SYNTHESIS AND CHARACTERIZATION OF THE POLYSTYRENE - ASPHALTENE GRAFT COPOLYMER BY FT-IR SPECTROSCOPY

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The creation of new polymer compounds to be added to asphalt has drawn considerable attention because these substances have succeeded in modifying the asphalt rheologic characteristics and physical properties for the enhancement of its behavior during the time of use. This work explains the synthesis of a new graft copolymer based on an asphalt fraction called asphaltene, modified with maleic anhydride. Polystyrene functionalization is conducted in a parallel fashion in order to obtain polybenzylamine resin with an amine – NH2 free group, that reacts with the anhydride graft groups in the asphaltene, thus obtaining the new Polystyrene/Asphaltene graft copolymer.

Keywords: asphaltene, polymer, maleic anhydride, copolymer, polystyrene. asphalt, physical properties , copolymer, polybenzylamine.

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La creación de nuevos compuestos poliméricos para ser adicionados al asfalto, ha llamado la aten-ción de manera considerable debido a que estas sustancias han logrado modificar las características reológicas y propiedades físicas del asfalto, con la finalidad de mejorar su comportamiento en el tiempo de uso. El presente trabajo explica, la síntesis de un nuevo copolímero de injerto a partir de una fracción del asfalto llamada asfalteno, la cual es modificada con anhídrido maleico. Paralelamente se rea-liza la funcionalización del poliestireno, resina polibencilamina, esta posee un grupo amina – NH_2 libre que reacciona con los grupos anhídro, injertados en el asfalteno, y así obtener el nuevo copolímero de injerto Poliestireno/Asfalteno.

Palabras Clave: *asfaltenos, polímeros, asfaltos, propiedades físicas, copolímeros, polimencilamina, anhídrido maleico, copolimero, poliestireno.*

INTRODUCTION

The great majority of natural macromolecules like the synthesized ones, by their molecular size are denominate polymers. This means that each one of them is composed by several simpler units, all of them identical or at least similar from the chemical standpoint, bound in a regular manner. These molecules are generated by a process named polymerization consisting in the binding of small molecules (monomers). These polymers are formed by two methods: first, by a chain reaction where molecules react with free radicals, either anions or cations. The second stage-based method consists in a series of independent reactions. In this second method, the monomer has more than one functional group that allows future reactions such as addition polymerization and condensation polymerization (Akelah & Sherrington, 1981; Frechet, 1981).

From the structural point of view, polymers are found in different varieties: linear polymers associated to the fact that all their reactions take place in heterogeneous media, with few diffusion problems and equal functional group accessibility. By contrast, crosslinked polymers with functional monomers are insoluble and easy to participate in selective reactions. Furthermore, polymeric chains with low crosslinking degree in appropriate solvents expose their functional groups to the reaction medium easily (Frechet, De Smet, & Farral 1979; Sherrington, 1984; Widdeckel,1984).

Reactivity of monomers in the copolymerization mechanism can differ in a reaction according to the concentration, nature of monomers, dispersion medium, initiator, and operation conditions such as temperature and pressure. Copolymers can be of different types according to the way parts couple among them. They are classified as random copolymers, alternating copolymers, block copolymers, and graft copolymers (Pulido & Salazar, 2001; Pepin, 2000; Quintana, Salazar, & Katime, 1993, 1994, 1995).

