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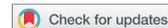
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Synthesis and Properties of Fumaric Copolymers as Potential Bitumen Modifiers

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ABSTRACT

New copolymers of dioctyl fumarate (DOF) and styrene (S) were synthetized by radical polymerization and used to modify bitumen. The poly(dioctyl fumarate-co-styrene) copolymers, PFS, were characterized by ^{1}H-NMR and FTIR spectroscopies and size exclusion chromatography (SEC) in order to determine their monomer composition and weight average molecular weights, respectively. The polymer-bitumen blending conditions were optimized and the samples analyzed by different methodologies. Fluorescence microscopy, rotational viscosity and differential scanning calorimetry (DSC) were used to study the morphological changes of blends during their manufacturing and the rheological and thermal behavior, respectively. All modified bitumen (MB) exhibited higher viscosity than the based bitumen (BB) under studied conditions and this effect was more evident for the MB containing the higher molecular weight polymer. The addition of polymers to BB enhances the bitumen viscosity and thus increased the energy required for the flowing (activation energy calculated by Arrhenius equation). Thermal and morphological analysis showed that all MB exhibited good polymer- bitumen compatibility, which could be consider as a good starting point for a potential applications of this new material in road engineering.

GRAPHICAL ABSTRACT
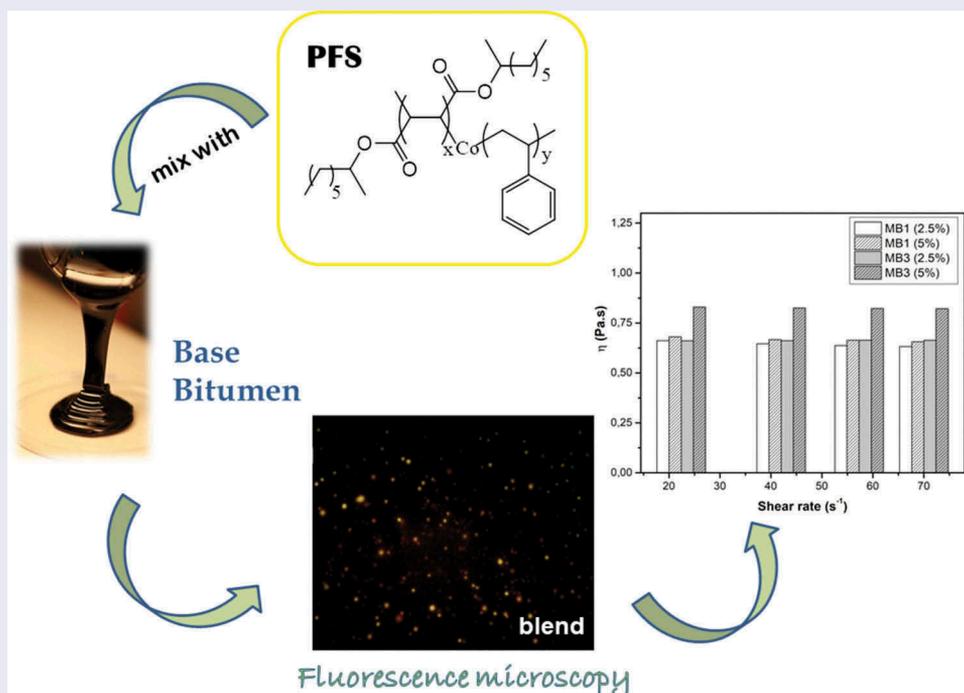
1. Introduction

Bitumen is one of the most widely thermo-viscoelastic materials used for the construction of highways and routes. However, in the last years have been noteworthy the greater demands that the pavements experience due to the greater loads and quantity of vehicles that transit them, which has prompted researchers to search for new materials. Actually, it is known that important properties such as thermal susceptibility, aging at environment and intermediate temperatures and resistance to rutting and fatigue can be improved through the incorporation of polymers [1–3]. This kind of material is known as polymer-modified bitumen (PMB) and a big number of different homo- and copolymers had been studied as potential modifiers [4,5]. Among them, plastomers such as polyethylene (PE), polypropylene (PP), ethylene–vinyl acetate (EVA), ethylene–butyl acrylate (EBA) and thermoplastic elastomers, for example styrene–butadiene–styrene (SBS), styrene–isoprene–styrene (SIS) and styrene–ethylene/butylene–styrene (SEBS) [5–7]. In many of these cases an effective polymer modification results in a thermodynamically unstable but kinetically stable system in which the polymer is partially swollen by the light components of bitumen [8]. Polacco et al 2015. have analyzed in detail the basic principles and fundamental aspects of the bitumen-polymer blends compatibility, highlighting the importance of the bitumen chemistry (source of the crude oil, nature chemistry, molecular weight and composition) as well as the nature and structure of the polymer (architecture and average molecular weight, M_w), in relationship to the bitumen-polymer interactions responsible of the optimal behavior of the PMB [9].

