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IMPROVEMENT OF COMPATIBILITY AND STABILITY ON POLYETHYLENE-MODIFIED BITUMEN BY USE OF AN AROMATIC EXTRACT AS COMPATIBILIZER

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ABSTRACT

Bitumen modification by polyethylene addition usually improves the mechanical properties of the binder and, therefore, the behavior in service of the bituminous mix: thermal susceptibility and rutting can be diminished, whilst the resistance to low temperature cracking may increase. To achieve this improvement it is necessary a good compatibility between the base bitumen and the polyethylene. Low compatibility between bitumen and polyethylene can lead to phase separation: the polymer-asphalt incompatibility translates into a deterioration of ultimate properties. The object of this research project was to determine if these problems can be diminished by using certain compatibilizer agents, e.g. an aromatic extract from the oil refinery. Compatibility and stability of the polyethylene modified bitumen were studied using conventional test methods and dynamic shear reometer (DSR). Blends of bitumen and polyethylene were prepared with neat bitumen (PMB) or bitumen with compatibilizer as component of the binder (PMBC) and then compared. The experimental results show that "colloid instability index"(IC) is a parameter that can be used to control the compatibility between bitumen and polyethylene. From polyethylene point of view, one of the parameters that govern is the "melt flow index" (MFI). Experimental results show that PMBC formulated with low IC bitumen and high MFI lineal polyethylene can be considered as stable binder.

Keywords: Polyethylene modified bitumen, binder stability, polyethylene-bitumen compatibility

1. INTRODUCTION

Bitumen as binder has a lot of advantages but also it has some disadvantages. Bitumen is a viscoelastic fluid and suffers for some important limitations due to high temperature sensitivity of his properties. This high thermal susceptibility causes stiffening at low temperature becomes fragile to light impacts so traffic charge cause crack initiation and propagation. At temperatures higher than 30-40ºC it has is too much low viscosity so rutting is presented in pavement (flows spontaneously or becomes permanently deformed even under slight mechanical stress). At usual summer temperatures of pavement surface (60°C), under traffic load, bitumen is not able to maintain the original shape of the pavement, thus leading to permanent deformation known as rutting. In low temperatures, the bitumen gets brittle and tends to crack, because the stiffer structure is unable to relax the internal stresses originating from traffic load. Both of these distresses are not avoidable for neat bitumen, resulting in a shorter pavement lifetime. To overcome these problems various modification of the neat bitumen are studied. The modification has to be done with respect to some requirements. First of all, of course, the modification has to be cost effective (reduced maintenance costs has to be taken in account). Secondly, a good compatibility with neat bitumen is required, especially in case of road paving, where high temperature storage specifications define temperature and period of storage during which the polymer should not separate from the binder. Moreover, the increase in viscosity shouldn't be very high when the bitumen is in its molten state, in order to allow the use of the existing paving apparatus and processes.

Plastomers i.e. polyethylene (PE), confer a high rigidity to the binder and strongly reduce deformations under load. These polymers are often used for bitumen modification in application such as roofing or other waterproofing uses. The limited use in road paving is motivated by the very high incompatibility of bitumen with saturated, non-polar aliphatic chains. Polyethylene modified bitumen (PMB) drives to products useful to manufacture binders with lower thermal susceptibility than bitumen and it can be applied to avoid rutting and stiffening in roads decreasing glass transition temperature. However, the major obstacle to widespread usage of polyethylene modified bitumen in paving practice has been their tendency towards gross phase separation under quiescent conditions at elevated temperatures. Most polymers occur to be insoluble, in some degree, in bitumen matrix, suffering from rapid coalescence followed by gravity induced flocculation and creaming; this results in a phase separation at high temperatures. In this case, pavement losses its ultimate properties and the existence of a separated second phase induces high cracking susceptibility.

One approach to overcoming this problem has been studying specialized mixing methods of physical mixture to obtain adequate dispersion of polymer in bituminous phase [1]. Further, there is a tendency for the homogenized bitumen and polymers to undergo gross phase separation, necessitating continuous stirring and local on-site preparation. Another approach is the steric or chemical stabilization of the polymer MB by adding additives, dispersing agents or functionalized copolymers. Most of these methods are based in the formation "in situ" of chemical bonding or cross-linking between the non-aqueous continuous phase and the insoluble polymeric particulates. [2]

In this paper we present the study of an aromatic extract (AE) from crude distillation as compatibilizer to get stabilized polyethylene – bitumen blends. Polyethylene has a non-polar, non-aromatic nature. Its low solubility parameter (15, 6 to 17, 4 $MPa^{1/2}$) reflects its incompatibility with a bitumen dispersion medium, which is more polar and aromatic. But it is likely to disturb the delicate colloidal equilibrium that exists between the various components in the bituminous binder. A possible way of diminishing this fact is to add a compatibilizer, i.e. an AE from the oil refinery, that reduces the "colloid instability index" [IC = (saturates + asphaltenes) ÷ (aromatics + resins)] of the binder, improving the stability of the colloid. This binder will have a composition more compatible with the polyolefin and it will reduce the phase separation in the PMB

2. EXPERIMENTAL

2.1 Materials.

Bitumen of penetration grades (pen) 90, 120 and 150 provided by REPSOL (Spain) from Maya and Arabian Light (AL) crude were used as base binder. Some of its properties are recorded in **table 1**. Bitumen from Maya crude has an asphaltic composition and from AL crude has a paraffinic composition.