Many studies have been conducted on polymeric mixtures as agents to enhance interface properties and control agents of immiscible polymers morphologies of (Brule, 1996; Cho, 1997; Q.F. An, *et al.,* 2003; Ruan,
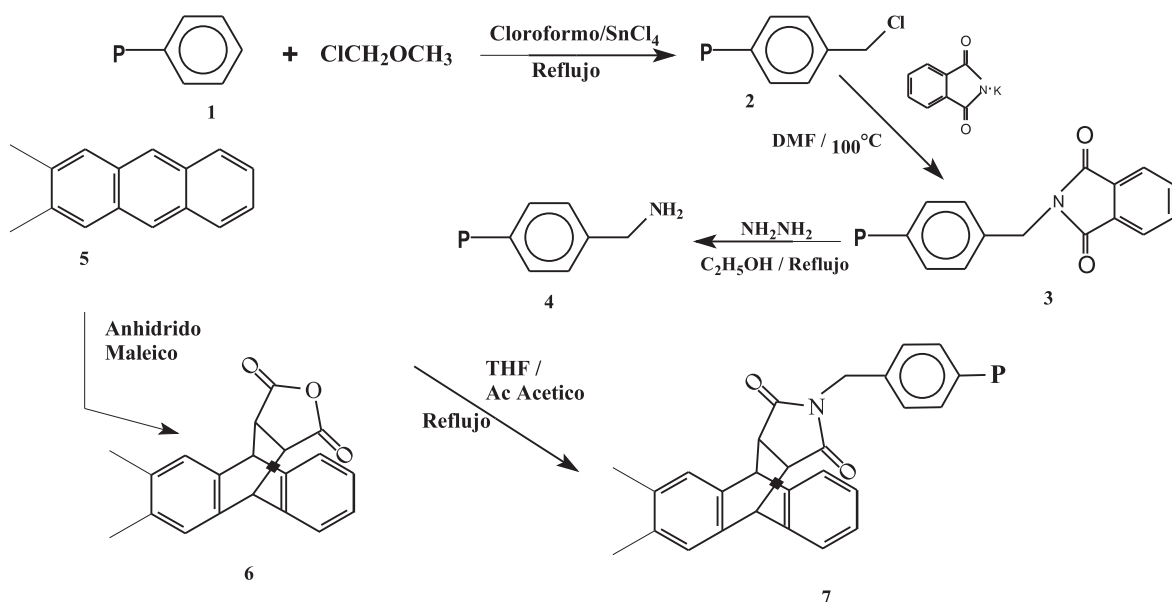

Figure 1. Synthesis path of the Polystyrene – Asphaltene graft copolymer: 1.Polystyrene, 2.Chloromethylation of Polystyrene, 3. resin synthesis Ftalimide, 4. Synthesis of Polybenzylamine resin, 5. Asphaltene, 6. Diels – Alder synthesis of Asphaltene – Anhidride

Davison, & Glover, 2005; Roedor, Oliveira, Becker, & Pires, 2005). The interface reagent has specific functional groups and can control and generate the type of desired copolymer in the interface by the reaction of the functional groups incorporated to each mixture component. There, they can control morphology in a wide variety of systems. Krauss, 1982; Shuler, 1990; Bouldin, and Collins, 1990; Lu and Isacsson, 1997; Hernández, Rodríguez, Blanco, and Castaño, 1997; among other authors, provide a more detailed explanation about this topic. The creation of new polymeric additives in asphalts has gained considerable attention, particularly regarding the modification of rheological, physical and chemical properties in order to improve stability and behavior over time.

Asphalt is composed by the heaviest petroleum components. This material can be utilized directly in pavement works or be submitted to other processes. Asphalt has mechanical properties such as high impermeability, adherence and cohesion. Furthermore, this material is able to withstand high instantaneous stress and flow under the action of permanent load (Collins,1986). Asphaltic materials are constituted by four generic fractions according to the SARA separation method: Saturated, Aromatic, Resin, and Asphaltene fractions. (Mcleod, 1987; ASTM D-3279- 1990, ASTM 4124-1991).

Several polymers are used nowadays to modify asphalts and each one fulfils different properties according their associated physical properties. For instance, the Ethyl Vinyl Acetate (EVA) produces high rigidity as a hard plastic material thus classifying it as an elastomer. Block copolymers such as Styrene – Butadiene (SB) and Styrene – Butadiene – Styrene (SBS) can increase asphalt elasticity since these compounds are also considered elastomers. (Krauss, 1982; Stathis & Nikos, 1994; Tjong, Xu, & Meng, 1999; Cortizo, Larsen, Bianchetto, & Alessandrini, 2004). Another group of elastomeric polymers such as rubber, latex, Butadien – Styrene rubber SBR increases asphalt ductility. (Becker, Méndez, & Rodríguez 2001; Chen, Liao, & Shiah, 2002; Shukla, Singh, & Bhanwala, 2003).