Homo- and copolymers of fumaric esters were synthesized under microwave conditions and their properties studied in our group for some years [10–12]. These polymers are characterized by high thermal stability, solubility in common solvents of varied polarity (THF, ethyl acetate, chloroform and toluene), glass transition temperature (Tg) values that can be regulated by the appropriated selection of comonomers, amorphous and transparent solid structure with high tensile strength. Due to those properties the fumaric polymers can be considered competitive with poly(methacrylic esters), which exhibit similar characteristics [13–15]. Thus, in the last years the interest in materials based on fumaric copolymers has grown in view of their potential applications; among which are those related to the biomedical area, such as scaffolds for bone and osteochondrogenic tissue engineering or membranes for transdermal drug delivery [13–18].

Based on our previous studies and considering the versatility of polyfumarate copolymers we postulated that this kind of polymers could act as good modifiers of bitumen properties. In addition, the raw materials for the synthesis of this type of polymers are easily available from local sources and the radical polymerization process is easy and widely used to produce mass polymers. The local source availability allows us to propose a new economical alternative of bitumen modifiers compare with those commercial available in the market. Therefore in this work we synthesized new poly (dioctyl fumarate-co-styrene), PFS, of varied comonomer composition and average molecular weight (M_w) in order to studied the effect of these variables on the morphology and compositions blends, as well as on the rheological and thermal properties of new modified bitumens (MB).

2. Experimental

2.1. Materials

Di-(octan-2-yl) fumarate (briefly: dioctyl fumarate, DOF) was synthesized and purified as previously described [18]. 2,2′-azobisisobutyronitrile (AIBN) were recrystallized from methanol. Styrene (St, Sigma-Aldrich, 99%) was purified by washing with a NaOH solution (10% wt.) and then distilled at reduced pressure. Ethylene-vinyl acetate copolymer (EVA) with 30% of vinyl acetate (as indicated by manufacturer) was used as modifying agent for blending comparison. This kind of copolymer is one of the most widely used as bitumen modifier and exhibited a statistical distribution of comonomers along to the linear macromolecular chain, similar to ours synthetic PFS copolymers. The weight average molecular weights (M_w) and polydispersity index (PDI) of this copolymer were determined by size exclusion chromatography: M_w = 92,500 g/mol and PDI = 3.97. Other reagents and solvents used were purchased from Merck and Sintorgan (PA). Bitumen was obtained from a local crude source (Argentina) and was used as base bitumen (BB).

2.2. Copolymer synthesis

The radical copolymerization of dioctyl fumarate and styrene was carried out in bulk and in solution (90%v/v, Toluene), both initiated with AIBN as initiator at 40 and 60 °C. Different amounts of each monomer were charged into the reaction vessel with the previously weighed mass of the initiator (20 mM). Then the reaction mix was purged with N_2 during 30 min. Finally, the reaction vessel was placed into a thermostatic bath

during different analysis times. The obtained PFS copolymers were isolated by methanol addition, purified by a solubilization–precipitation procedure (toluene: methanol, 1:5), and finally dried to get a constant weight for conversion estimation (Conv, %).

2.3. Modified bitumen preparation

The modified bitumen was carried out by mixing the base bitumen and the copolymer in a laboratory mill (E-asphalt, Model D-40) under high speed stirring. The equipment consists of a cylindrical mixing vessel (maximum capacity of 0.5 l; 6.0 cm internal diameter), built in stainless steel with double jacket for circulating oil and connection to a thermostat. The heat consists of a rotor with 2 paddles of 20 mm diameter and a stator with holes. The procedure was developed as follow: 100 ± 0,1 g of base bitumen was heat to 170 C in a mixer, and the PFS solid polymer was added (two different amounts of PFS were tested 2.5 and 5.0% by weight) by keeping the mixture to 2400 rpm for 5min, allowing the swelling of the polymer into the bitumen. Finally the mixing velocity was increased to 5800 rpm for 1 hour, at the same temperature, to obtain the complete incorporation and homogenization of both components.

2.4. Instrumental methods

A Shimadzu IR-435 spectrometer was used to record the infrared spectra of copolymers as a capillary film onto a sodium chloride (NaCl) window.

^{1}H-NMR spectra of copolymers were recorded with a Magneto Bruker UltraShield 14.1 T, 600 MHz at 35 C in CDCl$_3$.

The molecular weight distribution and average molecular weights were determined by size exclusion chromatography (SEC) with a LKB-2249 instrument at 25 C and a UV-Visible detector (SPD-10A Shimadzu). A series of four μ-Styragel columns (10^5, 10^4, 10^3, 100 Å pore size) was used with chloroform as eluent. The sample concentration was 4–5 mg ml^{-1} and the flow rate was 0.5 ml min^{-1}. Polystyrene standards supplied by Polymer Laboratories and Polysciences Inc. were used for calibration.

Glass transition temperatures (Tg) were measured using a scanning calorimeter (DSC, Q2000-TA Instruments). Samples (~10 mg) were weighed and scanned at 10 C min^{-1} from −30 to 150 C under dry nitrogen (30 mL min^{-1}). Three consecutive scans were performed for each sample: heating/cooling/heating.

Thermogravimetric (TG) analysis was performed in a TGA-Q500- TA Instruments. The measurements were done in a temperature range of 25–700 C, at 10 C min^{-1} heating rate, under nitrogen flux and using 10–15 mg of sample.

The standardized tests of BB and modified bitumen (MB) including penetration test (ASTM D5), softening point (ASTM D36), viscosity (ASTM D4402) and elastic recovery (IRAM6830) were studied.

