Tests Modification of the Particulate Additive Test (PAT), for the determination of the SBR polymer content on Asphalt Binders

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ABSTRACT

As it is in many countries, Costa Rica is implementing the use of polymer modified asphalts for road construction. A growing market offers various types of polymers that significantly improve the rheological properties of the asphalts, like SBR, SBS, rubber, EMA, EVA among others, which are commonly added at percentages between 1 and 5% mass / mass of binder. However, little research has been conducted on quantifying the amount of polymer incorporated to the asphalt binders.

This study presents a modification to the Particulate Additive Test (PAT) proposed by Bahia et al. (2001) to determine in a qualitative and quantitative way the presence of SBR type polymers on local asphalts (PG64-22). Two types of SBR polymers were used. However, the scope of this methodology does not include the identification of SBS polymers.

The results obtained show an acceptable rate of polymer recovery. The results can be later verified by means of the Fourier Transform Infrared Spectroscopy (FTIR). Also the solvents can be changed to apply this method for SBS type polymers or other polymers, turning this method into a quick, easy and low cost quality control tool to verify the amount of polymer added to the plant asphalt mixtures.

INTRODUCTION

The use of modified asphalt binders is becoming a very common practice around the world. In 2001 only, Bahia et al. calculated that around 15% of the total annual tonnage of the binders used were modified binders. This number has been increasing in the last few years from 16 state agencies in the USA back in 2002, to 34 agencies according to a 2005 survey by the Association of Modified Asphalt Producers (AMAP). It is then predictable that by now more and more agencies are getting into the use of this type of binders to improve the performance of asphalt pavements. Costa Rica, as it is expected, is also taking this step into the modified binders with the use of several commercial type modifiers like SBR and SBS polymers, among others.

The performance analysis of these modified asphalt pavements can be assessed in a more precise way if the amount and type of modifier is measure in the field. Reaching the homogeneity of the asphalt binder is a difficult process and for this reason it is easy to find different distributions of one polymer at different points of the road. Also, due to the cost increase on the in-place HMA, it is beneficial to be able to follow a procedure to make sure that the percentage of modifier that should be use in the mixture is actually being added, as a quality control tool for asphalt pavement construction. For this reason, an easy, quick and low cost test to determine the amount of SBR polymer on asphalt binders can be of great benefit.

The objective of this research effort is to develop a method to quantify the content of a polymer modifier in asphalt binder by means of a modification of the Particulate Additive Test (PAT) which was developed by Bahia et al. (2001) as part of the National Cooperative Highway Research Program (NCHRP), Project 9-10, "Superpave Protocols for Modified Asphalt Binders".

This project, was developed to verify whether the binder and mixture test methods of Superpave®, and asphalt-aggregate mixture design and analysis system developed under the Strategic Highway Research Program (SHRP), are suitable for use with modified binders (1). The project had basically two objectives: a) to make the necessary recommendations to Superpave asphalt binder tests when modified binders are used and b) to identify potential problems with the Superpave mixture performance tests, when using modified binders.

As a result of this project, a test for determining the type and amount of additive used on the modified binder was developed. This test was called the Particulate Additive Test (PAT) which basically separates the additive from the asphalt. Once the additive is separated, its type and characteristics can be determined. To perform this separation, the PAT includes two solvents: n-octane and toluene. The first one is supposed to separate any additive from the binder, being then and indicator of the presence of a modifier, while the second one separates only additives that are not likely to be soluble in asphalt(1). This test was performed on approximately 50 modified binders of various grades, showing the n-Octane is a good solvent that can dissolve most additives that are believed to be compatible with asphalt (1,2).

After reviewing this study very carefully, the Transportation Infrastructure Program (PITRA) of LanammeUCR, developed the following method, by following the PAT procedure, with some important modifications, to redirect the method to a gravimetric approach instead of a volumetric approach, and using in this case a different selection of solvents to separate the binder components. The approach followed was to look for high quality commercial solvents to achieve the polymer separation. Taking into account the environment and cost, it is proposed to recover the used solvents by means of the rotary evaporator (Rotavapor).

LanammeUCR is looking to create a tool to improve the quality control for the binder modification process. This first stage quantifies the SBR type polymers and in a second stage other polymers like the SBS and others are targeted to be isolated and quantified through the use of other well know solvents of common use.

The modification to the test is explained in detail through this document, including the results obtained in the process.

