Valorization of phosphogypsum wastes as asphaltic bitumen modifier

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ABSTRACT

The accumulation of phosphogypsum wastes from the fertilizer industries, which remain in regulated stacks occupying considerable land resources, is causing significant environment problems worldwide. In that sense, the scientific community is being pressured to find alternative ways for their disposal. In this research, we propose a novel application for phosphogypsum wastes, as a modifier of bitumen for flexible road pavements. Viscous flow tests carried out on bitumen modified with a phosphogypsum waste and doped with sulfuric acid demonstrated an extraordinary increase in viscosity, at 60 ºC, when compared to a counterpart sample which had been modified with gypsum, the main component of phosphogypsum. Similarly, a significant improvement in the viscoelastic response of the resulting material at high temperatures was also found. FTIR (Fourier transform infrared spectroscopy) scans provided evidences of the existence of chemical reactions involving phosphorus, as revealed by a new absorption band from 1060 to 1180 cm^{-1}, related to C−O−P vibrations. This result points at phosphorus contained in the phosphogypsum impurities to be the actual “modifying” substance. Furthermore, no C-O-P band was observed in the absence of sulfuric acid, which seems to be the “promoting” agent of this type of bond.

Keywords: phosphogypsum, bitumen, environment, valorization, rheology

1. INTRODUCTION

Phosphogypsum is the by-product of a wet manufacturing process in which phosphate ore is reacted with sulfuric acid and water to produce phosphoric acid [1]:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF \qquad (R1)$$

About 4.5-5 kg of phosphogypsum are generated for every kg of P_2O_5 manufactured. World phosphogypsum production is around 280 Mt per year. In Spain, the production of P_2O_5, and hence of phosphogypsum, is restricted to a large fertilizer industrial complex located in Huelva city (SW Iberian Peninsula). Over 2.5-3 Mt of phosphogypsum wastes are produced each year and deposited in a stack located less than 1 km away from the city [2]. On the 31st December 2010 the production of PG was stopped, there being nowadays stored in these piles around 100 Mt of PG. Similar phosphogypsum stacks can be found in more than 50 countries around the world, e.g. Engis (Belgium), Kavale (Greece), Siilinjärvi (Finland) or Florida (U.S.A.).

Phosphate rocks (mainly composed of fluorapatite, $Ca_5(PO_4)_3F$), contain high concentrations of metal impurities and some natural radionuclides (mainly from U-series) which during the industrial process, follow either the phosphate fertilizer or the residue generated, depending on the solubility of each element [3]. So, the effects of these stacks on the environment consist primarily of groundwater contamination with trace amounts of heavy metals and air pollution for radionuclides, the most threatening being Ra^{226} and its daughter product Rn^{222} [1,4-5]. Consequently, the presence of some U-series radionuclides in phosphate rock and its impact on the environment requires alternative ways of disposal of this kind of residue. As a matter of fact, 85 % of the worldwide production remains at present in regulated stacks which occupy considerable land resources and lead to serious contamination [6]. Due to these facts, the industry devoted to the production of phosphoric acid, and the related to them, are called NORM (Naturally Ocurring Radioactive Material) industries.

Numerous investigations have focused on the search of uses for the phosphogypsum wastes. Among them, phosphogypsum has been used as an agricultural fertilizer, in soil stabilization amendments [7], in the cement industry as setting regulator in place of natural gypsum [8], or as a raw mineralizer in the burning Portland cement clinker [9]. Unfortunately, the presence of impurities can negatively affect the performance of phosphogypsum in some of the above applications.

An application of phosphogypsum is its direct addition as a filler material in asphalt mixtures for roads construction [10]. However, a previous blend of phosphogypsum with the asphaltic bitumen, before this is used as binder of the mineral aggregates, may result of higher interest, as phosphorus compounds are well-known to improve its high temperature performance if compared to the original bitumen [11-13]. Consequently, the above alternative does not represent a disadvantage for the environment. Thus, on the one hand, bitumen constitutes a way for immobilizing these NORM radioactive wastes [14]. And, on the other hand, phosphogypsum is added in a concentration that only represents about 0.5 wt.% of the final asphalt mixture (composed of 95 wt.% aggregates and 5 wt.% bitumen, approximately).

As an alternative way of valorization of this kind of residue, in this study the feasibility of using a phosphogypsum waste from a fertilizers factory as a modifier of bitumen for the paving industry has been evaluated. In that sense, a basic rheological characterization, based on viscous flow tests at 60 ºC and dynamic shear temperature sweeps, have been carried out on different phosphogypsum-modified bituminous samples. Finally, in order to shed some light on the modification route and the chemical changes induced after the addition of this residue, simultaneous DTA/TG and modulated DSC tests, and FTIR scans were also performed.

2. EXPERIMENTAL

2.1. Materials

Bitumen, supplied by Construcciones Morales, S.A. (Spain), with a penetration of 40 dmm and R&B softening temperature of 52 ºC (according to EN 1426 and EN 1427, respectively) has been used as base material for the modification. Its chemical composition, expressed in terms of the SARAs (Saturates, Aromatics, Resins, Asphaltenes) fractions is 5.2, 48.3, 26.5 and 20.0 wt.%, respectively.

On the other hand, the phosphogypsum (referred to as PG, hereinafter) sample was collected from the phosphogypsum piles located at the surroundings of Huelva city (South-West Spain). Table 1 presents its average chemical composition, after 48 h at 50 ºC [15]. As expected, main contents of phosphogypsum are Ca and S (expressed as CaO and SO_3, respectively), which together make more than 90 wt.%. Major impurities are SiO_2, Fe_2O_3, Al_2O_3 and Na_2O, and, to a lesser extent, K_2O and TiO_2. It is important to note that 0.95 wt.% P_2O_5, which remains after the material washing, was also found [16]. In addition, in Table 1 is also shown its radioactive characterization [15].

