
Use of Waste Products as Bitumen Modifiers in Costa Rica

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ABSTRACT. Costa Rica is a tropical country that spans an area of 52,000 Km², but has a biodiversity that corresponds to 5% of the world. However, as is the case in most countries there are great difficulties in managing the non-biodegradable wastes that come from the Industry. Because of the volume of bitumen that is required each year, a feasible method of disposing waste materials is to use some of them as bitumen modifiers.

As part of this research, polyethylene bags, styrofoam, tire rubber, and car bumper material have been evaluated as possible bitumen modifiers. The homogenization process of the waste material inside the bitumen matrix was evaluated by means of Atomic Force Microscopy (AFM). Additionally, the properties of the waste materials were evaluated by means of physical-chemical and calorimetric tests, and the performance of the modified bitumen was analyzed by means of creep, multi stress creep recovery, and fatigue tests. The degradation temperatures of the waste materials were considerably above the bitumen modification temperatures.

The original bitumen corresponds to an AC-30 with a PG grading of PG 64-22. It was identified that all of the modifiers reduce the deformation by at least 50% after 250 loading cycles of repeated creep and with the exception of the polyethylene bag modified bitumen, all of the modified bitumens can be used in high traffic applications. Additionally, most of the modified bitumens exhibited a significant gain on fatigue resistance. Furthermore, using the waste materials as bitumen modifiers not only improves bitumen performance but is also a means of disposing of the material.

KEYWORDS: modified bitumen, recycling, waste materials, performance.

1. Introduction

The high performance requirements that asphalt pavements are currently subjected results in the need of ensuring that the bitumen properties to be used in a given project be adequate for withstanding the traffic and environmental demand. However, in many cases the high traffic volume, traffic loads, and tire pressures that an asphalt pavement will have to support require that the available bitumens be modified. The modification of the bitumen can serve two purposes: 1) ensure that the bitumen performs properly over a given range of service temperatures (change in high and low temperature grades), 2) improving the pavement response under specific critical service conditions (eg. high percentages of slow moving heavy vehicles), or 3) improving the durability and aging characteristics of the bitumen (Woo *et al.*, 2007).

Many types of materials can be added to the bitumen to serve as modifiers. The most common commercial modifiers consist of elastomeric polymers such as styrene-butadiene-styrene (SBS) and styrene-butadiene-rubber (SBR), which are polymers with a flexible matrix and large side chemical strains. Other types of polymers, such as plastomers, are also used (e.g. polyethylene and ethylene-vinyl-acetate [EVA]). Furthermore, materials such as hydrated lime, ash, crushed glass, elemental sulfur, polyphosphoric acid, and gilsonite are also used (Bahia *et al.*, 2001; West *et al.*, 1993; Styron *et al.*, 1993).

However, when considering the continuous increase in the cost of bitumens (NDOT, 2012) and the overall cost of modified bitumen with a typical commercial additive, the search for alternative modification materials becomes more attractive. In general, modified bitumen can increase the cost of the original bitumen between 60% and 150% (Coomarasamy *et al.*, 1998). In this sense, the use of recycled materials as feasible bitumen modifiers can be an economical alternative to typical commercial modifiers. Additionally, using recycled materials as bitumen modifiers has the increased benefit of reutilizing materials that in many cases end up in open pits where they can also result in a negative impact on the environment.

1.1. Recycled Materials as Pavement Modifiers

With the exception of recycled polyethylene, there is little experience in the use of recycled materials as bitumen modifiers. More specifically, most of the research on the use of recycled polyethylene has to do with crumb rubber (Palit *et al.*, 2004). Typically research on polyethylene modified bitumen results in improved fatigue and permanent deformation characteristics. Additionally, this type of modified bitumen exhibits lower temperature susceptibility and greater resistance to moisture damage (Gallego-Medina, 2003; Oda *et al.*, 2002). However, based on reported experiences, it seems that only in few cases (e.g. crumb rubber) the modification has been implemented for field application.

The authors believe that one of the reasons why the use of this type of materials as bitumen modifiers has not been widespread is the lack of available recycling plants that can readily process a given material into conditions that are optimal for its incorporation into the bitumen. The incorporation process in plant might also require some additional equipment / tuning. However, the global concern for more conscious waste management and minimization of waste is resulting in a growing trend on recycling and reprocessing materials.