Commercial grades polymers from Repsol Química were used. All of them are polymers of low density (LDPE) whith different "melt flow index" (MFI) and their properties and denomination are shown in **Table 2**.

The aromatic extract (AE) has 65-85% of aromatic hydrocarbons with C_{20}-C_{50} and upper 5% hydrocarbons with 4-6 condensed aromatic rings. Bitumen with AE was prepared with enough amount of AE to get binders with the same penetration that the neat bitumen, pen 90, pen 120 and pen 150. In **table 3 and 4** are shown the properties of these binders.

Table 1.- Neat bitumen properties

	UNE-EN Test	Bitumen from Maya crude			Bitumen from Arabian Light crude		
Penetration (1/10 mm)	124/84	150	120	90	150	120	90
Softening point (Ring and Ball) (ºC)	125/84	43,3	45,4	48,4	39,2	41,8	44,6
Penetration Índex	181/84	0,069	-0,04	-0,068	-1,55	-1,29	-1,21
Ductility 25ºC (cm)	126/84	>100	>100	>100	> 100	> 100	>100
Fraass breaking point (ºC)	182/84	-22	-18	-15	-27	-13	-10
Fractions (% wt) ASTM D4124							
ASPHALTENES		14,80	15,68	15,91	8,92	9,27	10,05
SATURATES		11,83	12,32	12,41	12,25	12,57	12,90
AROMATICS		34,80	33,58	33,29	42,31	41,90	41,29
RESINS		38,57	38,42	38,39	36,52	36,26	35,76
SOLUBILITY PARAMETER $(MPa)^{1/2}$		18,0244	18,0268	18,0274	17,8606	17,8581	18,8579
COLLOID INSTABILITY INDEX(IC)		0,3630	0,3889	0,3949	0,2679	0,2811	0,2976

Table 2.- Polyethylene properties

	Test method	*Unit*	**PE022 (LDPE)**	**PE033 (LDPE)**
Melt Flow Index(190ºC/2,16 Kg)	*ISO 1133 ASTM D-1238*	*g/10 min*	70	0,3
Density at 23ºC	*ISO 1183 ASTM D-792*	*Kg/m^3*	915	922
Softening Point VICAT (10N)	*ISO 306*	*ºC*	75	94
Hardness Shore D	*ISO 868 ASTMD-2240*		40	

Table 3. Characterization of blends with bitumen from AL crude

	ARABIAN LIGHT (AL)								
P25	150			120			90		
T_{rb}	38,9			40,5			43,3		
AE (%)	18,6			17,4			16,7		
Polyethylene	PE022								
%	5%	6%	7%	5%	6%	7%	5%	6%	7%
P25	115	107	95	107	91	76	72	51	37
T_{rb}	44,6	45,9	48,0	45,1	47,1	50,2	47,7	51,0	55,9
IP	-0,45	-0,27	-0,02	-0,52	-0,41	-0,07	-0,90	-0,88	-0,48
Storage Stability									
ΔP25	10	7	7	8	4	2	7	3	2
Δ T_{rb}	21	20	19	20	18	18	18	16	14
% solids (top)	8,3	7,9	5,3	8,7	8,5	8,6	9,8	9,5	9,2
% solids (bottom)	5,1	5,3	5,9	4,3	4,6	4,9	3,6	3,8	3,9
Stability Índex (IS)	3,2	2,6	1,8	4,4	3,9	3,7	6,2	5,7	5,3
Polyethylene	PE033								
%	5%	6%	7%	5%	6%	7%	5%	6%	7%
P25	113	100	91	103	86	69	71	49	36
T_{rb}	45,1	46,2	48,5	45,6	48,0	50,9	50,4	52,5	56,4
IP	-0,34	-0,39	0,00	-0,49	-0,32	-0,16	-0,21	- 0,62	-0,44
Storage Stability									
ΔP25	15	13	10	12	10	9	11	11	8
Δ T_{rb}	22	20	19	21	19	18	20	18	16
% solids (top)	8,9	8,8	8,6	9,8	9,5	9,3	12,1	11,9	11,4
% solids (bottom)	4,1	4,3	4,3	3,5	3,9	4,1	3,0	3,1	3,1
Stability Index (IS)	4,8	4,5	4,5	6,3	5,6	5,2	9,1	8,8	8,3

