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FULL LENGTH ARTICLE

Synthesis of phthalimide and succinimide copolymers and their evaluation as flow improvers for an Egyptian waxy crude oil

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Abstract This paper describes the synthesis, characterization and performance evaluation of three phthalimide and three succinimide copolymers of vinyl acetate, styrene and methyl methacrylate as flow improvers for waxy crude oil. The prepared copolymers were named as; (VA)Ph; (St)Ph; (MMA)Ph; (VA)S; (St)S and (MMA)S. These copolymers were characterized by FTIR and ^{1}H NMR spectroscopy. The molecular weights and nitrogen content of these copolymers were determined by using the GPC technique and the Kjeldhal method, respectively. The rheological properties of crude oil (with and without additives) were studied. From the obtained results, it was remarked that the styrene phthalimide copolymer (St)Ph exhibited the maximum pour point depression ($\Delta PP_{500\ ppm}$ = 30). The results of the rheological flow properties showed that the Bingham yield values (τ_β) for crude oil without additives at 15, 27 and 39 °C were 0.286, 0.131 and 0.075 Pa respectively, whereas the τ_β for the treated crude oil by the styrene phthalimide (St)Ph copolymer were 0.021, 0.0164 and 0.0081 Pa at 500 ppm at the same temperatures.

1. Introduction

Crude oil having high wax content causes many problems during production, storage and transportation [1]. The high wax crude oils are characterized by high pour point, high viscosity, high gel strength and abundant wax deposits [2]. When the waxy crude temperature is below the wax appearance temperature (WAT), wax crystals separate out from oil solution. If being continually cooled, more and more waxy crystals appear and interlock to form a network, which entraps the liquid oil, resulting in the gelation of crude oil [3]. This decreases the flow

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of the crude and increases the resistance to its flow, overloads the pump, reduces productivity and possibly plugs the well. For this reason, the inhibition of paraffin deposits is required to maintain the necessary well productivity [4]. Several options are available including stream heating, blending with lighter cutter stocks, mechanical scraping and use of chemical additives [5,6]. The preferred option is the use of chemical additives referred to as wax crystal modifiers, also known as pour point depressants (PPD), flow improvers (FI) and paraffin inhibitors [5]. Pretreatment with PPD is an attractive solution for transportation of waxy crude oil via pipelines. Polymeric additives which satisfy most of the requirements to act as pour point depressants and flow improvers for crude oil were synthesized and evaluated such as; poly long alkyl methacrylate, alkyl naphthalene copolymer [7], esters of oleic acid-maleic anhydride copolymer [8], copolymers of maleic anhydride and esters of n-alkyl alcohols with oleic acid and methacrylic acid [1], poly(styrene-co-alkyl methacrylate) [2], styrene-alkyl itaconate copolymer [9], hexa-triethanolamine oleate esters [10], poly-α-olefins [11,12], ethylene–vinyl acetate copolymers (EVA) [13], terpolymers like styrene/dodecyl methacrylate/octadecyl methacrylate having different molar ratios [11,14]. Also some diblock copolymers e.g. polyethylene-polyethylene propylene (PE-PEP) [15,16] and poly (ethylene-co-butene) (PEB) [17,18] are reported as good PPD. PPD modify the size and shape of crystals and inhibit formation of large wax crystal lattices [5,19,20]. Polymeric additives known as flow improvers or pour point depressants are generally used to lower the pour point, viscosity and yield stress of crude oil. In pipeline transportation, these additives improve the fluidity of waxy crude and reduce the extra pumping cost [8]. The designing of better additives requires a good understanding of the crystallization behavior of the paraffin molecules in the hydrocarbon fluids. Any additives which are as effective as PPD may be ineffective to reduce the viscosity and yield stress and enhance the flow ability [9]. All PPDs are structured so that the part of the molecules is like the paraffin wax crystals, this part functions by providing the nucleation sites and co-crystallizing with the paraffin waxes, while the other part of the structure, dissimilar to the wax crystals, blocks the extensive growth of the wax matrices [21]. PPD additives may work by number mechanisms [22,23]. They may serve as nucleating agents if they self-assemble or aggregate above the precipitation temperature of the wax. Facilitating nucleation can lead to a higher wax precipitation temperature. However, a lower precipitation temperature may result if there are many small nucleation sites that are not large enough to be detected. PPD may also bind to larger crystals and prevent particle–particle interactions from forming aggregates, volume spanning networks, or deposits. This can be termed steric stabilization or adsorption. PPD additives do not work by changing the amount of wax that comes out of solution [22,24,25] but by altering the crystal growth and structure. The following factors play an important role in the efficiency of pour point depressants [26,27]; (a) the number of pendant alkyl side chains and the length and distance between them are the important factors, (b) the solubility of the additives (which are generally polymers) in crude oil which depends on their average molecular weights, (c) if additives are copolymers then monomer to monomer ratio should be taken into consideration, (d) amorphous and crystalline parts of additives are very important in determining their efficiency, and (e) physical and chemical stability of additive [28].

The first object of this work is to prepare phthalimide and succinimide copolymers with vinyl acetate, styrene and methyl methacrylate. The second object is to evaluate their efficiency toward decreasing the pour point of the waxy crude oil. The third object is to perform these polymers as flow improvers via dynamic viscosity and the rheological parameters.

2. Experimental

2.1. Materials

The following chemicals were used; urea, acrylic acid, vinyl acetate, methanol, toluene, p-toluene sulfonic acid, ethanol and hydroquinone which were supplied from Sigma Aldrich chemicals company; phthalic anhydride and succinimide from Loba chemicals company; methyl methacrylate and styrene from Acros chemicals company; formaldehyde solution (37%) from El-Nasr pharmaceutical chemicals company; xylene and N,N dimethyl formamide from Morgan chemicals company. The initiator benzoyl peroxide was recrystallized from methanol.

2.2. Crude oil used

Egyptian waxy crude oil was submitted from Qarun Petroleum Company. Its physicochemical properties are listed in Table 1. The n-paraffin distribution of the isolated waxes was determined by gas chromatography analysis according to ASTM D 2887.

2.3. Esterification and polymerization reactions

To carry out the process of esterification and polymerization, it is necessary to prepare the following materials:

2.3.1. Synthesis of phthalimide

Equimolar amounts of phthalic anhydride and urea were refluxed with xylene as a solvent in a 250 ml three-necked flask equipped with a condenser and a thermometer. The temperature was raised to 140 °C and kept for 120 min with slow stirring. Then, it was cooled down to room temperature, filtered and dried in vacuum. The solvent was reclaimed from the mixture for reuse. As a result, a mixture of phthalimide and phthalic anhydride was obtained which was further treated with ethanol at 78 °C for 90 min. After cooling down to room temperature, the product was filtered and dried in vacuum. Finally, the phthalimide was obtained, (scheme 1a).

2.3.2. Synthesis of N-hydroxy methyl phthalimide

In a 250 ml flat bottom flask fitted with a condenser, 14.7 g of phthalimide was reacted with 5.5 ml of formaldehyde solution (37%) in the presence of distilled water (50 ml) as a solvent. The mixture was refluxed until clear solution, then the hot solution was filtered and cooled overnight. The product was filtered and dried, (scheme 1b).

2.3.3. Synthesis of N-hydroxy methyl succinimide

A suspension of succinimide (5 g) and 3 ml of formaldehyde solution (37%) in ethanol (100 ml) were refluxed in a 250 ml flat bottom flask for 4 h. After that, the whole mixture was kept in a refrigerator for 3 days to obtain a complete