Finally, with the goal to evaluate the modification route associated to the phosphogypsum waste, two other chemicals were used: a) H_2SO_4 (96 wt.%), supplied by Panreac, S.A. (Spain); b) commercial gypsum, $CaSO_4{\cdot}2H_2O$ (referred to as CG, hereinafter), supplied by Panreac, S.A. (Spain).

2.2. Samples processing

The different modified bitumens studied were prepared according to a general procedure which consisted in mixing molten neat bitumen with the different additives in a cylindrical vessel (60 mm diameter and 140 mm height) dipped in an oil bath. Satisfactory mixing was achieved by means of an IKA RW-20 stirring device (Germany) equipped with a four-blade turbine rotating at 1200 rpm. After processing, all the samples were covered with aluminum foil and stored in a freezer for further testing.

With regard to the phosphogypsum waste, three different modified samples were prepared. Thus, neat bitumen was mixed with 10 wt.% PG at 150 ºC for 1 h. Subsequently, the blend was divided into two parts: a) one was used as such ("PG-150" sample); b) the another one was mixed with 0.5 wt.% H_2SO_4 at 150 ºC for 30 min ("PG-H_2SO_4-150" sample). Moreover, with the aim to evaluate the influence of the processing temperature, an additional sample containing the same concentrations of PG and H_2SO_4 but prepared at 90 ºC was also evaluated ("PG-H_2SO_4-90" sample).

On the other hand, with the goal to look into the changes involved in the modification by phosphogypsum, two other binders were also prepared. Thus, neat bitumen was mixed with 10 wt.% CG at 150ºC for 1 h. Afterwards, the resulting binder was divided into two parts: a) the first one was used as such ("CG-150" sample); b) the second one was mixed with 0.5 wt.% H_2SO_4 at 150 ºC for 30 min ("CG-H_2SO_4-150" sample).

Finally, for the sake of reference, four more samples were considered. Thus, two binders were obtained by blending 0.5 wt.% H_2SO_4 and neat bitumen, at 90 or 150 ºC, for 1 h ("H_2SO_4-90" and "H_2SO_4-150" samples, respectively). The specific effects of temperature and agitation were assessed by subjecting the neat bitumen, without additives, at 150 ºC for 1 h (sample referred to as "blank", hereinafter). A reference bituminous sample containing 3 wt.% commercial SBS Kraton D1101 (“SBS-reference” sample) was also prepared by dispersing the rubber into bitumen with a Silverson L5M homogenizer, which produced an homogeneous dispersion.

2.3. Samples testing

Two different rheological tests were conducted on the bituminous samples using a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria): a) viscous flow measurements, at 60 ºC; and b) temperature sweep tests in oscillatory shear, from 30 to 100 ºC, at a heating rate of 1 ºC/min, a frequency of 10 rad/s and deformation of 1% strain (within linear viscoelastic interval). Serrated plate-and-plate geometry (25 mm diameter and 1 mm gap) was always used.

Simultaneous DTA/TG measurements were performed with a Seiko TG/DTA 6200 (Japan). Temperature ramps at 10 ºC/min, from 40 to 600 ºC, under N_2 atmosphere were carried out on 5-10 mg of sample.

Modulated Differential Scanning Calorimetry (MDSC) was performed with a TA Q-100 (TA Instruments, USA). Samples of 5-10 mg were always subjected to the following testing procedure: temperature range from -60 to 110 ºC; heating rate of 5 ºC/min; amplitude of modulation of ±0.5 ºC; a period of 60 s; and N_2 as purge gas, with a flow rate of 50 mL/min. In order to provide the same recent thermal history, all the samples were placed into hermetic aluminum pans and annealed for 24 h at room temperature before being analyzed.

Fourier transform infrared spectroscopy (FTIR) spectra were obtained with a Digilab FTS3500ARX (Varian, USA) apparatus. Neat bitumen and modified binders solutions were prepared by dissolving 0.7 g of each sample in 25 mL dichloromethane. The same volume of solution was always laid on a potassium bromide disk (32×3 mm), which was then exposed to ambient until the solvent was evaporated. Afterwards, the KBr disk was placed into the appropriate sample holder and the FTIR spectra were obtained in a wavenumber range of 400–4000 cm^{-1}, at 4 cm^{-1} resolution, in the transmission mode.

Bitumen SARAs fractions were determined by means of thin layer chromatography coupled with a flame ionization detector (TLC/FID), using an Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan). Determination was conducted through a procedure of sequential elutions as that described by Ecker [17], but with hexane, toluene and dichloromethane/methanol (95/5 vol/vol) as solvents.

In order to ensure the repeatability of the results, at least three tests were conducted on every sample studied.

3. RESULTS AND DISCUSSION

3.1. Rheological behaviour

The viscous flow curves, at 60 ºC (usually designated as the maximum expectable temperature to be reached in a pavement in warm climates), for the different phosphogypsum, commercial gypsum and reference bituminous binders are presented in Figure 1. All the samples present a Newtonian region, at low shear rates, followed by a shear-thinning drop beyond a threshold value of shear rate. This behaviour can be well-described by the Carreau’s model:

$$\frac{\eta}{\eta_0} = \frac{1}{\left[1+\left(\lambda\cdot\dot{\gamma}\right)^2\right]^s} \qquad (1)$$

where η_0 (Pa·s) is the zero-shear-viscosity, λ (s) is a time constant whose inverse approximately matches the threshold shear rate above, ‘s’ is a parameter related to the slope of the shear-thinning region and $\dot{\gamma}$ is the shear rate. Table 2 includes the fitting parameters η_0 and λ for the samples studied.