Table 4. Characterization of blends with bitumen from Maya crude

	MAYA								
P25	150			120			90		
T_{rb}	41,8			43,5			46		
AE (%)	18,2			17,0			15,0		
Polyethylene	PE022								
%	5%	6%	7%	5%	6%	7%	5%	6%	7%
P25	98	79	50	88	67	40	66	41	29
T_{rb}	46	49,6	56	48,3	51,6	60	53,6	59,8	64,6
IP	-0,52	-0,12	0,22	-0,16	-0,06	0,52	0,39	0,53	0,66
Storage Stability									
ΔP25	31	28	16	30	26	14	28	22	12
Δ T_{rb}	35	31	29	30	27	26	28	26	25
% solids (top)	14,9	14,6	14,3	17,3	16,8	16,7	22,0	21,7	21,4
% solids (bottom)	3,4	3,9	3.9	3,1	3,,2	3,3	2,2	2,2	2,7
Stability Index (IS)	11,5	10,7	10,4	14,2	13,6	13,4	19,8	19,5	18,7
Polyethylene	PE033								
%	5%	6%	7%	5%	6%	7%	5%	6%	7%
P25	93	72	42	81	62	33	60	33	19
T_{rb}	48,6	51	58,4	49,9	53,9	60,8	53	61,2	68,4
IP	0,09	-0,01	0,31	0,03	0,29	0,25	0,00	0,32	0,47
Storage Stability									
ΔP25	36	29	25	34	23	20	30	17	14
Δ T_{rb}	46	40	38	42	40	35	38	36	33
% solids (top)	20,0	19,8	19,7	21,9	21,3	21,2	24,3	24,0	23,1
% solids (bottom)	2,7	2,8	2,9	2,1	2,1	2,4	2,01	2,04	2,08
Stability Index (IS)	17,3	17,7	16,9	19,8	19,2	18,8	22,3	21,9	21,1

2.2. Preparation of bitumen polymer mixture

PMB were prepared in a high shear mixer Silverson lab mill, at 180ºC, 4 kg of bitumen was heated to fluid condition and added preweighted amount of AE. Mixing was then continued at 180 ºC for 20 minutes. After that, the preweighed amount of polyethylene was gradually added. The stirring was continued for a further 2 h at 180 ºC with higher rotating speed, 4000 rpm. At the end of the mixing, the mixture was transferred to an oven at 180 ºC. It was poured into molds for rheological testing. The bitumen mixture physical properties were investigated by measuring penetration (pen), softening point temperature (T_{rb} or RB), viscosity, storage stability and dynamic shear rheology. At least two replicates of each test were done.

Six different classes of bitumen (three pen from Maya and three from Light Arabian) were used in the present study and three concentrations of Polyethylene (5, 6 and 7%).

2.2. Characterization

The bitumen was characterized according to the standard procedures. Penetration tests were carried out at 25ºC according to NLT 124. The penetration of a standard needle under a standard load (50 g) was measured during 5 s and reported in tenth of millimeter. Softening point temperature (ring and ball test) of bitumen was measured according to NLT 125. In this test, two disks of sample were cast into shouldered ring, and then they were heated at a constant rate (5ºC/min) in a water bath using a special apparatus. The viscosity was measured by Brookfield Thermosel Viscometer model DV-II+, according to ASTM D4402 at elevated temperatures at 135, 145, 155 and 165ºC.

The rheological test was performed by measuring rheological curves with a Böhlin Dynamic shear rheometer (DSR) according to AASHTO TP5 Standard Test Method. The DSR measures the complex shear modulus (G*) and phase angle (δ) of PMB at the desired temperature and frequency of loading. Complex shear modulus (G*) can be considered as the total resistance of the mixture to deformation when repeatedly sheared. G* consists of two components: (a) storage modulus G' or the elastic part, and (b) loss modulus G″ or the viscous part. The parameter phase angle (δ) is used as a measure of the relative elasticity of the bitumen. A small sample of bitumen is placed between two round plates with a 1 mm gap at a frequency of 10 rad/s. The strain and torque were measured and input into a computer for calculating complex modulus and phase angle.

Storage stability (toothpaste tube test) was determined according to UNE-EN 13399. The sample in at least two toothpaste tubes was put into an oven at 180ºC ± 5ºC for 120 h. The tube was then cooled to room temperature and stored in a freezer. It was cut into three equal parts. The upper and lower parts were then melted and poured into the rings for ring and ball softening point test. The difference in penetration and in the softening point of respective top and bottom samples was reported.

In addition 2g of the samples obtained from the top and the bottom from the tubes, were diluted in 50 ml of Tetrahydrofuran (THF), vacuum filtered through a glass fiber filter of 2, 7 µm sieve. Because the polymers are no soluble in THF the weight of the filtered, referred to the initial mass will give the content of solids in the sample. The difference between the content of solids of the top and the bottom samples, defined as Stability Index (IS), will give a value of the segregation of polymer in the bulk bitumen, and it is an indirect measurement of compatibility.

Tables 3 and 4 shown experimental measures analyzed in next point.

