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Characterization of a novel terpolymer containing maleic anhydride-co-stearyl methacrylate-co-benhely acrylate for wax inhibition application

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Characterization of a novel terpolymer containing maleic anhydride-*co*-stearyl methacrylate-*co*-benhely acrylate for wax inhibition application

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Abstract. Wax deposition in petroleum pipelines is deliberated as one of the most severe operational issues, and extraordinary efforts have been made to remediate and prevent this flow assurance problem. Using, polymeric pour point depressants (PPD) as a wax control strategy to improve the fluidity of waxy crude oil and reduce the pour point have received significant attention. The purpose of the current research is to synthesize novel terpolymers which used as PPD and viscosity improvers. The synthesis process occurred *via* polymerization of stearyl methacrylate (SMA), behely acrylate (BA), and maleic anhydride (MA) monomers using free radical polymerization method in toluene as a solvent, and (1 wt%) benzoyl peroxide (BZP) as initiator. The chemical structure of the prepared terpolymer was characterized by FTIR and NMR. Also, the crystallization behavior of paraffin wax was investigated by differential scanning calorimetry (DSC). Experimental investigations furnish that the synthesized PPD showed high yield (87%) at the concentration (1:1:1) of BA-*co*-SMA-*co*-MA. From FTIR and ¹HNMR characterization results observed that maleic anhydride moiety, alkyl chain moiety, and methacrylate moiety are existing in the prepared terpolymer. Furthermore, DSC analysis showed that the glass transition temperature of the prepared terpolymer is weakly stated over a wide temperature range.

1. Introduction

The crude oil is a complex compound that consists of different hydrocarbons such as resins, asphaltenes, aromatics, and paraffin waxes [1-3]. Usually, in the grilling area or at high temperatures, the paraffin crystals stay liquefied in the crude. However, when the temperature decreases beneath the wax appearance temperature (WAT) the fluidity of crude oil becomes weak due to starting the precipitation of paraffin crystals in the crude and also on the inner wall of the pipeline [4-5]. The crystallization process of paraffin wax may lead to severe issues in the storage, production, and transportation due to loss in the flowing capability of crude oil as well as rising in the crude oil viscosity and some cases lead to blockage in the pipeline [6-7]. Paraffin wax could be successfully spread by using a little number of additives that are known as pour point depressants (PPD) [8-9]. There are different postulated mechanisms for such additives to form slight and regular shaped wax crystals, for instance, nucleation, adsorption, and co-crystallization which lead to increase in wax solubility [10-12]. Notably, there are no universal additives that can be effective for all types of crude oil. Consequently, the best wax inhibitor performance should be investigated for every well on an individual basis, and exact compatibility with the raw petroleum must be present. Many methods have



used to mitigate and prevent the issue of wax deposition, and some of these techniques are chemical treatment, thermal, electromagnetic, mechanical, bacterial. Nevertheless, chemical treatment practices using wax inhibitor has shown the best result to mitigate the wax precipitation in the oil and gas sector [5, 13-14]. Moreover, treating the wax deposition issue using polymeric additives as chemical treatment is considered as the most valuable and economical method to inhibit the wax precipitation. These polymeric compounds consist of the polar section which is chargeable for the modification of wax crystals morphology, as well as, contain hydrocarbon chain which extends the interaction between the additives and paraffin [6, 15]. A considerable number of sorts of polymeric additives have been created and utilized as PPDs to impact the formation manner of paraffin crystals [12, 15-17]. However, in recent decades close attention has been made on the methacrylate group and maleic anhydride polymers due to the highly polar functional groups that contain [15, 18].

Moreover, Dao in (2017) has proved that stearyl methacrylate and behenyl acrylate with vinyl acetate using AIBN as initiator gives high efficiency to reduce pour point temperature [19]. Furthermore, many other researchers have proven that maleic anhydride with other different monomers shows good results in reducing the pour point and yield stress of crude oil [20-21]. The goal of this study is to synthesize a newly terpolymer which working as a pour point depressant (PPD) using maleic anhydride with stearyl methacrylate and behenyl acrylate *via* free radical polymerization method to inhibit the wax precipitation in pipelines and reservoir formation. These three monomers integrated a new terpolymer which has not yet been invented by other researchers in wax inhibition field. Consequently, the significant effort of this research is to characterize the newly synthesized polymeric additives by confirming the chemical structure and rheological characteristics of the prepared terpolymer.