Some properties affected by the addition of polymers are: viscosity, fluidity, thermal susceptibility, flexibility and aggregate adhesion. In general terms, adding polymers to asphalt increases viscosity and decreases thermal susceptibility (Hernandez *et al.,*1997; Lundberg, & Peiffer, 1988; León, & Salazar 2003). Reduction in cracking, firmer mixtures at high temperature, and controlled viscosity are obtained when asphalt is modified by polymers. Furthermore, enhancement of other aspects such as stability, compatibility, improvement of strength against fatigue and resistance against aging and oxidation is attained (Lu, & Isacsson, 1998; King, 1999; Newman, 2003).

This study presents an infrared-based spectroscopy characterization of the compounds obtained in the stages leading to the synthesis of a new Polystyrene-Asphaltene (PS-ASP) graft copolymer. This copolymer has to be studied in further works as a compatibilizing agent in asphaltic mixtures in order to modify the rheological characteristics, the physical properties of the mixture and improve its performance with time.

EXPERIMENTAL METHODOLOGY

Materials

According to the AASHTO (American Association of State Higway and Transportation Officials) regulations, the physical properties of asphaltene obtained from Apiay asphalt are: 6,42 API at 25°C (298,15 K), 272,9 cst at 135°C (408,15 K) and Spark point of 291°C (564,15 K). Maleic anhydride of Analytical degree (Aldrich), Dextron Polystyrene, Paraformaldehyde 37%, Hydrochloric acid, Sulfuric acid, analytic n-Heptane, Tetrahydrofurane (THF), Acetic Acid, Triethylamine (TEA), N, N-Dimethylformamide, Chloroform and other reagents (Aldrich Co, The Merck and J.T Baker) were used and purified by conventional methods.

Instruments

The FT-IR Infrared Spectrocopy was used in the NICOLET AVATAR 360 FT-I.R E.S.P Spectrophotometer. The average molecular weight for polystyrene was determined by the viscosity method using a CANNON REF 50-K874 viscosimeter. The compatibilizing action

of the Polystyrene / asphaltene graft copolymer was studied by optic microscopy using a Nikon optic microscope, Photomicrographic Microflex PFX, coupled with a Nikon camera 6006.

Chloromethylation of polystyrene (2)

-Polystyrene average molecular weight (1). The viscosity method was employed by relating solvent flow times (Toluene) to of polystyrene solutions ti, to concentrations between 0,1g/dL and 1g/dL. The relative viscosity ($\eta_r = t_o/ti$), the specific viscosity ($\eta_{sp} = \eta_r - 1$), reduced viscosity ($\eta_{red} = \eta_{sp}/c$) and inherent viscosity ($\eta_{inh} = Ln.\eta_{red}/c$) were calculated. The viscous average molecular weight was obtained with the Mark-Houwink equation, $\eta = k*Mw^a$, where $K=1,7*10^{-4}$ and $a=0,69$. These are characteristic constants of polystyrene (Billmeyer, 1971; Collins, 1973).

- Chloromethylmethylether (CMME). 120 g of paraformaldehyde and 180 mL of methanol were mixed in a 500 mL round bottom flask with three entries, supplied with a thermometer, refrigerant, and an entry for the anhydrid hydrochloric acid obtained when concentrated HCl passes over an H_2SO_4 trap as dehydrating agent. The flask was injected intensely with bubbling anhydride hydrochloric acid until the formation of a two-layer solution. The system was kept in an isothermal bath between 1ºC (274,15 K) y 2ºC (275,15 K) during the whole reaction. The upper phase (CMME) was separated and stored in a dark flask with calcium chloride. After 40 h storage term, a distilled fraction between 56ºC y 58ºC (329,15 K and 331,15 K) was finally obtained (Pepper, Pasley, & Young 1953).