In the case of Costa Rica, high density polyethylene from the bags that are used to wrap bananas during production has recently been evaluated as a feasible bitumen modifier (Villegas-Villegas *et al.*, 2012). This has been important at the local level since the disposal of hundreds of tons of the material has become troublesome with the added complexity that the bags are impregnated with chlorpyrifos which is hazardous to humans and the environment. The initial results of using the bag as a bitumen modifier indicated that the bag provides an improvement on the resistance of the bitumen to permanent deformation and provide the added benefit of eliminating the chlorpyrifos from the environment since it degrades during the mixing process of the bitumen and the modifier.

Based on this experience is that the authors will evaluate the use of other waste materials that have been considered as feasible bitumen modifiers: styrofoam, car bumper, tire rubber, and polyethylene bags. More specifically, the objective of the paper is to assess the feasibility of incorporating the previous waste materials into the bitumen and to evaluate the related changes in its performance, specifically on plastic deformation and fatigue.

2. Materials and Analysis Methods

The tests to characterize the bitumen and modifiers were performed at the National Laboratory for Materials and Structural Models (LanammeUCR, Universidad de Costa Rica), in collaboration with the National Nanotechnology Laboratory (LANOTEC) and the Polymers Laboratory at the National Learning Institute (INA).

The base bitumen that was used is a viscosity grade AC-30 obtained from RECOPE (Costa Rican Petroleum Refinery). This bitumen corresponds to the most common bitumen used in Costa Rican roads. The waste polyethylene bags correspond to a high density polyethylene (HDPE). The car bumper material was identified as a thermoplastic olefin (TPO) which is a polymer filler blend which can include rubber, talc, carbon fiber, fiber glass, polypropylene, polyethylene, block copolymer polypropylene, or other fillers. The styrofoam corresponds to a polystyrene and tire rubber is typically a composition of three polymers: polyisoprene (natural rubber), polybutadiene and polystyrene-butadiene (Quek *et al.*, 2012). The main compounds in the analyzed waste materials are shown on Figure 1.

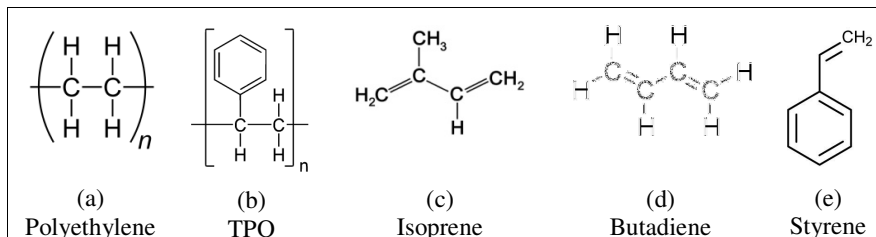


Figure 1. Main compounds in analyzed waste materials

2.1. Material Analysis

Both the waste materials and the modified bitumen were evaluated. The bitumen was characterized using the Superpave methodology, based on the PG grading of the material before and after the modification. The waste materials were analyzed based on their calorimetric curve, thermal transition, distribution in bitumen after modification, and overall quality.

The analysis of the waste materials was performed by means of Thermogravimetric Analysis (TGA), Differential Scanning Calorimeter (DSC) Sweep, and Fourier Transform Infrared (FTIR) Spectrometry. In the case of the material composition analysis and performance of the original and modified bitumen, Iatroscan Chromatography (original bitumen), Atomic Force Microscopy (AFM), and Fourier Transform Infrared (FTIR) Spectrometry were used. For analyzing the performance of the bitumen during its service life, the bitumen was aged using the Rolling Thin Film Oven (RTFO) and the Pressure Aging Vessel (PAV), and was analyzed using a Dynamic Shear Rheometer (DSR) under repeated creep (NCHRP 459), Multiple Stress Creep Recovery (MSCR) (AASHTO TP70-07), and fatigue under controlled displacement (NCHRP 459).

