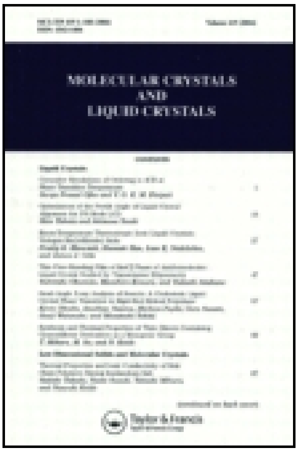

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Rheological and ^{1}H-NMR Spin-Spin Relaxation Time for the Evaluation of the Effects of PPA Addition on Bitumen

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Bitumens are currently modelled as a colloidal system and are the most used materials for road paving. Despite this large application, asphalts are still affected by some inconveniences that bring to road deterioration. This is prevalently due to temperature cycling which is related to the given local climate conditions and to the incident traffic load. In the last decades bitumen performances have been improved by means of different types of additives in order to match various expectations. This improvement is often the result of the indications given by traditional empirical standardized tests like penetration grade, temperature ductility and Fraas breaking point. The comprehension of the chemical mechanism that regulates the action of the used additives can greatly help in designing new and better performance materials. By means of a Stress Controlled Rheometer we present a laboratory evaluation of the rheological properties of a 70/100 bitumen which has been doped by different percentage of Polyphosphoric acid (PPA). In addition ^{1}*H-NMR measurements of proton transverse relaxation time* (T_2) *have been exploited in order to corroborate the rheological data. As a novel approach to the knowledge of bitumen macro-structures, we applied an Inverse Laplace Transform (ILT) to the measured echo decay. The results show the effect of PPA addition on bitumen mechanical behaviour.*

Keywords Bitumen; asphaltenes; rheology; NMR; Inverse Laplace Transform

Introduction

Bitumens are commonly employed as binders in road construction and roofing systems because of their thermoplastic nature, water resistance and adhesion properties.

Asphaltenes and maltenes are two of the major constituents in the bituminous materials, with asphaltenes as the dispersed phase and maltenes as the continuous phase [1]. Asphaltenes are formed by condensed polyaromatic structures containing alkyl chains, hetero-aromatic compounds with sulphur present in benzothiophene rings and nitrogen in pyrrole and pyridine rings. In addition, asphaltenes may contain polyfunctional molecules

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with nitrogen, as amines and amides; oxygen, nickel and vanadium metals complexed with pyrrole nitrogen atoms in porphyrin rings [1,2]. Considering their chemical composition, asphaltenes are the rigid portion of the material [3]. Maltenes are the soft part of the material and they are constituted by resins, aromatic hydrocarbons, olefins, cyclic saturated hydrocarbons and straight or branched chain saturated hydrocarbons (paraffins) [1]. The presence of both rigid and soft portions in the bitumen structure is at the basis of its liquid crystalline behavior [4].

Bitumens rheological behaviour is governed by the chemical-physics interactions of the individual constituents and it is strongly dependant on the temperature [5]. During the last years researchers focused their attention on the performances of bituminous materials. This is because of bituminous binders play a crucial role in the performance of the corresponding asphalt mix [6]. A frequent indication of the asphalt road deterioration is the occurrence of different types of cracks, such as those caused by traffic loading or temperature cycling, induced by frost heaving, and fissures formed at low temperature [7].