- Tin Tetrachloride IV, SnCl4. Tin tetrachloride was synthesized with the interaction of a chlorine current, Cl_2 (g), on metallic tin. Cl_2 (g), produced in the reaction between potassium permanganate and hydrochloric acid , is purified with sulfuric acid in a glass trap. The chlorine current passes through a glass tube equipped with a water cooling system and metallic tin inside. Furthermore, it has teflon plugs used as seals at the gas entry and exit tubes. Finally, the product is distilled after a 28 - hour storage term at about 114ºC (387,15 K) Jiménez (1942).

14 mL of chloroform and 4 g of polystyrene were added in a 125 mL round flask with two entrances, equipped with a condenser, a thermometer and magnetic agitation at room temperature. The solution was left under these conditions for a period of 20 minutes. Afterward, 7 mL of CMME were added with continuous agitation for 45 minutes. Then, 3 mL of CMME and 0,4 mL de $SnCl_4$ were added, drop by drop, to the mixture. The reaction was kept for a period of 8 hours. Upon the completion of the reaction, a white solid is observed. This white solid is more intense in the presence of ethanol. The solid was filtered with a 30 mL solution of 3:1 dionane-water, 20 mL of 1N 3:1 dioxane / hydrochloric acid, 10 mL of methanol and water until a negative test for chloride with a 2% silver nitrate alcohol solution was observed. Two more chloromethylation procedures were conducted in this study, changing the CMME, keeping the reaction time and the amount of polystyrene.

The functionalization degree was determined in each chloromethylation process, referred as the miliequivalent of the introduced group per gram of polymer using the Mohr's valuation method and the sodium fusion method. The inevitable crosslinking degree was determined by the reaction (Fischer, & Peters 1969; Bosch & Mateo,1993).

Ftalimide resin synthesis (3)

25 mL of N,N-Dimethylformamide (DMF) and 2 g of chloromethylated polystyrene were added to a round flask with 20-minute agitation and reflux. 0,6 g of Potassium ftalimide were added and the agitation was maintained for 8 hours. The solid formed was obtained after filtration and washing processes with methanol and distilled water (Belfer & Glozman, 1979; Salzberg *et al.,* 1942).

Polybenzylamine resin synthesis (4)

1,5 g of ftalimide resin and 25 mL of absolute ethanol were suspended in a 50 mL round flask. 0,4 mL of monohydrated hydracine were added after 20 minutes of soft heating and constant reflux and agitation. 35 mL of methanol were added after 8 hours. Then, the solid was purified with 20 mL of ethanol, 50 mL of 0,2 N NaOH solution and 100 mL of distilled water. The polymer obtained was placed in a heating stove for 4 hours at 50ºC (323.15 K) (Salzberg *et al.,* 1942).

Asphaltene (5)

The asphaltene fraction was obtained by precipitation with n-Heptane from a solid sample continuous extraction system. 70 g of Apiay asphalt and 250 mL of n-Heptane were deposited in an extracting recipient with siphon and lateral valve. Aftwerward, 300 mL of n-Heptane were placed in a 500 mL round flask with two entrances. The round flask was heated until the evaporation of an appropriate solvent amount. Vapors are conducted to the extracting recipient and condensed. This recipient is maintained with constant mechanical agitation for 50 minutes. After the agitation process, the system was left motionless for 20 minutes and the mixture was poured back into the 500 mL round flask through the lateral valve passage. This process repeated 7 times. Then, the asphaltene is purified and dried at 60°C (333,15 K) for 24 hours. The asphaltene extraction percentage was 20,5 %.

Diels-Alder synthesis of ssphaltene – maleic anhydride (6)

2 grams of asphaltene and 50 mL of toluene were placed in a 125 mL round flask with constant reflux agitation for 20 minutes. Then, 1,5 g of maleic anhydride were added, maintaining the reflux for 8 hours. The solvent was removed by distillation and the final product was washed with distilled water at 95°C (368,15 K) to remove any free anhydride in the reaction. Two more reactions were conducted, modfying the time, and keeping the amount of reagents (Fukusawa, & Masamune 1988; Larsen, Quay, & Roberts, 1991,1998).