3. Results

3.1. Characterization of the Waste Materials

The modifiers were incorporated into the bitumen as per the following dosage by weight of bitumen: polyethylene bag (3%, 4 x 4 cm fragments), car bumper (3%, material passing sieve No. 30), styrofoam (1,5%, as provided by recycling plant - approximately retained in sieve No. 8), and tire rubber (3%, material passing sieve No. 50). For reference purpose a commercial SBS (2,5%) and SBR (2,5%) were also included in some cases to compare to the waste materials.

Differential Scanning Calorimetry Analysis was performed to observe sample behaviour due to the change on temperature in a range from 25°C up to 200°C (Elseifi *et al.*, 2010; Daly *et al.*, 2010). Based on the data collected by the DSC analysis, the fusion temperature (T_f) and the glass transition temperature (T_g) were determined when possible. The T_f and T_g were then used in determining the optimum temperature at which the waste material can be incorporated into the bitumen. Figure 2 shows the DSC results for the 4 different waste materials.

Both the polyethylene bag and the bumper material (TPO) exhibit crystalline structures. Consequently, both of the materials exhibit a well defined T_f . In the case of the polyethylene bag, where the $T_f \approx 122$ °C, a higher modification temperature of 145 °C was selected to ensure that the viscosity of the bitumen was low enough so that the polymer was properly incorporated into the bitumen matrix. The modification process was performed in the laboratory by means of a low shear stirrer.

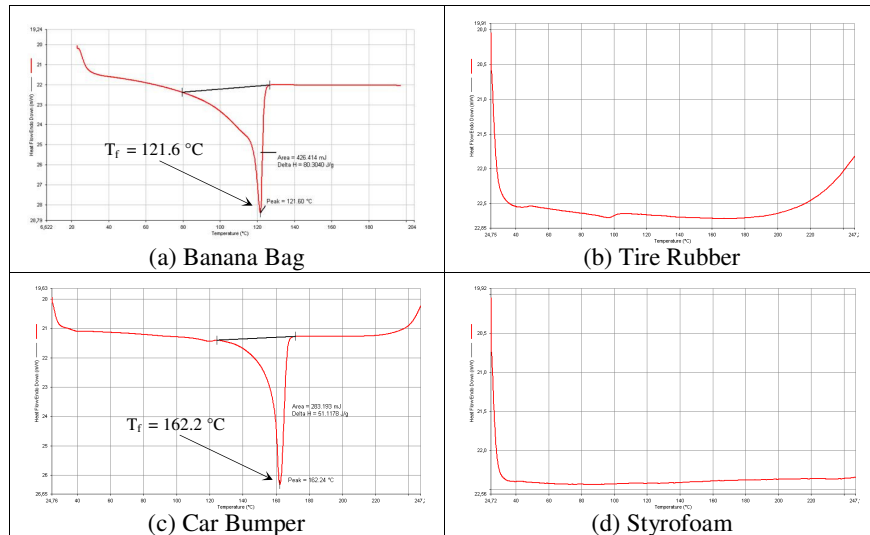


Figure 2. DSC analysis of waste materials

In the case of tire rubber and the styrofoam (polystyrene), due to their amorphous nature, do not present a well defined T_f , but exhibit a T_g . Based on the T_g the modification temperature can be defined at approximately 170 °C.

The Thermo Gravimetric Analysis (TGA) is used in determining the degradation temperature of the waste materials. A modifier that begins to degrade at a temperature below the bitumen modification temperature or the asphalt production temperature is not adequate since it will have lost its initial properties by the time the modification process is finished. In the case of the analyzed waste materials, all

degrade at temperatures above 200 °C and therefore, should be adequate for bitumen modification (Figure 3).