As observed in Figure 1, the neat bitumen shows a large Newtonian region, with viscosity of about 300 Pa·s, which extends up to 2 s^{-1}. The combined effect of temperature (150ºC) and agitation on the neat bitumen, evaluated by means of the so-called “blank” sample, does not seem to produce any significant variation in its flow behavior, as both viscosity and threshold shear rate values remain nearly the same. Even less significant was the effect observed at 90ºC (not shown). Consequently, the effect provoked by oxidation will not be considered in subsequent rheological tests.

With regard to the phosphogypsum sample (“PG-150” sample), the addition of 10 wt.% PG results in a poor viscosity increase if compared to the neat bitumen, which suggests that phosphogypsum acts merely as a “filler” and does not interact with the bituminous matrix. Moreover, similar increase in viscosity is observed after the addition of 10 wt.% CG (“CG-150” sample). However, a very remarkable increase in viscosity is noticed if 0.5 wt.% sulfuric acid is added to the PG sample prepared at 150 ºC (“PG-H_2SO_4-150” sample). Thus, viscosity undergoes an increase approximately from 400 up to 10^4 Pa·s. Similarly, an enhanced viscosity is obtained if the blending is conducted at 90 ºC (“PG-H_2SO_4-90” sample), although just up to 3000 Pa·s. This result demonstrates that modification is more effective when carried out at 150 ºC. In addition, the λ parameters provided by the Carreau’s model fittings reveal changes in their microstructure. Thus, higher values of λ (or inversely, lower values of the limit shear rate which marks the onset of the shear-thinning region) for the “PG-H_2SO_4-90” and, mainly, “PG-H_2SO_4-150” samples reveal the development of a more complex microstructure [18].

In order to explore the cause behind the high level of modification observed after addition of sulfuric acid to the phosphogypsum sample, the viscous flow behavior of a binder containing commercial gypsum (major component of phosphogypsum) and sulfuric acid, mixed at 150 ºC, was also evaluated (“CG-H_2SO_4-150” sample). As can be deduced from Figure 1, the viscous response shown for this binder is similar to that of a sample of bitumen to which only 0.5 wt.% sulfuric acid was added (“H_2SO_4-150” sample). As a consequence, this result reveals two important findings: on the one hand, some of the compounds contained in the PG fraction which is not $CaSO_4$ (about 8 wt.%) are the responsible for the viscosity increase observed, if compared to the increase due to the mere addition of sulfuric acid (“H_2SO_4-150” sample); on the other hand, the modification exhibited by the “PG-H_2SO_4-150” sample involves the activation of those “modifying” compounds present in the phosphogypsum by means of a strong acid as sulfuric acid. This provokes a viscosity enhancement, at 60 ºC, of more than one order of magnitude if compared to the “SBS-reference” sample.

In addition, Table 3 presents the values of penetration and R&B softening temperature tests. If compared to the neat bitumen, no variation is observed due to the combined effect of temperature and agitation (“blank” sample). With regard to the modifiers, similar effects (not very significant) are provoked by addition of phosphogypsum or commercial gypsum. Moreover, addition of 0.5 wt.% sulfuric acid is seen to produce a decrease of 25% in the penetration value, as well as an increase of 6 ºC in the softening temperature. However, synergestic effects are detected when this acid is added on a sample which has been previously modified with phosphogypsum. Thus, penetration goes down to 50% of neat bitumen’s value, whereas softening temperature increases 17 ºC. This result represents by far a larger degree of modification than that corresponding to the “SBS-reference” sample.

Apart from the viscous flow tests, dynamic shear temperature sweeps, from 30 to 100 ºC, were carried out on selected samples. Figure 2 shows the evolution with temperature of the loss tangent, a parameter which establishes a comparison of the viscous features relative to the elastic features of a material by dividing the viscous modulus by the elastic one ($\tan \delta = G''/G'$). Neat bitumen shows, in the entire temperature interval studied, a prevailing viscous behaviour, with values of $\tan \delta > 1$, mainly at the highest temperatures. After modification, the behaviour above described remains but in a lesser extent, and the samples show a reduced susceptibility to temperature variations. In that sense, the average slope values of the curves in Figure 2 within a temperature interval of up to 50ºC were calculated and displayed in Table 4. This demonstrates lower value of average slope for the "PG-H_2SO_4-150" sample, a result which suggests an enhanced resistance to temperature variations if compared to the original non-modified bitumen.

Interestingly, the "PG-H_2SO_4-150" sample presents a plateau region over an interval of intermediate temperature, approximately between 35 and 60 ºC. This region is similar to that found in the "SBS-reference" sample, which is a consequence of the deformation-relaxation produced on the polymer-rich dispersed phase during the oscillatory shear applied [19]. Instead, in the case of phosphogypsum sample, it could be related to new structures arisen from the interaction of certain compounds in the phosphogypum waste when those are activated by addition of sulphuric acid.

Moreover, data obtained from dynamic shear temperature sweeps, with a heating ramp of 1 ºC/min, were plotted in the form of $|G^*|/\sin \delta$ in Figure 3. This parameter was established by the Strategic Highway Research Program (SHRP) [20] in order to determine the binder's average seven-day maximum pavement design temperature (according to AASHTO M320, and by application of AASHTO T315). In our case, the actual aim was to present the results in such a way that the rutting resistance of the different samples at high in-service temperatures can be quantitatively compared [21]. In that sense, Table 4 displays the values of temperatures at which |G*|/sin δ ("rutting parameter") equals 1 kPa, established by SHRP as the temperature below which a specific binder will show a satisfactory performance. Hence, this method stands for an easy and time-saving way to establish a comparative analysis on the degree of improvement attained.