Generally bitumen composition is variable depending on its provenience and this strongly influences the rheological properties. For example, a bitumen that have a high waxes content is more sensitive to cracking or create plastic deformations of the paved asphalt [8] due to the crystal nature of these components. In order to reduce this phenomenon, bitumens should be able to relax the applied stress and at the same time their rigidity should not exceed a given value especially at low temperature [9]. In convenient applications, different types of additives, like waxes, polymers and acids (poly-phosphoric acid, PPA, as an example) are added to bitumens or to mixtures in order to improve their mechanical properties, with particular attention to the operative temperature conditions. To achieve good performance at both high and low temperatures, small quantities of PPA are used as a doping substance in bitumen formulation [8]. As matter of fact it was found that PPA can increase the stiffness of the material at intermediate and high temperatures. Unfortunately the asphalt mixture containing PPA showed an increased sensitivity to permanent deformation compared to mixture without the additive [8]. Besides the conventional tests, new approaches for the characterization of bituminous materials are developing [10–13]. Different rheological techniques are demonstrated to be a valuable and more sensitive way to asses bitumen properties [14]. Furthermore a deeper knowledge of the chemical composition as well as the morphology of the bituminous binder is essential to design new additives and the relative obtained materials. In this frame we performed rheological tests and exploited nuclear magnetic resonance trying to find new analytical approaches and a correlation between molecular organisation and mechanical behaviour. In the present work we have investigated straight and modified bitumen with different PPA content. Moreover for the first time we applied an inverse Laplace transform to the measured echo decays. This procedure allowed to distinguish different spin-spin relaxation times (T_2) that we can attribute to different macro-aggregates.

Experimental

Materials

The straight bitumen that we used in this study, has been produced in Venezuela and it has a 70/100 penetration grade. Polyphosphoric acid, 83.3% P_2O_5, or otherwise stated 115% H_3PO_4 equivalent [15], has been provided by ICL Performance Product LP (St. Louis, MO, USA).

Sample Preparation

The appropriate amount of PPA has been added to bitumen, at 120°C, to reach a level of 1 and 2% by weight. After mixing, the system has been heated up to 160°C (ARE, Velp Scientifica, Italy) and maintained at this temperature, under stirring at 600 rpm (RW 20 Digital, IKA, Germany), for 30 minutes in a sealed beaker to avoid any oxidation process. Afterwards, the resulting bitumen has been poured into a small sealed can and then stored in a dark chamber thermostated at 25°C to retain the obtained morphology. The samples for rheological tests have been rightly prepared; the bituminous material has been taken to the liquid status, increasing the temperature in a controlled way, then it has been poured directly on the plate of the rheometer preheated at 130°C. For the ^{1}H-NMR T_2 measurements, the samples have been introduced in a 5mm NMR tube, then heated up to 130°C and successively observed in cooling.

Methods

To explore the structural changes induced by temperature, a rheological characterization has been performed. In particular temperature-ramp test experiments have been performed on the bitumen. Rheological measurements have been conducted using a shear stress controlled rheometer SR5 (Rheometrics, USA) equipped with plate-plate geometry (gap 2.0 mm, diameter 25 mm). The temperature has been controlled by a Peltier system (±0.1°C). All the experiments have been performed in cooling. All the experiments have been carried out by using dynamic shear technique. The small amplitude dynamic tests provided information on the linear viscoelastic behavior of materials through the determination of the complex shear modulus [16].

$$G^{*}(\omega) = G'(\omega) + iG''(\omega) \tag{1}$$

where $G'(\omega)$ is the in phase (or storage) component, and $G''(\omega)$ is the out-of-phase (or loss) component.$G'(\omega)$ is a measure of the reversible, elastic energy, while $G''(\omega)$ represents the irreversible viscous dissipation of the mechanical energy. The rheological behaviour at different temperatures has been investigated by a time cure test (temperature-ramp test) at 1 Hz with a cooling ramp rate of 1°C/min. The applied shear stress of 100 Pa ensures to perform the dynamic rheological tests within the linear visco-elastic region.

NMR Measurement

For the ^{1}H spin-spin measurements a homemade NMR instrument has been used. It operates at a proton frequency of 15 MHz. Measurements have been performed at different temperatures ranging from 130 to 25°C with an error of ±0.1°C. A classic Carr-Purcell pulse sequence has been used to record the echo decay [17]. The applied width of $\pi/2$ pulse was 5.9 μs and that of π pulse was 11.8 μs. The τ delay time was 0.06 ms. In a basic NMR concept, at equilibrium, nuclei are distributed among the energy levels according to a Boltzmann distribution. Following any process that disrupts this distribution (e.g. absorption of radiofrequency energy), the nuclear spin system returns to equilibrium with its surroundings (the "lattice") by a first-order relaxation process characterized by a time T_1 called the spin-lattice relaxation time. To account for processes that cause the nuclear spins to come to equilibrium with each other, a second time T_2 is required. The T_2 is called the spin-spin relaxation time, because the relaxation is concerned with the exchange of energy between spins via a flip-flop type mechanism. It is defined according to:

$$\mathrm{v}_{\frac{1}{2}} \approx \frac{1}{\mathrm{T}_2} \tag{2}$$

where $\mathrm{v}_{\frac{1}{2}}$ is the linewidth at half height of a resonance line. In a perfectly homogeneous field the time constant of the decay would be T_2. However the real experiment is often characterized by field inhomogeneity. As a consequence, nuclei in different parts of the field precess at slightly different frequencies and quickly get out of phase with each other, causing the signal to decay with a different characteristic time T_2^*. This decay directly measures the decrease in the transverse magnetization M_{xy}, but due to the contribution of the magnetic field inhomogeneity it cannot be taken as a measure of T_2 [17].

A method for overcoming the inhomogeneity problem is to apply the Carr–Purcell technique [18]. This method may be described as a 90°, τ, 180°, 2τ, 180°, 2τ, 180°, 2τ, ... sequence (Fig. 1). The 180° pulses are applied along the positive y' axis, i.e., at 90° phase difference relative to the initial 90° pulse. The main advantage of such a multiple echo technique is its fastness as compared with other techniques based on single echoes. Consequently, it allows multiple accumulations of the echoes train signal which is an important issue in low-field experiments where the detection sensitivity is strongly reduced relative to the high-field experiments.

If the CP envelope, has a mono exponential decay, the relaxation time T_2 of the sample can be obtained by fitting the data to the following equation:

$$\mathrm{A} = \mathrm{A}_0 e^{-\frac{2\pi\tau}{\mathrm{T}_2}} \tag{3}$$

where A is the amplitude of the nth echo in the echo train and A_0 is a constant depending on the sample magnetization, filling factor and other experimental parameters. Usually the relaxation time varies all over the sample because of the sample heterogeneity or surface relaxivity differences, then a multi-exponential attenuation of the CP envelope should be observed. Hence if inside the sample, a continuous distribution of relaxation times exists, the amplitude of the nth echo in the echo train is given by:

$$\mathrm{A} = \mathrm{A}_o \int_o^{\infty} \mathrm{P}(\mathrm{T}_2) \exp\left(\frac{-2\pi\tau}{\mathrm{T}_2}\right) \mathrm{dT}_2 \tag{4}$$

where $P(T_2)$ is the T_2 relaxation time probability density. The last Equation suggests that the analysis of the experimental data using an Inverse Laplace Transform (ILT) might provide the relaxation time probability function. The ILT have been performed using an homemade software based on CONTIN [19, 20]. This is an iterative fitting software and

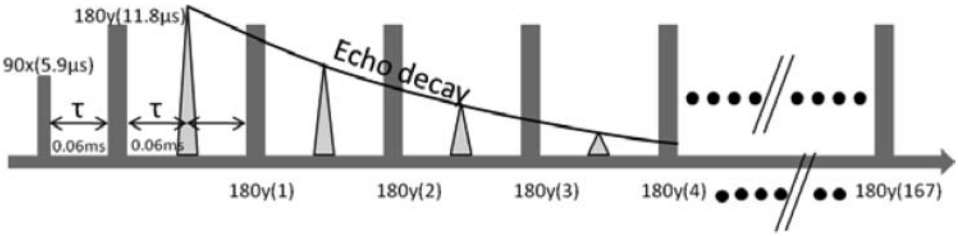

Figure 1. The echo detection pulse sequence used in the present paper.

it has been improved in order to extrapolate the data from the experimental T_2 decay. For a given CP decay, there are a certain different number of possible combinations of times which fit well the solution, especially in presence of signal noise. Therefore, the numerical ILT must be used with caution when interpreting the experimental results. As a matter of fact we cross-linked the ILT numbers with other experimental techniques.

