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Changing commercial EVA to improve its performance as pour point depressant: a study in waxy model oils at different wax concentrations

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Abstract

Different poly(ethylene-co-vinyl acetate) (EVA) based materials were evaluated as pour point depressants (PPD) in waxy model oils. Two commercial samples with different vinyl acetate (VA) (7 and 11 mol%) contents were modified by hydrolysis and used to prepare EVA-clay nanocomposites. The model oils were prepared up to 9.0 wt/wt% of wax (melting point in the range of 56-58ºC) in toluene. EVA7, modified and non-modified, exhibited the worst performance. At the lowest wax concentration (3 wt/wt%), EVA11, modified and non-modified, reduced the pour point (PP) from 15 ºC to <-24.0 °C. At 6.0 wt/wt% of wax, only hydrolyzed EVA11 and hydrolyzed EVA11-nanoclay were able to reduce the PP from 18 ºC to <-24 °C, at optimum concentration of 500 ppm. By increasing the wax concentration to 9.0 wt/wt%, the efficiencies of these two materials were reduced, but they were still able to reduce the PP from 24 ºC to ~14ºC. As expected, EVA11-nanoclay performs better than EVA11. Nevertheless, the presence of nanoclay in the nanocomposite with hydrolyzed EVA11 did not promote an improvement in its performance, suggesting that the effect of the OH group in the matrix overlaps in relation to the clay charge.

Keywords

EVA-clay nanocomposite; pour point depressant; waxy model oil

Introduction

The utilization of polymeric materials as flow improvers has seen a recent surge, driven by emerging petroleum industry challenges. One such challenge is the need to promote the flow of systems containing high molecular weight waxes, achieved through the incorporation of PPD additives [1-3]. Ideally, these materials should be incorporated at low concentrations in systems, thus considering the overall process cost. To ensure the effectiveness of a PPD, it's crucial that its chemical structure includes both apolar hydrocarbon chains and polar groups. This enables the PPD to co-crystallize with waxes and obstruct the formation of a crystalline network through steric hindrance. Additionally, in certain instances, the additive may prevent the precipitation of paraffins at elevated temperatures [2,4,5]. Different polymeric materials are utilized for this purpose, including polymers made from vinyl acetate, maleic anhydride, acrylics, methacrylics, and/or acrylonitriles monomers. The presence of polar groups in these materials facilitates morphological alterations in the crystals, aiding in the prevention of extensive three-dimensional paraffin networks [6–8]. Polymeric composites and nanocomposites have also stood out as PPDs and flow improvers [9-12]. EVA is one of the commercial polymer additives used as a PPD by industry. However, the material is not effective for all types of oil, in addition to showing poor performance in waxy model oils with high wax concentration [13,14].

Recent studies have shown that EVA:clay nanocomposites exhibit superior performance compared to the isolated EVA matrix [14].

Thus, this work investigated for the first time the PPD performance of a clay nanocomposite, produced using a hydrolyzed EVA matrix. Its performance was compared with different EVA-based materials: two commercial EVA samples with different VA contents, two hydrolyzed EVA samples (EVA-OH) obtained from the commercial samples and a second clay nanomaterial, produced with EVA-matrix. The performance of the materials was evaluated in PP tests on waxy model oils formulated with different wax concentrations.

Methodology

Chemical modification of EVA samples

Commercial EVA samples containing of 6.9 and 11.0 mol% VA groups, named EVA7 and EVA11 respectively, were modified through the hydrolysis reaction of VA groups, following Dutra's methodology [15]. In a reflux system, 10 g of EVA and 100 mL of toluene were added, which were kept under stirring and inert atmosphere for 24 hours at 50 °C. After this period, the temperature was raised to 70 °C, and drops of a methanolic solution of NaOH at 10 wt/v % were added to the system. Then, the temperature was raised to 110 °C for 2 h. At the end of the reaction, the material was precipitated at 60 °C with an aqueous solution of HCl at 20 v/v%. After filtration, the precipitate was kept in a vacuum oven for 3 days until complete drying. Table 1 presents the parameters used in the hydrolysis reactions. The EVA7 and EVA11 hydrolyzed samples were named EVA7-OH and EVA11-OH, respectively.