Analogously to the viscous flow results, Figure 3 reveals the successful combined effect of the phosphogypsum waste and sulphuric acid on increasing noticeably the complex modulus (and its derived "rutting parameter") and so, the resistance of the "PG-H_2SO_4-150" sample to permanent deformation at high in-service temperatures. However, the single contribution of the phosphogypsum results almost negligible. As a matter of fact, the values of temperature in Table 4 indicates an increase of 23 ºC for the "PG-H_2SO_4-150" sample and only of 1ºC for the "PG-150" sample, if compared to the neat bitumen. The improvement achieved by addition of SBS rubber at a concentration of 3 wt.% is only of about 7ºC, which represents less than one third the phosphogypsum sample's.

3.2. Modification and microstructure

Previous results for the "PG-H_2SO_4-150" sample hint at significant changes in its microstructure, which may be the consequence of chemical reactions, involving the phosphogypsum impurities. Hence, thermal analysis (TG/DTA and MDSC tests) and infrared spectroscopy (FTIR) may shed some light on this issue.

TG/DTA tests, which allow mass loss and thermal events to be determined simultaneously in an open system, were performed on four selected samples. For the pure commercial gypsum, Figure 4A shows a single DTG peak, with maximum at 130 ºC, which extends from 90 to 170 ºC and has a mass loss associated of about 21 wt.%.

This value agrees well with what is stoichimetrically expected for the complete dehydration of the structural water contained in gypsum, according to the two following reactions:

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 0.5H_2O + 1.5\ H_2O \qquad (R2)$$

$$CaSO_4 \cdot 0.5H_2O \rightarrow CaSO_4 + 0.5H_2O \qquad (R3)$$

In addition, DTA curve for commercial gypsum in Figure 4B displays an endothermic process due to the above phenomenon. Similar thermal response was observed for the phosphogypsum waste, which shows a mass loss slightly higher than that for the commercial gypsum.

On the other hand, neat bitumen presents a large mass loss, showing a DTG peak, with a maximum at 455 ºC, which extends over a wide temperature interval from 250 to 500 ºC. This peak involves the decomposition/volatilization of chemical compounds with very different molecular weights. Finally, the TG curve of the “PG-H_2SO_4-150” sample presents similar decay to the neat bitumen’s, but with an expected higher residue (24% if compared to 14.6% for neat bitumen).

Moreover, FTIR spectroscopy was carried out on the neat bitumen and three selected samples (“PG-150”, “H_2SO_4-150” and “PG-H_2SO_4-150”). As shown in Figure 5, a spectrum of absorption bands characteristics of certain chemical bonds was obtained for every sample. They all present, in the wavenumber interval scanned, three well-defined bands: the first, in the region 1760-1665 cm^{-1} due to the stretching vibration of the carbonyl (C=O) bond, and the second and third peaks, in the regions 1470-1350 and 1390-1370 cm^{-1} due to the bending vibration of the CH_2&CH_3 bonds and bending vibration of the CH_3 bond, respectively [22]. However, only the “PG-H_2SO_4-150” sample displays a new absorption band, from 1060 to 1180 cm^{-1}, related to C−O−P vibrations [23]. Therefore, FTIR results provide evidences of the existence of chemical reactions involving phosphorus contained in the PG fraction which is not $CaSO_4$ (about 8 wt.%), and which seem to be the responsible for the viscosity increase observed in Figure 1. In other words, phosphorus appears to be the “modifying” substance. On the other hand, they confirm that such chemical interactions between phosphorus and bitumen are not possible in the absence of a small amount of sulfuric acid, which seems to be the “promoting” agent of the C-O-P bond formation. Therefore, we may assume that the sulfuric acid addition, at 150 ºC, is able to release the phosphorus from the crystalline structure of phosphogypsum, allowing reactions with bitumen’s compounds.

Finally, in order to support further the above observations, modulated DSC tests were performed on three selected samples. They also disclosed changes induced in the bitumen microstructure. Figures 6A and 6B show the non-reversing heat flow thermograms and derivative heat capacity (dC_p/dT), respectively, for the neat bitumen and “H_2SO_4-150” and “PG-H_2SO_4-150” samples. According to Masson and co-workers [24, 25], the non-reversing heat flow curves for a neat bitumen present four clearly marked thermal events: i) a broad endothermic background which approximately extends from -40 up to 80 ºC; ii) and iii) two exotherms located at about -10 and 40 ºC, respectively; iv) an endothermic peak, at around 50 ºC. Masson and co-workers reported this endotherm to be related to the diffusion of relatively large structures, as those typically found in asphaltenic micelles. With this regard, enthalpy values associated to this thermal event can be calculated by mere integration of the corresponding peaks (see Figure 6A). Table 5, which presents these enthalpy values, demonstrates the largest value for the “PG-H_2SO_4-150” sample. This observation matches the idea of new structures, which form upon activation of phosphorus with sulfuric acid, and which would require a larger quantity of energy to melt. It is also significant, if compared to the neat bitumen, the increase in the enthalpy value corresponding to the sole addition of sulfuric acid.

Furthermore, derivative heat capacity for the neat bitumen in Figure 6B presents two well-defined events, with maximum peaks located at -30 and 3.5 ºC, respectively. According to Masson et al. [24, 25], they correspond to the glass transitions of saturates and aromatics, respectively, which are included in the maltene fraction. Thus, Table 5 presents values of these glass transitions temperatures determined from Figure 6B, which evidence a reduction in the temperatures at which the peaks T_{g1} and T_{g2} are located for the "PG-H_2SO_4-150" sample. In that respect, the second (exothermic) thermal event in Figure 6A derives from a time-dependent cold-crystallization of a certain quantity of saturates which, upon cooling from the melt, were unable to adequately crystallize. Hence, above the glassy state defined by $T > T_g$, their molecular mobility increases and the saturates segments order into crystalline domains [24-26]. Table 5, which also displays these second event temperatures (T_{2nd}), confirms lower values for the "PG-H_2SO_4-150" sample, the one for which, according to Figure 6B, the glassy state threshold was shifted to the lowest temperatures.

