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PREPARATION AND EVALUATION OF N-ALKYL METHYLACRYLATE-VINYL ACETATE - METHACRYLIC ACID TERPOLYMERS AS POUR POINT DEPRESSANT FOR FUEL

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Abstract

A variety of techniques have been employed in order to reduce problems caused by the crystallization of paraffin during the production. Four different alkyl chain length of n-alkyl methacrylate-vinyl acetate-methacrylic acid terpolymers were prepared and characterized by the infrared spectrometer, and the molecular weight of the prepared additives was determined by using gel permeation chromatography analysis. The performance of the prepared terpolymers as pour point depressants additives for fuel oil. The efficiency of the prepared compounds on pour point depressants for fuel oil increases by increasing the concentration of these additives and the alkyl chain length of n-alkyl methacrylate. The X- ray diffractometer patterns of wax in the absence and presence of investigated additives were studied. Comparison of morphologies and structures of waxy crystals in fuel oil beneficiated with and without a pour point depressant was made by micro photographic studies which show the modification in wax morphology due to the additive.

Keywords: *Terpolymers; Fuel oil; Pour point depressants; Wax modification.*

1. Introduction

Hydrocarbon fuel oils, for example, petroleum distillate fuels, contain n-paraffin waxes that tend to be separated from the oil in low temperature [1-2] The waxes generally crystallize as an interlocking network offine sheets, thereby entrapping the remaining fuel in cage like structures [3] and causing the cold flow problems such as blockage of fuel lines and filters in engine fuel system. Studies have shown that the network waxes amounting to as little as 1–2wt% of the sample are still capable of causing low temperature fluidity and operability problems in distillate fuels [4-5]. Highly waxy crude oils are characterized by a high pour point, viscosity, and yield stress, and exhibit non-Newtonian flow behaviour below pour point temperature [6-8] The flow properties of crude oil play a great role in its production storage, transport, and refining [9-11] pour point depressants (PPDs) to improve the cold flow properties of oils has been proven to be an effective and economical way [12]. In general, these additives have a wax-like paraffin part which provides the interaction between the additive and paraffin and a polar segment that is responsible for modifying the morphology of wax crystals [13-14].

Some characteristics of the additives should be considered: there should be a sufficient number of pendant alkyl groups with sufficiently long hydrocarbon chains, there should be an appropriate distance between the hydrocarbon pendant chains and there should be a suitable ratio of monomers for copolymer additives [15-16]. Many experimental and theoretical studies have been performed to reveal the pour point depressant mechanism and many hypothetical mechanism theories have been formed, in which adsorption, co-crystallization, nucleation, and improved wax solubility are the most widely accepted view points [17-18].In the present study, we have synthesized four alkyl methacrylate-vinyl acetate-methacrylic acid terpolymers with different long-chain alkyls by free radical polymerization and evaluated their influence on the flow properties of fuel oil.

2. Experimental

2.1. Materials

The following chemicals were used, methacrylic acid, dodecyl alcohol, hexadecyl alcohol, octadecyl alcohol, two linear saturated long chain alcohol blends NAFOL 20+A, and NAFOL 1822 B were supplied from Condea Chemical Company, the typical analysis is listed in Table 1. Vinyl acetate was purchased from Aldrich and distilled under reduced pressure before use. P-toluene sulphonic acid, dibenzoyl peroxide, and other common chemicals used were of laboratory grade reagents.

Table 1. Typical analysis of linear long-chain alcohol blends (NAFOL)

Properties	NAFOL 20+A	NAFOL 1822 B	Properties	NAFOL 20+A	NAFOL 1822 B
	Composition, wt %		Density g/cm^3 at 80°C	0.803	0.802
C16-OH	0.9	0.2	Solidification point,°C	56-60	63-65
C18-OH	24.3	15.0	Ester No. mg KOH/g	9.9	0.16
C20-OH	24.4	14.8	Acid No. mg KOH/g	0.05	0.01
C22-OH	38.2	69.8	Water, wt%	0.06	0.04
C24-OH	9.9	0.2	Flash point,°C	208	204
C26-OH	2.3	-	Iodine No. mg/100 mg	8.2	0.23
			Average carbon number (calculated)	C_{av}= 20	C_{av}= 22

2.2. Middle distillate fuel oil composition

Middle distillate fuel oil (FO) derived from the waxy western desert crude oil with physico-chemical characteristics given in Table (2) was used for evaluation of the performance of the synthesized additives. The n-paraffin content of the fuel oil tested was determined by urea adduction [19]. The fuel oil was subjected to gas liquid chromatographic analysis to determine the average carbon number and carbon number distribution.