Preparation of nanocomposite materials

The nanocomposite materials were prepared using the EVA11 and EVA11-OH samples as matrices, and the palygorskite (PALY) as filler. The matrix:filler ratio used in both materials was 95:5. Before preparation, PALY was organically modified with cetyltrimethylammonium bromide (CTAB) to allow its compatibility with the matrix. The preparation of the materials was carried out using the solution/solvent precipitation method [13,14]. Initially, a dispersion was prepared with a concentration of 2.78 wt/wt% of polymer + PALY in 10 g of toluene. After that, the systems were placed in an ultrasonic bath for 1 hour and then subjected to mechanical stirring at 80 °C until complete solvent evaporation. The produced film was placed in a desiccator and kept under reduced pressure until completely dried for a period of 48 h.

Size exclusion chromatograpy (SEC)

The molecular weight of the EVA7 and EVA11 samples was determined by size exclusion chromatography (SEC), using a Malvern Panalytical Viscotek GPC Max VE2001 Chromatograph, equipped with Shodex chromatographic columns (models KF-G 4A, KF-806M and KF-802.5) and refractive index, light scattering (high and low angle), and viscometric detectors. The calibration was performed using a monodisperse polystyrene standard. The samples were injected at concentration of 5 mg mL^{-1}, using THF as solvent and eluent.

Nuclear magnetic resonance (NMR)

The hydrolysis degree of the modified EVA samples was determined through proton nuclear magnetic resonance spectroscopy (^{1}H NMR) by integrating the signals corresponding to the proton directly linked to the carbon of the OH group and the protons of the CH$_3$ group of VA, centered at 3.59 and 2.03 ppm, respectively. The calculations were performed using Eq. (1).

$$\%\ \text{hydrolysis} = \frac{3 \times A_{3.64\text{-}3.54\ \text{ppm}}}{(3 \times A_{3.64\text{-}3.54\ \text{ppm}}) + A_{2.08\text{-}1.98\ \text{ppm}}} \times 100 \qquad (1)$$

Where $A_{3.64\text{-}3.54\ \text{ppm}}$ corresponds to the integration of the area under the signal at 3.59 ppm, and $A_{2.08\text{-}1.98\ \text{ppm}}$ corresponds to the integration of the area under the signal at 2.03 ppm.

The analyses were conducted on a Bruker Avance III NMR spectrometer of 500 MHz. The samples were prepared at concentration of 45 mg/mL, using CDCl$_3$ as the solvent and tetramethylsilane as internal standard.

Preparation of the additives and the model waxy oils

For the preparation of additives, the materials were dissolved in toluene and subjected to stirring and heating at 60 °C for 1.5 hours. The waxy model oils were prepared at concentrations of 3.0, 6.0, and 9.0 wt/wt%, using a paraffin (melting point in the range of 56-58 °C), containing *n*-paraffins ranging in size from C18 to C44 with a predominance of C28 [14,16]. For the preparation of the systems, the paraffin was dissolved in toluene and subjected to stirring and heating at 45 °C for 1.5 hours. In the additivation process, the materials were added at concentrations (C$_{\text{add}}$) of 500, 1,000, and 2,000 ppm. The additive was weighed in a beaker, and immediately after, the pre-heated model oil, was weighed into the same container. The additive-added system was subjected to heating and stirring at 45 °C for 1 hour.

Performance tests

The pure and additive-added systems with different materials were evaluated in pour point (PP) tests. The test was based on ASTM D97 standard, using a sequence of thermostatic baths configured at temperatures of 24, 0, –18, and –33 °C [17]. The analyses were performed in duplicate, with a maximum error of ± 1.5 °C.