4. CONCLUDING REMARKS

The potential utilization of phosphogypsum, by-product from fertilizer industries, as a bitumen modifier for paving industry was evaluated. It was found that, when activated with a small quantity of sulfuric acid (0.5 wt.%), the addition of 10 wt.% phosphogypsum leads to a notable improvement in the rheological response of the resulting material at high temperatures. Instead, poor level of modification was noticed when in such a formulation, phosphogypsum was substituted by the same concentration of commercial gypsum. With this regard, FTIR spectroscopy results provided evidences of the existence of chemical reactions involving phosphorus, as revealed by a new absorption band, from 1060 to 1180 cm^{-1}, related to C−O−P vibrations, which only appeared in the "PG-H_2SO_4-150" sample. Therefore, phosphorus seems to be the "modifying" substance to which the viscosity increase observed at 60 ºC is attributed. Furthermore, no C-O-P band was observed in the absence of sulfuric acid, which seems to be the "promoting" agent of this type of bond. On the other hand, it was registered a decrease of the thermal transition temperatures corresponding to saturates and aromatics, as well as an increase in the melting energy for the largest bitumen structures.

All these results may encourage industry to envisage the use of phosphogypsum wastes in paving applications. Thus, apart from the benefits for the bitumen performance, it may constitute an alternative way of managing this kind of residue and an efficient manner of immobilizing these low/intermediate radioactive wastes.

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Table 1. Chemical composition and radioactive characterization of the phosphogypsum waste.

Component	Percentage (wt.%)	Radionuclide	Concentration (Bq kg^{-1})
SO_3	52.41	^{238}U	97 ± 6
CaO	40.30	^{226}Ra	590 ± 34
F^-	3.34	^{230}Th	453 ± 15
SiO_2	2.40	^{220}Pb (^{210}Po)	624 ± 37
P_2O_5	0.95	^{232}Th	8.2 ± 0.7
Al_2O_3	0.40	^{228}Ra	8.0 ± 1.0
Fe_2O_3	0.23	^{228}Th	8.8 ± 0.9
Na_2O	0.13	^{40}K	< 18
TiO_2	0.04		
K_2O	0.03		
MgO	0.04		
CuO	0.01		
SrO	0.09		
ZrO_2	0.01		
BaO	0.02		
LOI[a]	2.40		

[a] Loss on ignition

Table 2. Carreau's model parameters for the samples studied.

Samples	η_0 (Pa·s)	λ (s)
Neat bitumen	$3.00 \cdot 10^2$	0.19
Blank	$3.18 \cdot 10^2$	0.18
PG-150	$3.80 \cdot 10^2$	0.14
CG-150	$3.72 \cdot 10^2$	0.24
PG-H_2SO_4-150	$1.00 \cdot 10^4$	5.55
H_2SO_4-150	$2.08 \cdot 10^3$	1.89
PG-H_2SO_4-90	$3.06 \cdot 10^3$	3.10
H_2SO_4-90	$2.31 \cdot 10^3$	1.89
CG-H_2SO_4-150	$2.46 \cdot 10^3$	1.91
SBS	$8.11 \cdot 10^2$	0.42

Table 3. Penetration values and Ring & Ball softening temperatures for the samples studied.

Samples	Penetration (dmm)	R&B softening point (ºC)
Neat bitumen	40	52
Blank	39	52
PG-150	35	54
CG-150	36	54
PG-H_2SO_4-150	21	69
H_2SO_4-150	31	58
PG-H_2SO_4-90	30	59
H_2SO_4-90	31	58
CG-H_2SO_4-150	30	59
SBS	33	56

Table 4. Average slope values of tan δ and temperatures calculated from Figure 4, for selected samples.

Samples	Slope tan $\delta^{35\text{-}50\ ºC}$	$T_{\lvert G^*\rvert/\sin\delta=1kPa}$ (ºC)
Neat bitumen	$1.9\cdot10^{-2}$	68.6
PG-150	$1.9\cdot10^{-2}$	69.7
PG-H_2SO_4-150	$6.0\cdot10^{-3}$	91.5
H_2SO_4-150	$9.0\cdot10^{-3}$	80.4
SBS	$7.7\cdot10^{-3}$	75.2

Table 5. Fourth event enthalpies (ΔH_{4th}), saturates and aromatics glass transitions temperatures (T_{g1} and T_{g2}) and second event temperatures (T_{2nd}) obtained from MDSC measurements, for selected samples.

Samples	ΔH_{4th} (J/g)	T_{g1} (ºC)	T_{g2} (ºC)	T_{2nd} (ºC)
Neat bitumen	1.28	-30.0	3.5	-8.0
H_2SO_4-150	5.10	-32.5	-1.5	-12.0
PG-H_2SO_4-150	6.90	-32.5	-5.0	-15.5

Figure captions

Figure 1. Viscous flow curves, at 60 ºC, for the neat bitumen, reference samples and the different modified binders studied.

Figure 2. Evolution of the loss tangent with temperature, for the neat bitumen and selected modified binders.

Figure 3. Evolution of the “rutting parameter”, $|G^*|/\sin\delta$, with temperature, for the neat bitumen and selected modified binders.

Figure 4. TG, DTG and DTA curves, between 40 and 600 ºC, under N_2 atmosphere for the neat bitumen, commercial gypsum (CG), phosphogypsum (PG) and “PG-H_2SO_4-150” sample.