Brookfield Model RVD-III Viscometer with a temperature control system was used for the viscosity test of base bitumen and MB (ASTM D4402). The measurements were carried out at different temperatures, 60, 135, 150 and 170 C.

The modified bitumen's morphology was analyzed by optical microscopy. Images were recorded and analyzed using a BX51 Olympus fluorescence microscope and a DP Controller image processor.

3. Results and discussion

3.1. Copolymer synthesis and characterization

The comonomers selection for the copolymer synthesis was based on their chemical nature, including an aliphatic and an aromatic substituent from DOF and St, respectively. At the same time, the glass transition temperatures (Tg) values of the corresponding homopolymers were consider for the selection. The radical copolymerization of DOF with St produce new copolymers (PFS) which structure and ^{1}H NMR spectrum (in chloroform) with the assignments of resonance signals are shown in Figure 1. The corresponding H assignations are (d, ppm): 6.40–7.40 (**H**-Ar), 4.81(–OC**H** (CH$_3$)–); 2.67 (>C**H**-C = O), 1.83 (-C**H**$_2$-, main chain), 1.55 (–(C**H**$_2$)$_5$–), 1.30 (C**H**$_3$-CH<) and 0.92 (C**H**$_3$). The structure was confirmed by FTIR analyses (NaCl, think film, cm^{-1}): 3050 (C-H, Ar), 2950, 2950 y 2860 (C-H aliphatic), 1738 (C = O), 1248 y 1118, (RO-C = O), 1600 (C = C, Ar ring), 763 and 697 (C-H, Ar monosubstituted).

It is known that for all copolymerization reactions the initial comonomer mixture (*f*) and copolymer compositions (*F*) are different due to the differences in reactivity of monomers. Considering that the properties of the copolymers depend on the content of comonomers in the macromolecular chain, it is always necessary to determine this parameter. Thus, the copolymer compositions were estimated from ^{1}H-NMR spectrum, using the integral ratio of the peaks of methyl (I_{CH3}) and aromatic (I_{Ar}) hydrogen at 0.92 and 6.40–7.40 ppm, respectively, by Eq. (1).

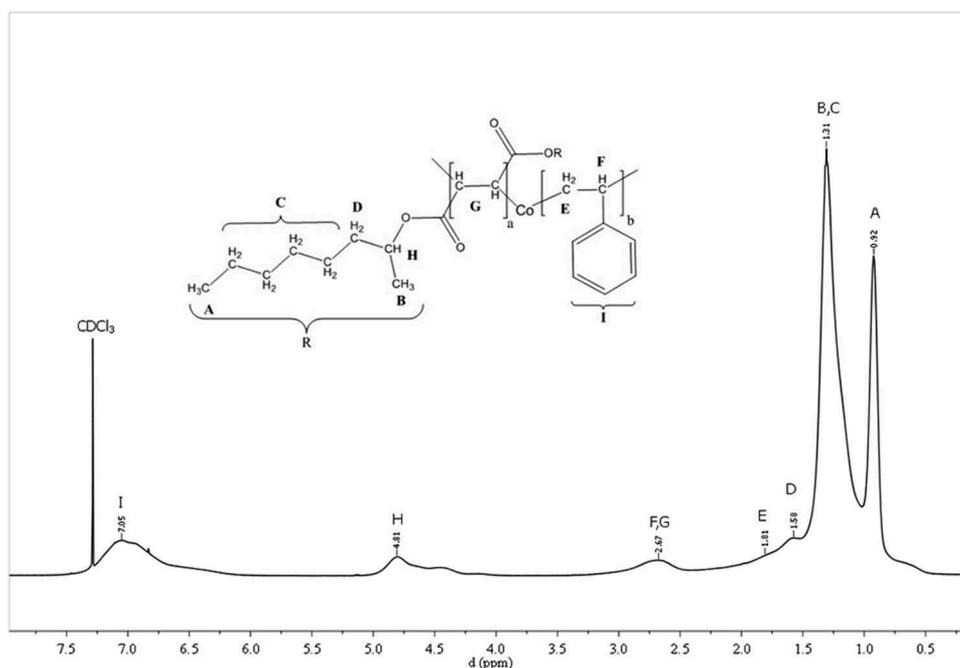$$F_{DOF} = \frac{5I_{CH3}}{5I_{CH3} + 6I_{Ar}} \qquad (1)$$

Figure 1. ^{1}H NMR spectrum CDCl$_3$ at 35 C of PFS3.

Table 1. Reaction conditions and properties of the copolymers.

Copolymer	f_{DOF}	t (d)	Conv (%)	M_W (g/mol)	PDI	F_{DOF}	IDT (ºC)	T_{max1} (ºC)	T_{max2} (ºC)
PFS1	75	3	25.0	45,300	2.15	60	275	325	360
PFS2	50	3	48.3	59,600	2.06	52	275	336	380
PFS3[a]	75	9	18.0	118,300	2.00	56	280	330	367

Reaction conditions: [AIBN] = 20 mM, 10% toluene, 3 or 9 days, 60 C
[a] In bulk at 40 C

Table 2. physical properties of base bitumen and modified bitumen.