Results and Discussion

Materials characterization

Table 2 presents the average molar mass and dispersion (Đ) values of the two commercial EVA samples. EVA11 exhibits higher average molar masses than EVA7, in addition to greater Đ.

Table 2. SEC results of EVA samples.

Sample code	$\bar{M}_n$ (Da)	$\bar{M}_w$ (Da)	Dispersity (Đ)
EVA7	12,900	84,700	6.56
EVA11	28,000	217,800	7.77

Table 1. Parameters used for EVA hydrolysis.

Modified sample	Origin sample	VA mol (n)	Theoretical hydrolysis degree (%)	NaOH mol (n)	MeOH/NaOH solution (g)
EVA7-OH	EVA7	0.0221	2	4.41×10^{-4}	0.1765
EVA11-OH	EVA11	0.0325	6	1.95×10^{-3}	0.7804

Table 3. Hydrolysis degree of modified EVA samples.

Sample code	Theoretical hydrolysis degree (mol%)	$A_{3.64\text{-}3.54\ ppm}$	$A_{2.08\text{-}1.98\ ppm}$	Experimental hydrolysis degree (mol%)
EVA7-OH	2	0.0041	1.0000	1.22
EVA11-OH	6	0.0400	1.0000	10.71

Analysis of the NMR spectra confirmed the chemical modification of the materials. Table 3 presents the calculated values for the hydrolysis degree of the modified EVA samples. None of the reactions achieved the theoretical degree of hydrolysis, with modification percentages obtained as 1.22% and 10.71% for the EVA7-OH and EVA11-OH samples, respectively.

Performance tests

Table 4 presents the results of the PP tests performed. All materials that showed any reduction at 3.0 wt/wt% of wax were analyzed at higher concentrations (6.0 or 9.0 wt/wt%) until reaching the efficiency limit.

Compared to unmodified EVA samples, EVA7 was able to reduce the PP of the model system to 3.0 wt/wt% of wax from 15.0 °C to a minimum of 1.5 °C at a C_{add} of 2000 ppm. Conversely, EVA11 was more efficient, reducing the PP of the model system at the same wax concentration to <–24.0°C at all evaluated C_{add}. This result aligns with literature that suggesting an optimal VA content to achieve the best PP reduction efficiency [18]. When increasing the wax content to 6.0 wt/wt%, EVA7 was no longer able to reduce the PP at any of the tested concentrations. EVA11, on the other hand, reduced the PP by 9.0 °C only at C_{add} of 500 ppm, with its efficiency decreasing as the additive concentration increased. This slight reduction justified the analysis of EVA11 in model systems containing 9.0 wt/wt% of wax; however, no efficiency was observed.

To assess the influence of increased polarity on the two EVA samples, they were partially hydrolyzed. EVA7-OH exhibited performance very close to its base material in the model system at 3.0 and 6.0 wt/wt% of wax, and therefore was not evaluated in systems with 9.0 wt/wt% of wax. This behavior suggests that only an increase in polarity, without an increase in the number of polar groups, does not affect the additive's action. The EVA11-OH sample also showed similar performance to its base material in the system containing 3.0 wt/wt% of wax; however, it was more efficient in the system with 6.0 wt/wt% wax at C_{add} of 500 and 1,000 ppm (Δ_{PP} = >–42.0 and –30.0 °C, respectively). This result justified the evaluation of this material in the model system containing 9.0 wt/wt% of wax, where efficiency (Δ_{PP} = –15 °C) was observed only at C_{add} of 500 ppm. This behavior confirms the improvement in efficiency with the increase in molecule polarity within its solubility limit in the organic environment in question [1,19].

The EVA11 and EVA11-OH samples, unlike what was observed for the EVA7-based samples,

Table 4. PP of pure and added model waxy oils.

