



Full Length Article

Synthesis and performance of maleic anhydride copolymers with alkyl linoleate or tetra-esters as pour point depressants for waxy crude oil



Emad A. Soliman^{a,*}, Marwa R. Elkatory^a, Ahmed I. Hashem^b, Hesham S. Ibrahim^c

^a Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, SRTA-City, New Bourg El-Arab City, 21934 Alexandria, Egypt

^b Chemistry Department, Faculty of Science, Ain Shams University, Egypt

^c Researches and Laboratorial Studies, El-Ameria Petroleum Refining Co. (APRC), Alexandria, Egypt

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ABSTRACT

The low-temperature flow properties of waxy crude oils are considered the determining factor in the pipeline transportation. Such properties are highly affected by the content, composition and structure of wax. Polymeric additives known as pour point depressants (PPDs) have been developed to control the growth habits of wax crystals to improve the cold flowability of waxy crude oils. The present study aimed to synthesize comb-shaped polymeric additives based on poly (alkyl ester of malenized linoleic acid) to lower the pour point of Egyptian waxy crude oil and study its impact on the growth of wax crystals. Such PPDs were first prepared by free radical polymerization of maleic anhydride with alkyl linoleate. The resultant copolymer was then esterified with fatty alcohol. These obtained polymeric derivatives were characterized by ¹H NMR, FTIR and Raman scattering spectral analyses. The crystallization behavior of paraffin wax was investigated by differential scanning calorimetry (DSC), X-ray diffractometry (XRD), photomicrography and scanning electron microscopy (SEM). The findings of these analyses showed that both of poly (alkyl linoleate-co-succinic anhydride) and poly (alkyl linoleate-co-tetra-esters) lower the crystallization temperature and enthalpies of paraffin wax, whereas photographs and SEM micrographs revealed that treating waxy oils with these pre-prepared polymeric additives led to suppress formation of the paraffin crystallites, and thus reduce the paraffin crystal size. Pour point measurements exhibited that the maximum pour point depression ($\Delta PP = 18\text{ }^{\circ}\text{C}$) was obtained by using poly (alkyl linoleate-co-tetra-esters) at dose of 3000 ppm.

1. Introduction

Global demand for non-conventional heavy and extra-heavy oil has been marginal until the end of the 20th century because of their high viscosity and composition complexity that cause many operational difficulties in the production chain that limit their economic viability. While, growing the energy demands in the beginning of the 21st century motivate some of the industrialized and emerging countries like, USA, Japan, China and India to handle such non-conventional resources that require significant technological developments and thus restructuration of the refining industries. The high viscosity and low API gravity of such oils are due to the high content of asphaltenes, paraffin wax, as well as a relative low proportion of low molecular weight compounds. The structural changes in these waxy crudes pass through three stages; wax precipitation, wax deposition and gelation. These phase and rheological behavior transformations (multi-phase flow) by which the oil is transformed from a simple Newtonian fluid into a complex non-Newtonian fluid result into abrupt rise in oil viscosity and high yield stress and

simultaneously deposition of wax and asphaltene on the inner walls of pipelines cause clogging of flow pipes or production lines and high-pressure drops [1]. Therefore, the reduction in mobility and flowability of these heavy and extra-heavy oils is considered one of the costly problems because it causes extra burden on the pumping system and consequently increase its power requirement and cost. Moreover, handling of such oils deals with another major problem on reuse of the pipeline after prolong shut down period which lead to costly downtime and expensive remediation techniques [2,3].

The solubility of paraffin wax is strongly related to the temperature where, n-paraffin waxes tend to be separated from oil when the temperature of crude oil falls below the wax appearance temperature (cloud point). Below cloud point, the waxes generally crystallize as an interlocking network of fine sheets, thereby entrapping the remaining liquid fuel in cage-like structures [4]. When the temperature approaches the pour point, the oil may gel completely causing the cold flow problems such as blockage of flow pipes or production lines [5,6]. The pour point is the lowest temperature at which oil will flow freely

* Corresponding author.

E-mail address: emadasoliman@gmail.com (E.A. Soliman).

under its own weight under specific test conditions [7–11]. Several mitigation strategies have been developed to overcome the deposition of wax and subsequently improve the low-temperature flow properties of waxy crude oil. Such strategies can be generally divided into two categories: removal and prevention [12]. Pretreatment (before pumping) with polymeric additives known as pour point depressants (PPDs) or flow improvers (FIs) is the most viable solution for this problem. Polymeric PPDs are widely used at a small dosage in pipeline industry to lower the gelation point (GP) / pour point (PP) to improve the low-temperature flow properties of waxy crude oil and facilitate pipeline transportation [13]. Such polymeric PPDs are homo- and copolymers of different monomers which have to be characterized by high solubility in the oil and have a versatile structure containing a wax-like paraffin part (typically mixture of long linear alkyl chains with 14–25 carbon atoms) along with a polar component (typically acrylate, methacrylate, acetate, etc.) that possess a high potential to interact with the growing wax crystals from the crude oil below its cloud point [14]. These potential interactions including nucleation, co-crystallization or adsorption where, if such materials are present in a comb-like shape, the pendant chains act as a wax-like paraffin part which provide nucleation sites and co-crystallize with oil's wax forming component, while the backbone and polar end groups block the extensive growth of wax matrices and limit such crystallization. Then, polymers that adsorbed on the growing wax crystals sterically hindered their growth, resulting into small crystals via modifying the growth habits and morphology of the wax crystals, which is generally orthorhombic, to a compact pyramidal or cubic form and preventing the growing wax crystals from agglomerating and forming a gel-like structure [15–22]. So, it had been shown that the more similar the polymer structure (backbone and pendant groups) to the wax components, the better its performance [23]. There are many polymeric compounds having such structural properties among which various types are available as commercial PPDs, for example, polymers of alkyl acrylates, alkyl methacrylates and alkyl esters of unsaturated carboxylic acids with α -olefins or long-chain alcohols, polyvinyl ethers copolymer of olefins and vinyl esters, particularly, ethylene vinyl acetate copolymers are used in the oil field in large quantity. Comb shaped polymers like alkyl esters of copolymers of maleic anhydride with styrene or alkyl esters of unsaturated carboxylic acids are also reported as good PPD. In the present work, comb-shaped copolymers of alkyl esters of linoleic acid with maleic anhydride and their alkyl esters were prepared with evaluating their performance as pour point depressants. The evaluation was carried out on Egyptian waxy crude oil via the rheological, photomicrography and scanning electron microscopy analysis to study the yield value and wax crystals modification, respectively.