Discussion

The present paper deals with the possibility of a more accurate description of the mechanical properties of bitumen if compared to the traditional standard empirical tests. These mechanical properties are the result of the chemical composition and phases arrangement of the molecular structures. So far, bitumen producers neglected, to a certain extent, the correlation of the molecular level with the macro-behaviour of the material. However there is a growing customer expectations in terms of given application performances. Hence bituminous materials are currently and always doped through substances that make the performance better for a given employment. On the other hand not always the mechanisms by which some additives act to dope bitumen are known. This is the case of PPA which is currently used by bitumen industry but it is still controversial its way to improve material performances. It is believed to reduce the size of the macro-polymers inside material leading to improved processing conditions, high temperature viscosity and storage stability. However, the mechanism of the chemical modification induced by PPA depends on the base bitumen. Here we investigated the effect of two different percentage of PPA onto a Venezuelan straight bitumen. Samples of pure materials have been added with a 1% and 2% of polyphosphoric acid. Rheology temperature-sweep experiments have been exploited to have some information on the structural changes induced by temperature, trying to better define a transition temperature range. In fact, in this experiment, the evolution of the storage and loss moduli is continuously monitored during a temperature ramp, at a constant cooling rate (1°C/min) and at a frequency of 1 Hz. Figure 2 shows the time-cure of the straight bitumen. No crossover between G' and G'' is observed, but the elastic modulus G' have

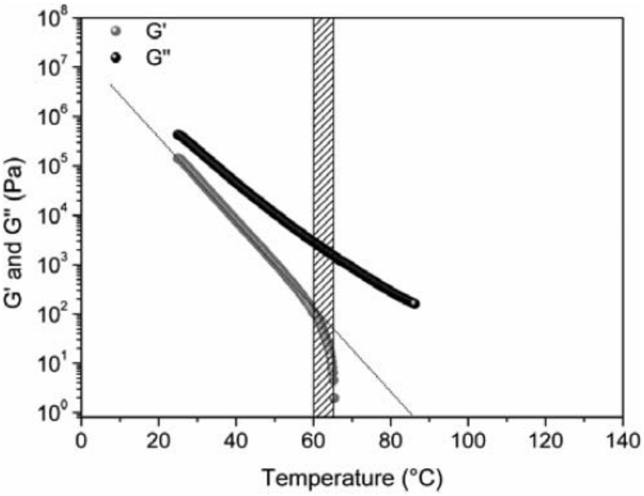

Figure 2. Time cure test at 1 Hz in the range 30–90°C of the straight bitumen. The two vertical lines define the temperature transition region.

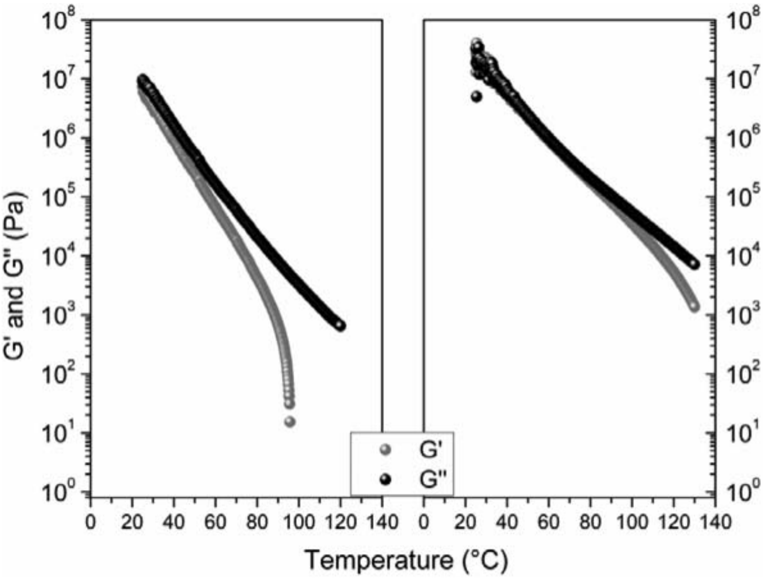

Figure 3. Time cure test at 1 Hz in the range 30–90°C of the bitumen modified with 1% and 2% PPA respectively.

a non-linear behaviour after 60°C. The starting point of the non-linear region of G′ can be considered as the beginning of the transition temperature region. The whole transition process from viscous to liquid regime ends when G′ modulus is no longer detectable.

