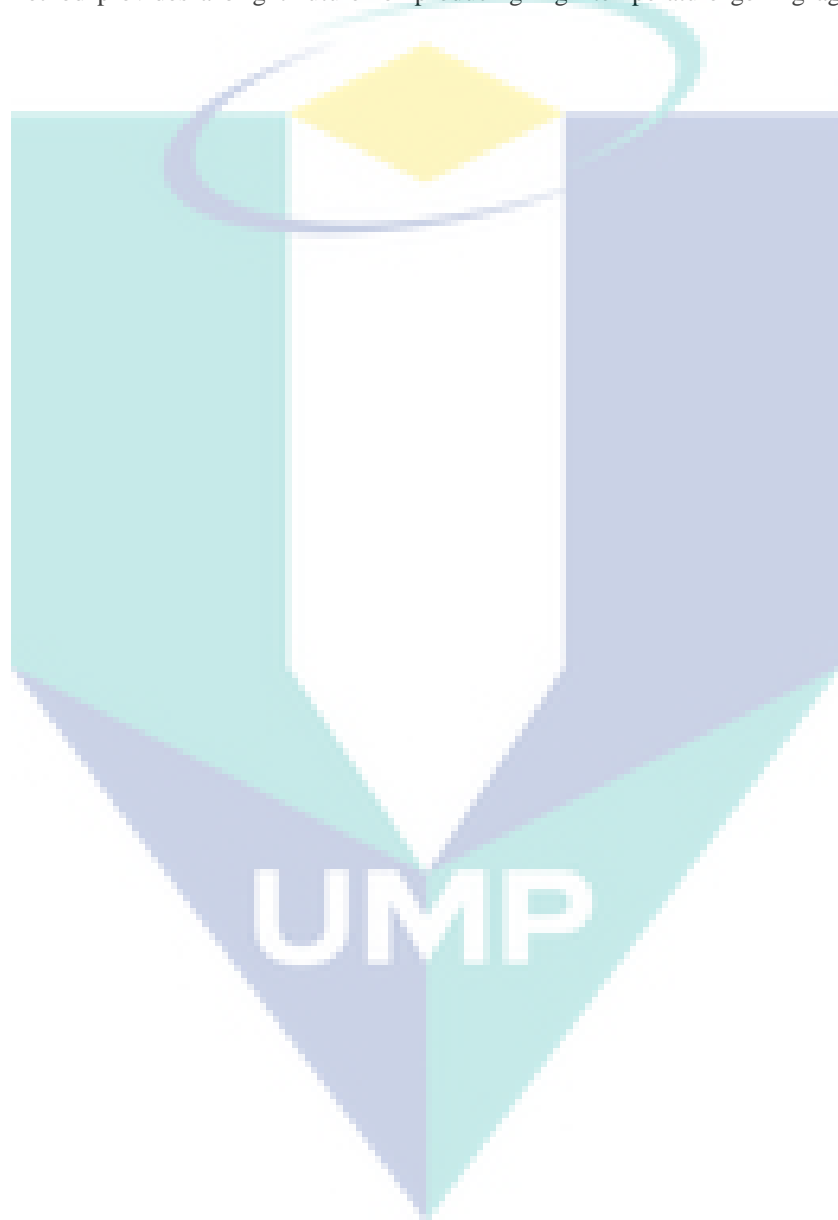


FIGURE 4. Elastic modulus (G') and viscosity modulus (G'') of DG and MDG

CONCLUSIONS

The usages of double helical biopolymer have been favorable due to their excellent properties at high salinity and high temperature reservoir. Diutan gum as one of the double helical biopolymer had been modified to improve its rheological properties. Diutan gum has been successfully modified by attaching quaternary amine group to its backbone. The result shows that the rheological properties of modified diutan gum have improved where the viscosity has increases from 98 cP to 117 cP and the suspension capabilities via G' and G'' are higher compare to diutan gum. This method provides a bright future for producing high temperature gelling agent for oil and gas applications.



CHAPTER 3

The Study of Cationic Modification of Welan Gum

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Keywords: Welan gum; Cationized polysaccharide; Quaternary amine group

Abstract. In the present study, welan gum (WG) was modified with quaternary amine group producing cationic welan gum (CWG) to enhance its thermal and viscosity properties. N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) was used as the source of quaternary amine group. The effect of CHPTAC amount in the presence of NaOH was investigated and analyzed using Fourier transform infrared (FTIR), Field emission scanning electron microscope (FESEM), thermal and viscosity analysis. The viscosity results were increases as the amount of CHPTAC increased. From the thermal analyses, it is observed that the CWG has better thermal resistance compared to WG. This study showed that modification of WG by attaching quaternary amine group on the hydroxyl group is promising for the exploration of high temperature reservoir.

Introduction

Polysaccharide is a polymeric carbohydrate molecule which derived from natural sources [1]. Welan gum (WG) is an example of natural polysaccharide that can be used in various application such as food, cosmetic, pharmaceutical, paper and textile and also oil and gas industry [2]. WG possessed an excellent properties as thickener, suspending agent, stabilizer and emulsifier [3]. Its structure consists of repeating unit of four saccharides which are D-glucose, D-glucuronic acid, D-glucose and L-rhamnose units and the side chain is L-mannose. WG is an anionic polysaccharide and it has the features of polyelectrolyte because the presence D-glucuronic acid [4].

Welan gum has a potential to be used in enhance oil recovery process due to good rheological properties such as higher storage modulus, loss modulus, elasticity and viscosity [5]. In addition, WG has a special characteristic where it is thermostable and the viscoelasticity is stable over a wide range of pH from 2 to 12 [6]. Those specialties have made WG contributed to many industrial applications apart from petroleum like food production, ink production and concrete [7]. Unfortunately, WG has its limitation which it can only sustained temperature up to 140 °C. This became crucial because the demand on thermally stable fluid at high temperature for petroleum industries.

In the present study, cationization of WG was conducted in order to improve its properties. The cationization was performed by substituting the hydroxyl group on WG backbone with

quaternary amine group (CHPTAC). The effect of different CHPTAC amount were investigated and observed through viscosity analysis. Moreover, the chemical, thermal and morphological properties are also studied using FTIR, DSC and FESEM.

Experimental

Materials. The welan gum (WG) was purchased from Permula Chemicals Sdn Bhd. The source of quaternary amine group which is 60 wt% of N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) was purchased from Sigma Aldrich. Other than that, 95% ethanol, absolute ethanol, sodium chloride and sodium hydroxide used throughout the experiment were also purchased from Sigma Aldrich.

Preparation of CWG powder and gelling fluid. CWG prepared by dispersing 20 g of WG in 50 ml of ethanol-water solution with the mass fraction of 85:15. After that, 1.5 ml of 40 wt.% sodium hydroxide aqueous solution was added to the mixture. The mixture was stirred at ambient temperature for 40 min. After that, CHPTAC (0.5 ml, 1.0 ml and 1.5 ml) was added to the mixture and stirred for 3 h at 70 °C for cationic modification. The cationic modification was cooled to room temperature and the product which is CWG was rinsed with the absolute ethanol. The CWG was dried at 80 °C in the oven until constant weight achieved.

In order to prepare the CWG gelling fluid, the CWG powder was simply mixed with 2% of NaCl brine solution. 500 ml of NaCl brine was stirred using IKA RW20 overhead stirrer and 4.8 g of CWG powder was slowly added into it. The speed was increased up to 1700 rpm when the mixture became viscous after adding the CWG powder. The gelling fluid was stirred for 5 h and left overnight to remove the bubbles.

Analysis of CWG powder and gelling fluid. The surface morphology of WG and CWG powder was observed on field emission scanning electron microscope (FESEM) at 1000 X magnification. Fourier transform infrared spectroscopy (FTIR) was carried out using Perkin Elmer Spectrum 100 FTIR-KBr instrument at scan ranges of 400 cm^{-1} up to 4000 cm^{-1} . The resolution was set at 2 cm^{-1} in order to detect the presence of quaternary amine group in CWG. The thermal analysis was performed on Netzsch Polyma Differential scanning calorimeter (DSC) to determine the glass transition temperature (T_g). The DCS was carried out at temperature range from 25 °C to 300 °C under nitrogen gas at a flow rate of 50 ml/min. In addition, the WG and CWG gelling fluid was characterized using Kinexus Lab+ rheometer. The viscosity measurement was performed at ambient temperature using plate-plate geometry and at constant shear rate which is 170 s^{-1} .

Result and Discussion

Structural characterization of CWG. The effect of cationization modification on the WG was observed using FESEM as shown in Fig. 1. The gelling fluid of WG and CWG was freeze-dried before observing the surface morphology. It can clearly be seen that WG in Fig. 1a has a smooth surface with small part of granular shape formed. However, after underwent cationization, most of the surface morphology of CWG (Fig. 1b) was converted to granular shape and has a rough surface suggesting that the quaternary amine group was successfully substituted on the surface of WG.

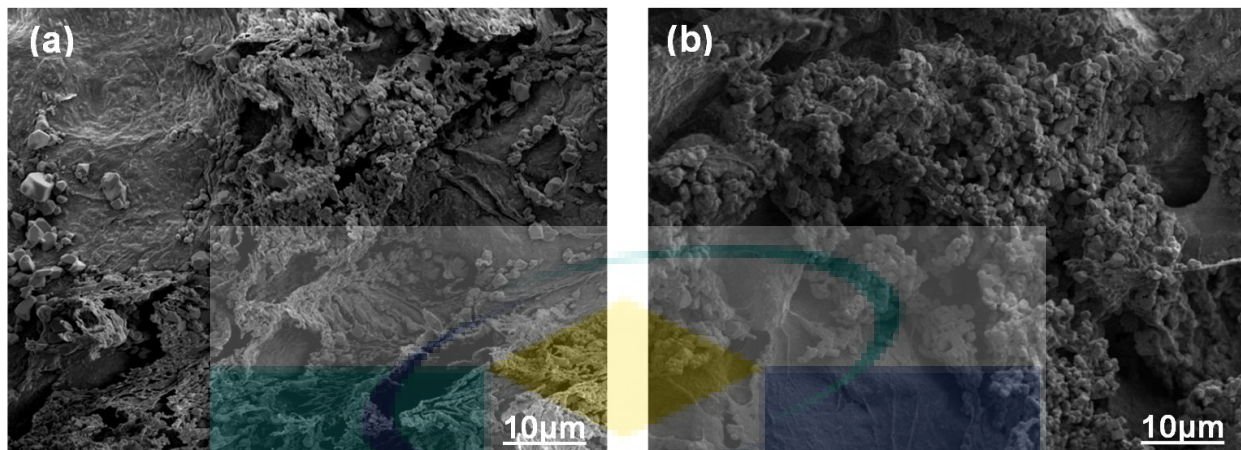


Fig. 1: Surface morphology of (a) welan gum and (b) cationic welan gum

The effect of cationization was further studied using FTIR. The FTIR results of WG and CWG with different amount of CHPTAC is shown in Figure 2. The appearance of new peak attributed to the C-N stretching vibration was presented in CWG 0.5, CWG 1.0 and CWG 1.5 in the range of 1421–1456 cm^{-1} which was not appeared in WG. The intensity of the peak was increases as the CHPTAC amount increased. This results are also supported by the study conducted by Pal and co-worker (2006) with the appearance of C–N cationic glycogen peak [8]. Apart from that, the cationic modification has broadened and decreases the intensity of O–H due to the substitution of quaternary amine group on hydroxyl of WG.