2. Experimental section

2.1. Chemical Materials

The material used in this study are stearyl methacrylate (SMA) (96%), behenyl acrylate (BA) (99%), maleic anhydride (MA) (<99%), which obtained as analytical reagents from Aladdin chemicals and used as received, as well as, Xylene ($\geq 98.5\%$) from Sigma- Aldrich as solvent in which the monomers dissolved. Also, benzoyl peroxide (75%) from Sigma- Aldrich used as an initiator of the reaction after the recrystallizing process from methanol.

2.2. Reaction yield

Typically, the efficiency of the chemical reaction in the polymeric synthetic is determined by the percentage of yield (%) [22]. The percent yield figures out by determining the amount of the monomers in the stoichiometry which known as theoretical yield. Whereas, the actual yield measured by determining the amount of the polymer after the chemical reaction carried out, and the percent yield can be measured using Equation 1 [23].

$$\text{Percent Yield} = (\text{Actual Yield} / \text{Theoretical Yield}) * 100 \quad (1)$$

2.3. Preparation of Terpolymer

The polymerization reaction conducted in a 200 mL three-necked glass flask which was equipped with a magnetic stirrer and thermometer, as shown in Figure 1. The produced terpolymer prepared by polymerizing of stearyl methacrylate, maleic anhydride, and behenyl acrylate monomers at the concentration (1:1:1) mole ratios under free radical polymerization method. The polymerization is ideally directed with constant stirring (400 rpm) at 80°C for five hours in the presence of 50 mL of toluene as a solvent and benzoyl peroxide (1 wt%) as an initiator under a nitrogen environment. The obtained terpolymers were precipitated in excess of methanol, then filtered and dried under vacuum at 40°C for 12 h.

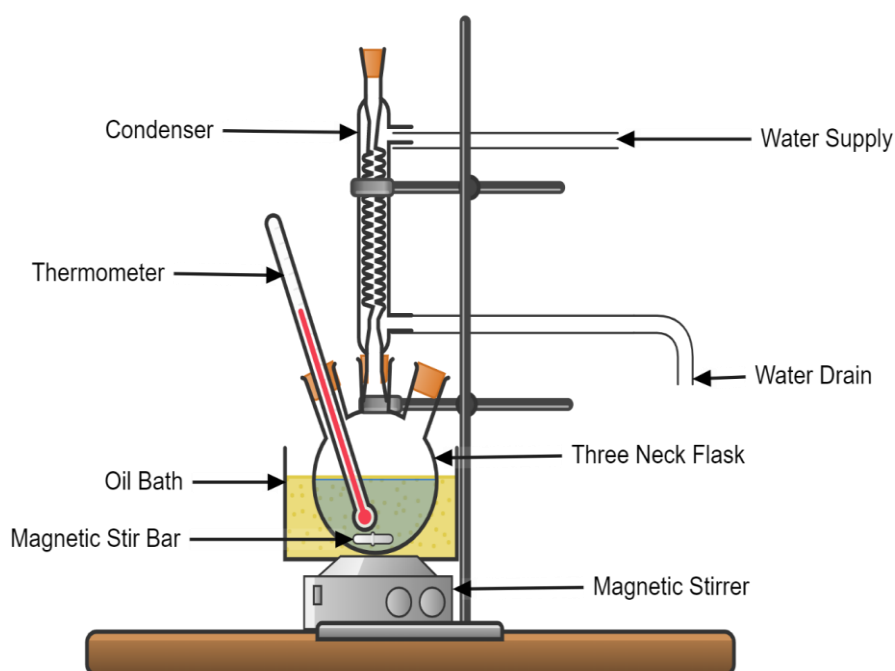


Figure 1. Experimental apparatuses.

2.4. Characterization of Prepared Terpolymer

To approve the chemical structure of the synthesized terpolymer Fourier transform infrared spectrometer (Nicolet iS5 FT-IR spectrometer) has been used. Also, H-NMR was conducted to determine unknown substances as well as the sample purity using Bruker ultra-shield plus 500MHz. Differential scanning calorimetry (DSC) was utilized to explore the response of polymeric additives to heating and also characterize the physical properties of the prepared terpolymer using TA Instruments Q1000 Differential Scanning Calorimeter.