Table 2. Physical characteristics of fuel oil

Properties	Methods	Result
Specific gravity at 60/60ºF	IP 160/87	0.8412
Kinematics viscosity at 40ºC (cSt)	IP 71/80	3.7
Cloud point (cp), ºC	IP 219/82	24
Pour point (pp), ºC	IP 15/67(80)	15
Sulfur content (wt%)	IP 266/87	0.231
Flash point, ºC	IP 34/82 (87)	123
Total paraffins content (wt%)	Urea adduct	20.3
n-paraffin (wt%)	GLC	19.9
Iso-paraffins (wt%)	GLC	0.40

2.3. Synthesis additives

2.3.1. Synthesis of n-alkyl methacylate

The methacrylic acid mono-esters were prepared by reacting 1 mole of methacrylic acid with 1.1 mole of a series of n-alkyl alcohols which having increasing number of carbon atoms dodecyl alcohol, hexadecyl alcohol, two linear saturated long chain alcohol blends NAFOL 20+A (C_{av}=20) and NAFOL 1822 B(C_{av}=22) using p-toluene sulphonic acid as catalyst, toluene as a solvent (100ml) and hydroquinone to avoid polymerization. The reaction mixture was conducted for 24 hours at the reflux temperature. Water was separated azeotropically using Dean-Stark apparatus. The excess of the residual alcohol was removed through distillation under vacuum; then the reaction mixture was extracted with n-hexane, washed several times with water to remove unreacted methacylic acid and the catalyst, and then dried under vacuum at 40C.

2.3.2. Synthesis of terpolymers

The above synthesized alky methacrylate, vinyl acetate and methacrylic acid dissolved in toluene in a 1:1:1 mol ratio were taken in a four-necked flask. In the beginning, the contents were subjected to nitrogen flushing for twenty minutes, then gradually heated to 95 °C. When the temperature of the reaction reached 95°C, benzoyl peroxide dissolved in toluene as an initiator was added drop by drop. The whole content was refluxed for 8 h. Finally, the thick slurry was distilled under reduced pressure, followed by precipitation in excess ethanol and vacuum dried for 24 h [20]. The prepared additives are named as MVM-12, M VM-16, MVM-20, and MVM-22, respectively.

2.4. Characterization of the prepared terpolymers

Infrared spectra for esters n-alkyl methacrylate and their terpolymers with vinyl acetate and metacrylic acid were recorded on FTIR spectrophotometer (Genesis Series) using the traditional transmission technique for KBr pellets.

Molecular weights and polydispersity of terpolymers were determined by using gel permeation chromatographic analysis (GPC) with a refractive index detector using column styragel HR THF 7.8X300 mm, equipped with a water 515 HPLC pump. THF was used as an eluent at a flow rate of 1ml/min. Aliquots (1ml) of each sample were diluted with an appropriate amount of THF and were shaken vigorously, then passed through a filter and injected into the GPC for analysis.

2.5. Evaluation tests

2.5.1. Pour point measurements

Pour points were measured by following the ASTM D97 method. An appropriate quantity of additive (250–2000 ppm) in 1 mL toluene was added to 50 ml fuel oil in a cylindrical test jar and the mixture was first heated to 45°C. The test jar was then placed in a digital pour point cooling bath, and the sample was cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which the movement of the specimen is observed is recorded as the pour point. The results are presented as pour point reduction in relation to the pour point of the fuel oil. The pour point reduction was calculated from the following equation: pour point reduction: $\Delta pp = pp_{pure} - pp_{add}$;
where PP_{pure} is the pour point of the pure fuel oil, and PP_{add} is the pour point of the fuel oil containing the additive.

2.5.2. X-Ray diffraction spectroscopy

The structure of the wax isolates from fuel oil and wax + 1500 ppm (MVM-22), and wax + 1500 ppm (MVM-12) were characterized using X-ray powder diffract meter, PANalytical X'Pert PRO MPD (Netherland). Cu Kα radiation with wave length= 1.5418Å was used at a rating of 40 kV, 40 mA. The diffraction patterns were recorded at room temperature in the angular range of 4-70º (2θ) with step size 0.02º (2θ) and scan step time 0.4 (s). The crystalline phases were identified using the ICDD-PDF database.

2.5.3. Microscopic Studies

An Olympus polarizing microscope model BHSP fitted with an automatic camera with a 35mm format was used to study the wax crystals of untreated and additive treated fuel oil at a temperature of -5°C below the pour point. The temperature of the tested lube oil sample was controlled on the microscope slide by an attached cooling thermostat. The adopted magnification was 100X.