Figure 5. FTIR spectra, from 2000 to 900 cm^{-1}, for the neat bitumen and selected modified binders.

Figure 6. Results of MDSC, for the neat bitumen and selected modified binders, in the form of: A) non-reversing heat flow thermograms; B) C_p-derivate curves.

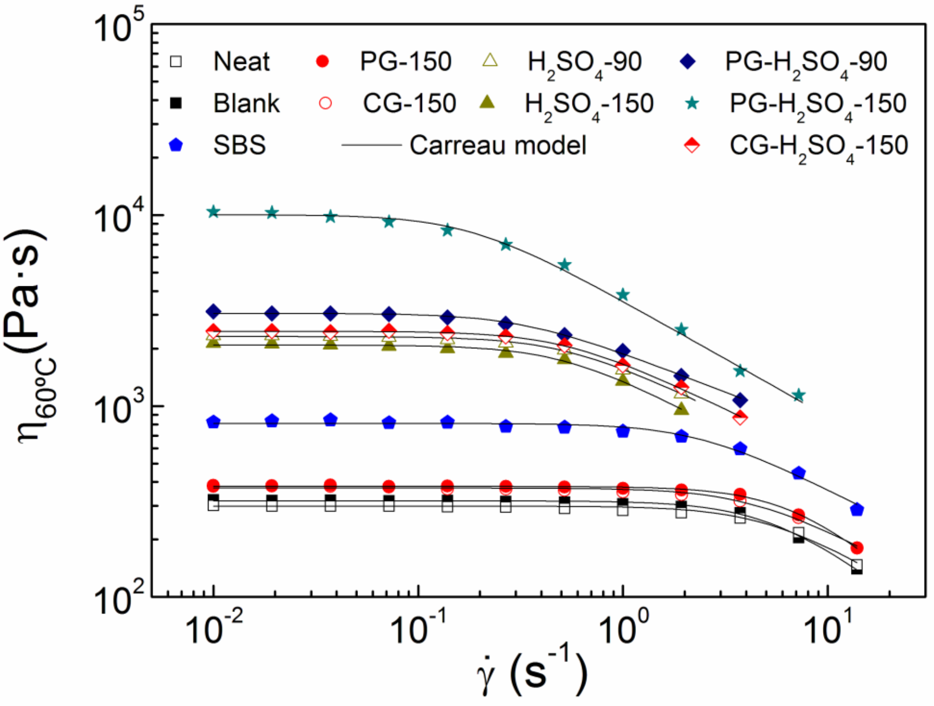

10^5
10^4
10^3
10^2
$\eta_{60^\circ C}$(Pa·s)
10^{-2}
10^{-1}
10^0
10^1
$\dot{\gamma}$ (s^{-1})
Neat
PG-150
H_2SO_4-90
PG-H_2SO_4-90
Blank
CG-150
H_2SO_4-150
PG-H_2SO_4-150
SBS
Carreau model
CG-H_2SO_4-150

Figure 1

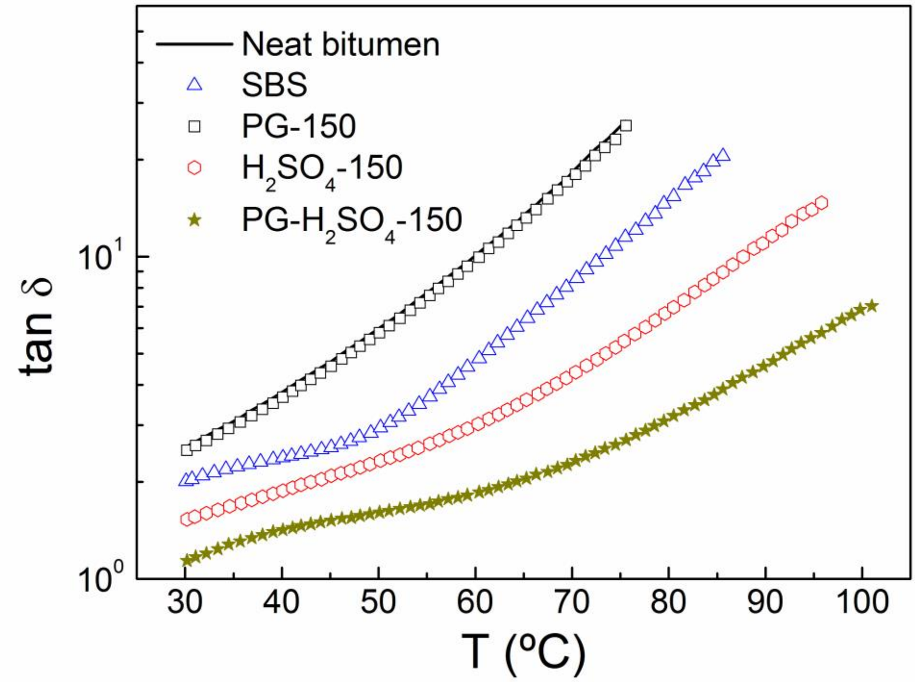
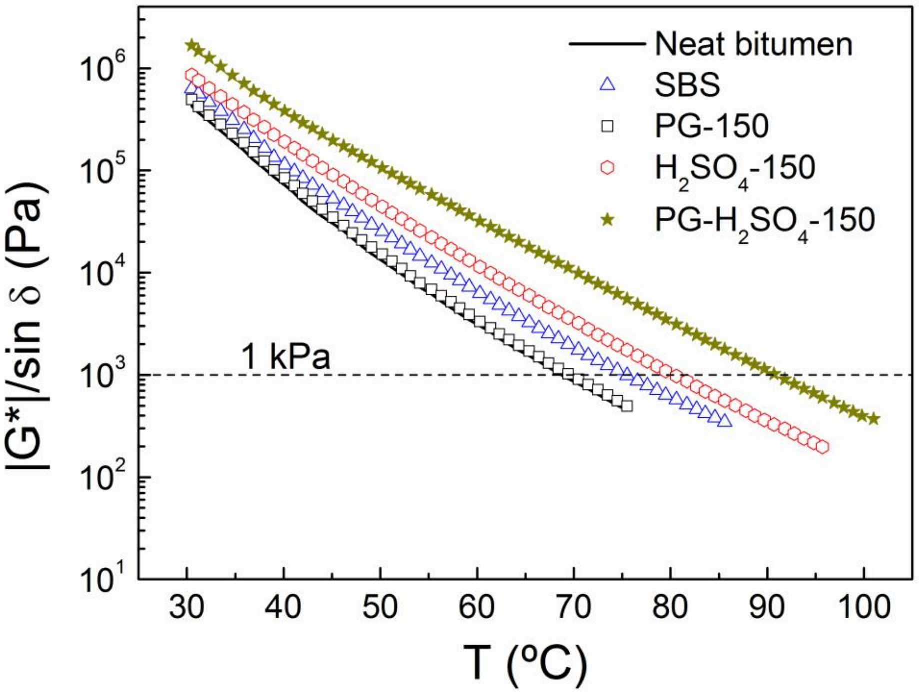