3. - RESULTS AND DISCUSSION.

Previous studies [3] on neat bitumen and bitumen with AE, both with the same penetration, have provided higher solubility parameter and lower IC for the last one as a consequence of their deferent chemical composition. Also the Black diagram (δ vs. G″) from the DSR results of both binders has been compared (**figure 1**). In the light of this figure, worse fatigue behavior and better rutting behavior for the bitumen with AE is shown when the bitumen is subjected to shear loading.

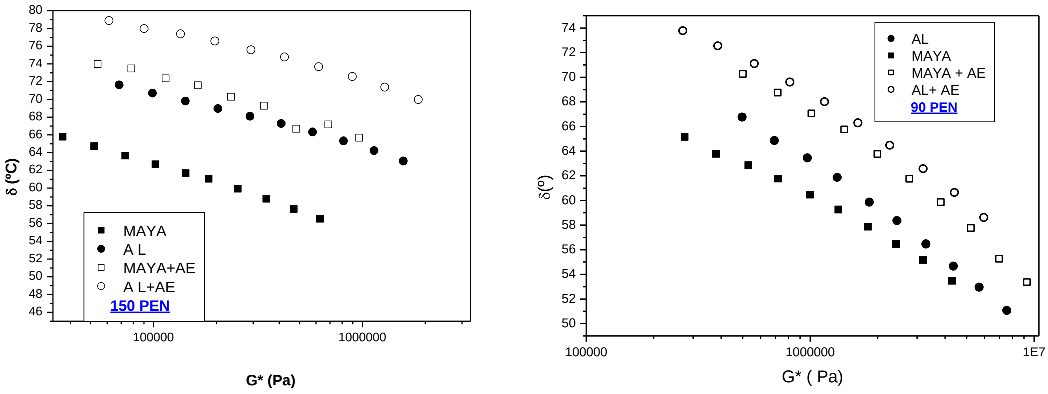

Figure 1,- Black Diagram. Neat bitumen and bitumen with AE. 20ºC

3.1. Effect on macroscopic properties (Penetration and Ring and Ball Tests).

From macroscopic properties point of view, and comparing similar bitumen, polymer in bitumen with AE produce less modification than polymer in neat bitumen. This fact is observed with AL bitumen as well as Maya bitumen and with PE033 as well as PE022. (**Figure 2 and 2 bis**)

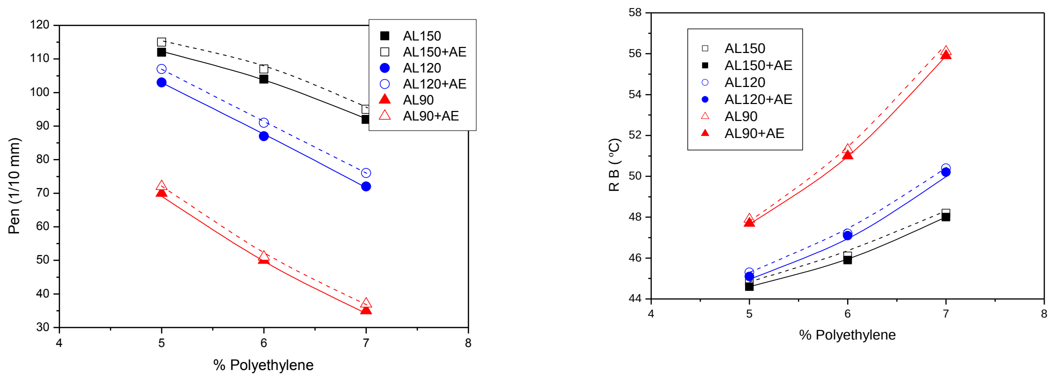

Figure 2- Penetration and Ring and Ball Tests. AL bitumen (with and without AE) with PE022

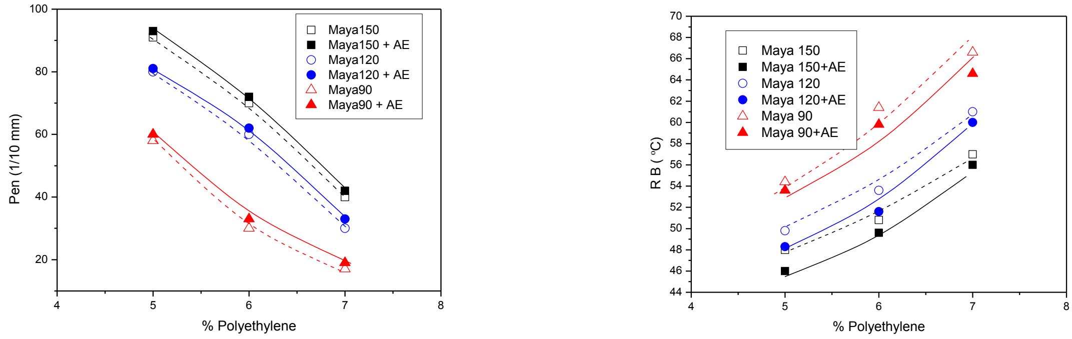

Figure 2 (bis)- Penetration and Ring and Ball Tests. Maya bitumen (with and without AE) with PE022.