3. Results and discussion

3.1. Chemical structure and characterization of the prepared terpolymers

By analyzing the most important signals in the FTIR spectra, it was confirmed that the four terpolymers share the same profile. According, the spectrum of compound acrylic acid which illustrates the O-H stretching band of the carboxylic group which appeared as a small broad band at 3443 cm^{-1}. It can be clearly seen the characteristic CH_3 and CH_2 of the alkyl group adsorption peaks at 2925 and 2854 cm^{-1}, the characteristic C = O stretching peaks of methacrylate at 1727 cm^{-1}, and the characteristic, and we can see the intensity of CH_3 and CH_2 bands increases with the increase of the length of alkyl groups [21]. The characteristic C =C is stretching vibration peak at 1639 cm^{-1} almost vanishes completely. This indicates that there exist alkyl chain moiety, methacrylate moiety, and vinyl acetate moiety in the prepared terpolymer.

The molecular weights and polydispersity index of the four terpolymers were determined using a gel permeation chromatograph the results are given in Table 3.

Table 3. Characterization of the synthesized terpolymer additives alkyl methacrylate-vinyl acetate-methacrylic acid

Additive designation	Composition	M_w (g/mol)	Poly dispersity index
MVM-12	Terpolymer (dodecyl methacrylate-vinyl acetate – methacrylic acid)	11350	1.70
MVM-16	Terpolymer (hexadecyl methacrylate- vinyl acetate – methacrylic acid)	15660	2.03
MVM-20	Terpolymer (NAFOL 20+A methacrylate-vinyl acetate - methacrylic acid)	20351	2.42
MVM-22	Terpolymer (NAFOL 1822 B methacrylate- vinyl acetate – methacrylic acid)	22980	3.09

3.2. Pour point

The pour point of the fuel oil sample is 15°C. The reduced extent of the four terpolymers with different n-alkyl chain lengths MVM-12, MVM-16, MVM-20 and MVM-22 at various concentrations to pour point is shown in Table 4 and Figure 1. It can be seen from Figure 1, the n-alkyl chain length and concentration of PPDs have very important effects on the reduction extent of pour point.

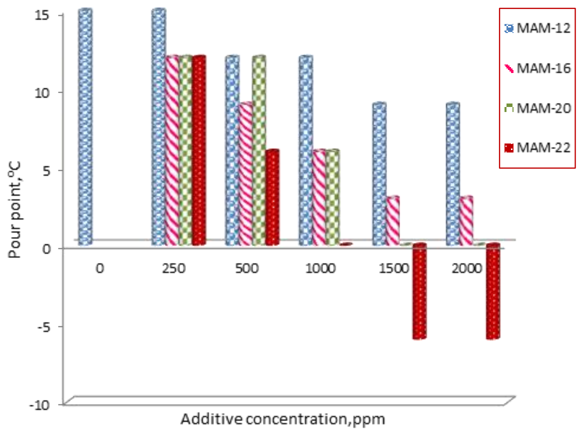


Figure 1. Relation between additive concentration and pour point depressant for fuel oil

The influence of n-alkyl chain length of terpolymers is closely related to the content of the corresponding n-alkane in the fuel oil, especially for their influence on the PP. The effects of the PPDs on reducing PP sometimes are in consistent, because PP is closely related to the formation of the three-dimensional network. MVM-22 exhibits the best considerable reduction on PP. At a concentration of 1500ppm, MVM-22 reduces the PP by -6°C and (reduces the PP by 21°C) and has a better effect on reducing PP with MVM-20 (reduces the PP by 15°C). In the pour point tests that were conducted with various samples methacrymlate terpolymers, we note that for a given size of a pendant hydrocarbon group, an increase in the proportion of these groups increases the performance of the additive. Also, for a given terpolymers composition, increasing the size of the alkyl group improves the performance of the additive. The effect of the four terpolymer additives MVM-12, MVM-16, MVM-20 and MVM-22 on pour point for sample fuel oil are shown in Table 4. With increasing the concentration of the additives an increase in their activity was observed and as a result, a great depression of pour point was achieved. This means that at these concentration ranges the additives may co-crystallize with the paraffins and modify their crystals, at higher concentrations of additives, the side way growth becomes more difficult for the wax crystals (4).