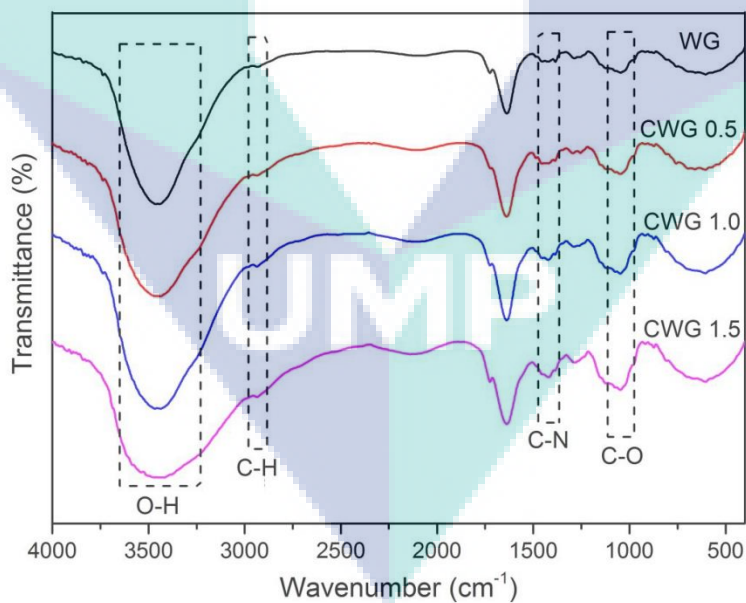


Fig. 2: FTIR spectrum of WG and CWG

Thermal analysis of CWG. Thermal analysis of WG and CWG with different amount of CHPTAC was characterized using DSC and the results are shown in Table 1 and Fig. 3. From Table 1, it is showed that CWG with 0.5 ml CHPTAC has the highest glass transition (T_g) temperature which observed at 146.5 °C. It is well-known that C–N is a polar group which has the strongest effect on T_g . When cationization conducted on WG, the polarity of the CWG increased and developed strong intermolecular interactions between chains which hinder molecular motion and caused the increasing of T_g . However, as the CHPTAC amount increased on CWG 1.0 and CWG 1.5, their T_g were slightly decreased into 142.2 °C and 143.5 °C, respectively. This might be due to the insufficient of NaOH as catalyst for the reaction to occur with quaternary amine. According to Kavaliauskaite et al. (2008), the amount of NaOH in cationic modification had big influence on the reaction rate [9].

Table 1 Glass transition value of WG, CWG 0.5, CWG 1.0, and CWG 1.5

Samples	T_g [°C]
WG	141.2
CWG 0.5	146.5
CWG 1.0	142.3
CWG 1.5	143.5

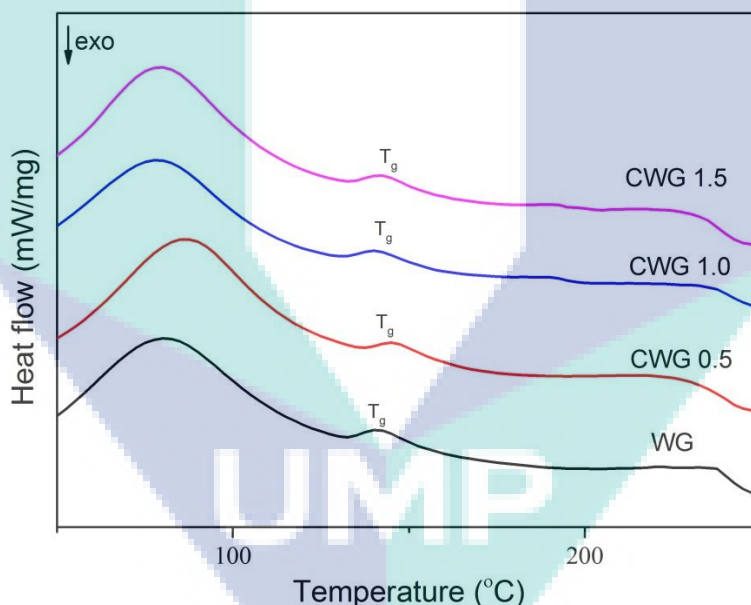


Fig. 3: DCS spectrum of WG and CWG

Viscosity analysis. Fig. 4 shows the viscosity results of gelling fluid prepared from WG and CWG. The WG gelling fluid recorded a viscosity value of 148 cP. After cationization, the highest amount of CHPTAC (1.5 ml) formed the highest viscosity at 188 cP, followed by 1.0 ml with 178 cP and 161 cP for the 0.5 ml CWG. The viscosity increments are directly proportional to the CHPTAC amount. Higher amount of CHPTAC indicated more CHPTAC monomer grafted onto the WG. This findings was similar with the results reported by Singh et al. (2016) which proved that the increasing viscosity of cationic guar gum was due to the presence of longer CHPTAC chain linked on the polysaccharides [10]. From this analysis, it was proved that

the modification of original WG with the use of CHPTAC as quaternary amine group was successfully substituted to the surface back bone of WG.

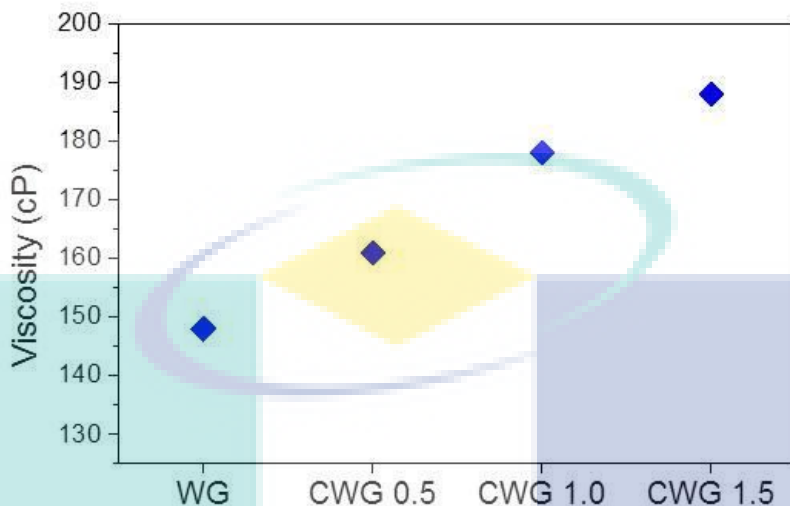


Fig. 4: Viscosity of WG and CWG at shear rate 170 s^{-1}

Conclusions

Cationic modification on WG has been performed to extend the properties of CWG. The present results indicate that CHPTAC were successfully substituted onto WG which confirmed by FTIR and surface morphology. Higher concentrations of CHPTAC created more chain with WG thus increase the viscosity. The high viscosity of CWG gelling fluid provides a strong gel chain simultaneously improve the CWG thermal stability compared to WG. As for overall, the CWG developed in this study has a high potential to be used as a gelling agent for high temperature well intervention application.

CHAPTER 4

Rheological and Thermal Stability of Cationic-Modified Diutan Gum Biopolymer

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ABSTRACT

Cationic diutan gum (CDG) biopolymer has been developed by incorporating a quaternary amine group on diutan gum (DG) structure to improve the thermal and rheological properties. The modification was performed by mixing DG with different N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) concentration to produce CDG in the presence of sodium hydroxide. The FTIR results confirmed the incorporation of cationic moieties onto the CDG chains. The surface morphology observed through FESEM showed that the smooth surface of DG was converted to a connective spherical reticular structure upon CHPTAC modification. The viscosity of CDG gelling fluid was increased after modification due to electrostatic chain interaction. Rheological properties showed that plateau-like region was observed which signifying a stable gel response towards frequency. Thermal stability analysis using static

thermal aging test showed the CDG was stable up to 170 °C suggesting this biopolymer can withstand the high-temperature requirements of the upstream petroleum industry.

Keywords: Diutan gum; Cationized polysaccharide; Rheological behavior; CHPTAC; Petroleum industry.

1. Introduction

In the upstream petroleum industry, assistive-fluids such as drilling, fracturing, and completion fluids are generally injected into the petroleum reservoir for oil exploration and production. A thickening agent such as polymers are usually used to produce the assistive-fluids by dissolving the polymer in either water, monovalent, or divalent brines base fluid (Zhou, Deville, & Davis, 2015). The most extensively used polymer for this application is synthetic hydrolyzed polyacrylamides (HPAMs) due to its availability and ability to be custom-made into desired molecular weight as well as variation in the degree of hydrolysis. However, the usage of these synthetic polymers is vulnerable to reservoir temperature and salinity due to the amide functional group hydrolysis rate increment producing more acrylic acid on the HPAM backbone which leads to the loss of thickening ability (Pu, Shen, Wei, Yang, & Li, 2018). It is reported that at 50 °C with the presence of divalent ions, the HPAM hydrolysis rate was prolonged. At 60–70 °C, the hydrolysis rate was moderate and turned to rapid as the temperature increased to 90 °C (Ryles, 1988). Due to this issue, various efforts have been made to develop polymers that are eco-friendly and able to withstand the high temperature and salinity requirements of the upstream petroleum industry.