Sample	Penetration (dmm)	Softening point (ºC)	Viscosity 135 ºC (Pa.s)	Elastic recovery (%)
BB	96	40.4	0.52	-
MB1	76	50.2	0.67	8
MB2	72	53.3	0.79	8
MB3	68	55.3	0.87	9
MB4	52	56.6	1.14	17

where F_{DOF} represents the DOF composition in the copolymer.

Table 1 shows the polymerization conditions: the reaction time, DOF monomer mole fraction in the initial monomer mixture (f_{DOF}), DOF monomer mole fraction in the copolymer (F_{DOF}), the conversion, the weight average molecular weight (M_W), and the polydispersity index (PDI) of the copolymers synthesized.

Thermal stability of synthesized copolymers were analyzed by thermogravimetric analysis (TG), in order to select the adequate temperature for the modified bitumen preparation, considering to avoid the initial degradation of copolymers at this temperature. As can

be seen in Table 1, all copolymers showed higher initial decomposition temperature (IDT) than a homopolymer structurally related [12], and also copolymers seemed to decompose in a two-stage process, at T_{max1} and T_{max2} characteristic temperatures.

3.2. Bitumen blend and morphological characterization

The samples were prepared with the base bitumen and using two different contents of each copolymer (2.5 and 5.0%) for each of the three different polymer synthetized. The applied methodology for the bitumen blend preparation was according to our previous procedure published [19]. EVA copolymer with M_w = 92,500 g/mol and PDI = 3.97 was used for the bitumen blend comparison which is a linear random copolymer as PFS synthesized in the present work. In other words, EVA has ethylene and acetate aleatory units in its structure, i.e. polar functional groups able to improve the interaction with bitumen [9] as well as is expected for the fumaric styrene copolymer synthetized. On the other hand, although the octyl ester group in the PFS is slightly more hydrophobic than EVA's acetyl component, their content in the PFS copolymer is higher, which would compensate for the structural differences between both copolymers.

The corresponding modified bitumen was identified as MB1, MB2, MB3 and MB4, each of them including one of the synthetized copolymers PFS1, PFS2, PFS3
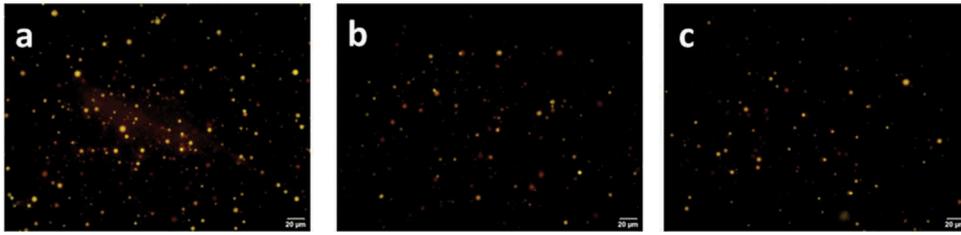
Figure 2. Fluorescence micrographs of MB2 sample obtained under the following conditions: a) 5.0%, 10 min; b) 5.0%, 60 min, c) 2.5%, 60 min. Mixing conditions: 5800 rpm at 170 C. Magnification 40X.

and EVA, respectively. Table 2 shows a resume of physical properties of base bitumen and modified bitumen (MB) carried out by standardized tests.

Fluorescence microscopy was used to observe the compatibility polymer-bitumen through the distribution between the polymer-rich phases (which can be seen as slightly bright tone) and the bitumen-rich phases (which can be seen as black in the picture).

Figure 2(a,b) shows the image of the MB2 bitumen blend (5%) obtained at 5800 rpm after 10 and 60 min of blending. At short time, it was possible to see polymer droplets heterogeneously dispersed over a continuous bitumen phase. After 60 min of blending, due to the swelling of the polymer-rich phase and their