Synthesis of polystyrene / asphaltene graft copolymer (7)

0,2 g of asphaltene modified with maleic anhydride and 0,13 g of benzylamine resin were placed in a round flask together with 7 mL of THF and 3 mL of acetic acid. The reaction was submitted to reflux during 16 hours with constant agitation. Upon the end of the reaction, 5 mL of methanol were added to the mixture. The product was initially purified with 20 mL of THF and 20 mL of methanol. Then, 6 mL of 1:1 benzene/ toluene solution and 3 mL of triethylamine were added. The mixture was submitted to reflux for 4 hours. The solvent was distilled and the product was filtrated and washed again with 15 mL of THF, 15 mL of methanol, 20 mL of 0,5 M HCl and 50 mL of water. Finally, the obtained copolymer was dried at 60°C (333,15 K) for 4 hours in a heating stove.

RESULTS

Polystyrene characterization

The average molecular weight for a zero concentration ($\eta.inh = 0,7404$) was established by adjusting tthe concentration values and inherent viscosities (Table 1) to the minimum square, using the Mark-Houwink ratio:

$$\eta = k*Mw^a; \quad 0,7404 = 1,7*10^{-4} *Mw^{0,69}$$
$$Mw \cong 187905 \text{ g/mol} .$$

Bands of the IR spectrum for polystyrene correspond to their functional groups, C-H aromatic tension 3081,2 cm^{-1} - 3001,11 cm^{-1}; 2923,91 cm^{-1} and 2850,40 cm^{-1} CH$_2$ asymmetric and symmetric tension; 1943,19 –1728,23 cm^{-1} aromatic ring monosubstitution; 1452,28 cm^{-1} deformation CH$_2$ + C=C of the aromatic ring; 1069,65 cm^{-1} flexion C-H in the plane (Figure 2).

Table 1. Flor and viscosity times

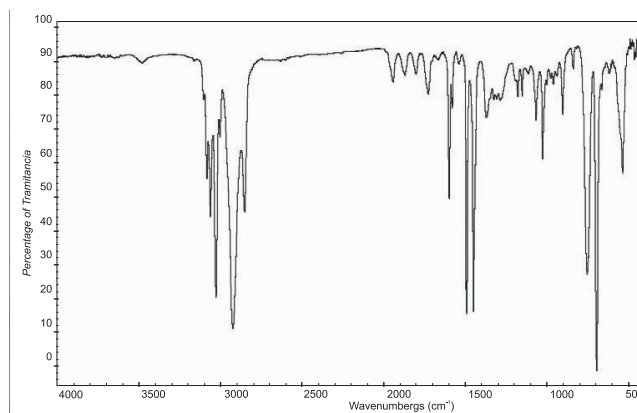| Conc. g/dl	Time	Ln. ηr	$\eta.inh$
Toluene, to.	200,09		
0,196	230,93	0,1429	0,7291
0,448	276,01	0,3216	0,7179
0,6	305,92	0,4242	0,7070
0,948	359,90	0,5871	0,6923
1,006	399,34	0,6910	0,6869

Figure 2. IR Polystyrene spectrum.

Solubility tests in toluene, benzene, THF, and Chloroform were conducted. Results indicate that the polystyrene used is of the linear type.

Polystyrene Chloromthylation

- Chloromethylmethylether characterization

Signals between 2995,35 cm⁻¹ y 2943,95 cm⁻¹ are observed in the IR spectrum of the chloromethylating agent. These signals correspond to the asymmetric and symmetric tension of CH_3, 1118,46 cm⁻¹ asymmetric stretching C-O-C, 1042,91 cm⁻¹ symmetric stretching C-O-C, and a medium intensity record in 923,64 cm⁻¹ corresponding to the characteristic stretching vibration of the C-Cl bond. The main physical properties such as refraction index and boiling point were 1,397°C and 61 ± 2,648°C (275,798 K) respectively. Table 2 shows the results for the functionalization and crosslinking degrees for polystyrene chloromethylation with different CMME quantities.