Currently, biopolymers have been the focus owing to its environmental feature and superior tolerance to temperature and salinity. Biopolymers are usually having a distinctive linear structure, double or triple helical structure, rigidity and charge-free chains which enhance the thickening capability and stability in severe reservoir conditions. Various biopolymers have been studied including hydroxyethylcellulose (HEC) (Abbas, Sanders, & Donovan, 2013), carboxymethylcellulose (CMC) (Marques, Balaban, Halila, & Borsali, 2018), guar gum (GG) (S. Wang, He, Guo, Zhao, & Tang, 2015), xanthan gum (XG) (Jang, Zhang, Chon, & Choi, 2015), welan gum (WG) (Gao, 2016), and scleroglucan (Fariña, Siñeriz, Molina, & Perotti, 2001). HEC and CMC are usually used for low-temperature applications (<90 °C) as the apparent viscosity decreased to below 10 cP (Bai, Shang, Wang, & Zhao, 2018). Meanwhile, for XG, WG, and scleroglucan, the fluid can withstand temperature up to 100–120 °C (Castillo, Valdez, & Fariña, 2015; Gao, 2015; Y. Li et al., 2017). Among these biopolymers, XG has been the most extensively studied as drilling, fracturing, and pipeline cleaning fluid. XG fluid exhibits a pronounced shear-thinning behavior with a low power-law index due to the molecule aggregation through hydrogen bonding and biopolymer entanglement, which improve injectability for field operation (Pu et al., 2018). However, the application of commercial biopolymers was limited since the oil and gas exploration moving toward the high-temperature (above 120 °C) reservoir condition (Barnes et al., 2008). Therefore, finding a new biopolymer which can endure high temperature and salinity are necessary.

Diutan gum (DG) is a high molecular weight bacterial polysaccharide produced through aerobic fermentation of *Sphingomonas* sp. It is an anionic biopolymer which consists of a repeating unit of β -1,3-D-glucopyranosyl, β -1,4-L-glucuronopyranosyl, β -1,4-D-glucopyranosyl, and α -1,4-L-rhamnopyranosyl, and a two saccharide L-rhamnopyranosyl side-chain attached to

the (1 → 4) linked glucopyranosyl residue (Banerjee et al., 2009; Sonebi & McKendry, 2008). Currently, DG is primarily applied in the cement and concrete industries. The DG has been used as a viscosity modifying agent in cement slurries because of its effectiveness in controlling bleeding by the formation of a viscous gel (Sonebi, 2006; Zhang, Weissinger, Peethamparan, & Scherer, 2010). Typically, the DG will act as a thickening, binding, emulsifying, suspending, and stabilizing agent when applied in specific applications. However, the study of DG for the upstream petroleum industry has rarely been reported. An exciting investigation of DG rheological properties has been reported (Xu, Gong, Dong, & Li, 2015). Their findings showed that DG gelling fluid could be produced at a very low concentration (0.12 g/L). Besides, the gelling fluid is stable towards temperature range from 25–75 °C and virtually independent to the cationic environment (Na⁺ and Ca²⁺) due to its perfect double helix molecular conformation. In another study, the DG biopolymer was found insensitive toward salt and shearing time when compared with HPAM. The viscosity was stable after 90 days of aging at 85 °C, and 16% of oil recovery was obtained in the core flooding test (Liang, Han, Chen, Su, & Feng, 2019). As the current state-of-art has proved that DG possessed excellent rheological properties, a question arises as to whether surface functionalization on DG will further progress or deteriorate its properties.

Several techniques have been previously conducted to modified polysaccharides such as nonionic (Z. H. Wang et al., 2011), anionic (Tarus et al., 2014), and cationic (H. J. Prado & Matulewicz, 2014) modifications. Cationization of polysaccharide has been widely conducted to improve the properties of the polysaccharide. The modification of cationic moiety with anionic biopolymers can generate inter-polyelectrolyte complexes with hydrogel-like structures, expanding the former utilization. Until now, several chemical modifications involving the

cationic moiety were performed on polysaccharide. For examples, cationic dextran was used in clay suspension separation (Ghimici, Morariu, & Nichifor, 2009), cationization on starch and konjac glucomannan as flocculating agent (Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2008; S. Pal, Mal, & Singh, 2005; Tian, Wu, Liu, & Xie, 2010; Yu, Huang, Ying, & Xiao, 2007), study on the quaternized chitin (Chen et al., 2010), GG as flocculating agent and for coal fine suspension (Sagar Pal, Mal, & Singh, 2007), structural and rheological properties of kappa (κ)-carrageenans (Covis et al., 2016), pullulan for gene transfection carrier (Jo, Okazaki, Nagane, Yamamoto, & Tabata, 2010) and XG as thickener and stabilizer of emulsion (Shi, Wei, Luo, Tan, & Cao, 2017). N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) or known as liquid cationic etherification agent has been commonly deployed to enhance the properties of polysaccharides because of their stability and non-toxicity (Moral, Aguado, & Tijero, 2016; Héctor J. Prado, Matulewicz, Bonelli, & Cukierman, 2011). The cationization reaction using CHPTAC generally begins with the formation of alkoxide on the polysaccharide hydroxyl group in the presence of NaOH (or other bases) aqueous solution. The alkoxide will then attacks the epoxide on the quaternary amine group of CHPTAC formed in-situ by the alkaline medium, and it opens the epoxide to form the hydroxy ether (H. J. Prado & Matulewicz, 2014). Recently, cationic XG has been synthesized by Shi and co-workers to enhance its rheological property by attaching quaternary amine groups to the XG backbone (Shi et al., 2017). Their results showed that viscosity, elastic and viscous modulus, and thermal stability were significantly improved compared with bare XG.

In the current study, the cationic diutan gum (CDG) was prepared by quaternary amine groups from CHPTAC grafting on the hydroxyl groups of DG. The effectiveness of cationic moiety modified on DG was studied by calculating the degree of substitution (DS), Fourier

transform infrared (FTIR), and CHNS, while the surface morphology was observed using field emission scanning electron microscope (FESEM). Furthermore, the rheological properties (viscosity, elastic and loss modulus) and thermal stability of the gelling fluid produced using DG and CDG were also investigated using rheometer and static thermal aging test, respectively.

2. Experimental

3.1. Material

The DG was supplied by Permula Chemicals Sdn Bhd. An aqueous solution of CHPTAC (60 wt.%), sodium hydroxide (NaOH), sodium chloride (NaCl), absolute ethanol and 95% ethanol were purchased from Sigma Aldrich. All chemicals were used without any purification.

3.2. Cationic modification of diutan gum (CDG)

The cationization of DG was conducted by reacting DG with a cationic CHPTAC monomer. The procedure to prepare CDG is described as follows: 30 g of DG was dispersed in 100 ml of ethanol-water solution (the mass fraction of ethanol is 85%). The solution was then mixed with 2.5 ml of 40 wt.% NaOH aqueous solution to control the pH of the mixture. The mixture was stirred at ambient temperature for 40 min. Afterward, a different amount of CHPTAC (0.5 – 4 ml) was added into the mixture and stirred at 70 °C for 2 h for the cationization process. Then, the mixture was cooled to room temperature and washed thoroughly with absolute ethanol. The

CDG powder is finally obtained after drying at 80 °C overnight and labeled CDG1 – CDG6 as summarized in **Table 1**.

3.3. Determination of DS by elemental analysis

The elemental analyses (carbon, hydrogen, nitrogen, and sulfur) of the DG and CDG were performed on CHNS elemental analyzer (EQPCL 200 Elementar, Germany, Vario Macro Cube). The DS was determined by elemental analysis of nitrogen. The following equation which adapted from (Haack, Heinze, Oelmeyer, & Kulicke, 2002; Héctor J. Prado et al., 2011) was used to calculate the DS:

$$DS = \frac{(403 \times \%N)}{1400 - (152 \times \%N)} \quad (1)$$

where 403 is the molecular weight of the average unit of DG. %N is the percentage of nitrogen on a dry basis. 14 is the atomic weight of nitrogen and 152 is the molecular weight of the cationic substituting group.

3.4. DG and CDG powder characterizations

The FTIR spectra of the DG and CDG powder were recorded using Spectrum One (Perkin Elmer, USA) using KBr technique. The pallet was scanned with resolution 2 cm⁻¹ at wavenumber 4000 to 600 cm⁻¹. The morphology of the DG and CDG were examined using FESEM (JEOL) at an accelerating potential of 5 kV. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo, Switzerland thermal analyzer. Approximately 2 mg of powder was placed in a platinum crucible and subjected to heating from 25 to 600 °C in a nitrogen

atmosphere with a heating rate of 10 °C/min. The glass transition temperature (T_g) of the powder was determined using Netzsch Polyma 214 differential scanning calorimetry (DSC). The DG and CDG were heated at a temperature from 25 °C to 200 °C (10 °C/min) under a constant flow of nitrogen gas (40 ml/min).

3.5. Preparation of DG and CDG gelling fluid

The gelling fluid was prepared by mixing 2.4 g DG or CDG powder in 500 ml of 2 wt.% NaCl brine solution. The solution was stirred using IKA RW20 overhead stirrer at 2000 rpm in a 1 L beaker for 3 h at ambient temperature to achieve a homogeneous solution. The gelling fluid was kept stationary for overnight to eliminate bubbles formation.

3.6. Rheological analysis of DG and CDG gelling fluid

The rheological properties (viscosity and viscoelasticity) of DG and CDG fluid were determined via Malvern Kinexus Lab+ rheometer using plate and plate geometry. In order to measure the apparent viscosity of the fluids, a plate and cone-plate have been used at a shear rate of 170 s^{-1} at ambient temperature. The viscoelasticity of fluids was determined by determining the linear viscoelastic region (LVER) through stress sweep testing in the range 0.01 Pa to 300 Pa at a frequency of 1 Hz. A frequency sweep testing is conducted from 0.1 to 10 Hz within the indicated LVER region.

3.7. Thermal stability of DG and CDG gelling fluid using static thermal aging test

The thermal stability was performed by pouring the gelling fluid (80% of the Teflon liner capacity) in closed-system autoclave steel. The autoclave steel was inserted in an oven at ambient temperature and heated at targeted temperature (100–180 °C) for 1 hour. The gelling fluid was then cooled to room temperature, and the initial and final viscosity of the gelling fluid was determined at a shear rate of 170 s^{-1} .