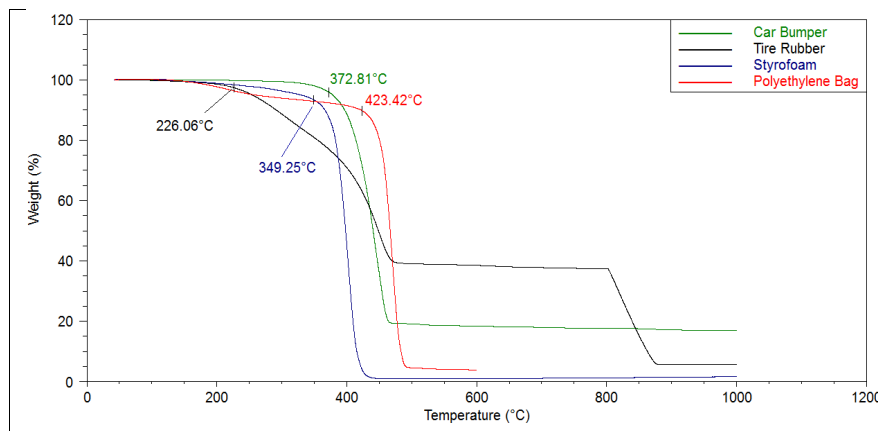


Figure 3. TGA analysis of waste materials

3.2. Characterization of the Virgin and Modified Bitumen

A chromatography analysis made with the Iatroscan chromatographer show that the SARA fractions of the virgin bitumen are distributed as follows: Saturated 5,4%, Aromatics 35,3%, Resins 41,4% and Asphaltenes 17,9% (Stability index = 0.3).

The binder characterization was performed following the Superpave methodology for the original bitumen, the short term aged bitumen (RTFO) and the long term aged bitumen (RTFO+PAV). Table 1 shows the Superpave characterization results for the unmodified and modified bitumens at the three different aging conditions.

To characterize the performance of the bitumen, the repetitive creep test was used. The results are shown on Figure 4. The test which is performed at 70°C consists of subjecting the sample to 250 load cycles (the selected temperature corresponds to a base PG grade that all the modified bitumens meet). The applied shear stress is 100 Pa, the defined creep time is 1,0 second, and the recovery time was 9,0 seconds according to test specifications (NCHRP 459).

The figure indicates that all of the modifiers results in a cumulative permanent deformation significantly lower than that of the unmodified bitumen. The polyethylene bag, which showed the smallest improvement resulted in a cumulated permanent deformation approximately 50% lower than that of the unmodified bitumen. The remaining modifiers performed exceptionally well and resulted in permanent deformations smaller than those exhibited by bitumens modified with SBS and SBR that have been used in Costa Rica.

Table 1. Rheology analysis of the modified bitumen

G*/sinδ ≥ 1 kPa, Original Bitumen					
Test Temperature	64 °C	70 °C	76 °C	82 °C	True PG
AC-30	1,78	0,89	0,47	----	69,0
Polyethylene Bag	3,11	1,53	0,80	----	73,9
Car Bumper	----	2,92	1,47	0,78	79,6
Styrofoam	3,63	1,79	0,91	----	74,2
Tire Rubber	----	2,45	1,28	0,70	78,4
SBR	3,00	1,52	0,81	----	73,9
SBS	3,60	2,04	1,19	----	78,0
G*/sinδ ≥ 2,2 kPa, RTFO-aged Bitumen					
Test Temperature	64 °C	70 °C	76 °C	82 °C	True PG
AC-30	5,97	2,94	1,47	----	72,4
Polyethylene Bag	11,31	5,55	2,77	1,35	77,8
Car Bumper	----	----	2,88	1,50	78,4
Styrofoam	----	4,65	2,33	1,20	76,5
Tire Rubber	----	----	2,51	1,34	77,2
SBR	9,23	4,87	2,60	1,19	76,8
SBS	13,84	8,13	4,89	2,17	82,4
G*·sinδ ≤ 5 MPa, PAV+RTFO-aged Bitumen					
Test Temperature	Intermediate Temp. (°C)	MPa			
AC-30	22	4,14			
Polyethylene Bag	22	4,14			
Car Bumper	25	4,44			
Styrofoam	25	4,15			
Tire Rubber	22	4,34			
SBR	13	4,20			
SBS	22	4,89			