MATERIALS USED IN THE STUDY

One asphalt binder source was used in the study since it is the only one produced in Costa Rica by the Costa Rican National Petroleum Refinery (RECOPE). This asphalt is classified as an AC-30 according to the classification currently used in Costa Rica which corresponds to a PG64-22. Two different types of Styrene-Butadiene-Rubber (SBR) were used as modifiers at different percentages (3.5% and 1.6%), according to Table 1. These types of modifiers have been used in the country as adhesion enhancers. The modification of the binder was conducted at a temperature of 150°C by means of a low shear mixer. Both modified binders changed their PG grade as shown in the table.

TABLE 1 Materials used for the study.

Binder Identification	PG of the Binder	Percentage of Polymer used	Polymer used
LPI (Original)	64-22	0.00	-
LPI + 2.5% m/m SBR (A)	70-22	2.50	UP-70
LPI + 1.6% m/m SBR (B)	76-13	1.60	Butonal NX-1138

Regarding the solvents used for this study, n-octane is originally used for the PAT, however it is considered a very expensive solvent (2) which sometimes is even difficult to get. For this reason it is convenient to look for alternate solvents with similar chemical properties in order to get similar results during the test procedures. Some chemical and physical properties of the solvents used for this study are shown on Table 2.

TABLE 2Physical and Chemical Properties for the solvents suggested.

Solvent	Boiling Point (°C)	Solubility Parameter, δ	Vaporization Latent Heat /cal	Chemical Formula	Density, g/cm^3
n-Octane	125.6	7.6	-	C_8H_{18}	0.7025
n-Heptane	98.4	7.4	76	C_7H_{16}	0.6838
n-Hexane	69.0	7.2	88	C_6H_{14}	0.6600
Toluene	110.6	8.9	83	C_7H_8	0.8669
Xylene	~138.5	8.8	82	C_8H_{10}	0.8801
Iso-Octane	99.3	6.9	-	C_8H_{18}	0.6919
Dichloromethane	39.75	9.9	79	CH_2Cl	1.3255
Trichloroethylene	86.9	9.3	57	C_2HCl_3	1.4559
Iso-propanol	82.5	11.5	159	C_3H_8O	0.7851
Methanol	64.7	14.3	263	CH_4O	0.7915

The main objective is to separate the polymer from the asphalt using one solvent or a mixture of them, taking always into consideration the variable of cost of the chemicals and also the environmental impact that their residues can cause. It is important to remember that most of these chemicals are dangerous toxic substances and their manipulation must be done by qualified personnel. For this study, some dangerousness parameters are considered regarding health, flammability, reactivity, skin absorption and also the Maximum Allowed Concentration (MAC). These parameters are shown in Table 3. Flammability and MAC are considered the most important parameters of all these. As it is shown, all the chemicals are highly flammable and the higher the MAC level, the greater risk they represent to human health.

TABLE 3Chemicals' Information (4 is extreme and 0 is minimum)

Solvent	Health Hazard	Flammability Hazard	Reactivity Hazard	Contact Hazard	MAC /ppm[a]
n-Octane	1	3	0	1	500
n-Heptane	1	3	0	1	500
n-Hexane	2	3	0	1	100
Toluene	2	3	0	2	200
Xylene	2	3	0	1	200
Iso-Octane	1	3	0	1	510
Dichloromethane	2	3	0	2	500
Trichloroethylene	2	3	0	2	100
Iso-propanol	1	3	0	1	400
Methanol	2	3	0	2	200

[a] MAC: by definition, the average concentration of solvent in the environment that can be applied on a repeated exposure (8 hours a day, 5 days a week) during a professional work life length, without causing a harmful health effect.

In all cases, the use of Personal Protection Equipment is mandatory during the testing. The separation testing was performed with Dichloromethane with a MAC value of 500 and n-Hexane with a MAC value of 100.

TESTING PROCEDURES

The Particulate Additive Test (PAT) device can be built in many ways with different filtering systems. Many commercial suppliers are in capacity of selling the different pieces. The configuration of the device used for this modification uses a 75µm filter on a metallic ring placed over a Buchner Funnel. This configuration was proposed by the Materials and Pavements Unit at LanammeUCR. A scheme of the original configuration developed by Bahia et al. (1) is shown on Figure 1.