3. Results and discussion

3.1. DS from elemental analysis

The elemental analysis result and the DS of DG and CDG are presented in **Table 1**. The elemental analysis result showed that there are no significant changes in the percentage of carbon (%C). As the cationization reaction using CHPTAC begins with the formation of alkoxide on the polysaccharide hydroxyl group (**Fig. 1a**), it is expected the percentage of hydrogen (%H) will decrease. This can be seen when the %H decreasing from 5.54% to 3.81% as the CHPTAC concentration increased. The alkoxide will then attacks the epoxide on the CHPTAC formed in situ by the alkaline medium, opens the epoxide ring to form the hydroxy ether and grafted on the DG structure (**Fig. 1b**). Nitrogen was not observed in the DG sample. However, after underwent cationization, the percentage of nitrogen (%N) was increasing from 0.72 to 0.83 showing that CHPTAC has been grafted in the CDG structure. Calculating the DS using the %N also creating a similar trend, which increases from 0.23 – 0.26 but not significant compared to the result

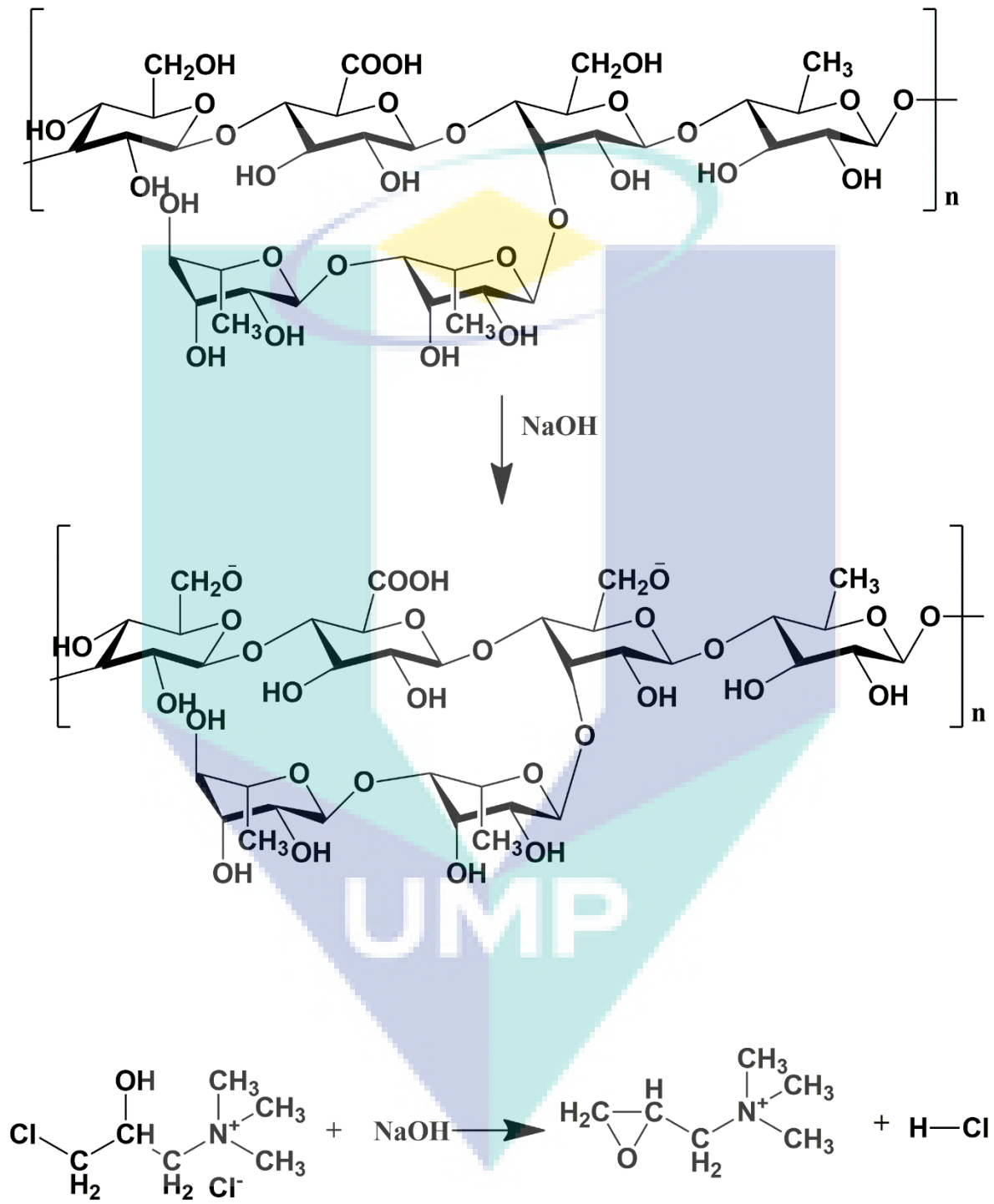
reported by Prado et al. (2011). This could be due to the insufficient NaOH because an equivalent of NaOH is necessary for generating the epoxide on CHPTAC. Moreover, NaOH is also required to ionize the hydroxyl groups on the DG structure, which are the nucleophiles of the reaction.

Table 1

CHNS data, DS and viscosity of DG and CDG gelling fluid.

	CHPTAC (ml)	C (wt%)	H (wt%)	N (wt%)	DS	Viscosity cP
DG	0	38.45	4.27	0	0	104
CDG1	0.5	38.32	5.54	0.72	0.23	115
CDG2	1.0	38.05	5.55	0.73	0.23	112
CDG3	1.5	38.61	4.03	0.75	0.24	102
CDG4	2.0	38.35	4.08	0.77	0.24	80
CDG5	3.0	37.56	3.93	0.80	0.25	60
CDG6	4.0	38.22	3.81	0.83	0.26	48

(a)



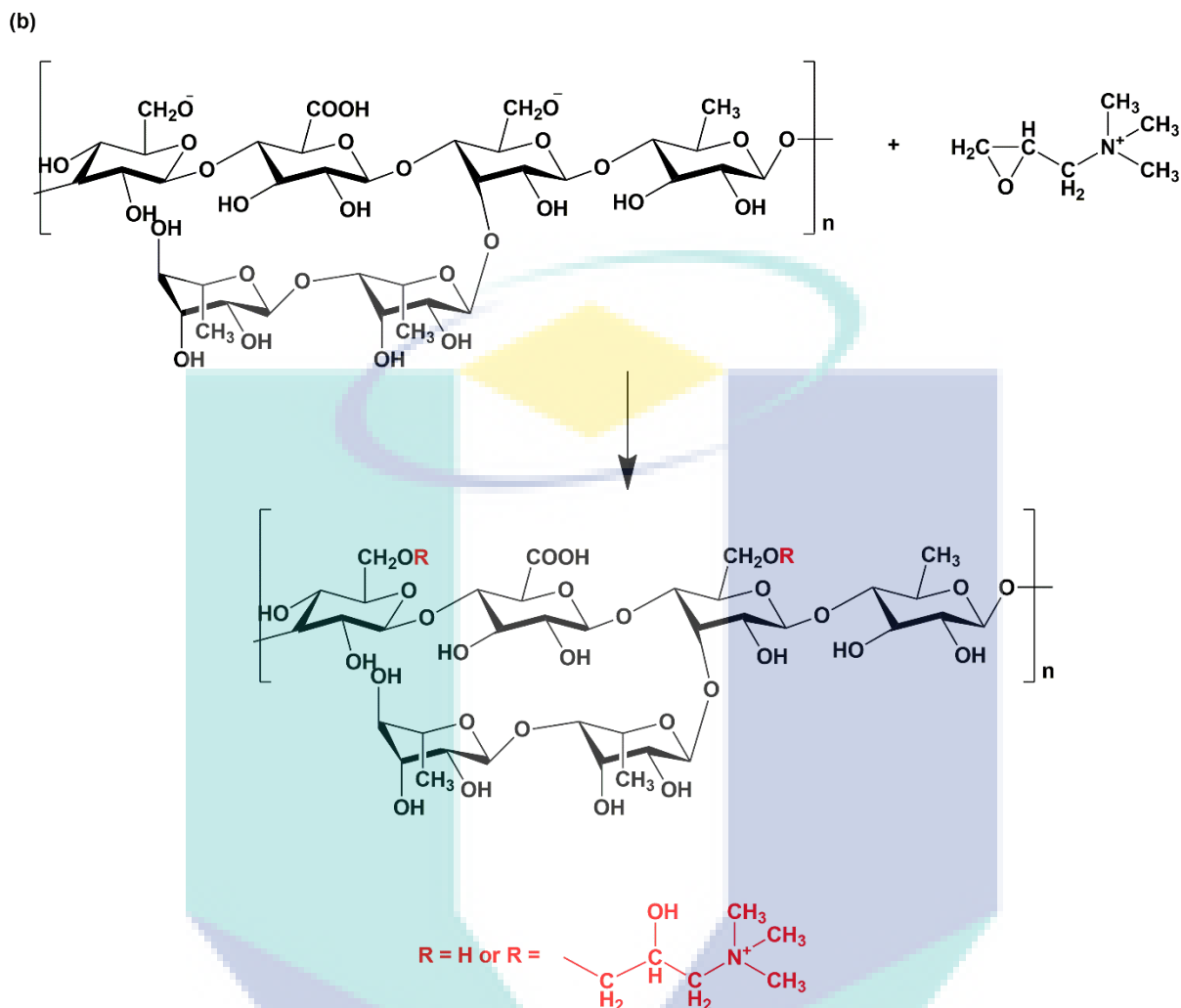


Fig. 1. Schematic representation for the CDG synthesis; (a) activation with NaOH, (b) reaction of DG with CHPTAC.

3.2. Functional group analysis on DG and CDG via FTIR

Fig. 2 illustrates the FTIR spectra of DG and CDG synthesized with different CHPTAC concentrations. The band centered at 3420 cm^{-1} was attributed to the stretching vibration of O—H groups on the DG and CDG backbone. The peak at 2934 and 2885 cm^{-1} corresponded to the asymmetric and symmetric stretching vibration of C—H. The significant band at $\sim 1730 \text{ cm}^{-1}$ is

attributed to the adsorption of the C=O bonds in the acetyl groups (Diltz & Zeller, 2001). The C–C and C–O stretching vibration can be observed at approximately 1600 cm^{-1} and 1000 cm^{-1} , respectively (Xu et al., 2019). Cationic modification on DG using CHPTAC has led to some significant changes in the original DG spectrum. First, the intensity of the O–H peak was slightly decreasing after the cationic modification due to the substitution of a quaternary amine group on the hydroxyl group of DG. It is observed that the peak intensity at 1259 cm^{-1} was increasing resulted from the new C–O bond formed between DG and CHPTAC. Besides, the appearance of a new peak at 1406 cm^{-1} is attributed to the C–N stretching vibration was clear evidence of the incorporation of cationic moieties onto the DG chains. This result was also supported by the study conducted by Pal and co-worker (2005) with the advent of CHPTAC peak at 1400 cm^{-1} which assigned to the C–N (S. Pal et al., 2005).