3. Results and Discussion

3.1. Fourier Transform Infrared (FTIR) Spectroscopy

The chemical structure of the prepared terpolymer was characterized by FTIR spectrometry. Figure 2 demonstrates the FTIR spectra of the prepared BA-co-SMA-co-MA copolymer and clearly illustrates that the influential absorption band at 2916 and 2849 cm^{-1} attributed to stretching vibration of C-H bonds of methyl and methylene group as the similar findings that have been indicated previously by Darvishi et al. [24]. The figure also shows characteristics of C=O stretching peaks of maleic anhydride at 1781 cm^{-1} and sharp absorption peak of the characteristic C=O at 1728 cm^{-1} for stearyl methacrylate as similar observation by Song et al. [25]. The bending vibration peaks of the C-H bonds appear at 1466 and 1379 cm^{-1} , and weak asymmetrical stretching vibration peaks for the epoxy group appears at 835 and 959 cm^{-1} . As well, the typical medium absorption peak of characteristic $-\text{CH}_2-$ in long-chain alkyl are distinguished at 720 cm^{-1} , and these results are in line with previous findings by M. A. Zhou et al. [18]. Therefore, the result represents that maleic anhydride moiety, alkyl chain moiety, and methacrylate moiety are existing in the prepared terpolymer and absence of bands between 1640-1680 cm^{-1} which typify C=C group designate the completion of polymerization and this result in line previous reported by other researchers [26].

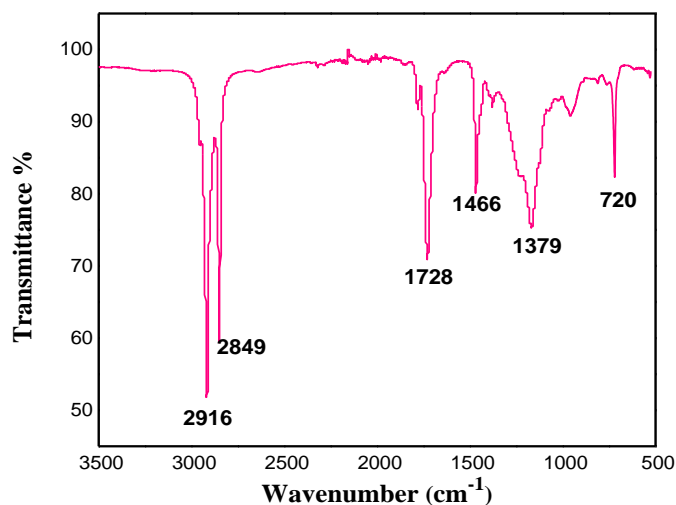


Figure 2. FTIR spectra of (BA-co-SMA-co-MA) terpolymer.

3.2. Proton Nuclear Magnetic Resonance ($^1\text{H NMR}$)

Further characterization utilizing $^1\text{H NMR}$ analysis has been conducted to accumulate more information on the chemical structure of the prepared terpolymer (BA-co-SMA-co-MA). Figure 3 represents the $^1\text{H NMR}$ spectra of the synthesized polymer (1:1:1-mole ratio of BA-co-SMA-co-MA). The chemical shifts for terpolymer showed a peak at 0.86 ppm was due to methyl of methacrylate chain, whereas the other peaks which ranged between 1.1-1.6 ppm characterized for methylene protons of acrylate chain these results are in accordance with conclusions stated by observation by Upadhyay et al. [27]. Besides, the spectra of the proton showed chemical shift at 3.7 ppm, and 4.1 ppm were due to the group of methylene which adjacent to an oxygen atom ($-\text{OCH}_2$) of methacrylate and behenyl acrylate respectively, a similar pattern of findings was obtained by Song et al. [25]. Nevertheless, the peaks of the proton of maleic anhydride polymeric state are not observable as the similar results reported by Mingan in 2015 [18]. These results designate that the alkyl chain moiety and methacrylate moiety are existing in the prepared terpolymer and same results have also been confirmed by FTIR analysis.