Material Code	C_{add} (ppm)	Wax concentration (wt/wt%)					
		3.0		6.0		9.0	
		PP (°C)	Δ_{PP} (°C)	PP (°C)	Δ_{PP} (°C)	PP (°C)	Δ_{PP} (°C)
No additive	–	15.0	–	18.0	–	24.0	–
EVA7	500	6.0	–9.0	18.0	0.0	–	–
	1000	7.5	–7.5	16.5	–1.5	–	–
	2000	1.5	–13.5	16.5	–1.5	–	–
EVA7-OH	500	10.5	–3.0	18.0	0.0	–	–
	1000	4.5	–10.5	15.0	–3.0	–	–
	2000	4.5	–10.5	15.0	–3.0	–	–
EVA11	500	<–24.0	>–39.0	9.0	–9.0	21.0	–3.0
	1000	<–24.0	>–39.0	15.0	–3.0	24.0	0.0
	2000	<–24.0	>–39.0	15.0	–3.0	24.0	0.0
EVA11-OH	500	<–24.0	>–39.0	<–24.0	>–42.0	10.5	–15.0
	1000	<–24.0	>–39.0	–12.0	–30.0	21.0	–3.0
	2000	<–24.0	>–39.0	15.0	–3.0	21.0	–3.0
EVA11:PALY	500	<–24.0	>–39.0	3.0	–15.0	21.0	–3.0
	1000	<–24.0	>–39.0	3.0	–15.0	22.5	–1.5
	2000	<–24.0	>–39.0	18.0	0.0	21.0	–3.0
EVA11-OH:PALY	500	<–24.0	>–39.0	<–24.0	>–42.0	12.0	–12.0
	1000	<–24.0	>–39.0	–9.0	–27.0	21.0	–3.0
	2000	<–24.0	>–39.0	9.0	–9.0	21.0	–3.0

$\Delta_{PP} = [PP_{added\ system} - PP_{pure\ system}]$; maximum PP error = ± 1.5 °C showed better performance at lower concentrations. The enhanced performance achieved by these materials at lower concentrations could be related to the hydrodynamic volume of the polymer: reducing the molecule's hydrophobicity would promote greater solubility in toluene, expanding the hydrodynamic volume in solution. Consequently, the ethylene segments capable of interacting with the waxes would become more available, thereby promoting the greater PP reduction observed for these materials. On the other hand, the expansion of the polymer coil would decrease the intermolecular distance between species at high concentrations of the material in the system, leading to increased polymer-polymer interaction and resulting in the observed loss of efficiency.

When evaluated in systems containing 3.0 wt/wt% of wax, EVA11, EVA11-OH, EVA11:PALY, and EVA11-OH:PALY were able to reduce the PP to <–24 °C at all C_{ADD}. At the concentration of 6.0 wt/wt% of wax, EVA11:PALY was more efficient at C_{ADD} of 500 and 1,000 ppm and showed similar efficiency at 2,000 ppm, confirming what has been reported in the literature [14]. EVA11-OH:PALY was only slightly better than its base material at C_{ADD} of 2,000 ppm, exhibiting similar efficiencies at the other concentrations. Like the base materials, none of the nanocomposites were able to reduce the PP in systems containing 9.0 wt/wt% of wax. The presence of PALY in the polymer matrix can enhance the efficiency of unmodified EVA; however, in the EVA11-OH:PALY sample, the effect of the OH group in the matrix structure outweighed that of the clay mineral fillers. This behavior may be related to the greater availability of polar groups (-OH) along the polymer chain compared to the charges occluded on the surface of the mineral bound to the polymer matrix.

Conclusions

All materials produced demonstrated efficiency as PPDs in low wax concentrations (3.0 wt/wt%). In these systems, samples EVA7 and EVA-OH exhibited the lowest performance, reducing the PP to a maximum of 1.5 and 4.5 °C, respectively. In contrast, all EVA11-based samples reduced the PP to <-24.0 °C. In model oils at 6.0 wt/wt% of wax, only EVA11-OH and EVA11-OH:PALY were able to reduce the PP to <-24 °C, but only at a C_{add} of 500 ppm, having a reduction in its performance with the increase C_{add} in the system. In systems with 9.0% w/w wax, this behavior was maintained, where again only these two materials showed some reduction in PP, albeit slight.