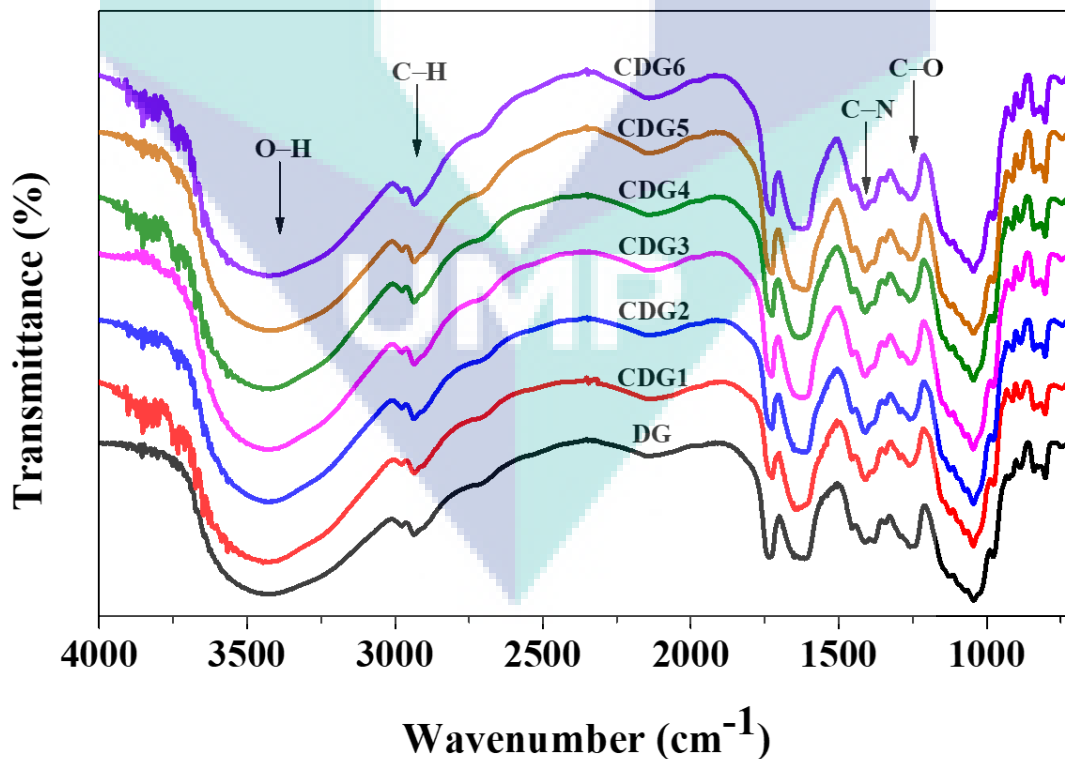


Fig. 2. FTIR spectra for DG and CDG at different CHPTAC concentration.

3.3. Surface morphology of DG and CDG via FESEM

FESEM is an excellent instrument to probe the polysaccharide's morphology. **Fig. 3(a)-(g)** shows the surface morphology of DG and CDG at various CHPTAC concentrations observed at 5000x magnification. As shown in **Fig. 3(a)**, the DG surface showed a smooth with proper assembled multilayered granular structure. Significant changes were observed on the DG surfaces after CHPTAC modification. For instance, the smooth surface of DG was converted to a connective spherical reticular structure which observed in **Fig. 3(b)**. When the CHPTAC concentration increased, the spherical structure was converted into nearly cubic shape (**Fig. 3(c)**). Further increased in CHPTAC concentration has shown the bigger size cubical shape structure became dominant, not connected, and agglomeration was observed **Fig. 3(d)-3(g)**. Comparing the result with previous studies, cationic modification of polysaccharides showed identical findings on agarose (Héctor J. Prado et al., 2011), and XG (Shi et al., 2017) which showed smooth surface morphology for the native agarose and xanthan. Cationization on the polysaccharides has converted the smooth surface to branched reticular structure and became more remarkable at higher CHPTAC concentration.

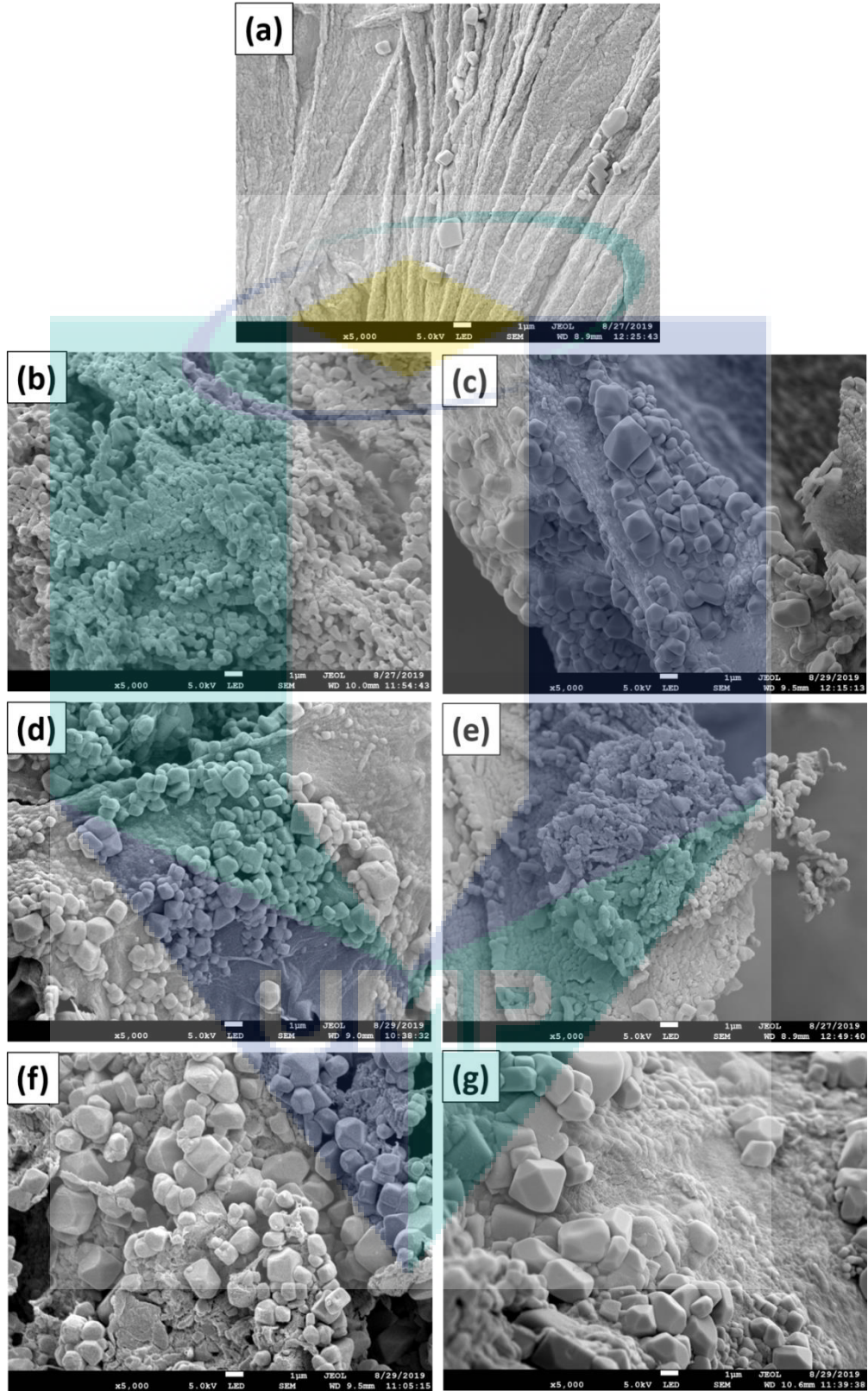


Fig. 3. FESEM morphology of DG (a) and CDG at various concentration (b)–(g).

3.4. Thermal properties of DG and CDG via TGA and DSC

Thermal decomposition of DG and CDG were performed on thermogravimetry analyzer (TGA) in a temperature range from 20 – 600 °C, as shown in **Fig. 4**. There are two regions of decomposition have been observed on the TGA thermogram of DG and CDG. The first decomposition has occurred below 100 °C while the second decomposition happened from 229 to 274 °C. The early decomposition region is attributed to the desorption of physically bound water or moisture from the surface of the DG and CDG. After that, the DG and CDG samples were stable up to 220 °C before the advent of the second decomposition. The second decomposition was a rapid degradation of all samples with an average weight loss of ~45% which is due to the decomposition of DG and CDG backbone (Zohuriaan & Shokrolahi, 2004). Incorporation of CHPTAC has caused slight increase in the thermal stability of CDG (256 °C) compared to DG (250 °C) because of the increased electrostatic attraction between the chains overcoming the mutual repulsion of positive charges of the loaded cationic moiety. The increased in electrostatic attraction hence increase the force to break the chains, which also reported for GG (Sagar Pal et al., 2007).

