



Production of EVA:MMT nanocomposite and its evaluation as flow improver using model systems and doped crude oil

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Abstract

Influenced by the temperature, wax precipitation is a serious problem in the oil industry, impairing the flow of oil, reducing productivity, and increasing costs. To prevent this problem, chemical additives can be used, and a new branch of research involves the application of polymeric nanomaterials. In this work, poly(ethylene-co-vinyl acetate) (EVA): Montmorillonite (MMT) nanocomposite was produced to compare its efficiency with EVA in waxes systems and a crude oil doped with waxes. It was verified that the nanocomposite presented efficiency as pour point reducer, which can be attributed to its intercalation in the polymer matrix, allowing an efficient steric hindrance in the waxy systems.

Keywords

Wax precipitation; Pour point reducer; polymeric nanomaterials

Introduction

Among the many organic compounds present in the crude oil, waxes are high mass molar hydrocarbons, and they present specific characteristics such as low water solubility and low chemical reactivity. Hydrocarbon chains from 18 carbon atoms are solid at room temperature and atmospheric pressure, and alkanes of less carbon number may be solidified at low temperatures [1]. Thus, the waxes precipitation is a challenge for the production and transport of crude oil in pipelines and during logistics activities. At temperatures below the wax appearance temperature (WAT), the oil waxes begin to precipitate and form crystals. Thus, wax crystals leave out the solution and promote a balance between liquid and solid phases. As the wax solubility decreases with the temperature, a larger amount of wax precipitates and the aggregation of the crystals can cause the deposition on the tube wall, a significant increase in oil viscosity and the oil no flow [2-4].

An efficient preventive method to avoid or minimize the problems caused by wax crystallization is the use of polymeric additives. In addition to conventional polymers, polymeric nanocomposites are a promising alternative as pour point depressants and flow improver due to their ability to modify the morphology and crystal size and/or prevent their agglomeration [5].

Thus, in view of the operational challenges and economic factors, it is necessary to establish a better relationship between the oil composition and the efficiency of the additives as pour point

reducers. Montmorillonite (MMT) is an interesting clay mineral for the study of polymeric nanocomposites due to its characteristics, such as high aspect ratio, and good ability to separate clay layers in the polymer matrix [6-8]. Thus, MMT was selected for this study due to its lamellar structure, which may contribute to the intercalation of the clay mineral with the polymer. Therefore, this work aims to evaluate the efficiency of a polymeric nanocomposite of poly(ethylene-co-vinyl acetate) (EVA) with montmorillonite, as pour point reducer and flow improver in waxy model systems and a crude oil doped with commercial waxes.

Methodology

Preparation of mineral sample and polymeric nanocomposite

The mineral sample used in this work was montmorillonite (MMT). The clay sample was processed from the following procedure: i) crushing with jaw crusher (background spacing of 2 cm by 1 min); ii) wet grinding with bar mill (1000 rpm for 30 min); iii) wet granulometric classification with sieves of #325 mesh (corresponding to fraction less than 44 µm); iv) filtration and subsequent oven drying v) ball mill grinding (with 25 spheres of 2 cm).

Then, the MMT was organically modified with cetyltrimethylammonium bromide (CTAB) to allow the compatibility with the hydrophobic polymer, the poly(ethylene-co-vinyl acetate) (EVA).

Polymeric nanocomposite based on EVA (10 mol% of vinyl acetate) was produced using the solution method, using toluene as the. The EVA:MMT nanocomposite was produced at 90:10 ratio and identified as EVA:MMT.

Preparation of model systems

For the preparation of model systems, waxes with the melting points of 44-46 °C and 56-58 °C were used and called P01 and P03, respectively [9]. For these systems, toluene was used as solvent. The concentrations of 5 wt/v% and 5.5 wt/v% of waxes and 500 mg/L of the additive were used. Petroleum was also used for the study, named Petro17, with 0% wt/wt of n-alkanes and 24.62% wt/wt of cycloalkanes and API 17. Due to the absence of n-alkanes in the natural composition of this oil, petroleum systems were doped with P03 under the same conditions as the model systems.

