

Experimental Study on Microwave-Assisted Preparation of Hydrophobic Modified Guar Gum for Fracturing Fluid

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Summary: Hydraulic fracturing plays a significant role in developing low permeability reservoir. The modified guar gum is an effective method to enhance the guar gum fracturing fluid properties. The hydrophobic modified guar gum was prepared by microwave-assisted. The effect of different reaction condition on viscosity and water-insoluble of modified guar gum was studied. The optimum reaction condition was obtained as following: 80 °C reaction temperature, 8-10 min reaction time, 100 W microwave power, 8mL NaOH solution, 3mL 1-bromooctadecane. Fourier Transform Infrared Spectroscopy (FT-IR) characterization and Thermal Gravimetric Analysis (TGA) were conducted to prove that the hydrophobic modified guar gum was synthesized successfully. Microwave assisted heating is useful to improve the hydrophobic modified guar gum efficiency and viscosity.

Keywords: Guar gum; Fracturing fluid; Viscosity; Microwave-assisted; Water-insoluble.

Introduction

Petroleum, as a fossil fuel, is a renewable energy source for transport, and a major part of chemical makeup of many plastics and synthetics. With the development of low permeability reservoir increasing, hydraulic fracturing is playing a more and more role in improving the oil yield [1]. The properties of fracturing fluid have huge influence on result of fracturing. Guar gum fracturing fluid occupies a large proportion in water-based fracturing fluids, due to the wide source and environment friendly. However, guar gum fracturing fluid has disadvantages of the large quantity of residues after gel breaking and high concentration. The guar gum derivatives can overcome those shortcomings. Lots of researches were conducted to synthesis novel guar gum derivatives [2-4]. These researches mainly focus on conventional methods to synthesize modified guar gum for fracturing fluid. The 2-hydroxy-3-butoxypropyl guar gum was synthesized with guar gum as material, using n-butyl glycidyl ether as the hydrophobic reagent, sodium hydroxide as catalyst and isopropanol as solvent. The result showed that the hydrophobic modified guar gum can reduce the crystallinity and improve the thermal stability [5]. Hydrophobically modified hydroxypropyl guar gum was prepared through the introduction of long chain hydrophobic monomers (1-bromododecane molecule) to hydroxypropyl guar gum (HPG) molecular chain. The results of rheological property showed that BD-

HAHPG have viscosity increasing, thermal resistance, salt tolerance and shear resistance properties [6]. The radiation dosage of γ -radiation source ⁶⁰Co has large influence on viscosity and graft ratio. This study can provide a new perspective for relevant study [7].

Recently, the microwave-assisted chemistry develops rapidly. The microwave-assisted can enhance the reaction speed tens and hundreds times [8, 9]. The study on microwave-assisted synthesis of modified guar gum is rarely reported. Cationic guar gum was prepared by microwave-assisted using 3-chloro-2-(hydroxypropyl) trimethylammonium chloride as cationic etherifying agent. Experimental results showed that comparing with traditional synthesis method, the reaction time decreased to 16% and the rate of reaction efficiency increased by using microwave [10]. However, there is no report on microwave-assisted preparation of modified guar gum for fracturing fluid.

In this paper, the microwave-assisted hydrophobicity guar gum derivatives were synthesized and the effect of different factors on the derivative properties was studied. The optimum reaction condition was also obtained to provide reference for relevant research.

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Experimental

Reaction formula

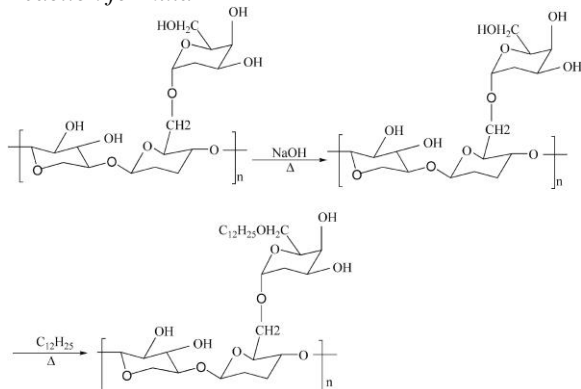


Fig. 1: Reaction formula.

Through the etherification reaction between guar gum and 1-Bromododecane, the modified guar gum is synthesized. Reaction molecular formula is shown in Fig. 1.