In next figures (**figure 3**) the influence of percentages of both polymers in Penetration and Softening Point of the mixtures are shown. It can be observed that PE033 (with high MFI) and in Maya bitumen provoke higher modification in neat binder than PE022 polyethylene (with low MFI) and in AL bitumen.

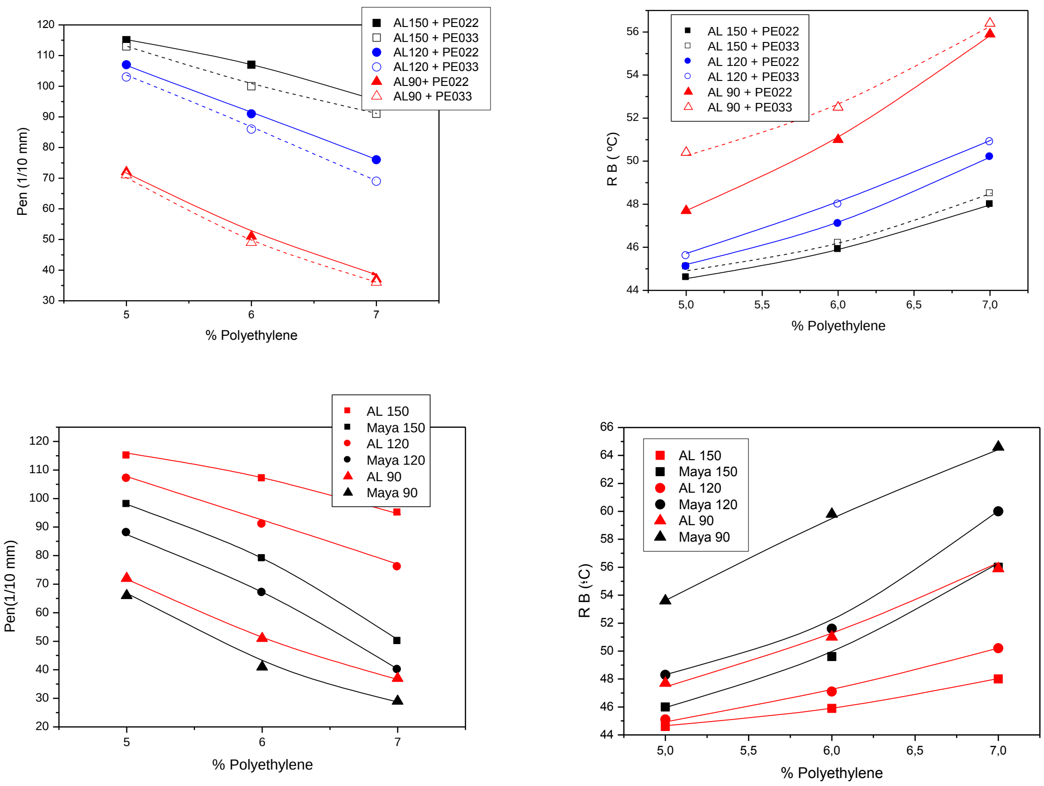

Figure 3- Penetration and Ring and Ball Tests. Maya and AL bitumen with AE (pen 90, 120 and 150). PE033 and PE022.

3.2. Effect on storage stability

From a macroscopic point of view, system is heterogeneous with Maya bitumen and a little more homogeneous with AL bitumen, but an increase in viscosity of the mix when it was storage at 160ºC for 3 days has not been observed. This fact means that colloidal equilibrium of binder is not broken (that happens when additive is not added). Therefore, the presence of AE in bitumen modified with PE prevent from breaking the binder colloidal equilibrium into bituminous phase and polymeric phase (**figure 4**).