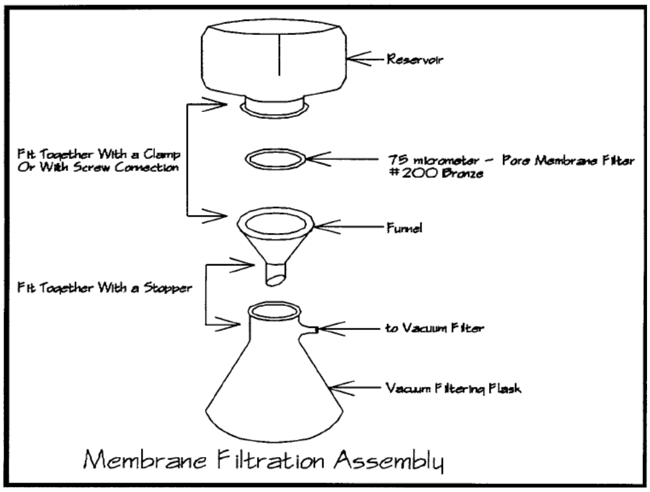

FIGURE 1 PAT Testing Scheme (Source: NCHRP Report 459)

The procedure followed for the testing is based on the original procedure with slight differences to accommodate the use of the new solvents. The complete suggested procedure is as follows.

Proposed Procedure to Estimate the SBR Polymer Content on Asphalt Binders

1- Three replicates of this test have to be done to assure its precision and accuracy.
2- Heat and agitate the modified asphalt binder to be analyzed at 135 ± 3°C in a 1000 mL beaker until it is fluid enough to pour.
3- Weigh a 75 µm membrane filter on a semi-analytic scale at room temperature y register the mass to the 0.001 g (M_2).
4- Pour 200 mL of n-hexane or n-heptane into a 250mL Erlenmeyer Flask and heat it to a temperature of 80°C. Prolonged heating processes generate unwanted evaporation losses of the solvent. These gases are flammable. To make a third replicate the flask has to be filled again with the solvent and heated in the oven since it can be dangerous to heat higher quantities of solvent.
5- Once the modified asphalt binder is fluid and homogeneous, zero a 250 mL Erlenmeyer Flask (with a known mass to the 0.001g) and weigh 10 ± 1 grams on a precision scale of 0.1g. Get the mass to the 0.001 g of the flask with the sample and write down the mass of the binder sample alone by subtraction to the 0.001g (M)
6- To the Erlenmeyer flask that contains the 10 ± 1 grams of the binder sample, add 100 mL of n-hexane ACS (or n-heptane) previously heated at 80°C. Shake gently to dissolve. Maintain the 80°C temperature for 10-12 minutes while the modified asphalt binder fully dissolves. Work on one replicate at a time.
7- Ensemble the filtration device as it is shown in Figure 2. Make sure the membrane filter is well placed.
8- On a 500 mL wash bottle, pour 200 mL of n-hexane (or the solvent used) and write its name on the bottle. On a second wash bottle pour 400 mL of Methylene Chloride. Do not use the solvents directly from their bottle; pour the necessary quantity on a 400 mL glass beaker.
9- When the asphalt binder is completely dissolved, turn on the device and filter the solution by decantation using a glass agitator to make sure the solution is well distributed on the 75 µm filter. When using the configuration on Figure 2, make sure not to reach a level of solution above the height of the filter (9 mm) to avoid the loss of the sample. The sample must be transferred from the Erlenmeyer flask on a quantitative way. Rinse the flask with n-hexane until the full sample passes the separation filter.
10- Once the filtration is over, turn off the device and use the n-hexane wash bottle to clean the filter. Using the glass agitator, mix the filter residue while washing until the liquid that comes out of the filter is clear of straw color.
11- Replace the vacuum flask that contains n-hexane with a dry and clean one. The solvent can be recovered by means of the rotary evaporator. An alternative to follow for this procedure is explained at the ASTM D5404 procedure.
12- Using the wash bottle containing the Methylene Chloride, moisten and mix the filtration residue very carefully with an agitator, making sure of not wasting the sample. Continue adding the solvent and mixing while using the vacuum device until the liquid that comes out of the filter is clear or straw color. It is convenient to wash the Erlenmeyer containing the sample with Methylene Chloride and filter the liquid to make sure that the full sample was transferred.
13- Remove the filter containing the residue and leave it at room temperature on a dryer for 60 minutes.
14- Get the mass of the filter and residue to the 0.001g (M_1).
15- Get two other replicates of the residue, by following the whole procedure described above.
16- Remove the vacuum flask containing the Methylene Cholride. This solvent can be recovered by means of the rotary evaporator. An alternative to follow for this procedure is explained at the ASTM D5404 procedure.

17- Calculate the percentage mass of SBR polymer particles bigger than 75µm of each replicate by using the following equation.

$$\text{SBR Polymer content, m/m/ \%} = [(M_1\text{-}M_2)/M] \times 100$$

Where,

M_1 = mass of the filter and residue in grams
M_2 = mass of the filter in grams
M = mass of the modified asphalt binder used (~10 ± 1) in grams

FIGURE 2 PAT Proposed Testing Scheme (Source: LanammeUCR)

TESTING RESULTS AND DATA ANALYSIS

The results obtained from the modified PAT procedure are shown on Table 4. Seven samples were modified with a 2.5% of emulsified polymer SBR. The latex was incorporated to the asphalt by using a shear mixer for three hours at 155°C. The results obtained for asphalt binder modified with another SBR polymer at 1.6% are also shown on the table.