solubilization, a decrease of droplets size and more homogeneous droplets size distribution was observed. This behavior could be attributed to the rapid migration of maltenic compounds to the polymer-rich phase together with the effect of the better homogenization of the blend, which suggest that the compatibility between polymer and the type of base bitumen used was greatly improved. In order to quantify the polymeric phase size distribution, images (Figure 2(a,b)) were analyzed respect to their size and the results are presented on Figure 3. As can be observed, the polymer drop average size decreases with the elaboration time: 3.8 ± 0.1 µm and 2.9 ± 0.3 µm at 10 and 60 min, respectively. At short times, the polymer-rich phase is not completely
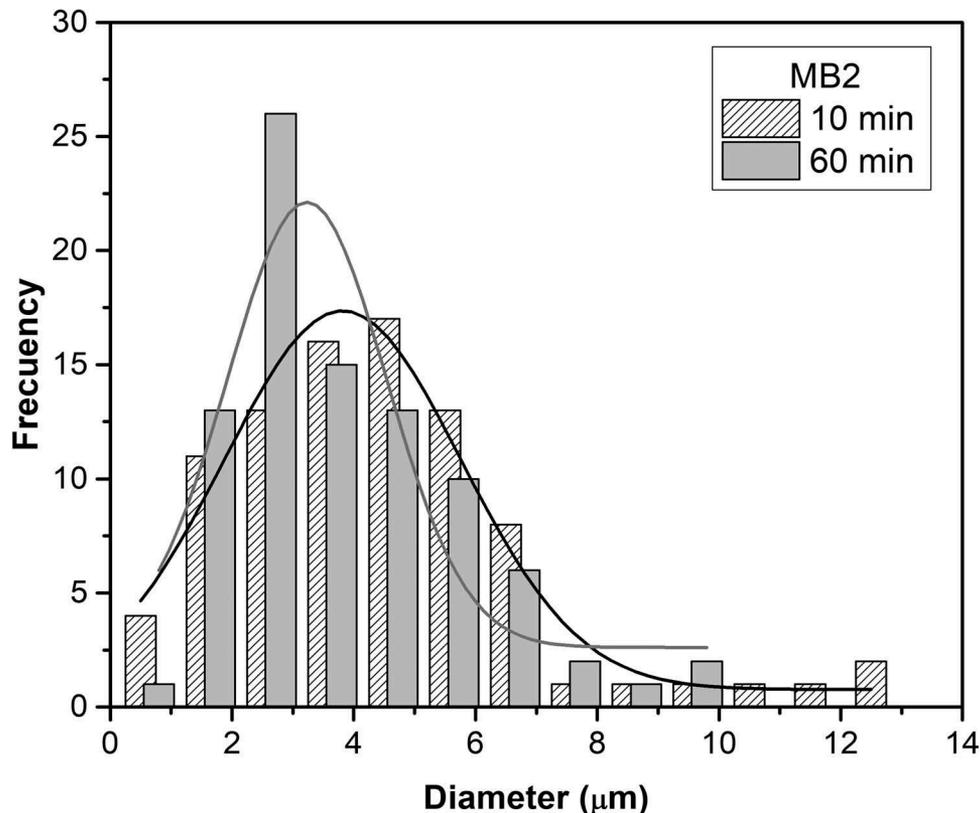
Figure 3. Drops size distribution of MB2 at 10 and 60 min after mixture (5800 rpm).

integrated with the bitumen-rich phase and higher drops size were observed.

The effect of polymer concentration can be seen for comparison between Figure 2(b,c), for 5.0 and 2.5%, respectively. Although no significant variation in morphology is observed, the decreased on the polymer content is clearly detected.

Comparing the morphologies of modified bitumen presented in Figure 4(a–c), it can be seen that the size of the drops and their distribution are comparable. These observations indicate similar kind of interaction between polymer-bitumen phases and thus comparable compatibility. No effect of the weight average molecular weight or polymer composition was observed, suggesting that these macromolecular characteristics had no influence on the copolymer solubility in the bitumen. On the other hand, MB4 (containing 5.0% EVA), prepared under the same experimental condition, exhibited a very different morphology (Figure 4(d)). The image, in Figure 4, shows an intertwined phase structure with neither phase dominating the overall system. Inversion of phases at highest concentrations (> 5%) was observed and previously reported [20, 21].

3.3 Rheological behavior of blends

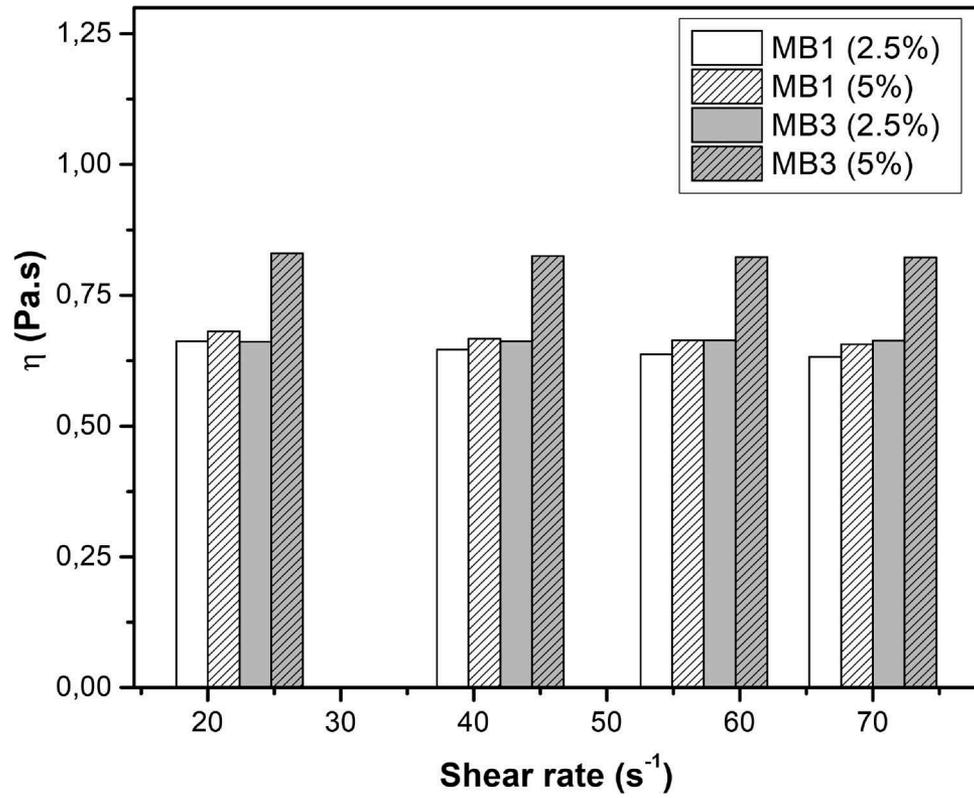The effect of the copolymer concentration on the rotational viscosity in function to shear rate for all modified bitumen, was not evident. However, the MB3 sample exhibited some differences, as can be seen in Figure 5, which present the results in comparison with to those of the MB1 sample, as an example. This result could be attributed to the highest average molecular weight of the PFS3 copolymer in the MB3 bitumen (see Table 1). A similar behavior was previously verified for modified bitumen including SBS copolymers of different average molecular weight [19, 22].