Neat bitumen
SBS
PG-150
H_2SO_4-150
PG-H_2SO_4-150
tan δ
10^1
10^0
30
40
50
60
70
80
90
100
T (ºC)

Figure 2



10^6
10^5
10^4
10^3
10^2
10^1
|G*|/sin δ (Pa)
30
40
50
60
70
80
90
100
T (ºC)
1 kPa
Neat bitumen
SBS
PG-150
H_2SO_4-150
PG-H_2SO_4-150

Figure 3

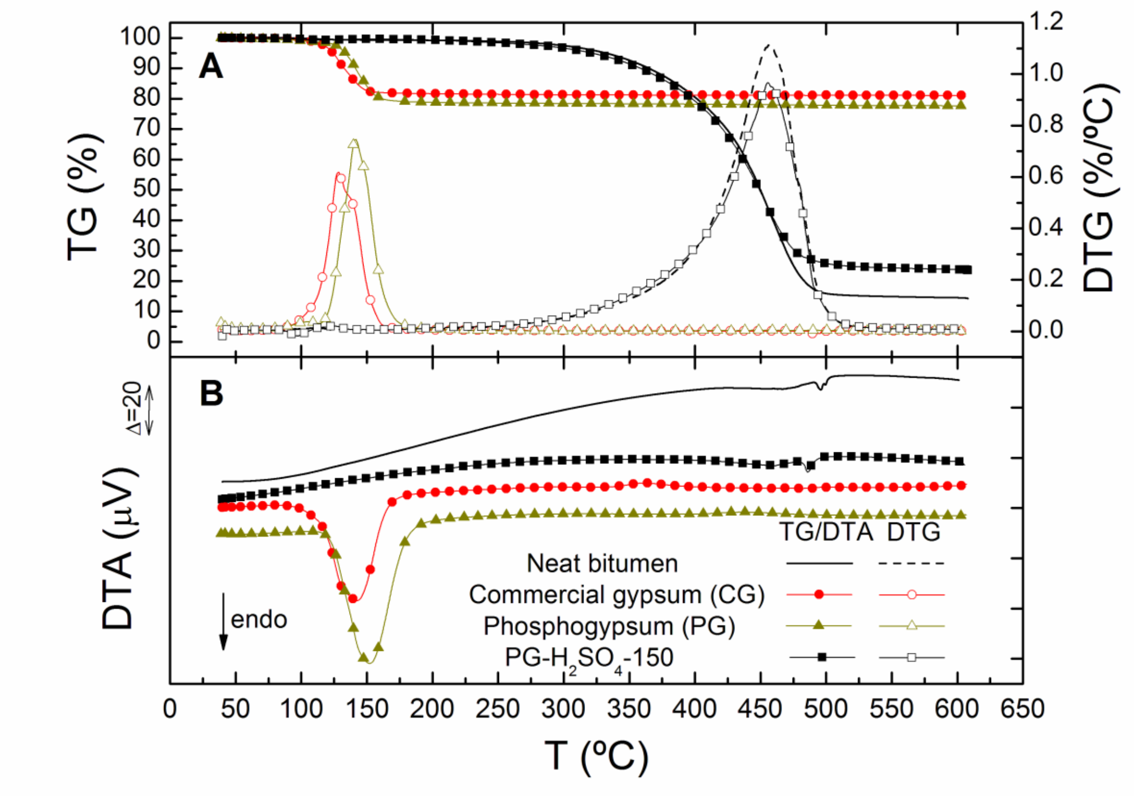

A
B
TG (%)
DTG (%/ºC)
DTA (μV)
T (ºC)
Δ=20
endo
TG/DTA DTG
Neat bitumen
Commercial gypsum (CG)
Phosphogypsum (PG)
PG-H2SO4-150
0 10 20 30 40 50 60 70 80 90 100
0.0 0.2 0.4 0.6 0.8 1.0 1.2
0 50 100 150 200 250 300 350 400 450 500 550 600 650