Material

Guar gum, NaOH, Isopropanol, 1-Bromododecane, 1-Bromotetradecane, 1-Bromohexadecane, 1-Bromooctadecane were bought from Sinopharm Chemical Reagent Co., Ltd. Atmospheric pressure microwave reactor, Thermostatic water bath kettle, centrifugal machine, drying oven, FT-IR spectrophotometer (Shimadzu Corporation, Japan), TGA instrument, magnetic stirrers, rotational viscometer (ZNN-D6, Qingdao Hengtai Electrical and Mechanical Equipment Co., Ltd) and boiling flask-3-neck were used.

Methods

Guar gum samples (3 g) were slurried in 25 mL isopropanol and 10 mL NaOH water solution for 2 h at 45 °C. Then 3 mL modifier (1-Bromododecane) was added, and the slurry was continuously stirred for 10 min at 60 °C heated by microwave and in an inert atmosphere (nitrogen). The resultant of reaction was filtered and washed, and then was dried in the oven at 80 °C for overnight. The production was used without further purification in subsequent synthesis. All conditions remain unchanged unless otherwise specified. Viscosity and water-insoluble are important parameter for the performance evaluation of guar gum fracturing fluid. Greater viscosity will improve the sand carry ability and less water insoluble can reduce the permeability damage. Therefore, the viscosity and water-insoluble

were chosen to evaluate the modified guar gum according to General technical specifications of natural plant gum for fracturing (SY/T-2007).

Fourier transform infrared spectroscopy (FT-IR)

The Fourier Transform Infrared Spectroscopy (FT-IR) of guar gum and modified guar gum were recorded in solid state, using KBr pellets with a FT-IR spectrophotometer between 400 cm^{-1} and 4000 cm^{-1} . The FT-IR is shown in Fig. 8.

Thermal gravimetric analysis (TGA)

The TGA of guar gum and the modified guar gum was carried out with TGA instrument. The study was performed up to 600 °C, starting from 30 °C, in an inert atmosphere (nitrogen). The heating rate was uniform in all cases at 10 °C/min. The results are shown in Fig. 9.

Results and discussion

The effect of heating temperature on guar gum properties

Table-1: The effect of heating temperature on guar gum properties.

Temperature, °C	30	40	50	60	70	80
Viscosity, mPa·s	129±4.2	135±4.1	138±2.7	144±3.3	148±2.5	155±4.3
water-insoluble, %	11.5±0.9	8±0.82	4±0.45	2.2±0.25	2.0±0.18	1.8±0.14

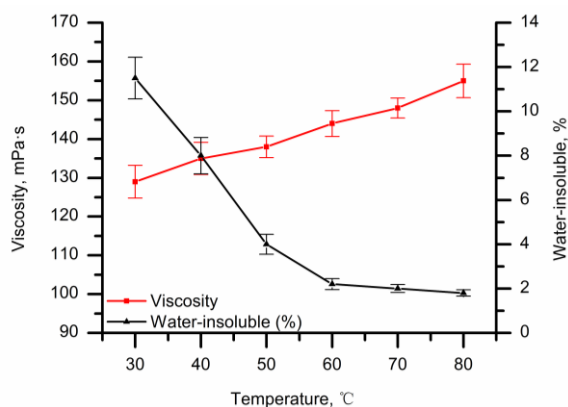


Fig. 2: The effect of heating temperature on guar gum properties.

Keep other reaction conditions constant. The reaction was conducted in different temperature heated by microwave. As shown in Fig. 2, as temperature increased, the viscosity increased. This is may be because high temperature can improve the reaction speed. At high temperature, more 1-Bromododecane connects with guar gum chain and

more hydrophobic modified guar gum was obtained. Considering the boiling point of isopropanol, the maximum temperature is 80 °C. As temperature increased, the water-insoluble decreased gradually. When the temperature raised from 30 to 60 °C, the water-insoluble decreased sharply, when the temperature was greater than 60 °C, the water-insoluble unchanged.

The effect of heating time on guar gum properties

Table-2: The effect of heating time on guar gum properties.

Time,min	2	4	6	8	10	12	14
Viscosity, mPa·s	128±2.	138±4.3	150±4.5	155±3.3	140±4.	122±0	100±3.8
water-insoluble, %	12.5±0.68	10±0.46	7.2±0.56	5.3±0.365	3.5±0.275	2±0.2	1.8±0.12

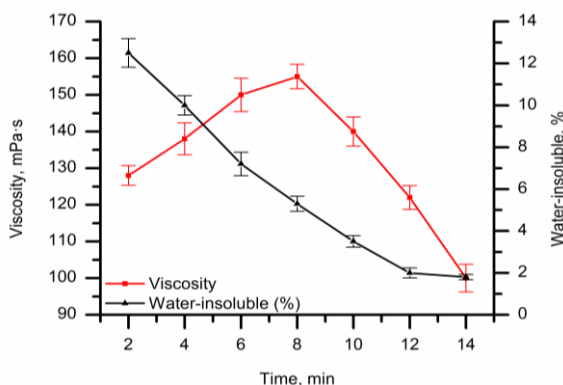


Fig. 3: The effect of heating time on guar gum properties.