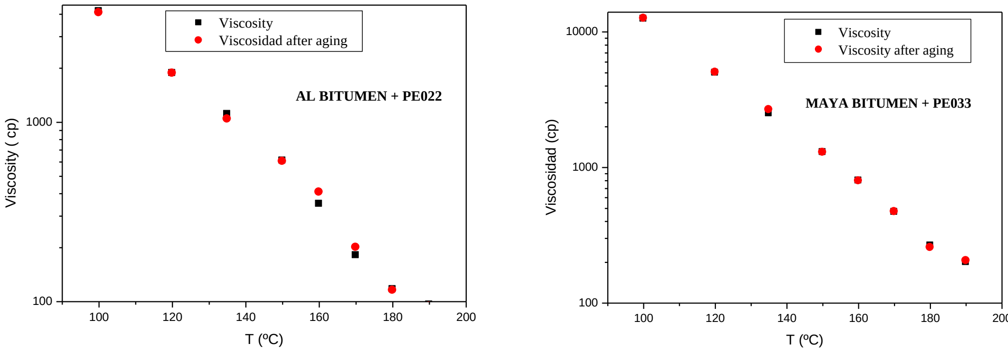

Figure 4.- Viscosity after aging at 160ºC for 3days. Pen = 90

In mixes in which Maya bitumen is used as base binder and AE is added a light polymeric phase is observed in its surface when it remains at high temperature, but this phase can be dispersed with conventional propeller stirrer at 100 rpm. If stirring stop the polymeric phase is formed another time and the process can be repeated for three times. The viscosity is maintained in each case (**figure 5**). Capacity of recuperation of the viscosity by simple stirring confirms that the colloidal equilibrium of the binder modified with PE has not been broken when an AE is used as compatibilizer. It is well known that broken colloidal equilibrium do not might inverted by stirring.

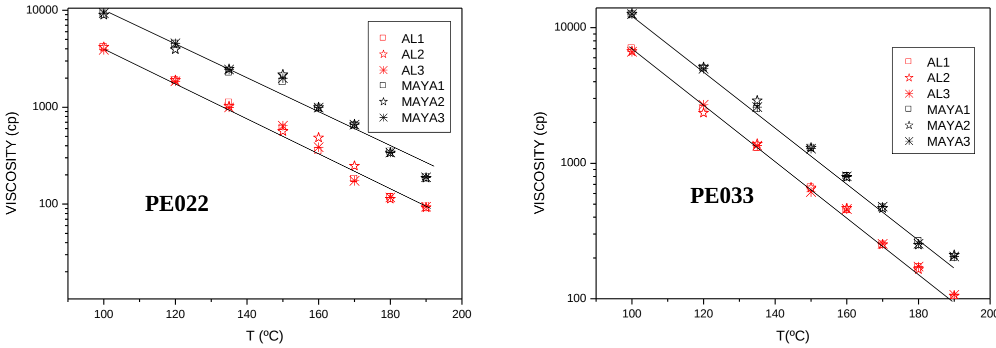

Figure 5.- Viscosity repeated for 3 times. Pen = 90. 5% indicated PE

In mixes in which AL bitumen is used as base binder and AE is added, produce less heterogeneity than Maya bitumen and better compatibility than mixes without AE: it is shown in storage stability test results. In this case polymeric phase is also dispersed with conventional propeller stirrer at 100 rpm.

Figure 6 shows macroscopic properties after storage. Modified binder with AL bitumen (90 pen) and AE mixed with PE022 meets with spanish specification for modified bitumen [4] about penetration, but not for softening point

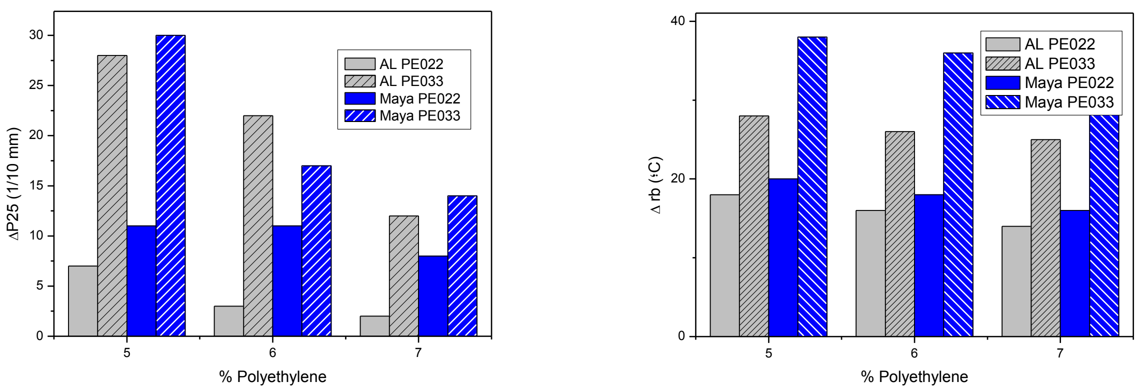

Figure 6.- Macroscopic properties after storage. Bitumen pen 90 with AE

It can be observed also in figure 6 that influence of polyethylene grade on mix stability is more significant than influence of bitumen composition and its origin. Modified binder with Maya bitumen, AE and PE022 presents less Δpen25 after stability test than mix with AL bitumen, AE and PE033. Actually, modified binder with AL bitumen, AE and PE033 can be included in Spanish specification for modified bitumen.

With respect to the influence of consistence of neat bitumen on storage stability of the mix, as harder is the bitumen, less difference on penetration between lower and upper part of the test tube is detected (**figure 7**). As we verified on previous works, this tendency agree with results for neat bitumen with PE and disagree with results of Stability Index. **Figure 8** shows that Stability Index (IS) of blend Al bitumen with AE and PE022 are low enough to be considered as a stable binder. Similar results are observed in blend with PE033 and are agree with stability test results (figure 7). However, binders with less consistence (high penetration index) are more stable (less Stability Index) than binders with lower penetration index.