Figure 4

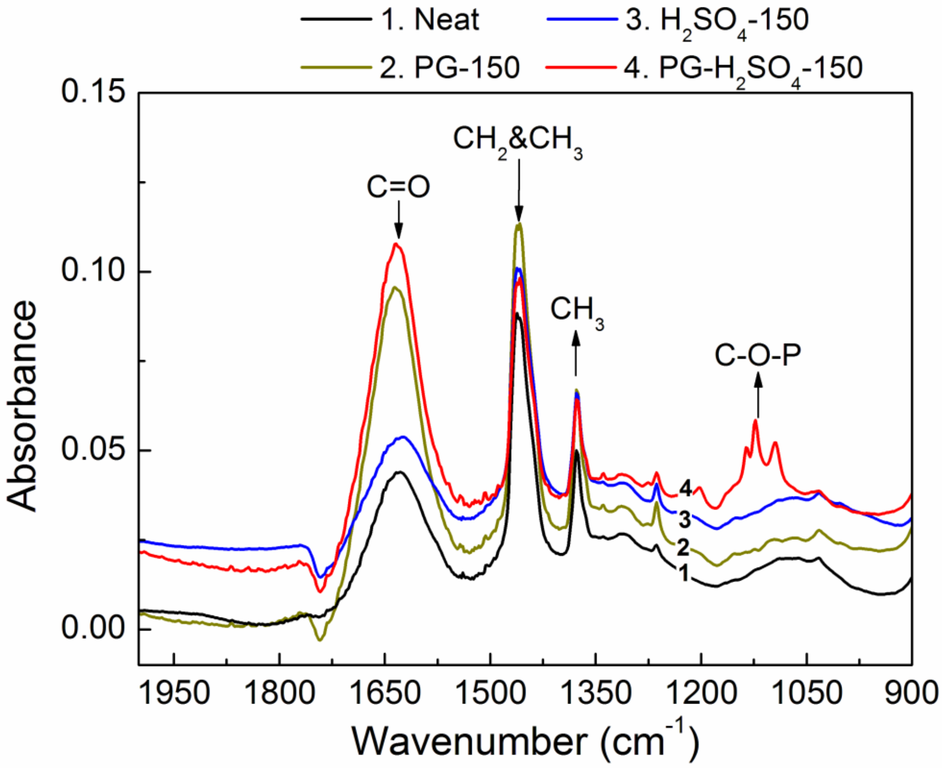

1. Neat
3. H$_2$SO$_4$-150
2. PG-150
4. PG-H$_2$SO$_4$-150
Absorbance
0.15
0.10
0.05
0.00
C=O
CH$_2$&CH$_3$
CH$_3$
C-O-P
4
3
2
1
1950
1800
1650
1500
1350
1200
1050
900
Wavenumber (cm^{-1})

Figure 5

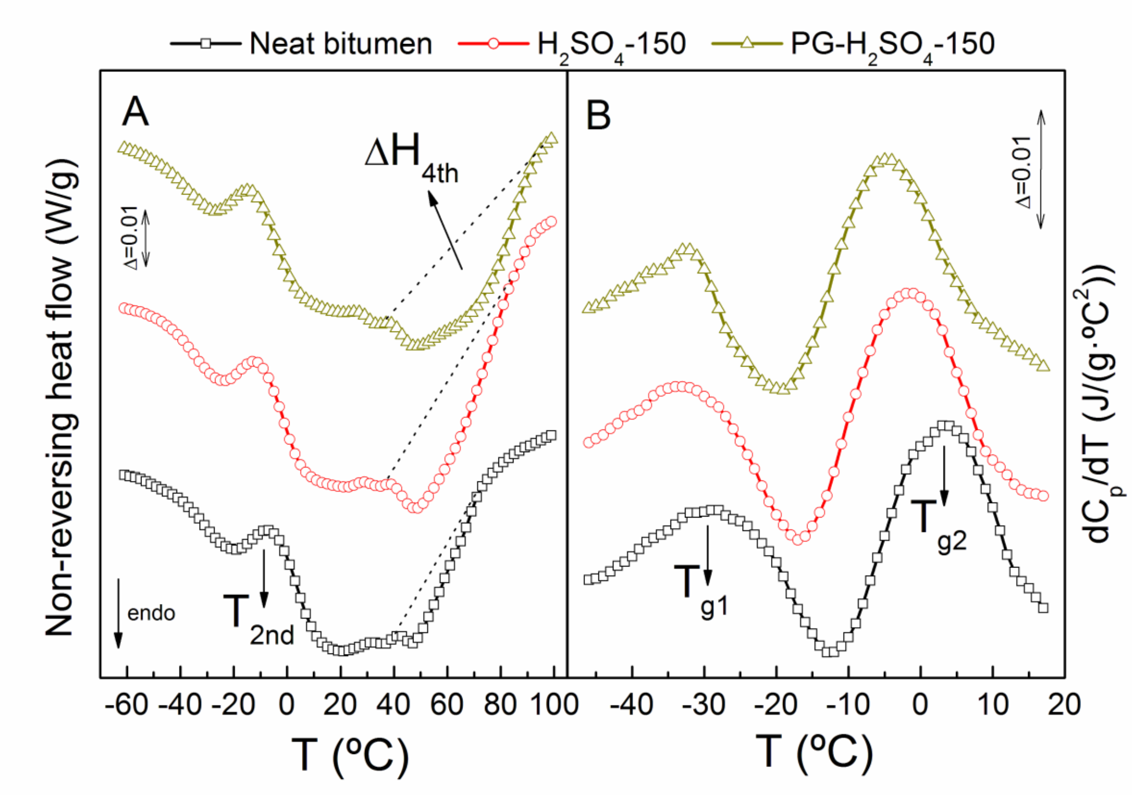

Neat bitumen
H2SO4-150
PG-H2SO4-150
A
B
ΔH4th
Δ=0.01
endo
T2nd
Tg1
Tg2
Non-reversing heat flow (W/g)
dCp/dT (J/(g·ºC2))
T (ºC)
-60 -40 -20 0 20 40 60 80 100
-40 -30 -20 -10 0 10 20

Figure 6