The effect of reaction time on modified guar gum is shown in Fig. 3. The result showed that the viscosity increased first and decreased then with the increasing reaction time. The viscosity reached the maximum at 8 min. This may be because that at initial period, the etherification reaction speed was greater than decomposition of guar gum, when time was greater than 8 min, the decomposition of guar gum speeded up and was greater than etherification. In contrast, the result indicates that the reaction time is significantly shorter than conventional methods [11, 12]. The water-insoluble decreased with the time increasing, this may be a consequence of decomposition of water-insoluble materials.

The effect of microwave power on guar gum properties

Table-3: The effect of microwave power on guar gum properties.

Power, W	100	300	500	700	900
Viscosity, mPa·s	153±4.5	153±3.3	147±3.2	135±4.0	130±2.2
water-insoluble, %	2.2±0.21	2.5±0.19	2.4±0.12	2.3±0.2	2.6±0.22

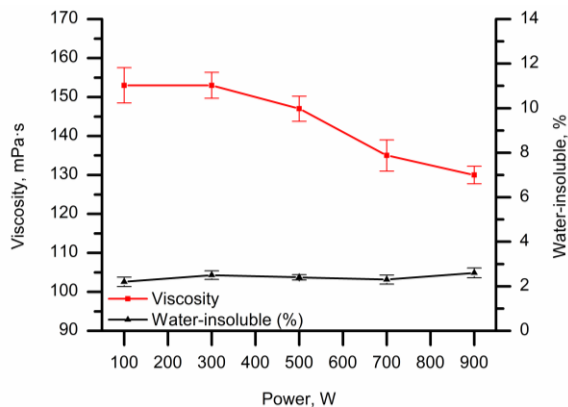


Fig. 4: The effect of microwave power on guar gum properties.

The effect of microwave power is shown in Fig. 4, the result showed that with the power increasing, the viscosity decreased slightly. That may be because that high power needed less time to heat the same temperature. The power has little influence on water-insoluble. Further studies should be conducted to research the effect of the power.

The effect of NaOH dosage on guar gum properties

Table-4: The effect of NaOH dosage on guar gum properties.

Dosage,mL	2	4	6	8	10	12	14
Viscosity, mPa·s	130±3	139±6	152±5	155±4	148±2	137±3	110±4
water-insoluble, %	3.4±1	6.1±8	5.34±5	4.2±3	2.93±2	3.12±1	4.21±1

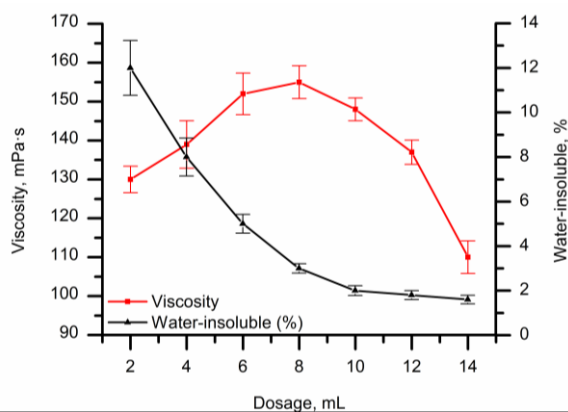


Fig. 5: The effect of NaOH dosage on guar gum properties.

The effect of NaOH is shown in Fig. 5. The result showed that with the NaOH dosage increasing, the viscosity increased when the NaOH water solution was lower than 8 mL, and decreased when the NaOH water solution was greater than 8 mL. The water-insoluble decreased with the NaOH dosage increasing. This may be because that NaOH can

catalyse the water-insoluble materials into water-soluble materials.

The effect of modifier dosage on guar gum properties

Table-5: The effect of modifier dosage on guar gum properties.