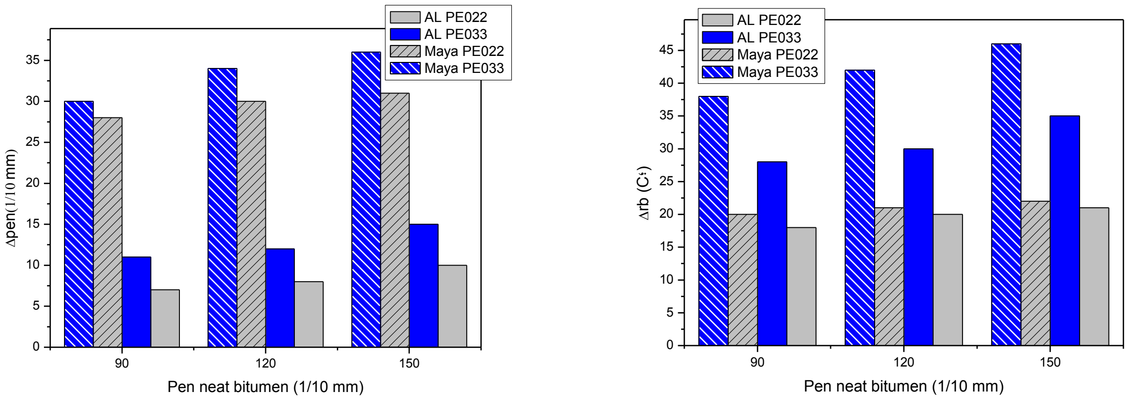

Figure 7. - Properties after storage. Stability test. 5% polyethylene.

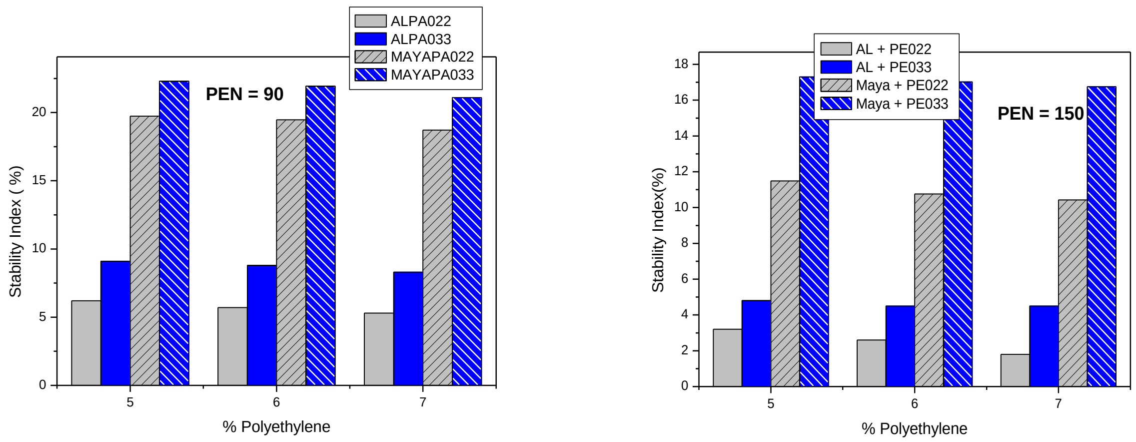

Figure 8.- Stability Index

Actually, the more enlightening measure about storage stability is the IS, so we can confirm that AL bitumen with AE result in more stable blends with PE than blend with Maya bitumen with AE, and also that storage stability increases diminishing consistence of the neat bitumen. When soft bitumen is blended with PE, the coalescence of PE particles is avoided because of more ratio oil/ asphaltenes: this effect is the determining factor in coalescence of PE in opposite to the effect of decrease in density that increase phase separation speed.

Figures 9 and 10 shows a comparison of the storage stability data of modified binder with and without AE. From the results (figure 9) it can be stated that AE diminishes differences between upper and lower fraction of the tube on Penetration index and softening point. Also (figure 10) can be stated that this fact don´t depend on PE grade or MFI and stability of modified bitumen with AE is better for blends made with bitumen of paraffinic composition (AL). On the other hand, the IS indicate better compatibility when bitumen is modified with PE022 (MFI = 70) in regard to PE033 (MFI = 0,3) as modifier: as higher is the MFI of the PE, lower is the IS of the blend an better stability