Generally, the modified bitumen showed non-Newtonian behavior within the temperature range of 110 to 160 C. Figure 5 shows that, the effect of shear rate on the viscosity was not significant in the range of the shear rate analyzed, and also at all tested temperatures (data no shown), suggesting that this region correspond to the plateau of Newtonian viscosity behavior [23].

The analysis of the viscosity-temperature relationship is very important from the practical point of view due to it is related with the behavior of the modified bitumen in service life as well as on the rheological changes that modified bitumen suffer during their manufacturing process [19]. In order to evaluate all the MB rheological behavior at high temperature, the rotational viscosity from 60 to 170 C was studied for each sample. Figure 6 shows the decreased of the rotational viscosity with the increase of the temperature, as is expected, for both base bitumen and modified bitumen. All MB exhibited higher viscosity than the BB, and this effect was more evident for the MB3, which include
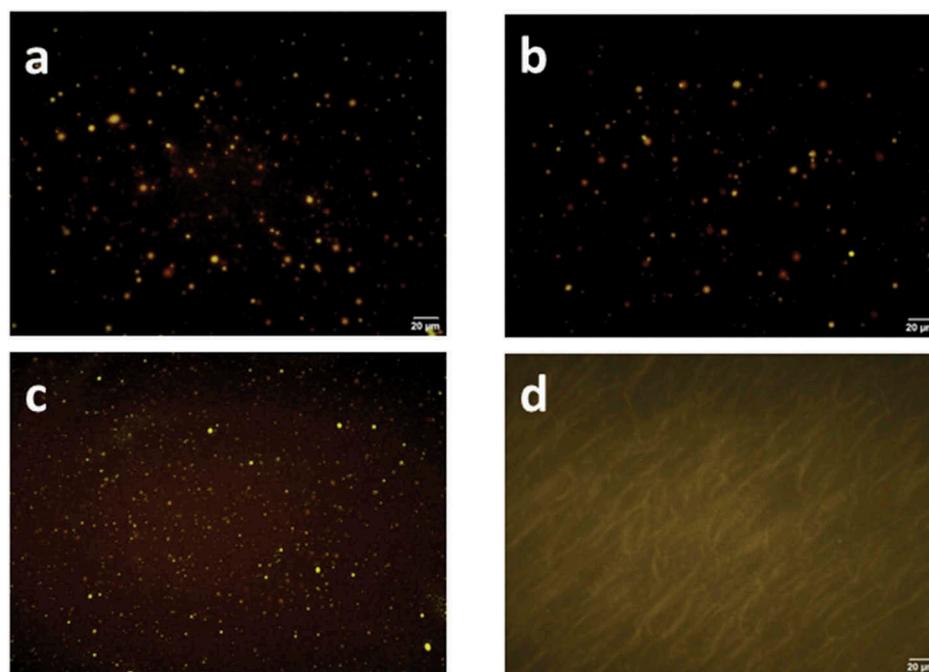
Figure 4. Fluorescence micrographs of modified bitumen (5%): a) MB1, b) MB2, c) MB3 and d) MB4. Mixing conditions: 60 min, 5800 rpm at 170 C. Magnification 40X.

Figure 5. Effect of the polymer concentration on the viscosity in function of the shear rate for MB1 and MB3 samples. Temperature of the measurement: 135°C.
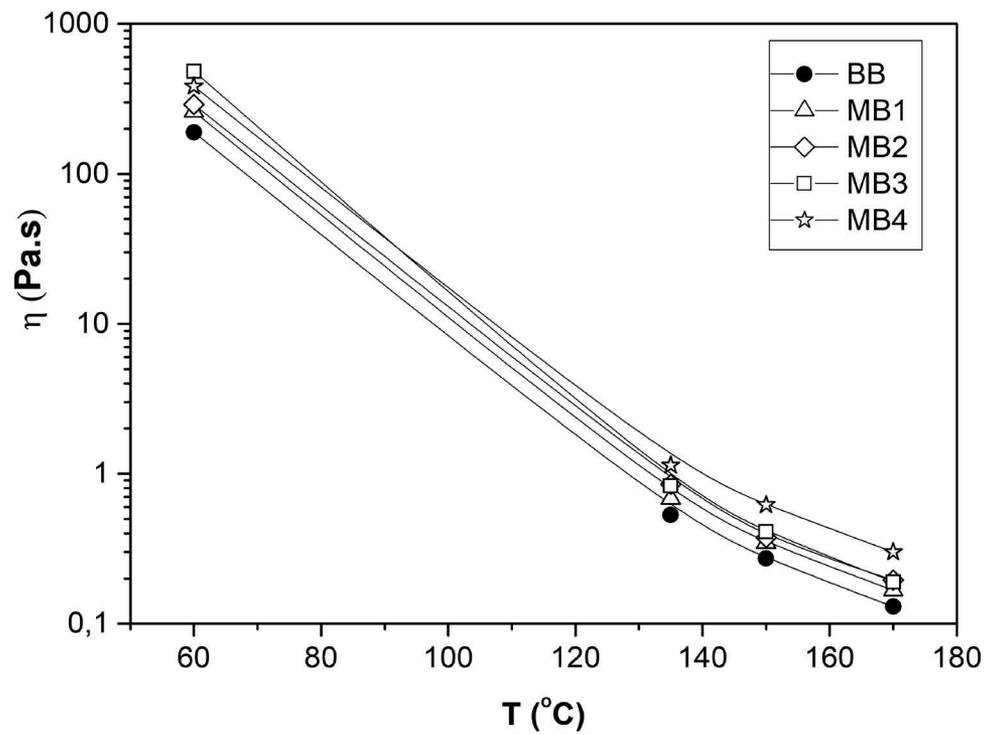
Figure 6. Rotational viscosities of modified bitumen (5%) in function of the temperature.