Figure 3 shows the time-cure experiments for the 1% and 2% PPA modified bitumen. They show a similar behaviour of G′ and G″ in comparison with the straight bitumen. It is worthy to note that G′ and G″ of the modified bitumens, are higher than those of the straight bitumen and in addition G′ is closer to G″. This indicates that the doped material is more elastic. Moreover for the sample containing 2% PPA it can be observed a crossover between G′ and G″ along temperature. This behaviour is the result of a structural modification that occurs passing from a gel-like to a viscous material through a large visco-elastic region.

Table 1 reports the softening range temperatures for the three investigated bitumen. The addition of PPA shifts the transition range to higher temperatures.

The same samples have been investigated by means of ^{1}H-NMR spectroscopy. T_2 relaxation times were measured for all of the samples at different temperatures. The T_2 time can be used as a measure of the softness of a given material. The relaxation process, in fact, is more efficient when the material is more rigid, that corresponds to shorter relaxation times. As matter of fact, higher temperatures correspond to longer T_2 times,

Table 1. Temperature range transition of the straight, 1% and 2% PPA modified bitumen

	Starting Temperature	Final Temperature
Straight Bitumen	60.1	65.4
Bitumen + 1% of PPA	87.0	95.6
Bitumen + 2% of PPA	121.8	129.8

bitumen is not an exception. As mentioned above the T_2 time is usually extracted from an exponential decay which is the envelope of the recorded echo signals. When the material is not homogeneous, the measured T_2 is averaged over all of the contributions of the different macro-structures. Considering bitumen models, one can roughly distinguish between a rigid (asphaltenes) and a soft fraction (maltenes) inside the substance. These two parts have a different intra-molecular arrangement and interactions and it is reasonable to think that they relax-back to the equilibrium in different times, contributing to the measured echo envelope differently.

A sophisticate mathematical process to extract the T_2 distribution times is to apply an Inverse Laplace transform (ILT) to the measured echo envelope. Figure 4 shows the echo decay and the ILT results for the straight bitumen at 25°C and 65°C.

It is worthy to note that at 25°C two very close T_2 distribution times can be observed. The first distribution corresponds to the “rigid” part while the second to the “soft” one. However these times distributions (peaks) are really close each other and this means that the whole structure is quite homogeneous with a mutual exchange of spin energy between the soft and rigid fractions. At the transition temperature of 65°C, the ILT reveals that the T_2 distribution times are longer, as we expected for temperature effects, but now the two macro structures can be absolutely differentiated. We attributed the largest T_2 peak to the oil phase inside bitumen (maltenes fraction). This result falls into the transition temperature range obtained by rheology.

The same experiments have been conducted for the two modified bitumens. Figure 5 shows the obtained results for the sample containing 1% PPA. The trend and the shape