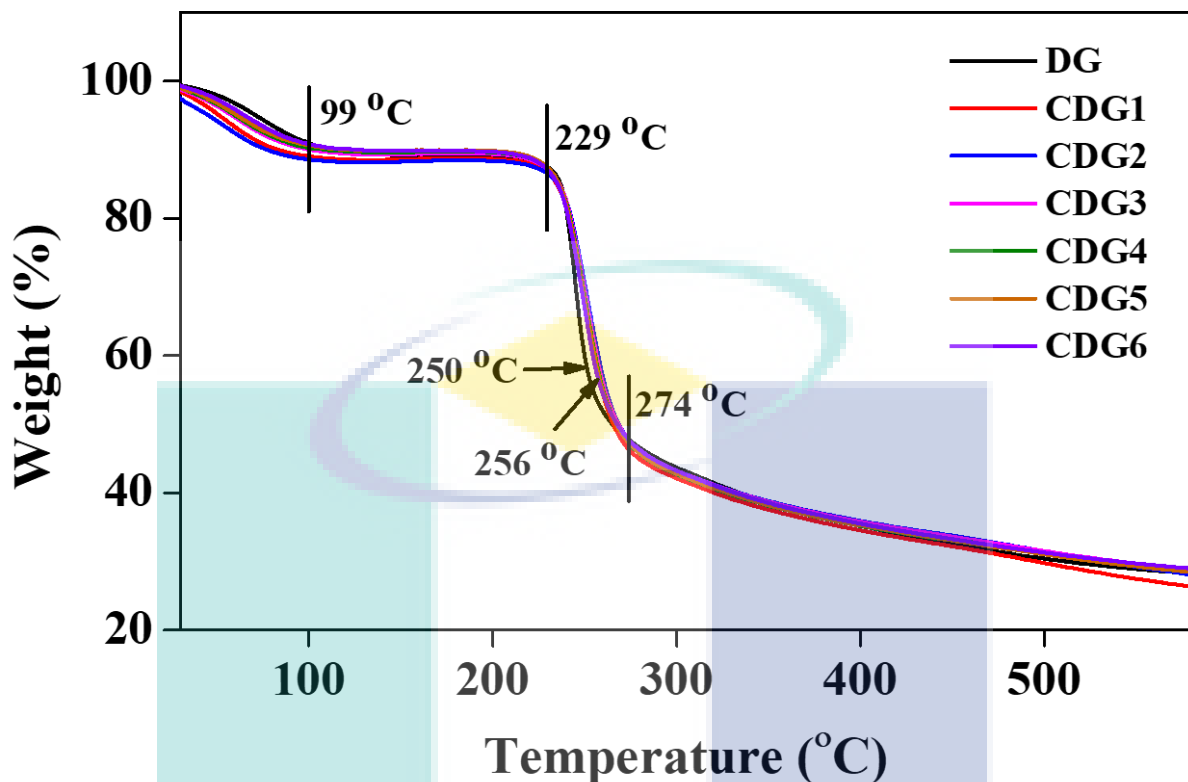


Fig. 4. TGA weight loss curves for DG and different concentrations of CDG.

The thermal properties of DG and CDG were further analyzed using DSC to investigate the thermal transitions that occurred on DG after the cationic modification. Fig. 5 shows the glass transition temperature (T_g) for the DG (86 °C) and CDG in the range of 88 – 92 °C. The relatively weak and broadened glass transitions can be ascribed to the semi-crystalline nature of the DG and CDG samples. The endothermic peak of CDG was broader compared to DG samples indicated the disintegration of an intramolecular interaction between the amorphous region due to the etherification process (Ren, Sun, Liu, Lin, & He, 2007). It was also observed that the T_g peak for CDG was slightly shifted to higher temperature indicating the T_g for the CDGs were improve due to the cationization process which had increased the electrostatic attraction between the chains.

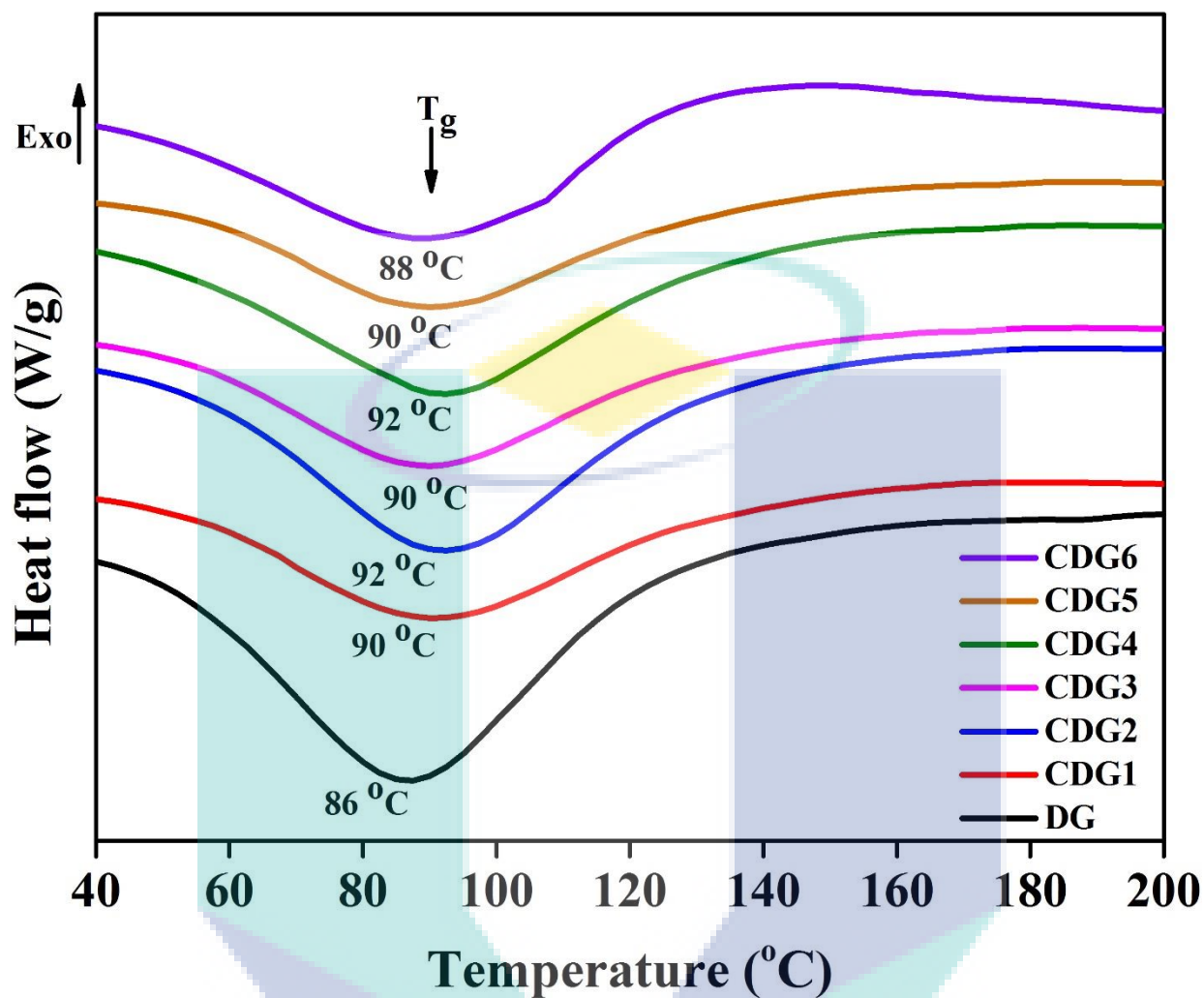


Fig. 5. DSC glass transition temperature (T_g) curves for the DG and different concentrations of CDG.

3.5. Rheological analysis

The cationization of DG and CDG has shown an interesting result in terms of viscosity. **Table 1** shows the gelling fluid (DG and CDG) viscosity at 25 °C. As shown in **Table 1**, the DG gelling fluid recorded a viscosity of 104 cP. Cationization had increased the viscosity of CDG1 and CGD2 by ~10% to 115 and 112 cP, respectively. The modification had offered a sturdy

electrostatic interaction and this improved intertwining network between the chains (Shi et al., 2017). However, the CDG3, CDG4, CDG5, and CDG6 showed a constant decrement in viscosity. Since the quantity of NaOH is fixed in this study, therefore employing higher CHPTAC concentration hindered the CHPTAC substituted on the hydroxyl group of the DG but promotes agglomeration process. This result was also supported by the morphology observed through FESEM which increasing CHPTAC concentration produced bigger cubical structure, not connected and agglomeration.

To have a better understanding of the viscoelasticity properties of the DG and CDG gelling fluids, a dynamic viscoelasticity measurement test was performed. The rheological properties of gelling fluid are strongly influenced by the state of the polymer gel. According to Deshpande (2009), a highly concentrated gelling fluid will show a gel-like response, inferring dynamic elastic modulus (G') to be higher than viscous modulus (G'') and both being almost constant concerning frequency (Deshpande, 2009). A weak gelling fluid will show a crossover point between G' and G'' . This crossover frequency is associated with a relaxation time characteristic for the onset of the terminal or flow region for the fluid. The dependence of the G' and G'' on the oscillation frequency for DG and CDG gelling fluid are shown in **Fig. 6**. As shown in the rheogram, the G' is larger than G'' for DG, CDG1, CDG2, CDG3, and CDG4 and no crossover was observed. A plateau-like region was seen which signifying a stable gel response towards the frequency due to the interaction of the neighboring DG or CDG biopolymers (H. Li, Chen, Lu, & Hou, 2012). In the case of CDG5 and CDG6, the G'' is higher compared to G' indicating the viscous modulus is dominating in the oscillation frequency. A crossover was also observed at frequency ~ 0.5 Hz and ~ 1.0 Hz, respectively. In addition, the G' and G'' trend was also increased as the frequency increased which indicative of a weak gel-like structure (Covis et al., 2016).