the polymer with the highest average molecular weight (see Table 1). The behavior of that sample is similar to the MB4 which had EVA copolymer.

The viscosity-temperature relationship of bitumen can be represented well by Arrhenius Eq. (2):

$$\eta = A\exp\left(\frac{E_a}{RT}\right) \qquad (2)$$

where η is the viscosity of the bitumen, A is the pre-exponential factor, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (in K) and E_a is the activation energy for flow (J mol^{-1}). This last parameter has been related with thermal susceptibility of the bitumen and has been found that it depends of different molecular characteristics, such as molecular weight, molecular weight distribution, nature, architecture and concentration of included polymer, as well as the aging of the modified bitumen [24, 25]. Eq. (2) can be rewrite in natural logarithm form:

$$\ln\eta = \ln A + \frac{E_a}{RT} \qquad (3)$$

Thus, a plot of lnη versus $1/T$ allows obtaining the E_a values through a linear extrapolation. Using this methodology the data presented in Figure 6 were analyzed and the results presented in Table 3. As can be observed, the addition of PFS modifier enhances the bitumen viscosity and thus increased the energy required for flow. The effect of the polymer content on the E_a is not clear, except in the sample MB3 where an increase of the E_a is observed. These results suggest that, within the range of temperature tested, these modified bitumen will be more sensitive to temperature changes than the unmodified one. Similar results were found for different type of polymers, such as SBS, high-density polyethylene (HDPE) or HDPE blend, between others [24].

As Table 3 shown the EVA addition leads to a decrease in the E_a values, according to a previously reported result [21]. It is evident that the chemical structure of the modified polymers has influence on the activation energy, which could be interpreted as different polymers may have different interactions with the bitumen components which change the flow resistance of the final MB [25]. Thus, the flow

Table 3. Activation energy (kJ mol^{-1}) for BB and modified bitumen.

Sample	Polymer concentration (%)		
	0	2.5	5.0
BB	83.2 ± 3.9		
MB1		84.5 ± 4.1	84.1 ± 4.2
MB2		84.6 ± 4.2	83.7 ± 3.8
MB3		83.8 ± 5.2	89.7 ± 4.6
MB4		-	81.8 ± 4.3

resistance is strongly influence by the rate of change of viscosity with temperature or shear rate, experimental conditions that will be determined during the mixing and compaction process. A higher E_a value demands a higher compaction effort of bitumen mixtures in their application, because it is necessary to overcome a greater energy barrier for the material to flow during this process and hence the importance of the evaluation of this parameter.

3.4 Thermal characterization

Differential scanning calorimetry (DSC) was used to characterize the thermal behavior of the base bitumen and the modified bitumen. The multicomponent nature of bitumen, including aromatics, paraffins, asphaltenes and resins compounds [26], is evident from DSC measurements. The DSC trace of BB (Figure 7) reveals different thermal events: a glass transition (Tg) at −27.3 C followed by two endotherms near to 40°C which in our thermogram appears overlapped. These observations are in agreement to other authors whom have related the Tg close to −30 C to the transition of the maltenic components (saturates and aromatics) [27–29]. Systematic works by Masson et al [28–32] on bitumen and its fraction demonstrate that the transitions above 20 C are difficult to analyze and to assign to a given fraction, except when measurements are made by modulated DSC. Under such conditions they assigned the endotherm peaks to the saturated alkane segments, resins, and asphaltene mesophases.

The PFS copolymers exhibited a single Tg value, which is in between the Tg values of the corresponding homopolymers (Table 4), as was expected based on the monomer content and the monomeric statistic distribution into the copolymer structure [18, 33].