Table 4. The effect of additives on the pour point of fuel oil

Additives designation	n-alkyl side chain	Additive concentration, ppm	PP, ºC	ΔPP, ºC
MAM12	12	0	15	0
		250	15	0
		500	12	3
		1000	12	3
		1500	9	6
		2000	6	6
MAM16	16	0	15	0
		250	12	3
		500	9	6
		1000	6	9
		1500	3	12
		2000	3	12
MAM20	20	0	15	0
		250	12	3
		500	12	3
		1000	6	9
		1500	0	15
		2000	0	15
MAM22	22	0	15	0
		250	12	3
		500	6	9
		1000	0	15
		1500	-6	21
		2000	-6	21

PP = pour point ΔPP = pour point depression

3.3. X-Ray diffraction measurements

X-Ray diffraction investigation of wax in the absence and presence of prepared additives (1500 ppm). The particle size of wax with in the presence of 1500ppm MVM-22 and wax with 1500ppm from MVM-12 were determined by using the Scherer equation [22].

$d = \frac{B\lambda}{\beta cos\theta}$, where d is the mean particle diameter; B is Scherer constant (0.89); λ is wave length of the x- ray beam = 1.5405Å; β is full -width half maximum FWHM of diffraction lines, and θ is the diffraction angle.

The computed values of particle size Table 5 showed increasing the order of wax with 1500 ppm of MVM-22 = 4.47 < wax with 1500 ppm of MVM-12= 5.88 < Wax = 9.41.

Table 5. X-Ray Diffraction results of the wax and wax with additives

Sample	Pos, [2θ]	FWMH(o)	d-spacing, [Å]	Rel. intensity, [%]
Wax	21.4033	0.2952	4.17095	100.00
	22.2754	0.1574	3.75442	31.60
Wax+MVM22	21.4305	0.3129	4.1522	100.00
	23.7275	0.3346	375044	31.45
Wax+MVM12	21.2772	0.2952	4.17596	100.00
	19.1588	0.2362	4.63264	31.6

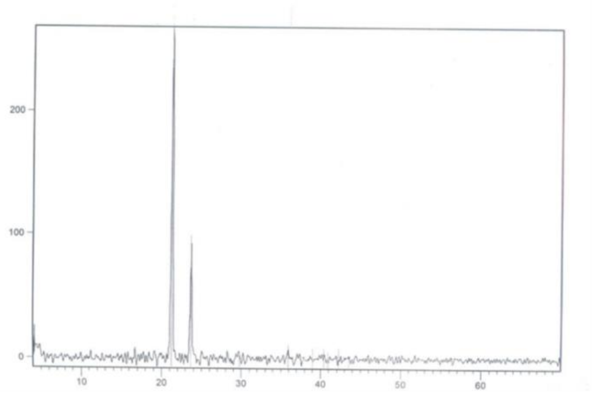


Figure 2. XRD spectra for wax in presence of 1500ppm from MVM-22

The PPD additives are considered to be well in the primitive molecular orientating and nucleating process. MVM-22 is considered more efficient than MVM-12. Figure 2 represents the XRD spectrogram for MVM-22 additives. The PPD molecules will get into the lattice part of wax crystal cells causing a change in the surface properties of the wax crystals. It will also bring the n-alkane molecules to deposit on the surface of the wax crystals. Adsorption can also decrease the plane density, but the changes of the surface properties of the wax crystal are different from those with co- crystallization.

3.4. Mechanism studies

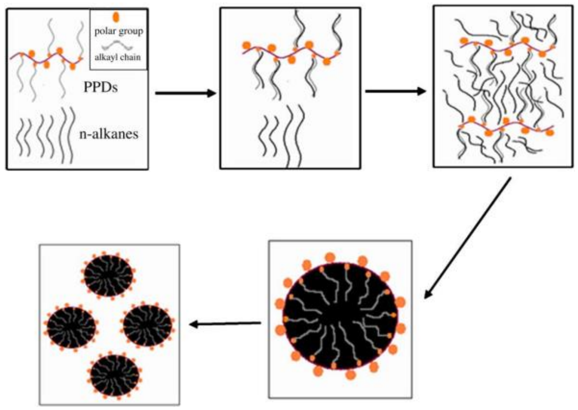
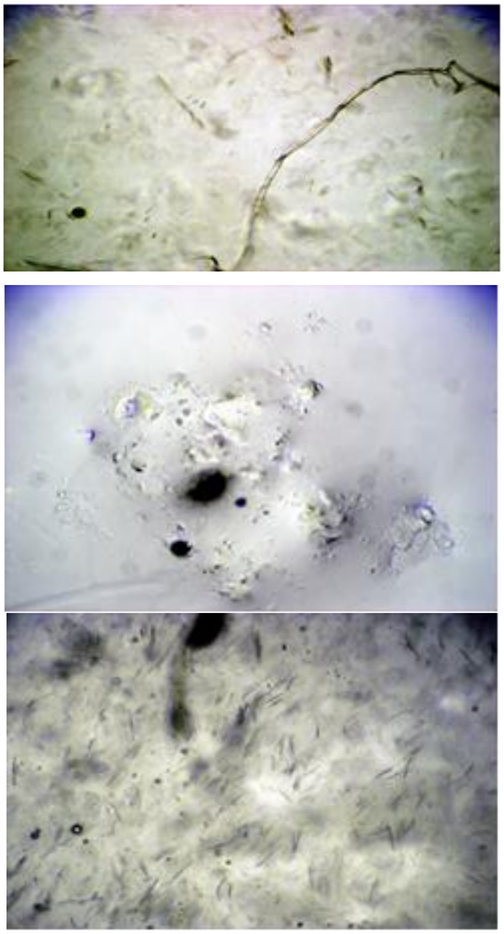