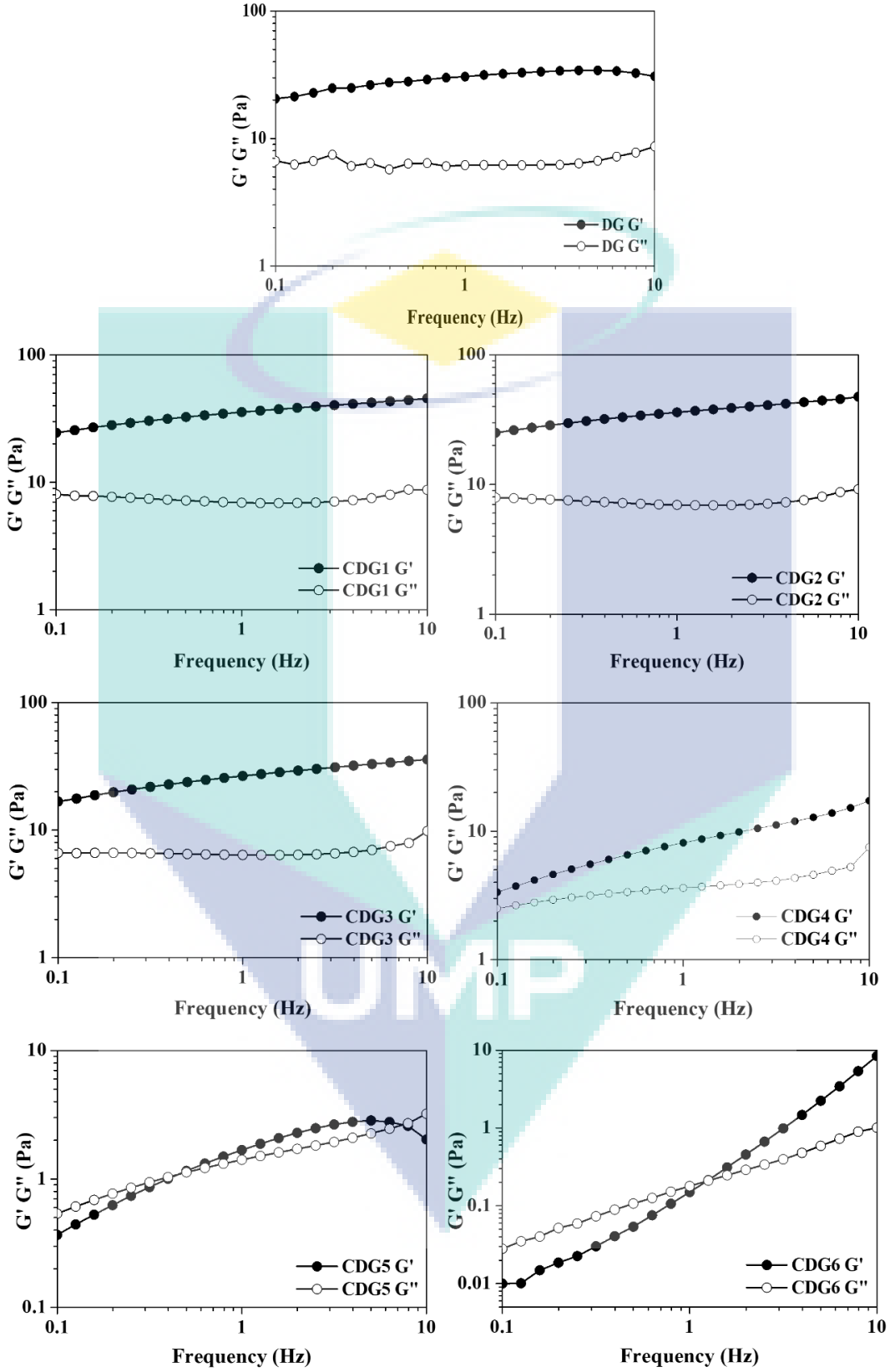


Fig. 6. The dependence of elastic modulus (G') and viscous modulus (G'') of DG and CDG.

3.6. *Effect of temperature on viscosity of DG and CDG gelling fluid tested using static aging test*

The effect of temperature on the viscosity of DG and CDG has been investigated as shown in **Fig. 7**. CDG2 gelling fluid has been selected and compared with DG gelling fluid as it produced stable viscosity among other CDGs. Both gelling samples were tested in a closed-system autoclave to avoid evaporation and heated in the range of 100 – 180 °C using an oven for a static aging test. CDG2 has higher viscosity compare to DG. The viscosity recorded after the static aging test showed both samples were stable up to 160 °C. As the temperature increased to 170 °C, both DG and CDG2 viscosity begin to decline by 11% and 8% respectively. At this temperature, the motions of the molecules have accelerated and decrease the van der Waals forces and hydrogen bond. Hence, decreased the entanglements of macromolecules and weaken the gelling fluids network (Liang et al., 2019). At 180 °C, a massive viscosity decrement was observed due to the breaking of the gelling fluid network.

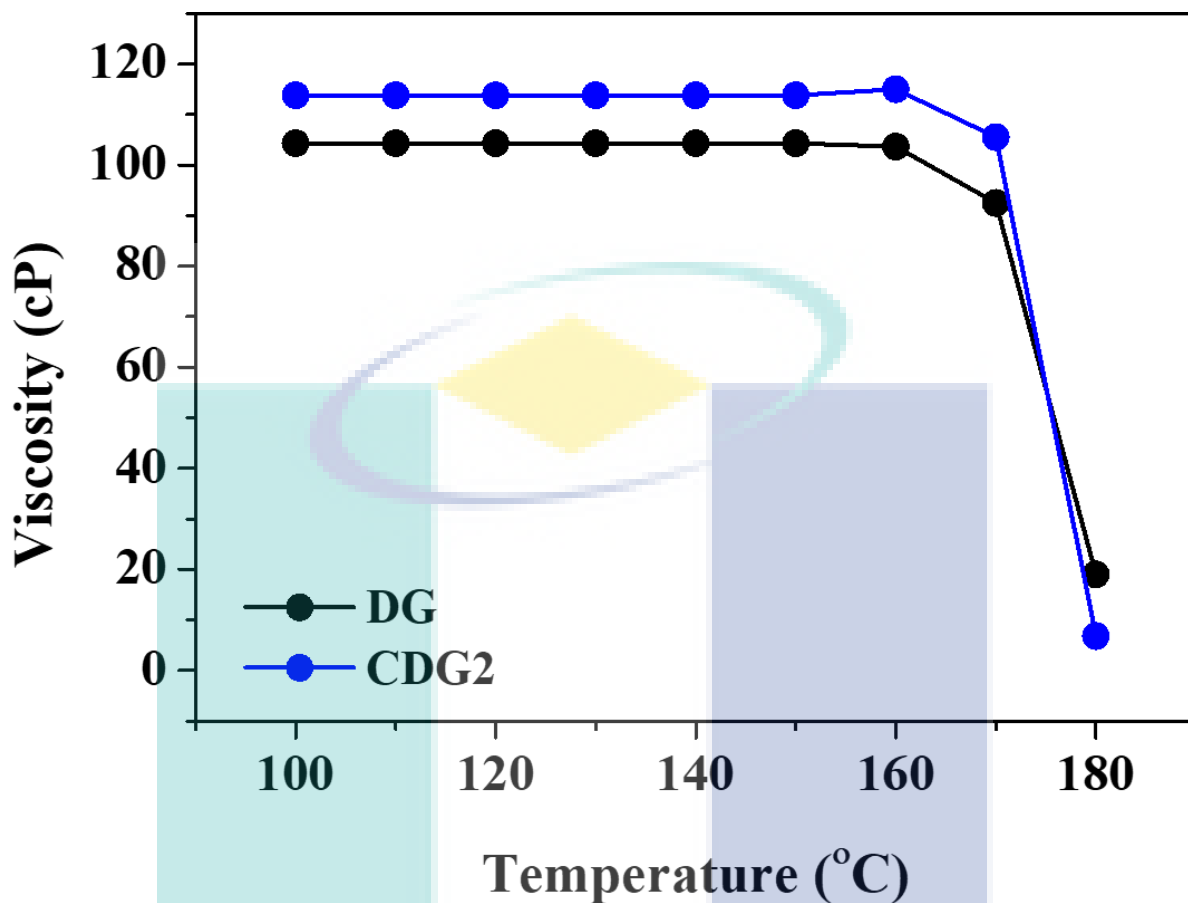
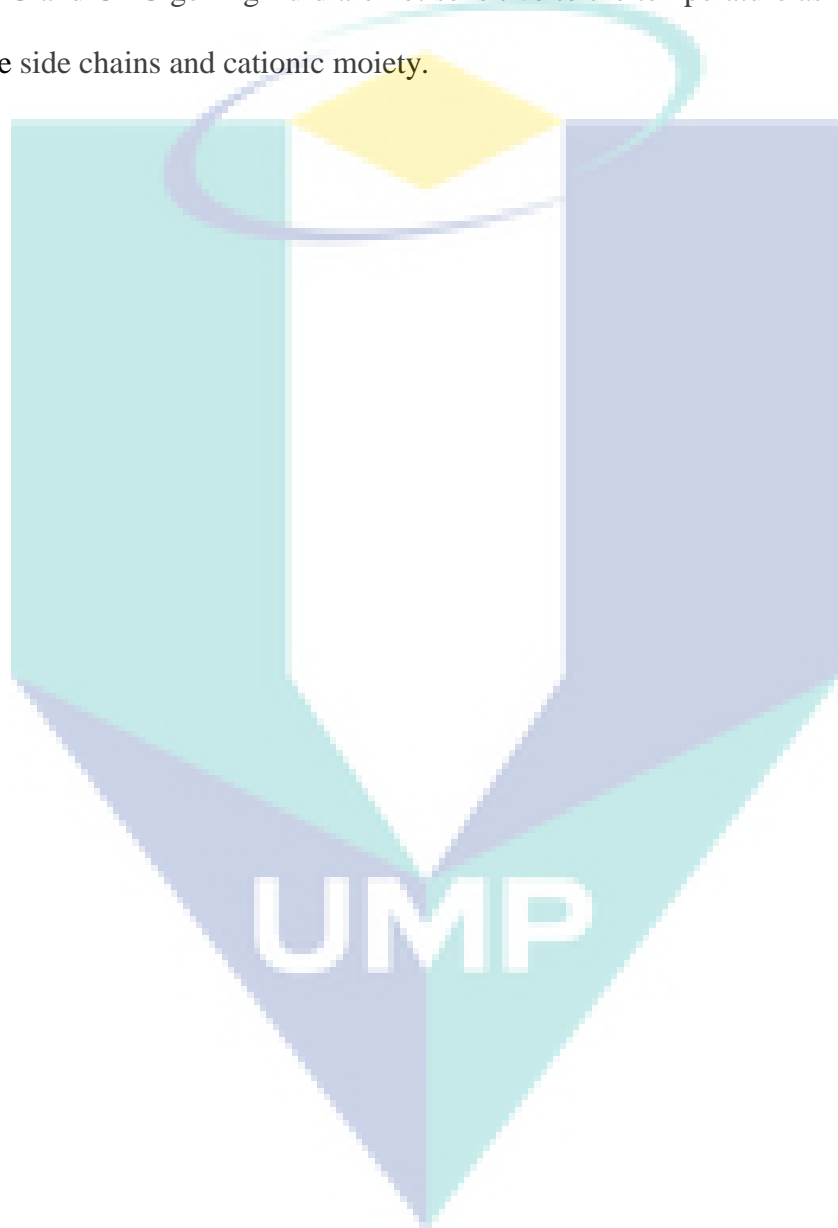


Fig. 7. Effect of temperature on the viscosity of DG and CDG

4. Conclusions

DG has been successfully modified with different concentrations of CHPTAC. Cationic modification on DG using CHPTAC was proved with the appearance of a new peak at 1406 cm^{-1} attributed to the C–N stretching vibration on the IR spectrum. An increasing viscosity was observed at a low concentration of CHPTAC but decreased after further addition of CHPTAC. The viscosity supposed to be increased as the amount of CHPTAC increased. Yet, this phenomenon is only possible if the optimum concentration of NaOH in each case was employed. Rheological properties showed that plateau-like region was observed which signifying a stable

gel response towards frequency due to G' is larger than G'' for DG and CDG. The viscosity recorded after the static aging test showed both samples were stable up to 170 °C suggesting these biopolymers can withstand the high-temperature requirements of the upstream petroleum industry. The DG and CDG gelling fluid are not sensitive to the temperature as it is stabilized by the disaccharide side chains and cationic moiety.