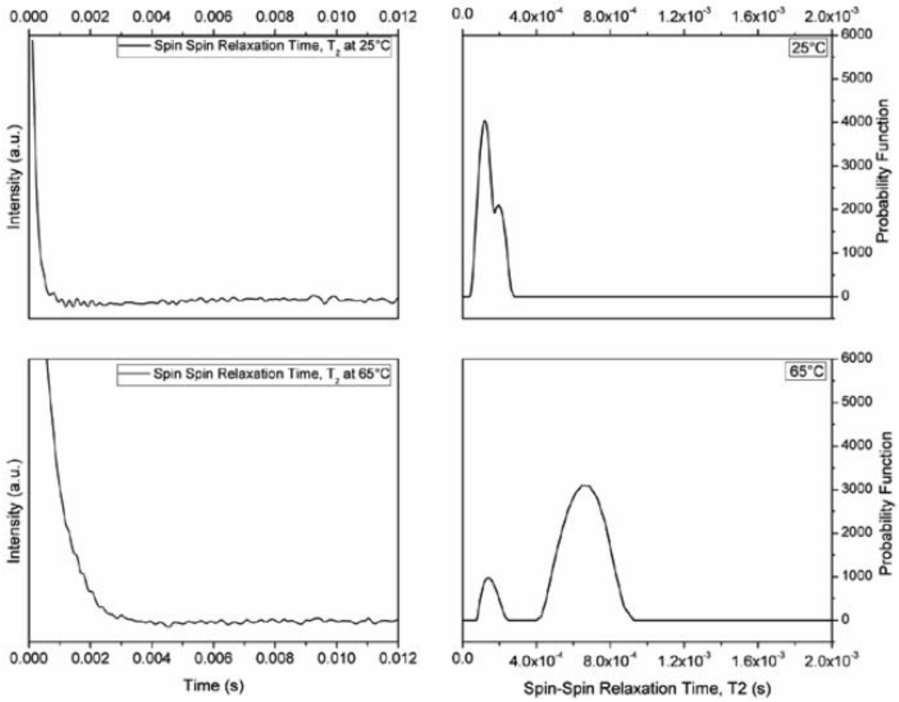

Figure 4. a) The echo intensity envelope versus time in a CP relaxation experiment in the case of straight bitumen at 25°C and 65°C. b) Relaxation times distribution of straight bitumen at 25°C and 65°C obtained by ILT.

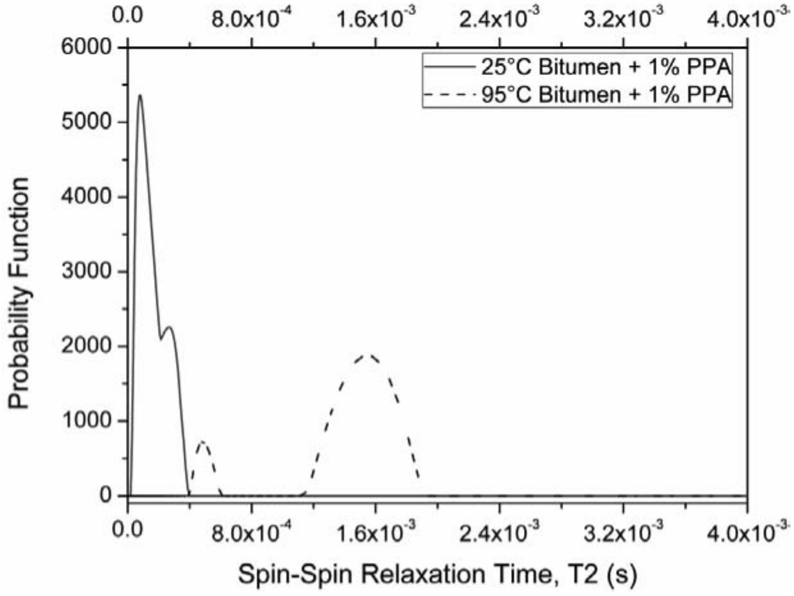

Figure 5. Relaxation time distribution of bitumen 1% PPA modified at 25°C (solid line) and 95°C (dashed line) obtained by ILT.

of the extracted peaks are very similar to those of the straight bitumen. However the transition temperature is shifted towards higher values (about 95°C, dashed line). Also for this modified sample we can say that there is good homogeneity at room temperature while at the transition temperature we attribute the largest T_2 peak centred at 1.6×10^{-3} s, to the soft part of the material. The calculated spin-spin relaxation times are shorter than the T_2 times of the straight bitumen. This is due to the enhanced rigidity after the addition of 1% PPA. The transition temperature as measured by applying the ILT is still in agreement with the rheology findings.