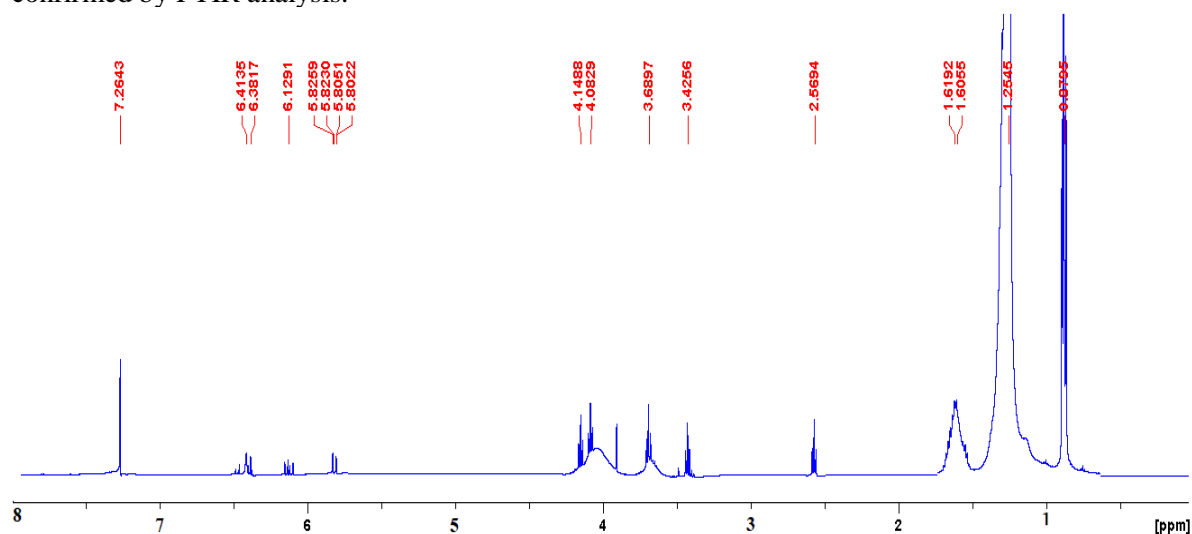


Figure 3. $^1\text{H NMR}$ spectra of the prepared terpolymer.

3.3. Differential Scanning Calorimeter (DSC)

Phase transitions and thermal properties for the prepared polymer are significant for the utilization of polymeric materials. Therefore, the thermal properties of the prepared terpolymer have been characterized using DSC. As observed from DSC analysis data in figure 3, the prepared terpolymer relies upon the sort and structure of monomers and these results are consistent with what has been found in the previous literature by Karažija et al. [28]. Also observed from figure 3, at the temperature -60 C° to approximately -10 C° the terpolymer is in the glassy state, while at the temperature ranged from -10 C° to 40 C° , the glass transition of the synthesized terpolymer is observed. With additional heating, the crystalline phase of terpolymer melts. Furthermore, the temperature of the glass transition of synthesized terpolymer is weakly stated over a wide temperature range, and without apparent completion surpasses into an endothermic peak as a similar conclusion that obtained by Liu et al. [29]. This is because of the relaxation process in the glass transition phase, as reported previously by Beiner et al. [30]. Consequently, for more precise determination and comprehensive examination of phase transition, additional methods ought to be used as well.

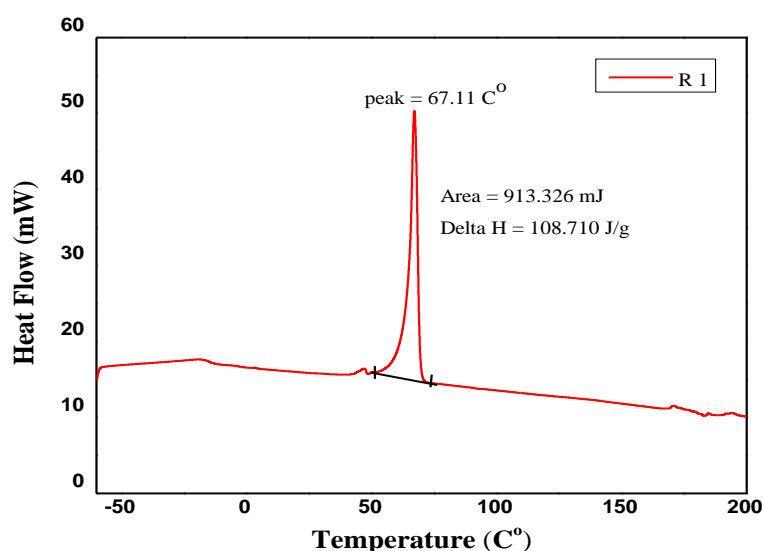


Figure 4. DSC curve of the synthesized terpolymer.