CONCLUSIONS

In conclusion, the cationic modification on the surface of double helical biopolymer structure (diutan and welan gum) have extended their properties. The thermal properties have improved accordingly with the improvement of the viscosity of the biopolymer. This is due to the generation of inter-polyelectrolyte complexes with hydrogel-like structures when modify the anionic biopolymer with cationic moiety. The improvement of the electrostatic attraction between the chains has overcoming the mutual repulsion of positive charges of the loaded cationic moiety. Hence, increase the force to break the chain where making it more stable at high temperature. The cationic biopolymer showing good gel stability upon exerted frequency where almost of the sample showing greater elastic modulus (G') compares with viscous modulus (G''). This is because of the strong intertwining network between the chains.

All of these positive responses have answered the needing on finding a sturdy biopolymer which can endure the high-temperature reservoir and meet others requirements and challenging of the upstream petroleum industry. Furthermore, the utilization of environmentally friendly, biocompatible and biodegradable material have become a world concern and this study have meet those requirement by using biopolymer instead of synthetic polymer to accomplish the industry demand.

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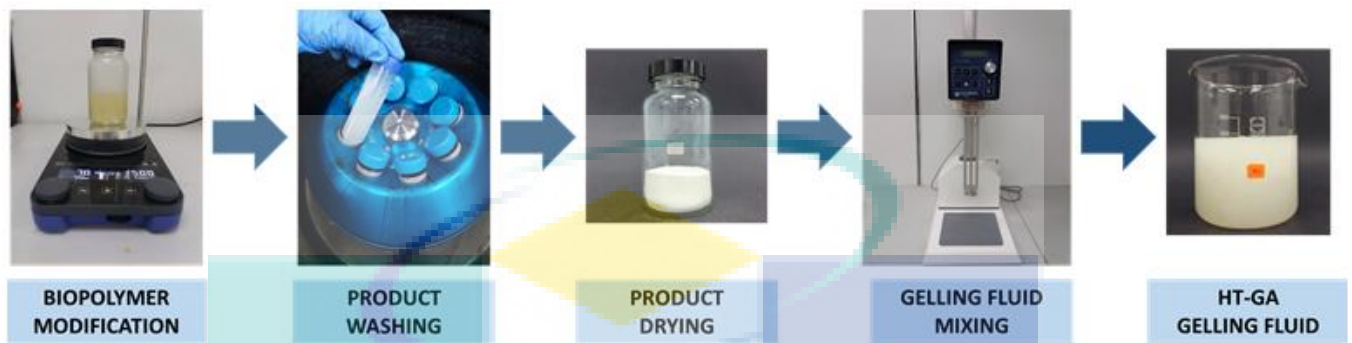
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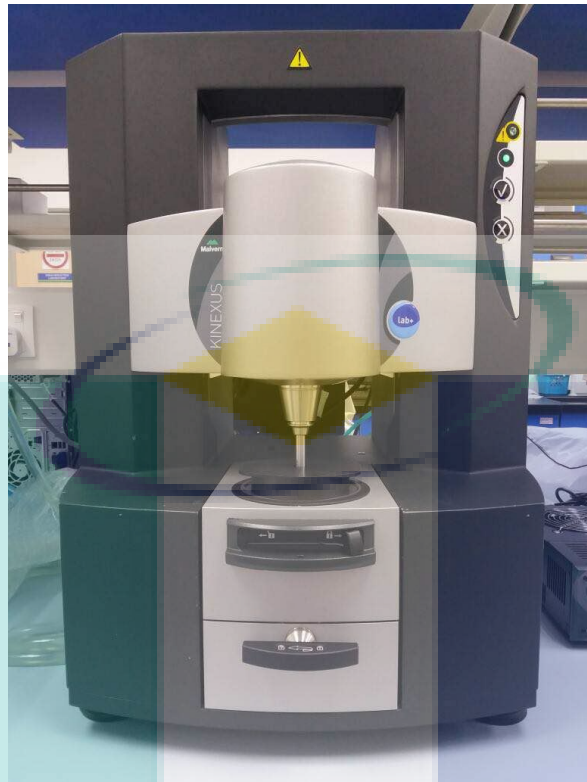
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APPENDIX



1. Process for cationic biopolymer modification

2. Stainless Steel Autoclave set with Teflon liner for static aging test



3. Malvern Kinexus Lab+ rheometer

UMP

HIGH TEMPERATURE GELLING AGENT FOR OIL AND GAS APPLICATIONS



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PRODUCT BACKGROUND

- Utilization of viscous fluid in a wellbore have been a common practice to enhance oil and gas hydrocarbons production.
- The viscous fluids are usually produced by hydrating common gelling agent such as hydroxyethyl cellulose, guar gum and xanthan gum in water or aqueous solution.
- As the oil exploration shifted towards higher-temperature reservoir, the common gelling agents are no longer usable because of degradation upon exposed to high temperature.
- To overcome this problem, UMP in collaboration with Neo Solutions Sdn Bhd have produced high-temperature gelling agent (HT-GA)
- HT-GA price is 75% cheaper compared to high temperature

BENEFITS AND APPLICATIONS

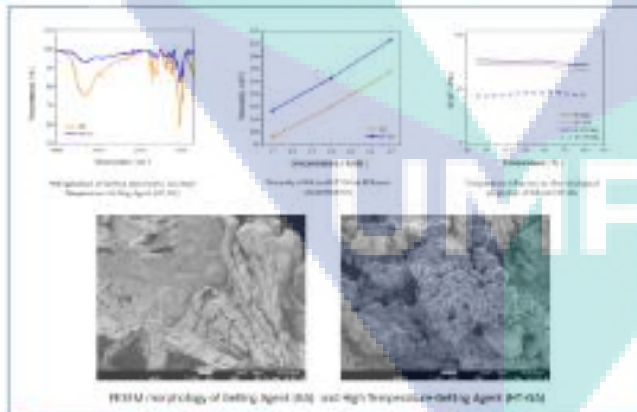
- BENEFITS**
- Produced from natural sources polymer, environmentally friendly.
 - Thermal stability up to 350°C.
 - High viscosity at low polymer loading
 - Excellent suspension capabilities
 - Easily mixed in freshwater, seawater or monovalent brines.
- APPLICATIONS**
- Polymer flooding for enhance oil recovery (EOR)
 - Hydraulic fracturing
 - Wellbore cleanout operation



PRODUCTION PROCESS



PRODUCT CHARACTERISTICS



MARKETABILITY & PRICE ESTIMATION

Global gelling agent market is expected to grow significantly from USD 2.795 in 2015, to USD 13.915 in 2023.

Material	Temperature (°C)	Product Density	HT-GA Price (USD/MT)
Guar gum	25	1.2	280.00
HT-GA	25	1.2	80.00
GA	275	1.2	80.00
HT-GA	275	1.2	15.00
HT-GA	300	1.2	15.00

TECHNOLOGY READINESS LEVELS (TRLs)



PATENT

INTERNATIONAL PATENT

AWARDS

- GRAND PRIX, INNOVATION, TECHNOLOGY & RESEARCH CONGRESS, UTM
- FINAL AWARDS BEST INNOVATION AWARD, INNOVATION, TECHNOLOGY & RESEARCH CONGRESS, UTM

COLLABORATOR

PROJECT LEADER: DR. RASDI ROSLAN
 COLLABORATOR: NEO SOLUTIONS

4. Poster ITEX 2018

HIGH TEMPERATURE GELLING FLUID FOR OIL AND GAS APPLICATIONS

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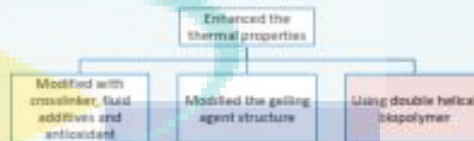
Email: rasidi@ump.edu.my

Introduction

- Utilization of a viscous fluid in a wellbore have been a common practice to enhance the production of oil and gas hydrocarbons (Serafi & Liang, 2014).
- The viscous fluid are produced when a thickener or gelling agent such as polymer was added into water or an aqueous solution.
- Various polymers were known for this purpose including a number of polysaccharides such as guar gum, guar gum derivatives (Wang et al., 2015), xanthan gum (Tan et al., 2015), carboxymethyl cellulose (Esmailirad et al., 2016) and hydroxyethyl cellulose (Brode et al., 1986).
- Diutan gum (DG) recently have been study as a promising gelling agent for oil and gas exploration because it has a great potential to be used in a harsh reservoir conditions.
- DG is a natural and environmentally friendly high molecular weight microbial polysaccharide obtained from *Sphingomonas* sp.

Motivation

- Oil exploration has shifted toward higher-temperature reservoir.



Proposed idea

- Modification on diutan gum (double helical biopolymer)

Diutan gum (DG) → Cationic diutan gum (CDG)

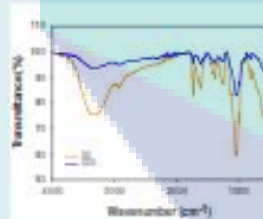
Methodology

CATIONIC MODIFICATION OF DG AND GEL PREPARATION

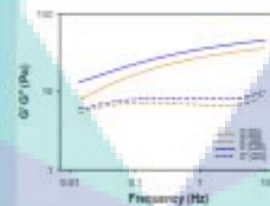


* N-(3-chloro-2-hydroxypropyl)trimethyl ammonium chloride (CHPTAC)

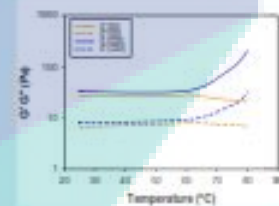
RESULTS



FTIR spectrum of diutan gum (DG) and cationic diutan gum (CDG)



Dynamic modulus of diutan gum (DG) and cationic diutan gum (CDG) on frequency



Temperature influence of diutan gum (DG) and cationic diutan gum (CDG)



Viscosity of DG and CDG

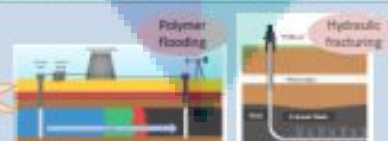


Surface morphology of DG and CDG gel

- ✓ Cationic-modified Diutan Gum
- ✓ High viscosity at low polymer loading
- ✓ Stable suspension capabilities
- ✓ Good thermal properties.

Applications

- Well Clean-up
- Hydraulic fracturing
- Drilling fluid
- Polymer Flooding for enhance oil recovery (EOR)



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