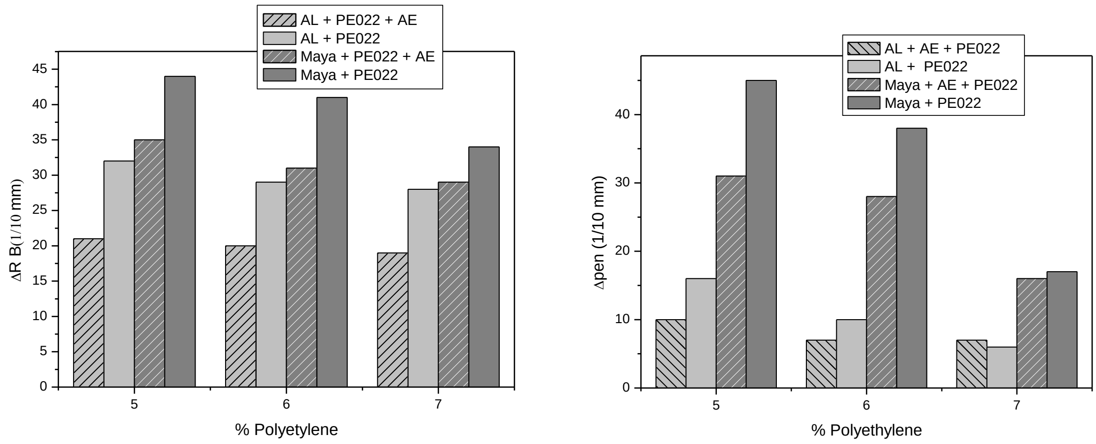

Figura 9.- Comparison between properties after storage. Stability test. Neat bitumen and bitumen with AE. Pen 150.

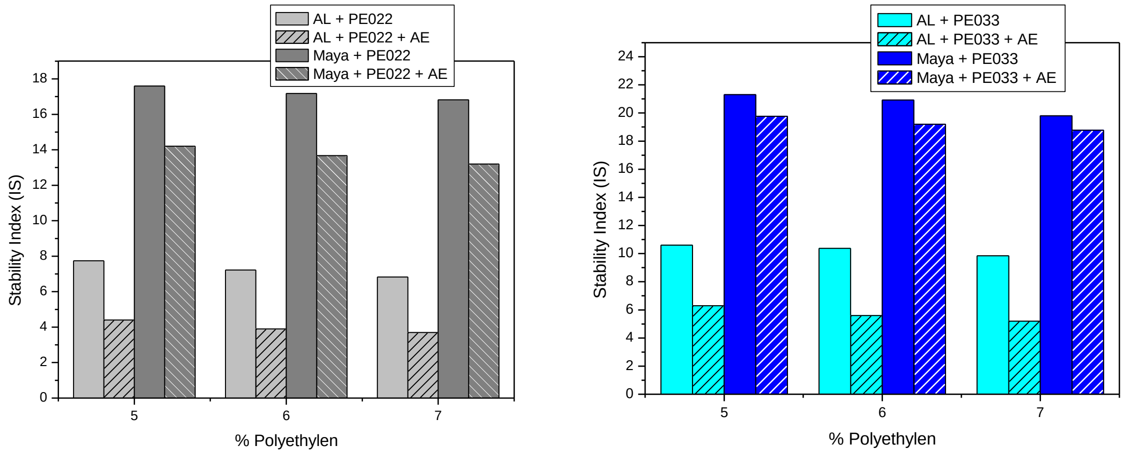

Figura 10.- Comparison between IS of conventional bitumen and bitumen with AE. Pen = 120. PE022 and PE033

5. CONCLUSIONS

Bitumen made with AE produce more stable blend with PE than conventional bitumen. In **table 4** can be observed that AE in bitumen diminishes its colloidal instability index (IC): that means that less IC implicate higher storage stability for PE modified bitumen. The hypothesis of this work (decreasing the IC adding AE as part of the binder increase the storage stability of PE modified Bitumen) has been probed. Since AL bitumen with AE modified with the two PE grades (PE022 and PE033) can be considered stable binder on storage, experimental results indicate that systems with storage stability enough can be got with LDPE of wide range of MFI whenever bitumen with IC up to 0,24 are used.

Table 4.- Comparison between IC of conventional bitumen and bitumen with AE

BITUMEN (Pen)	Arabian Light (90)	Arabian Light (120)	Arabian Light (150)	Maya (90)	Maya (120)	Maya (150)
CONVENCIONAL BITUMEN						
Colloidal instability (IC)	0,298	0,281	0,268	0,395	0,389	0,363
BITUMEN WITH AE						
Colloidal instability (IC)	0,238	0,233	0,226	0,335	0,321	0,304

In any case, the presence of AE in the composition of the binder infers a better compatibility in polyethylene modified bitumen and a less modification in macroscopic properties of the modified binder relative to neat bitumen. This tendency has consequences on fabrication process because of the need to use more polymer/ binder ratio to get similar macroscopic properties. This fact should be at a disadvantage, but it is compensate for the advantage of get compatible systems with high storage stability.

The main conclusions of this study are:

- The increase of the aromatic hydrocarbons amount in the binder with an AE from the crude distillation, avoid that the PE breaks the colloidal equilibrium of the binder.
- Stabilized PE modified bitumen could be get with paraffinic base bitumen (AL) that has low IC. An approximate upper limit of 0,24 is suggested for the IC
- High MFI polyethylene is required to get modified binder that meet the Spanish standards for PMB

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