Figure 3. Schematic drawing of operating mechanism of terpolymers in fuel oil

The probable mechanism is shown in Figure 3 At wax appearance temperature, the alkyl chain of the PPDs co-crystallized with the corresponding n-alkanes in the fuel and became the nuclei of wax growth. With the temperature decrease, other n-alkanes in the fuel oil gradually precipitated out in the nuclei and the PPD molecules in a closer position combined with each other through n-alkanes. Thus wax crystals gradually grow. The polar groups of the PPD molecules play a very important impact on the morphology of wax crystals. Due to the strong polarity of the polar group on the methacrylic acid, wax crystals are easy to form sphere or ellipsoid, which has a smaller specific surface. The system has low surface energy and is more stable. As the polar groups distributed on the surface of wax crystals, wax crystals are difficult to bond together to form a three-dimensional network. But when the size distribution of wax crystals is very uneven, the smaller particles tend to get together with the bigger ones. The system is more stable.

3.5. The effect of terpolymer additives on wax crystal modification

The photomicrography of waxy fuel oil without treatment showed a column large wax crystal (PP=15^{o}C), Figure 4(a) to compare with The photomicrography of treatment the fuel oil with 1500 ppm from MVM-12, MVM-16, MVM-20 and MVM-22 terpolymer additives illustrated in Figure 4(b, c, d, e) respectively. From in section of this Figure 4, it can be observed that the wax crystals configurations have been modified to involve many fine dispersed crystals as shown in Figure 4(d, e). In this case, the wax modification in the order MVM-22 > MVM-20 > MVM-16, i.e. from these obtained data it can be concluded that there is a correlation between wax modification and measured flow parameters.



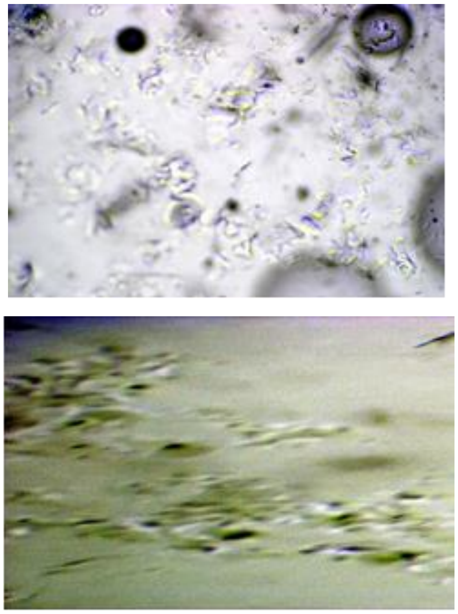


Figure 4. Photomicrographs of (a: FO untreated) and (b: FO+ 1500 ppm MAM-12), (C: FO+1500 ppm MAM-16), (d: FO+1500 ppm MAM-20) and (e: FO+1500 ppm MAM-22)

a PP=15	b PP=3
c PP=0	d PP=0
e PP=-6	

4. Conclusions

Four alkyl methacrylate – vinyl acetate- methacrylic acid terpolymer additives with different alkyl groups from C_{12} to C_{22} and different were prepared, purified and characterized by FTIR and GPC their effects on pour point properties of the fuel oil were investigated.

In the pour point tests that were conducted with various samples of n- alkyl methacrylate –vinyl acetate- methacrylic acid terpolymers, we note that for a given size of a pendant hydrocarbon group, an increase in the proportion of these groups increases the performance of the additive. Also, for a given terpolymer composition, increasing the size of the alkyl group improves the performance of the additive.

With increasing the concentration of the additives, an increase in their activity was obtained, and as a result, a great depression of pour point was achieved.

Study X-ray diffraction of wax and wax with different additives. Photomicrographic analysis showed that a clear effect of the terpolymer additives on the wax crystal modification which is in agreement with the above results

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