The DSC thermograms corresponding to the modified bitumen (MB, Figure 7) present a profile similar to the base bitumen. A slightly shift of the Tg value at higher temperatures of MB1 and MB3 were observed, because that samples has more fumaric fraction in copolymer than PFS2 in sample MB2 (Table 4). This behavior could be attributed to the copolymer swelling by the maltenic fraction, considering the chemical nature of the modifying copolymers, which suggest good interaction bitumen-polymer. On the other hand, sample MB2 exhibited a lower Tg than the BB Tg's. In this case the incorporated copolymer (PFS2) possibly has long branches in their microstructure, due to the high conversion attained during the polymerization (48.3%, Table 1), as was previously observed [18, 34, 35]. It is known that when a radical polymerization reaches high
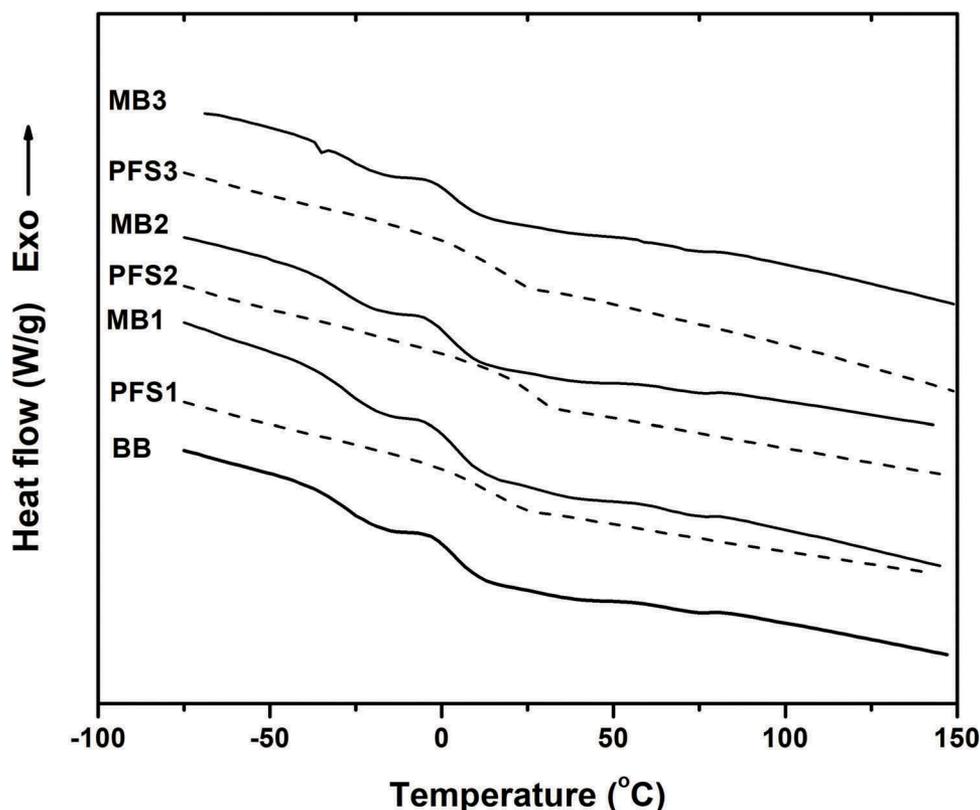
Figure 7. DSC curves of base bitumen (BB), PFS-modified bitumen (MB, 5%) and pure PFS copolymers.

Table 4. DSC thermogram data of base bitumen and modified bitumen containing 5% PFS at a heating of 10°C/min.

Sample	F_{DOF}	T_g (°C)	T_1 (°C)	T_2 (°C)
BB	-	−27.3	40.5	74.9
PFS1	60	17.5		
MB1		−26.8	40.1	74.4
PFS2	52	27.0		
MB2		−28.7	40.2	75.4
PFS3	56	21.0		
MB3		−26.9	39.5	73.0

conversions (> 20%), chain transfer reactions could be occur generating branches in the final structure of the obtained polymer which significantly affect the material properties. That structural characteristic could be responsible of the strongest interaction polymer-polymer and polymer-bitumen compare with MB1 and MB3 resulting in a decrease of the Tg of the blend. The other thermal transitions (above 20 C) did not show significant changes, which suggest that those copolymers did not exhibit important interactions with other bitumen fractions. Our results indicate that as higher is the fumaric composition present in the copolymer, the corresponding bitumen binder Tg value will be higher. In that way MB2 present the better thermal behavior and therefore its copolymer could improve low-temperature properties of BB.

4. Conclusions

In this work three new fumaric copolymers were obtained by radical polymerization with different average molecular weight and monomer composition. The effect of those macromolecular characteristics on the morphology, rheological and thermal properties of new modified bitumen were analyzed.

The experimental conditions in the modified bitumen preparation were optimized for attained an efficient blending. The analysis of the morphology of the mixtures showed that after 1 h of mixing at 170 C, the polymer-bitumen compatibilization is achieved. Although the effect of the copolymer concentration on the rotational viscosity in function to shear rate was not evident, all modified bitumen exhibited higher viscosity than the base bitumen under the analyzed condition. As the average molecular weight of copolymer increase the viscosity of the modified bitumen has a significantly increase. Both morphological analysis by fluorescence microscopy and thermal properties demonstrated good polymer-bitumen compatibility for all prepared blends . According to viscosimetric and thermal studies MB2 shows lowest activation energy and Tg than MB1 and MB3 suggesting an improvement of the thermal behavior. The

present work constitutes the basis for future research on the interaction and compatibilization of new fumaric polymer binders – bitumen. It's a new subject for the bitumen industry and a new gate in the field of investigation.

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