Table 2. Characterization of Chloromethylated Polystyrene

CMME mL	GF meqcl/g	% Cl	GE mmol/g	PS-Cl g.*
10	2,23	7,91	9,01	5,12
14	2,51	8,95	10,13	5,22
17	3,04	10,9	16,17	5,92

*PS-Cl Chloromethylated polystyrene

Modified polystyrene exhibits a chloromethyl group due to the appearance of an about 1267 cm⁻¹ band and an increase in the band of 840,67 cm⁻¹ due to the sum of the (CH_2Cl + $-CH_2$-) groups. The difference in band intensity is directly related to the functionalization degree reached thus confirming the reaction by the method employed.

Synthesis of ftalimide resin

The chloromethylated bands in 1267 cm⁻¹ and 840 cm⁻¹ corresponding to the CH_2Cl and CH_2Cl + CH_2 tension vibrations were eliminated in the reaction with potassium ftalimide. New tension signals appear for the carboxyle group at 1718 cm⁻¹ C=O, bond tension

between 1391 cm⁻¹ and 1346 cm⁻¹ for C-N-C and 1167 cm⁻¹ for the C-O group tension.

Polybenzylamine (P-NH2) resin Synthesis

The band assigned to the C=O group dissapeared in this synthesis. An N-H tension band appears close to 3400 cm⁻¹ and a flexion weak N-H_2 band appears between 1650 cm⁻¹ and 1640 cm⁻¹. The out-of-plane aromatic C-H tension band increases due to the substitution. A tension band at 1383,5 is obtained due to the C-N bond, indicating polystyrene ammination (Figure 3).
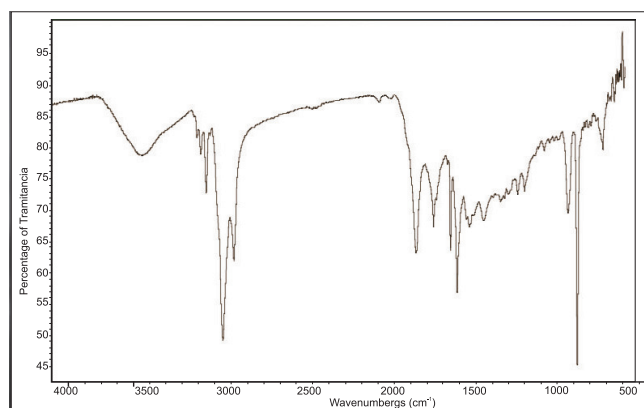

Figure 3. IR Spectrum of polybenzylamine resin

Obtaining asphaltenes

Asphaltenes show signals that correspond to aliphatic and aromatic structures. They show a band at 3452,25 cm⁻¹ whose origin is the OH tension and another band at 3024,32 cm⁻¹ as a result of the aromatic CH tension. Furthermore, asymmetric and symmetric elongation CH_2 band at 1598,9 cm⁻¹ corresponds to the C=C aromatic double bond. Signals between 1080 cm⁻¹ and 1030 cm⁻¹ appear in the region for heteroatom vibration frequency such as sulphur and nitrogen.

(Figure 4). band at 1598,9 cm-1 corresponds to the C=C aromatic double bond. Signals between 1080 cm-1 and 1030 cm-1 appear in the region for heteroatom vibration frequency such as sulphur and nitrogen. (Figure 4).