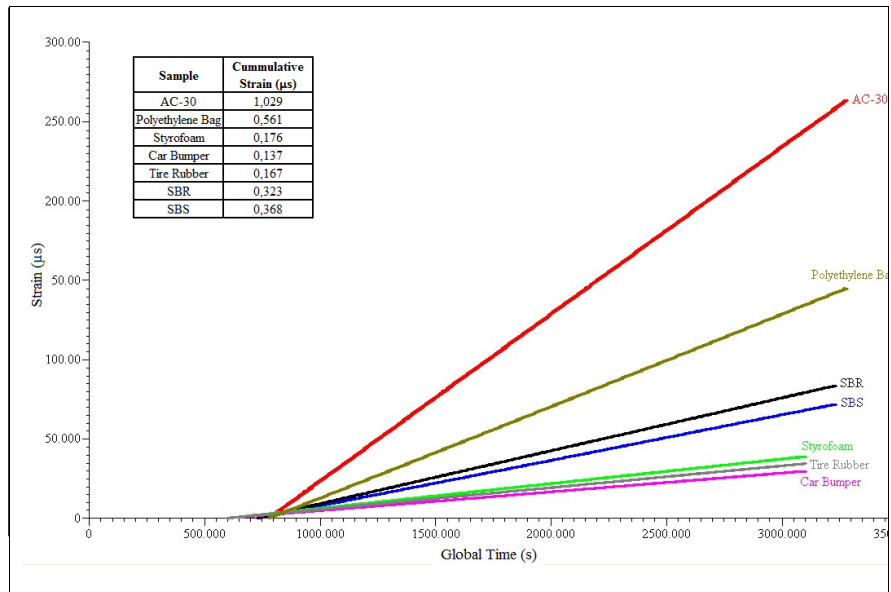


Figure 4. Repeated creep comparison for the unmodified and modified bitumens

Table 2 shows the performance of the bitumen modified with the different materials, when analyzed with the Multiple Stress Creep Recovery (MSCR) test for permanent deformation. The results confirm the observations from Figure 4 and indicate that for several of the cases the modified bitumen can be used in high demand projects. More specifically, the bitumen modified with car bumper, Styrofoam, tire rubber and commercial SBS can be applied to high traffic pavements. This is important since, based on the MSCR criteria, the unmodified bitumen should only be used in low volume roads (high performance gain).

Table 2. Results of the MSCR Test (ASTM – D7405)

Polymer	Result	J _{NR@3,2KPa}	$\frac{(J_{NR@3,2KPa} - J_{NR@0,1KPa})}{J_{NR@0,1KPa}}$
AC-30	---	7,344	0,22
Polyethylene Bag	Standard Traffic	3,180	0,26
Car Bumper	High Traffic	1,476	0,25
Styrofoam	High Traffic	1,952	0,24
Tire Rubber	High Traffic	1,831	0,32
SBR	Standard Traffic	3,284	0,37
SBS	High Traffic	1,575	0,26

Traffic Conditions	J _{NR@3,2KPa}	$\frac{(J_{NR@3,2KPa} - J_{NR@0,1KPa})}{J_{NR@0,1KPa}}$
Standard Traffic (< 1x10 ⁷ ESALs)	< 4	< 0,75
High Traffic (1x10 ⁷ – 3x10 ⁷ ESALs)	< 2	< 0,75
Very High Traffic (> 3x10 ⁷ ESALs)	< 1	< 0,75