4. Conclusion

A newly synthesized terpolymer has been characterized using FTIR, NMR, and DSC. The synthesis process occurred *via* polymerization of stearyl methacrylate, benzyl acrylate, and maleic anhydride monomers using free radical polymerization. The chemical structure of the prepared terpolymer has been confirmed using FTIR (Fourier transform infrared spectroscopy), and NMR (Nuclear Magnetic Resonance). Experimental investigations furnish that the synthesized PPD has high yield 87% at the concentration (1:1:1-mole ratio of BA-co-SMA-co-MA). From FTIR and ^1H NMR results observed that maleic anhydride moiety, alkyl chain moiety, and methacrylate moiety are existing in the synthesized terpolymer. Furthermore, DSC analysis reported that additional methods ought to be used as well to obtain precise determination and comprehensive investigation of phase transition.

Acknowledgments

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References

- [1] Chen W, Zhang X, Zhao Z and Yin C 2009 *Fluid Phase Equilibria* **280** 9–15
- [2] Duarte L, Filgueiras P, Silva S, Dias J, Oliveira L and Castro E 2016 *Fuel* **181** 660–9
- [3] Kasumu A, Arumugam S and Mehrotra A 2013 *Fuel* **103** 144–7
- [4] Jung K, Chun B, Park S, Lee C and Kim S 2011 *J. Appl. Poly.Sci.* **120** 2579–86
- [5] Aiyejina A, Chakrabarti D, Pilgrim A and Sastry M 2011 *Int. J. Multiphase Flow* **37** 671–94
- [6] Al-Sabagh A, Eldin M, Morsi R and Elsabee M 2009 *J. Petro. Sci. Eng.* **65** 139–46
- [7] Yao B, Li C, Yang F, Zhang Y, Xiao Z and Sun G 2016 *Fuel* **184** 544–54
- [8] Ghosh P and Das M 2014 *J. Petro. Sci. Eng.* **119** 79–84
- [9] Han S, Song Y and Ren T 2009 *Energy & Fuels* **23** 2576–80.
- [10] Chen W, Zhao Z and Yin C 2010 *Fuel* **89** 1127–32
- [11] Fang L, Zhang X, Ma J and Zhang B 2012 *Industrial & Eng. Chem. Research* **51** 11605–12
- [12] Liu T, Fang L, Liu X and Zhang X 2015 *Fuel* **143** 448–54
- [13] Elbanna S, Abdelrhman A, Alhussaini A and Khalil S 2017 *Petro. Sci. Tech.* **35** 1047–54
- [14] Jennings D and Breitigam J 2009 *Energy & Fuels* **24** 2337–49
- [15] Wu Y, Ni G, Yang F, Li C and Dong G 2012 *Energy & Fuels* **26** 995–1001
- [16] Cao K, Zhu Q, Wei X and Yao Z 2015 *Energy & Fuels* **29** 993–1000
- [17] Lü Y, Zhang X and Yao G 2011 *Energy & Fuels* **25** 2115–8
- [18] Zhou M, He Y, Chen Y, Yang Y, Lin H and Han S 2015 *Energy & Fuel* **29** 5618–24
- [19] Than D, Chuong T and Tuy D 2017 *AIP Conf. Proc.* **1878** p 020002
- [20] Soliman E, Elkatory M, Hashem A and Ibrahim H 2018 *Fuel* **211** 535–47
- [21] Xu J, Xing S, Qian H, Chen S, Wei X and Zhang R 2013 *Fuel* **103** 600–5
- [22] Isacgarcía J, Dobado J, Calvoflores F and Martínezgarcía H 2016 *Academic Press* **8** 29–43.
- [23] Sheldon R 2012 *Chem. Society Reviews* **41** 1437–51
- [24] Darvishi A, Zohuriaan M, Marandi G, Kabiri K, Bouhendi H and Bakhshi H 2013 *Designed Monomers and Polymers* **16** 79–88
- [25] Song Y, Ren T, Fu X and Xu X 2005 *Fuel Processing Tech.* **86** 641–50
- [26] Atta A, Elghazawy R, Morsy F, Ali M and Elmorsy A 2013 *Global J. Sci. Res. Chem.* **13** 21–7
- [27] Upadhyay M, Saha D and Ghosh P 2018 *J. of Scientific & Industrial Research* **77** 652–6
- [28] Karažija T, Vidović E and Jukić A 2013 *Polymer Eng. & Sci.* **53** 2299–307
- [29] Liu G, Zhang L, Yao Y, Yang L and Gao J 2003 *J. Appl. Poly. Sci.* **88** 2891–6
- [30] Beiner M 2001 *Macromolecular rapid communications* **22** 869–95