Figura 4. Aspahaltene IR spectrum.
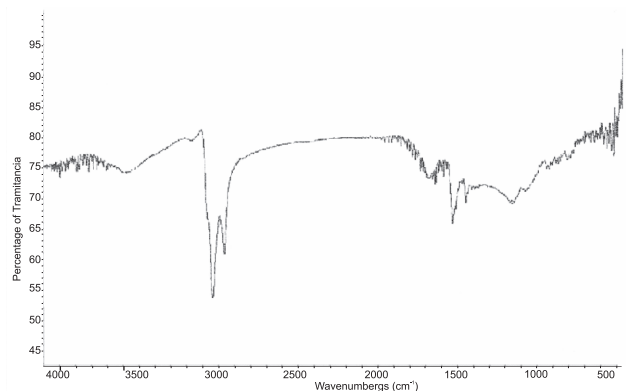

Figure 5. Asphaltene / maleic anhydride IR spectrum asfalteno

Asphaltene / maleic anhydride

Asphaltene was modified with different concentrations of maleic anhydride, keeping constant temperature. Based on the results and on the weight increment, it was established that the Diels-Alder reaction between asphaltene and maleic anhydride tends to reach an approximate constant value at 20%, as it is reported in the following table:

Table 3. Modification of asphaltene with maleic

Time, h.	Duct.	% Increment
6	2,362	18,1
12	2,384	19,2
18	2,396	19,9

The greatest interaction is observed in the zone whose wavelength ranges between 1900 cm^{-1} and 1600 cm^{-1}. As maleic anhydride concentration increases, the tension signal intensity C=O also increases around 1780 cm^{-1} and 1700 cm^{-1}, becoming more evident due to the contribution of the carboxyle groups from the anhydride molecule in the aromatic systems. The signals corresponding to the aromatic ring tension is reported around 1600 cm^{-1}. Flexion of the methyl groups at 1455 cm^{-1} and 1375 cm^{-1} is observed. Signals originated by C-O tension are evident again around 1223 cm$^{–1}$. Then, in the region between 900 cm^{-1} and 675 cm^{-1}, polysubstitution signals are confirmed in aromatic systems. (Figure 5). One characteristic between pure and modified asphaltenes is the notable band enlargement caused by the superposition of vibration modes of their complex molecules.
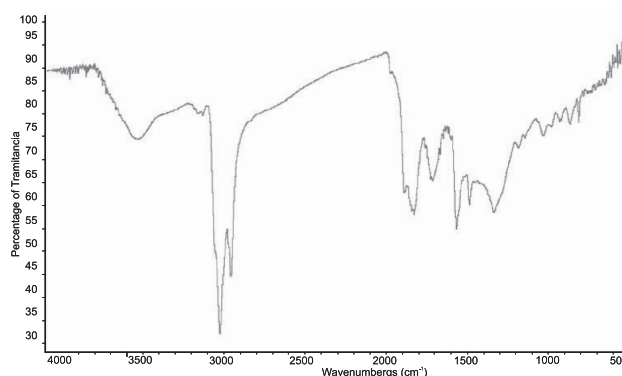
Modified asphaltene – polybenzylamine resin copolymer (amino-PS-co-ASP-AM)

For this research section, modified asphaltene with the greatest concentration of the anhydride group was selected. Then, this compound was submitted to reaction with different benzylamine resin concentrations (Table 4), keeping constant temperature and agitation.

Table 4. Polybencylamine Resin (P-NH$_2$) vs asphaltene-maleic anhydride (Asf-AM)

P-NH$_2$ g.	Asf-AM g.	Copolym g.	% Increment
0,065	0,1	0,106	63,2
0,101	0,1	0,168	66,3
0,129	0,1	0,214	65,99

Increased yield in copolymer formation (amine-PS-co-ASP-AM) is observed as a reaction product between the anhydride groups (O=C-O-C-=O) of the modified asphaltene and the amino functional groups present in the participant polybezylamine resin. Due mainly to the equilibrium between the crosslinking degree and its moderate chlorine percentage found in the starting functionarized polystyrene where it participates as an active site.