Characterization techniques and performance tests of model systems

To characterize the composite produced, Fourier transform infrared spectroscopy (FTIR) was used to identify the chemical structure of the materials through energy absorption by the bonds in the sample molecules [10]. The materials were analyzed by the attenuated total reflection mode (ATR), with four sweeps in the range from 4000 to 400 cm^{-1} with resolution of 4 cm^{-1} .

X-ray diffraction spectrometry (XRD) technique was performed to investigate the crystalline phase of the material and verify the mixing degree of the polymeric nanocomposite by the observation of the peak corresponding to the clay crystalline plane. The sample was scanned in the 2θ angle range from 4 to 70° with steps of 0.01° for MMT.

Thermogravimetric analysis (TG) was performed in the range of 30 to 800 °C, at 10 °C/min, inert atmosphere. By this analysis the clay mineral was identified in the composite by the ash content.

Scanning electron microscopy (SEM) was performed to identify the characteristic of the clay mineral dispersed in the polymeric material. The microscope used was coupled to an EDS diffraction analyzer, allowing the identification of chemical elements in the composite.

For the study of the performance of additives in model systems and doped crude oil, rheological tests were performed to determine the flow behavior and the temperature at which the minimum quantity of waxes crystals is required so that Arrhenius behavior does not occur, called crystallization temperature (TC). The rheological tests were performed from 40 to 5°C at 200 s^{-1} for model systems and 50 to 5°C at 100 s^{-1} for petroleum systems. The wax appearance temperature (WAT) was determined by microcalorimetry (μDSC) cooling the system from 80 to -20 °C at 0.8 °C/min.

The optical microscopy analyzes were performed to study the waxes morphology and infer about modifications caused by the additives action. The

tests were performed in dark field to better define the results and the sample was cooled from 30°C to 0 °C at 0.8 °C/min rate and the micrographs were obtained at 8 °C. The pour point test was based on the ASTM D97 (ASTM D97-2012) standard.

Results and Discussion

FTIR spectra showed the adsorption bands. Both the composite and EVA presented bands at 2916 and 2849 cm^{-1} , which are assigned to the CH_3 and CH_2 groups, respectively, and 1235 cm^{-1} , assigned to the C-O-C bond. The adsorption bands at about 915 cm^{-1} , 3626 cm^{-1} , 1030 cm^{-1} and 460 cm^{-1} were assigned, respectively, to the $\text{Al}_2\text{-OH}$, -OH, Si-O-Al and Si-O-Al (octahedral Al) groups related to MMT. Thus, it can suggest the formation of polymeric nanocomposite [5,11,12].

Through the thermogravimetric analysis (TGA), with the derivative of the weight change of pure and organically modified clay mineral, the presence of the CTAB was identified at about 240°C, as shown in Fig. (1), and the majority presence of the polymer in the composite was evidenced through the graph of the weight loss of composite.

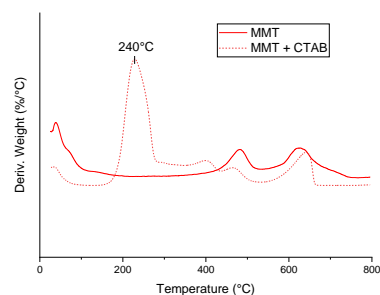


Figure 1. Derivative of weight percentage of pure and organically modified clay minerals.

In the MMT diffractograms, shown in Fig. (3), the characteristic peak of the clay mineral (MMT) was observed at 5.75° (15Å) and the EVA:MMT composite peak shifted to 4.4° (20Å). It was identified a peak displacement for lower angle values suggesting the increase in the interlayer spacing of the silicate, which is due to the EVA chains intercalation in the galleries of montmorillonite.