Although it has previously been found that the presence of clay mineral in the EVA matrix improves the efficiency of the additive, the presence of PALY in the EVA11-OH:PALY did not promote an improvement in the material's performance, suggesting that the effect of the OH group in the matrix overlaps in relation to the clay charge. In this case, the costs, advantages, and disadvantages of the nanocomposite production process must be considered.

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Responsibility Notice

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References

[1] Steckel L.; Nunes R.C.P.; Rocha P.C.S.; Ramos A.C.S.; Alvares D.R.S.; Lucas E.F. *Fuel* 307, 121853, 2022.

[2] Yang F.; Zhao Y.; Sjöblom J.; Li C.; Paso K.G. *J. Dispers. Sci. Technol.* 36, 213-215, 2015.

[3] Xia X.; Li C.; Sun G.; Zhao K.; Zhang J.; Yao B.; Yang F. *Pet. Sci.* 19, 2472-2482, 2022.

[4] Fang L.; Zhang X.; Ma J.; Zhang B. *Ind. Eng. Chem. Res.* 51, 11605-11612, 2012.

[5] Kozhabekov S.S.; Zhubanov A.A.; Toktarbay Z. *Oil Gas Sci. Tecnol.* 74, 28-37, 2019.

[6] Al-Sabagh A.M.; Betiha M.A.; Osman D.I.; Hashim A.I.; El-Sukkary M.M.; Mahmoud T. *Energ. Fuel. 30*, 7610-21, 2016.

[7] Al-Sabagh A.M.; Betiha M.A.; Osman D.I.; Mahmoud T. *J. Appl. Polym. Sci. 136*, 47333, 2019.

[8] Kelland M.A.; *Production Chemicals for the Oil and Gas Industry*. 2nd ed., New York, CRC Press, 412 p, 2014.

[9] Lvov Y.; Abdullayev E. *Prog. Polym. Sci. 38*, 1690-1719, 2013.

[10] Luo J. *Compos. Sci. Tecnol. 63*, 1607-1616, 2003.

[11] Kym Y.H.; Sim B.; Choi H.J. *Colloids Surf. A 507*, 103-109, 2016.

[12] Ghouil B.; Harabi A.; Bouzerara F.; Boudaira B.; Guechi A. Demir M.M.; Figoli A. *Mater. Charact. 103*, 18-27, 2015.

[13] Alves B.F.; Rossi T.M.; Marques L.C.C.; Soares, B.G.; Lucas E.F. *Fuel 332*, 125962, 2023.

[14] Alves B.F.; Silva K.M.S.; Silva C.A.; Celestino, G.C.; Nunes R.C.P..; Lucas E.F. *Fuel 333*, 126540, 2023.

[15] Dutra R.C.L.; Lourenço V.L.; Diniz M.F.; Azevedo M.F.P.; Barbosa R.V.; Soares B.G. *Polymer Bulletin 36*, 593-600, 1996.

[16] Oliveira L.M.S.L.; Nunes R.C.P.; Melo I.C.; Ribeiro Y.L.L.; Reis L.G.; Dias J.C.M; Guimarães R.C.L.; Lucas E.F. *Fuel Proces. Technol. 149*, 268-274, 2016.

[17] ASTM D97. Standard Test. Method for Pour Point of Petroleum Products, 2012.

[18] Machado A.L.C.; Lucas E.F. *J. Pet. Sci. Eng. 32*, 159-165, 2001.

[19] Alves B.F.; Pereira P.H.R.; Nunes R.C.P.; Lucas E.F. *Fuel 258*, 116196, 2019.