2. Materials and methods

2.1. Materials

Maleic anhydride, oleic acid, octadecanol, *p*-toluene sulphonic acid and toluene were obtained as analytical reagents from Aldrich chemical, and used as received. The initiator benzoyl peroxide was recrystallized from methanol.

2.2. Crude oil used

Egyptian waxy crude oil (Alamin) obtained from El-Amieria Refining Company. Their physicochemical properties are listed in Table 1.

2.2.1. Esterification of linoleic Acid;

Linoleic acid was esterified with octadecanol (fatty alcohol of molecular formula $C_{18}H_{38}O$) in the presence of conc. sulphuric acid as a catalyst. The product was neutralized using $NaHCO_3$ solution. Water was separated azeotropically using Dean-Stark apparatus. After the completion of the reaction, the organic layer was separated and dried

Table 1
Physico-chemical characteristics of Egyptian heavy crude oil (Alamin).

Physico-chemical parameters	Method	Values
Density (g/cm^3)	ASTM D1298	0.8180
API Gravity	ASTM D1298	41.38
Kinematic Viscosity (C.St.) @60 °C	ASTM D445	7.43
@ 100 °C		3.67
Pour Point, PP (°C)	ASTM D97	24
Wax Content (%)	UOP46	12.40
Asphaltene Content (%)	ASTM D6560	1.32
Water Content (% vol.)	ASTMD-4006	0.10
Sediment (%m/m)	ASTMD-473	0.034
Water and sediment (% vol.)	ASTMD-4007	0.15
Salt content (PTB)	ASTMD-3230	85
Ash content (% wt.)	ASTMD-482	0.018

over anhydrous Na_2SO_4 [24].

2.2.2. Preparation of Copolymers;

The pre-prepared *n*-alkyl linoleate were copolymerized with maleic anhydride in toluene at molar ratio of 1:2. The polymerization was conducted under inert static nitrogen gas condition in presence of benzoyl peroxide as initiator (1% w/w) at 90 °C for 20 h. with constant stirring. The copolymer was precipitated in the petroleum ether 40/60, then filtered and washed by petroleum ether 40/60. The product was dried at 60 °C [25,24].

2.2.3. Esterification of Copolymers;

The obtained copolymers were esterified with octadecanol at molar ratio. The esterification reaction was conducted in 100 ml xylene as a solvent, *p*-toluene sulphonic acid as a catalyst in the three-necked bottom flask equipped with a dean-stark. The reaction was carried out at 145–150 °C for 15 h. and then the temperature was slowly raised to 160–165 °C up to end of the reaction. The resultant esters were precipitated and washed by acetone and then dried and collected [24] (Scheme 1).

2.3. Characterization of structural properties of polymeric additives

2.3.1. Proton nuclear magnetic resonance (1H NMR) Spectroscopic analysis

Proton nuclear magnetic resonance spectra of poly (*n*-alkyl linoleate-*co*-succinic anhydride) (Poly (AL-*co*-SA)) and its esterified form, Poly (*n*-alkyl linoleate-*co*-tetra-ester) (Poly(AL-*co*-TE)), were obtained using JEOL 500 MH NMR spectrometer, Japan at 500.2 MHz Samples dissolved in deuterated chloroform $CDCl_3$ were analyzed by a 5 mm ^{13}C - 1H dual probe head at 25 °C. The spectra were accumulated into 32 K data points and processed using exponential multiplication with 2 Hz line broadening into 128 K spectra. For the resulting spectra 25,000–35,000 scans were accumulated. All spectra were accumulated under identical conditions using power gated Waltz decoupling with 25-degree measurement pulse and 1 s prepulse delay [26].

2.3.2. Fourier Transform Infrared (FTIR) Spectroscopic analysis

The structure of the prepared poly (AL-*co*-SA) and its derivative esterified with fatty alcohol (octadecanol) (Poly (AL-*co*-TE)) was confirmed by using FTIR Shimadzu 8400 S spectrometer (Shimadzu, Japan) after their preparation in form of KBr pellets. About 4–8 mg of the crushed sample was mixed with 200 mg of potassium bromide and was further ground in an agate mortar with pestle. The mixture was then transferred to a die and pressed into a disc in a vacuum press at 80 KN. The spectra (128 scans at 2 cm^{-1} resolution) were collected with the frequency range of 4000–400 cm^{-1} . The FTIR spectra were Fourier-deconvoluted with a resolution enhancement factor of 1.5 and a bandwidth of 15 cm^{-1} . KBr sample discs were measured in the transmittance mode (T%).

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