Modifier dosage, mL	1	2	3	4	5
Viscosity, mPa·s	130±3.0	146±3.4	154±2.6	155±3.1	155±4.0
water-insoluble, %	2.6±0.22	2.9±0.28	2.5±0.22	3±0.34	2.8±0.33

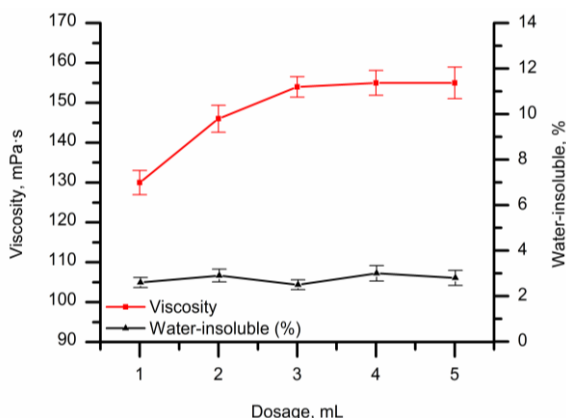


Fig. 6: The effect of modifier dosage on guar gum properties

The effect of modifier dosage is shown in Fig. 6. The result showed that 3 mL modifier was enough for the etherification reaction. And the modifier dosage had little influence on water-insoluble.

Different modifiers (1-Bromododecane, 1-Bromotetradecane, 1-Bromohexadecane, 1-Bromooctadecane) were used, and the effect of them is shown in Fig. 7. The result showed that the viscosity increased when the length of modifier carbon chain increased. The modifier dosage had little influence on water-insoluble materials.

Fourier transform infrared spectroscopy (FT-IR) analysis

Fourier Transform Infrared Spectroscopy (FT-IR) of guar gum and modified guar gum is shown in Fig. 8. The result showed that the peak of two samples was similar which indicated the main structure was similar. The peak at 2925 cm^{-1} was strengthened, which indicated the long chain alkyl was added. 1379 cm^{-1} , 1437 cm^{-1} were asymmetric stretching vibration and symmetric stretching vibration of $-\text{CH}_2-$ and $-\text{CH}_3$, which indicated the strengthen of alkyl. $1000-1200\text{ cm}^{-1}$ strengthen that were stretching vibration of C-O and C-O-C, which indicated the Ether bond was improved. In a summary, we believe that the long carbon chain

hydrophobic modifier is added.

The effect of modifier type on guar gum properties

Table-6: The effect of modifier type on guar gum properties.

Modifier type	1-Bromododecane	1-Bromotetradecane	1-Bromohexadecane	1-Bromooctadecane
Viscosity, mPa·s	152±3.3	155±2.3	158±2.8	162±3.5
water-insoluble, %	2.6±0.22	2.8±0.15	2.9±0.12	3.2±0.13

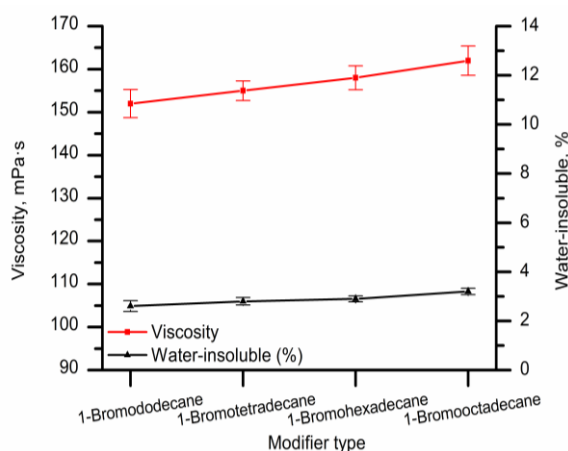


Fig. 7: The effect of modifier type on guar gum properties.

The Thermal Gravimetric Analysis (TGA) is shown in Fig. 9. The result showed that at intinal period, guar gum lost weight slightly and losed sharply at the temperature of $280-350\text{ }^{\circ}\text{C}$, and changed slightly agian when the temperature was greater than $350\text{ }^{\circ}\text{C}$. The weight loss of the modified guar gum is less than that of guar gum. Compared with guar gum, when the weight loss is same, the temperature of modified guar gum was improved. It can be concluded that the guar gum meclular changes and the thermal stability enhances.

Compared with conventional methods, microwave-assisted preparation of hydrophobic modified guar gum can shorten reaction significantly and don't effect the modified guar gum properties (Chen *et al.* 2014, Zhao *et al.* 2011).