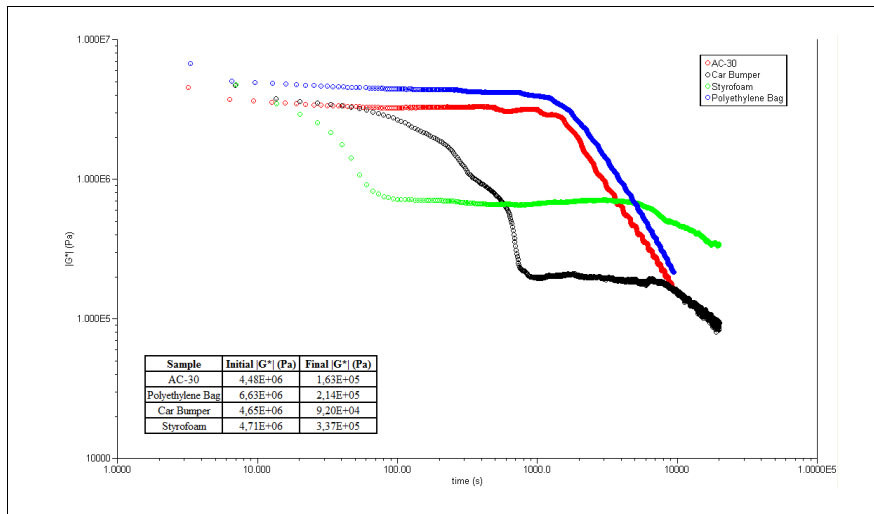


Figure 5. Fatigue analysis for the unmodified and modified bitumens

Fatigue analysis was also performed. The analysis was performed at 25°C using an angular frequency of 10 rad/s, under strain controlled mode (10%) following NCHRP 459 recommendations (the selected temperature corresponds to a base PG grade for intermediate temperatures that all the modified bitumens meet). The results are shown in Figure 5. It was found that, with the exception of the polyethylene bag modified bitumen, the tertiary stage the modified bitumens is increased over 5 times that of the unmodified bitumen. This is an indication that the fatigue resistance of the modified bitumen is increased.

The analysis of the modifier distribution on the bitumen was performed using Atomic Force Microscopy (AFM). This test shows information on the topography and the tridimensional environment of the sample, and also on the roughness of the material. The AFM images of the distribution of modifiers within the bitumen matrix are shown on Figure 6. The image shows the differences in the way that the modifier is incorporated into the bitumen. Note that in the case of tire rubber there are particles that were not properly incorporated into the bitumen. This is an indicator that the material should be incorporated to the bitumen in smaller particles than the ones used.

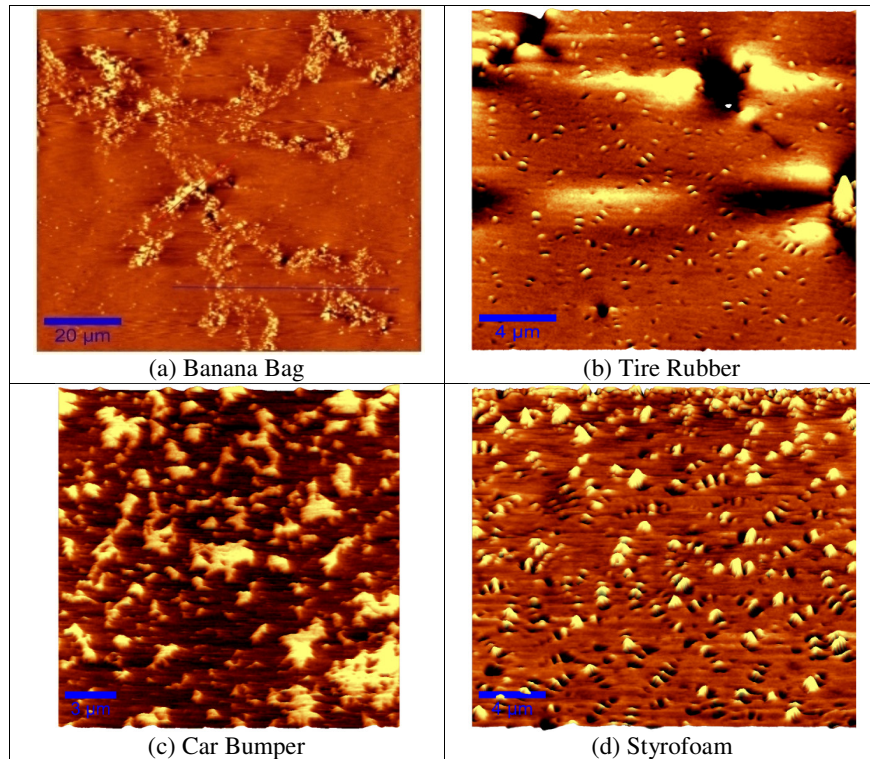


Figure 6. *AFM topography for modified bitumens*

Finally, infrared spectroscopy was performed for all the samples (Figure 6) to characterize the molecular structure of the materials (Kuptsov, 1994; Wei *et al.*, 1996). The FTIR spectrum of the unmodified bitumen has the following characteristic bands: 2851-2920 cm^{-1} high intensity CH_2 bands which are associated to saturated hydrocarbons, 1600 cm^{-1} medium intensity and 1500 cm^{-1} low intensity $\text{C}=\text{C}$ (Ar) bands can be associated to aromatic hydrocarbons, the 1340 cm^{-1} medium intensity C-N bands correspond to aromatic amines, and the 1170 cm^{-1} and 1030 cm^{-1} low intensity R-O-Ar are alkyl-aryl-ethers.