When comparing the copolymer formed to the preliminary compounds, it is possible to observe the substitution of the splitting band around 1780 cm^{-1} and 1700 cm^{-1} of modified asphaltene. Elimination of the N-H$_2$ weak flexion band in polybenzylamine between 1650 cm^{-1} and 1640 cm^{-1} is observed. Then, the new compound shows a clear intensity at approximate 1700 cm^{-1} for the carbonil group and a clear region between 1390 cm^{-1}-1370 cm^{-1} that corresponds to the C-N-C tension (Figure 6).
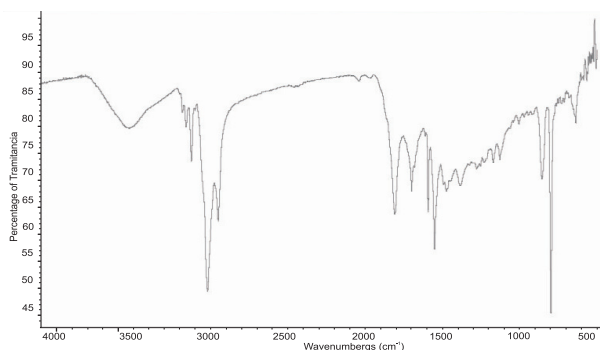
Figura 6. IR Spectrum of modified asphaltene - polybenzylamine Copolymer (amine-PS-co-ASP-AM)

Optic microscopy studies reveal the formation of two domains (phases) for the polystyrene-asphaltene mixture in a weight ratio 50/50 w (Figure 7). The induced effect of phase decrease in the mixture as a result of the addition of 1% of the new copolymer (Figure 8) is mainly due to the reduction in the interface tension of the polystyrene-asphaltene mixture, thus obtaining greater mixture homogenization finally.
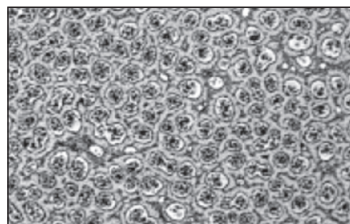

Figure 7. Asphaltene – polystyrene mixture 50/50 weight, magnification X 40
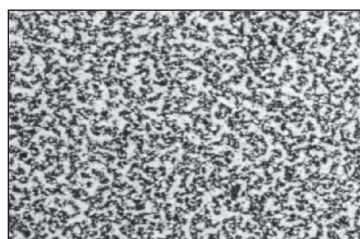

Figura 8. Asphaltene-polystyrene mixture 50/50 weight, with 1% of copolymer. magnification X 40

The corresponding IR spectra for each prepared resin from polystyrene to the amine-PS-co-ASP-AM copolymer are indicated in this work. Besides, clear modifications are observed as different functional groups are introduced. These groups are finally appreciated in each polymeric support. The optic characterization conducted

for each mixture proved that this copolymer forms different materials as the ones expected from a simple physical mixture. Therefore, based on the results, a new copolymer acting as compatibilizing agent for asphaltic mixtures was obtained.

Finally, the conduction of further studies for the application of the copolymer obtained in asphaltic mixtures is recommended in order to obtain suitable work conditions at industrial level for this process. The objective is to implement favorable modifications in the mixture rheological characteristics and physical properties.

CONCLUSIONS

- The Infrared spectroscopy analysis confirms the asphaltene - maleic anhidride Diels-Alder reaction with good selectivity. This reaction is characterized by the appeareance of bands corresponding to the new structure of the carboxyle group.

- Due to the high average molecular weight of polystyrene, this compound has an irreversible chain cross-linking. This problem can decrease the concentration of supporting active centres.

- A weight increment was obtained upon the completion of the copolymerization final synthesis of polybezylamina and the duct (modified asphaltene). This increase was induced by the selectivity of the amino group to form a macrostructure of imide character which is the target substance of this work.

- Characterization by optic microscopy proves that obtaining this new material from simple graft polymer reactions facilitated the capacity of improving heterogeneous mixture incompatibility, thus representing and advancement aiming a the application and use in the asphalt industry.

- In order to go deeper into this topic, it is recommended to continue with this research line for the creation of new materials from functionarized polymers, able to react chemically with asphalt components.

ACKNOWLEDGMENTS

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