TABLE 4Results obtained from the SBR polymer recovery

Sample	Asphalt Binder mass /g	Recovered Polymer mass /g	% of SBR polymer
LPI IV (Original)	12.460	0.000	0.000
LPI IV + 2.5 % m/m SBR (A) 1	9.989	0.233	2.332
LPI IV + 2.5 % m/m SBR (A) 2	10.464	0.246	2.351
LPI IV + 2.5 % m/m SBR (A) 3	9.765	0.256	2.621
LPI IV + 2.5 % m/m SBR (A) 4	9.435	0.219	2.321
LPI IV + 2.5 % m/m SBR (A) 5	9.383	0.246	2.622
LPI IV + 2.5 % m/m SBR (A) 6	11.482	0.290	2.526
LPI IV + 2.5 % m/m SBR (A) 7	9.483	0.209	2.204
LPI III + 1.6 % m/m SBR (B) 1	9.919	0135	1.351

The washing procedure can be critical for this test. It should be done with the solvent until the passing liquid is clear. An insufficient washing process would implicate a bigger recovered mass, due to the presence of asphaltenes. In the other hand a very intensive washing process may force the polymer particles to go through the filter. The use of a N°325 screen is possible for this test, even though its effectives hasn't been proven.

Solubility tests were performed on the SBR emulsified polymers. Water was evaporated on both polymers in an oven at 70°C. Once they were dry, 2.000 grams of each sample were placed on a 250 mL Erlenmeyer and 100 mL of solvent was added. The samples were shaken for 60 minutes to try to dissolve them and later they were decanted very carefully. The change on the mass of the sample due to dissolved material is calculated. The results obtained are shown on Table 5.

TABLE 5Results obtained from the SBR polymer solubility (Loss Percentage)

Sample	% Solubility on Trichloroethylene ACS	% Solubility on Dichloromethane ACS	Previous Process
SBR (A) UP-70	1.36	1.23	Water Evaporation at 70 °C
SBR (B) Butonal NX-1138	0.34	1.58	Water Evaporation at 70 °C
SBS	Not recoverable	Not recoverable	-
Elvaloy	Not recoverable	Not recoverable	-

The loss percentages are very low meaning that more than 98.4% of the polymer is recoverable. For the cases of Elvaloy and SBS, these have a greater solubility, and the loss is very big once the asphaltenes are washed with the solvent. For this reason, it is not possible to recover the polymers.

Information about the solubility tests of common polymers and several solvents of common use in the laboratory are shown on Table 6. This information can be very useful to determine which solvent is effective at separating a polymer from the asphaltenes. For example, to separate the asphaltenes from the Elvaloy, Dichloromethane can be used at a temperature near to 0°C. Additionally, a biodegradable solvent Carroll DG90 is also included.

TABLE 6 Solubility results for several solvents

Solvent	SBR (A)	SBR (B)	SBS	Elvaloy	Asphaltenes
n-Hexane ACS	Insoluble	Insoluble	Insol+Swe	Insoluble	Insoluble
n-Heptane ACS	Insoluble	Insoluble	Insol+Swe	Insoluble	Insoluble
Toluene ACS	Soluble	Soluble	Part. Solub.	Soluble	Soluble
o-Xylene ACS	Insoluble	-	Part. Solub.	Part. Solub.	Soluble
o-Xylene ACS Cold	Insoluble	-	Part. Solub.	Part. Solub.	Part. Solub.
Iso-Octane ACS	Soluble	Soluble	Part. Solub.	Insoluble	Soluble
Iso-Octane ACS Cold	-	-	Insoluble	Insoluble	Insoluble
n-Octane ACS	Insoluble	Insoluble	Insol+Swe	Insoluble	Insoluble
Methanol ACS	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Ethanol ACS	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Iso-Propanol ACS	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

TABLE 6 Solubility results for several solvents (Contd)