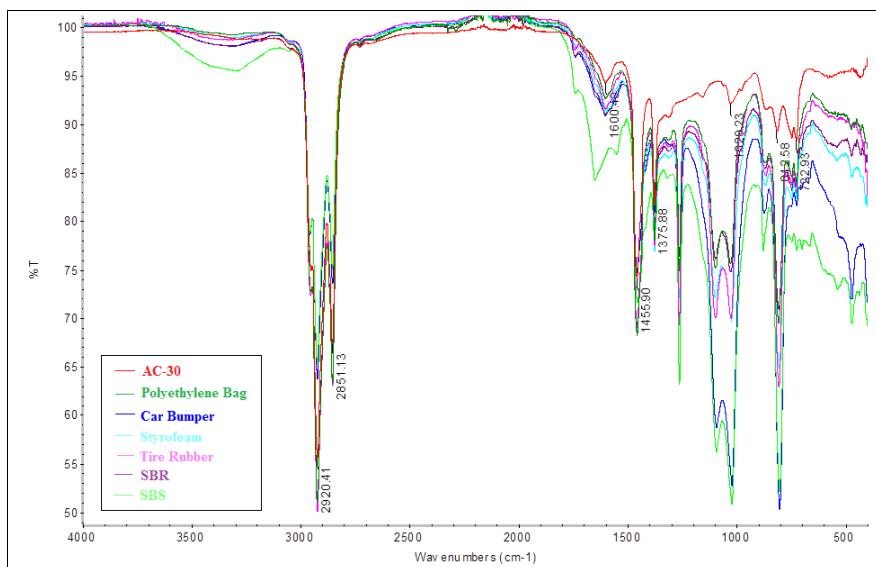


Figure 6. IR spectra comparison for unmodified and modified bitumens

It should be highlighted that the last 4 bands in the spectrum are the ones that show an important change when the modifiers are incorporated into the bitumen. These bands are the ones that can be associated with a performance improvement in the bitumen. Note that the spectrum bands between 1000 and 1200 cm^{-1} are the ones that show the largest increase due to the modification. Additionally, the 800 cm^{-1} band has very low intensity in the case of the unmodified bitumen but shows an important increase when the modifiers are incorporated. The increments are related to changes in the content of aromatic hydrocarbons and aromatic amines. For reference purposes, the SBS modified bitumen shows the largest increment in the aforementioned bands and the polyethylene modified bitumen shows the smallest increase.

4. Concluding Remarks

The evaluated waste materials resulted in an increase of the PG grade by 6 °C or 12 °C, depending on the modifier. Additionally reductions in permanent deformation of more than 50% and increases in fatigue resistance were recorded. Based on the previous, all of the modified bitumens (with the exception of the polyethylene modified bitumen) can be used in roads with heavy vehicle traffic – main roads.

Consequently, the research effort shows an effective method for not only improving the bitumen performance, but most importantly then use of the waste materials also has a positive effect on the environment. Instead of dumping the waste materials in open pits or incinerating them, and based on the dosage used in the present study, 4 kg of material can be used per cubic meter of asphalt.

However, based on the experience of the authors some aspects need to be highlighted: 1) Because of the heterogeneous nature of the materials (different production plants and waste collection locations) it is important that prior to using any of the materials used in this study, or similar materials, an analysis should be performed to characterize the material and ensure that it is chemically similar to the materials that have been used in previous times. 2) The size of the modifier particles is of extreme importance. This was observed in the present study in the case of the tire rubber material that was used as modifier: smaller particle sizes of the modifier ensure that the material incorporates more homogeneously into the bitumen matrix. 3) It is convenient to perform further analysis to determine if modifying the bitumen at high temperatures is convenient, or if elevating the temperature of the bitumen will result in detrimental effects in the medium-long term due to aging. And finally, 4) the adherence properties of the bitumen need to properly measured to check the possibility of a reduction in the cementing capacity of the bitumen, regardless of the experienced performance gains.

5. Acknowledgements

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