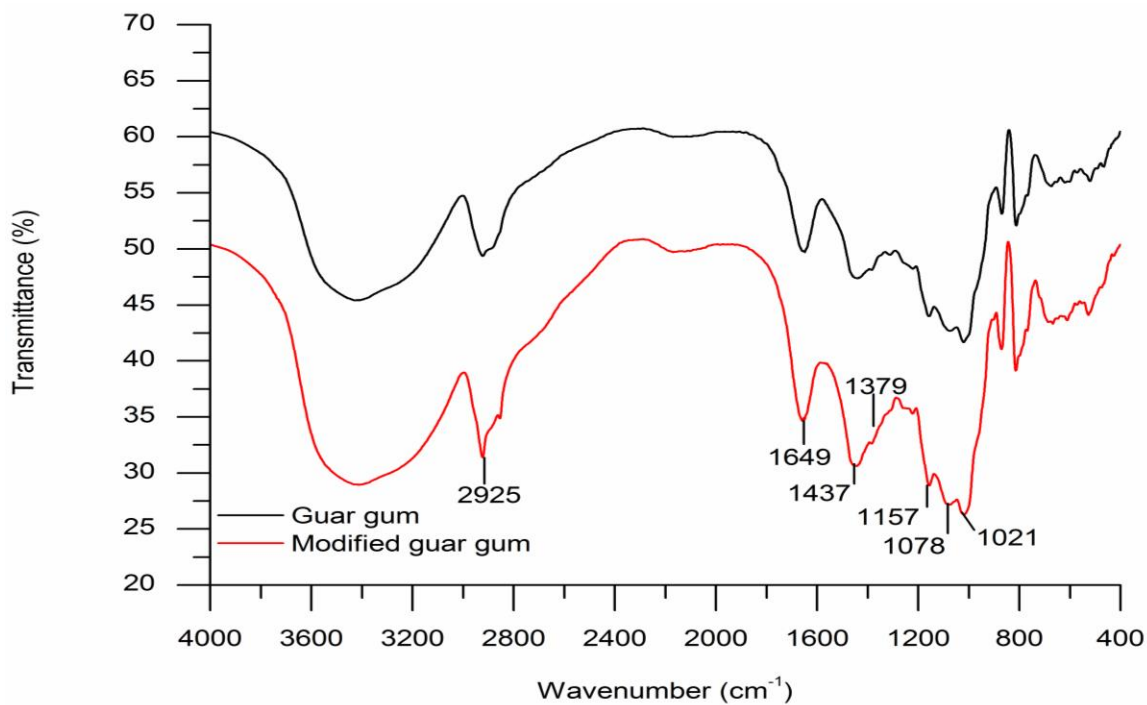


Fig. 8: Fourier Transform Infrared Spectroscopy.

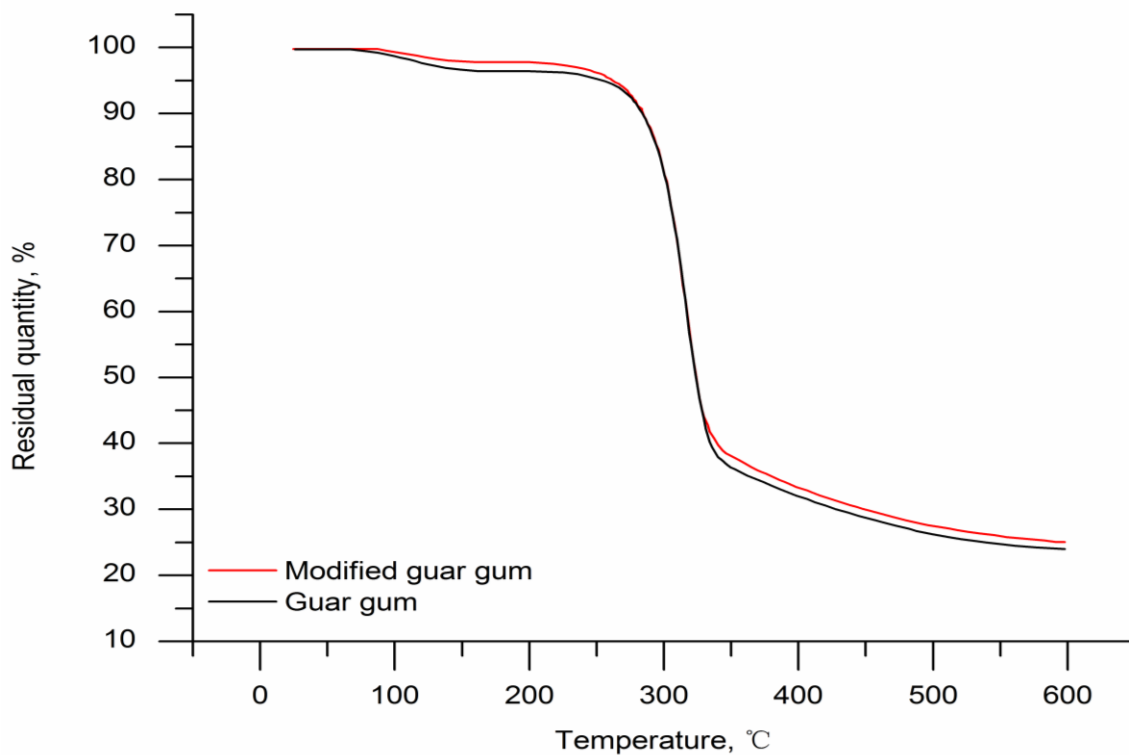
Thermal gravimetric analysis (TGA)