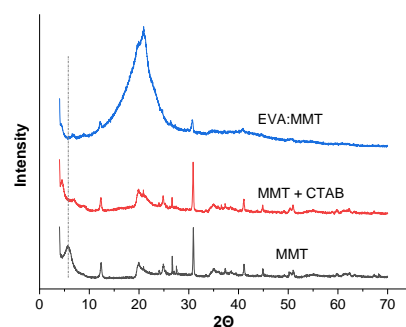


Figure 2 – Diffractogram of EVA, Montmorillonite and EVA:MMT

By the scanning electron microscopy, it was observed that MMT was more aggregated before the organic modification. This occurs due to the intercalation of clay mineral with CTAB, which facilitates its layer's separation, modifying the morphology of the clay mineral and increasing the organophilic characteristic, allowing its interaction with the polymer [13]. The EDS spectra of clay minerals showed the presence of Al, Mg, O and Si, characteristics of aluminosilicates, and other compounds, which were considered impurities due to the natural origin of clay minerals. In the nanocomposite, the presence of carbon (C) predominates due to the high concentration of polymer.

From the pour point tests, it was observed that in the system with 5 wt/v% of P01, which has the smallest chain length, the pour point was reduced from 4.5 to $<-24^{\circ}\text{C}$ when using both EVA:MMT and pure EVA. Comparing the system with P03, which has the higher chain length, the influence of the wax chain length in the additives action was evident because EVA was not able to reduce the pour point in the system with 5 wt/v% of P03. Thus, it was verified that the composite was more efficient than EVA. For 5.5 wt/v% of P03 containing 500ppm of EVA:MMT, the composite was able to reduce the pour point from 21 to $6\pm 1.5^{\circ}\text{C}$, and EVA was not able to reduce the pour point of this system. The pour point of the doped crude oil with 5.5% of P03 (Petro17 + P03) was the same found in the pure model system (toluene + P03), which proves that toluene is an adequate choice of solvent and suggests that the tests in model systems can reproduce those in the crude oil.

For 5.5 wt/v% of Petro17 + P03 containing 500ppm of EVA:MMT, the composite was able to reduce the pour point from 21 to $-19.5\pm 1.5^{\circ}\text{C}$, and EVA was not able to reduce the pour point of this system. Thus, as in the model systems, the nanocomposite was a better pour point reducer than the EVA in doped crude oil.

By rheology, it was verified that the nanocomposite slightly reduced the viscosity below WAT of both the waxy model system and doped crude oil.

By microcalorimetry, it was possible to determine the WAT of the systems. It was evident that the additives, despite acting effectively as flow improvers and pour point reducers, were not able to significantly change the WAT of the waxy model systems or the doped crude oil.

By optical microscopy containing 5.5 wt/v% of wax, it was verified that the additives acted reducing the crystals size. The morphological changes promoted by the additives contributed to the flow assurance of the model systems. The sizes of the crystals were smaller when using the nanocomposite when compared to that using only EVA. It may be one of the reasons for the better performance of the nanocomposite. The micrographs are shown in Fig. (3).

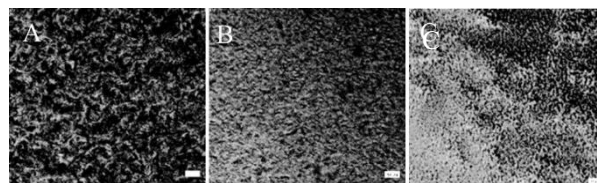


Figure 3 – Micrographs of model systems with 5.5% wt/v of P03: A- No additive, B- EVA; C-EVA:MMT.

Conclusions

The results of this work revealed that the EVA:MMT composite was efficiently produced. The characterization analyses proved the nanomaterial structure and contributed to explain its better performance as pour point reducer than the pure EVA. Although they have not modified the WAT, the nanocomposite reduced the crystals size and improved the flow. This result was attributed to the MMT intercalation in the polymer matrix, optimizing the nanomaterial's property and allowing an efficient steric impediment in waxy and petroleum systems.

Acknowledgments

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Responsibility Notice

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