For the last sample, which contains 2% PPA (Fig. 6), we have registered the largest transition temperature deviation from the straight bitumen (Fig. 4). Indeed the sample turned from gel to liquid phase at a temperature around 130°C. Also in this case the transition temperature observed by NMR analysis is similar to that determined by rheological measurements. However we can make some new and interesting considerations. At room temperature we can clearly recognize three peaks underlying the echo envelope fitting. This means that the highest PPA content might induce the formation of a third macro-structure inside the material. As a matter of fact, the third peak indicates a inhomogeneity of the material that can cause processing and application problems. This macro-structure is a relatively soft component and it is evidenced by the smallest peak shown in Fig. 6. Indeed this peak falls into the same times region at both low and high temperatures. This indicates that the new structure seems not to be affected by temperature. On the other hand at high temperatures only two peaks are found, similarly to the straight and 1% PPA modified bitumens. In addition for the bitumen added with 2% PPA at 125°C, we observed that the T_2 peak centred at 2.6×10^{-3} s is wider and shorter than the correspondent peak for the 1% PPA sample (Fig. 5). This is probably due to a more fragmented structure as relaxation times are spread throughout a larger time range.

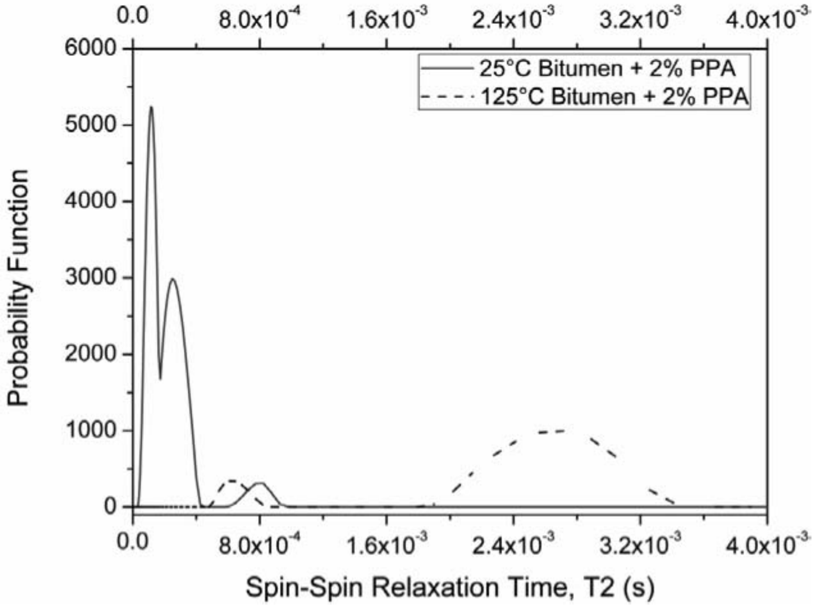

Figure 6. Relaxation distribution times of bitumen 2% PPA modified at 25°C (solid line) and 125°C (dashed line) obtained by ILT.

Conclusions

Commercial bitumen classification is still based on empirical standardized tests. Also the effects of doping substances on bituminous materials are evaluated by conventional methods. Here we reported a new analytical approach to improve the usual bitumen classification and the evaluation of the chemical changes caused by a given additive.

A common modifier, PPA, has been added to a Venezuelan 70/100 straight bitumen. Two PPA percentage were used to evaluate the effects of an excess of doping substance along temperature. Rheology and ^{1}H-NMR spin-spin relaxation times were used to assess the softening point of the three materials and their response to specific solicitations. Results were in agreement to what expected and to literature. It was found that a 1% of PPA can shift the transition temperature towards higher values and the systems remain stable. The sample containing 2% of PPA showed a huge transition temperature shifting as it was found around 130°C. However the last sample resulted more heterogeneous because of new structures appeared after the modifier addition, precluding practical application. In addition the Inverse Laplace Transform revealed itself as a valuable way to study the macrostructure of bitumen when this technique is supported by other methods.

Further investigations are needed to clarify the nature the nature of the interaction between PPA and the bitumen network.

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