Fig. 9: Thermal Gravity Analysis.

Conclusion

The hydrophobic modified guar gum was synthesised with microwave-assisted. The effect of different reaction conditions was studied. The result showed that temperature, reaction time and NaOH dosage have large influence on viscosity. The water-insoluble decreased with temperature, time and NaOH dosage increasing. The microwave power and modifier type have little influence on water-insoluble. The optimum reaction time is 8 min, which is much shorter than conventional methods (6-8 h). The optimum reaction condition was obtained as following: 80 °C reaction temperature, 8-10 min reaction time, 100 W microwave power, 8 mL NaOH solution, 3 mL 1-bromooctadecane. Microwave-assisted is useful to improve the hydrophobic modified guar gum efficiency and viscosity.

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Reference

1. Y. Wang, Y. Lu, Y. Li, X. Wang, X. Yan and Z. Zhang. Progress and application of hydraulic fracturing technology in unconventional reservoir. *Acta Petrolei Sinica*. **33** 149 (2012).
2. S. Pal, A. S. Patra, S. Ghorai, A. K. Sarkar, V. Mahato and S. Sarkar. Efficient and rapid adsorption characteristics of templating modified guar gum and silica nanocomposite toward removal of toxic reactive blue and congo red dyes. *Bioresource. Technol.* **191** 291 (2015).
3. Kamaljit Singh Sokhal, Dasaroju Gangacharyulu, Vijaya Kumar Bulasara, Effect of guar gum and salt concentrations on drag reduction and shear degradation properties of turbulent flow of water in a pipe, *Carbohyd Polym*, **181** 1017-1025 (2018).
4. Mudgil, D., Barak, S. and Khatkar, B.S. Guar gum: processing, properties and food applications—A Review. *J Food Sci Technol*, **51** 409 (2014).
5. X. J. Xue, Y. D. Shen, X. J. Lai, W. Lei and J. B. Zhao. Preparation and rheological property of 2-hydroxy-3-butoxypropyl guar gum. *Funct. Mater.* **43** 88 (2012).
6. X. Zhao, D. Qiu, S. Li and K. Sun. Research on the synthesis of hydrophobically associating hydroxypropyl guar gum. *Special.* **28** 41 (2011)
7. X. F. Zhao, P. J. Yao, and Y. A. Wei. Preparation of guar gum-maa radiation grafted copolymers and its application. *Technol. Develop. Chem. Indust.* **37** 1 (2008).
8. M. Likhitha, R. R. Sailaja, V. S. Priyambika, and M. V. Ravibabu. Microwave assisted synthesis of guar gum grafted sodium acrylate/cloisite superabsorbent nanocomposites: reaction parameters and swelling characteristics. *Int. J. Biol. Macromol.* **65** 500 (2014).
9. D. Ashok Rao, V. H. Sreenivas, and Peddolla. Microwave-assisted synthesis of 2-(4, 5-dihydro-5-(tetrazolo [1, 5-a] quinoline-4-yl)-1h-pyrazol-3-yl)-substituted phenols. *Heterocycl. Commun.* **19** 363 (2014).
10. X. L. Dai, G. Q. Cao, and C. Yang. Study on microwave-assisted synthesis of cationic guar gum. *Appl. Chem Indust.* **40** 2150 (2011).
11. F. Chen, X. G. Wang, R. S. Yang, M. L. Yu. and Q. Wang. Synthesis and property analysis of hydrophobic modification guar gum. *Adv. Mater. Res.* **22** 1046 (2014)
12. J. Zhao, Y. Shen and L. Wang. Synthesis of Hydrophobic Modified Guar Gum Thickener and Correlation. *Polym Mater Sci Eng.*, **10** 58 (2011).