Solvent	SBR (A)	SBR (B)	SBS	Elvaloy	Asphaltenes
Oil Ether ACS	-	-	Part. Solub.	Insoluble	Insoluble
Acetone ACS	Insoluble	Insoluble	Insol+Swe	Insoluble	Insoluble
Dichloromethane ACS	Insoluble	Insoluble	Part. Solub.	Soluble	Soluble
Dichloromethane ACS Cold	-	-	Part. Solub.	Insoluble	Soluble
Trichloroethylene ACS	Insoluble	Insoluble	Part. Solub.	Part. Solub.	Soluble
Tetrahydrofuran ACS	Soluble	Soluble	Soluble	-	Soluble
Carbon Tetrachloride ACS	Soluble	Soluble	Soluble	-	Soluble
Ethyl Acetate ACS	-	-	Soluble	Insoluble	-
Acetonitrile ACS	-	-	Insoluble	Insoluble	Insoluble
Diethyl Diamine ACS	-	-	Insoluble	Insoluble	-
Kerosene	-	-	-	-	Insoluble
Carroll DG90	-	-	Part. Solub.	Part. Solub.	Soluble

Part Solub: Partially Soluble
Insol + Swe: Insoluble + Swelling presence

FINDINGS AND CONCLUSIONS

This test method is valid for SBR type Polymers, being necessary to check the applicability for other polymer types. The test was not successful on recovering SBS type polymers.
The test was designed considering the Particulate Additive Test with a few modifications to make it applicable to determine the SBR type polymer content mixed with the asphalt binder. The test method suggested can be use either for qualitative and quantitative purposes. The effectives of these types of modifiers are well known when improving the properties and performance of asphalt mixtures.However, recovering the polymer after being added to the binder requires a big effort since the asphalt matrix is very complex and also when polymers are added, the homogeneity of the binder is not always achieved. The results obtained during the repeatability testing (Table 4), confirm this last statement, since the percentage of recovered polymer was not fully precise when comparing with the original amount of polymer added.
Not polar solvents like n-hexane and n-heptane cause precipitation and flocculation of the asphaltenes of higher molecular weight along with the added modifiers. Polar solvents like the Toluene and citric based cleaners fully dissolve the asphalt binder. These results were also noted by Bahia et al. during project 9-10 (1).
The solvents Dichloromethane and Trichloroethylene don’t interact enough with the SBR type polymers, which make them ideal to achieve the separation. The testing with the two commercial SBR polymers didn’t show a significant loss of the polymer during the whole procedure. These are however halogenated solvents and for this reason they are not an environmental friendly option.
Future research on this matter will be related to the identification of the recovered polymers by means of the Fourier Transform Infrared Spectroscopy (FTIR) to compare them with the original spectra. Also some other solvents are to be analyzed to evaluate the capacity of recovering SBS type polymers and other common use polymers.

RECOMMENDATIONS

This method is recommended as a simple and quick test with a low cost device and chemical materials, in comparison with the use of the FTIR and calibration curves. The test can be used on a qualitative way to prove the presence of SBR polymer or a quantitative way to determine the amount of polymer mixed with the asphalt binder, which can work as an excellent quality assurance tool in the field. If it is necessary to recover an SBS polymer, it is recommended the use of a different solvent since this method can only recover this polymer partially.

REFERENCES

1. National Cooperative Highway Research Program, NCHRP, “Report 459 Characterization of Modified Asphalt Binders in SuperPave Mix Design”, Appendix I Standard Test Method for Determining the Content of Solid Additives in Asphalt Binder Using the Particulate Additive Test (PAT) Device, C-1-1 a C-1-4, 2001.
2. Federal Highway Administration, FHWA, U.S. Department of Transportation, “Evaluation of the Particulate Additive Test, Publication NO. FHWA-HRT-04-110, 32 pages, 2004.
3. *AASHTOStandard Specifications for Transportation Materials and Methods of Sampling and Testing*. “Standard Method of Test for Solubility of Bituminous Materials.” AASHTO Designation: T 44-97. Washington, D.C., 25th edition, 2006.
4. *ASTMAmerican Society for Testing and Materials. “Standard Method of Test for Solubility of Asphalt Materials in Trichloroethylene.”* ASTM Designation: D 2042-09. ASTM standards online, USA, 2012.
5. ASTMAmerican Society for Testing and Materials. “Standard Test Methods for Quantitative Extraction of Bitumen from Bituminous Paving Mixtures.” ASTM Designation: D 2172-11. ASTM standards on line, USA, 2012.
6. ASTM American Society for Testing and Materials.“Standard Practice for Recovery of Asphalt from Solution Using the Rotary Evaporator.” ASTM Designation: D 5404-11.ASTM standards on line, USA, 2012.
7. Grzybowski, K. The Minuses of Plus Specifications. Association of Modified Asphalt Producers, February 2005. Available at http://modifiedasphalt.org/educational-library/case-studies#_2005. Accessed July 29, 2012.