

RHEOLOGICAL BEHAVIOUR OF POLYMER-MODIFIED
BITUMINOUS MASTICS: A COMPARATIVE ANALYSIS
BETWEEN PHYSICAL AND CHEMICAL MODIFICATION

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ABSTRACT

Mastic, a bitumen/filler blend which naturally forms when bitumen is mixed with aggregates is the actual product used to bind coarse mineral particles in the asphalt mixtures. As a result, the characterisation of mastics is essential to improve the understanding of the response and performance of asphalt concrete pavements. On the other hand, the lack of experimental data concerning the behaviour of mastics and, above all, polymer-modified mastics has been lately claimed. In that sense, this work presents a comparative analysis between the effect that “physical” and “chemical” modification by polymers exert on mastics prepared by blending modified binders with different contents of calcium carbonate, ranging from 65 to 80 wt.%. Tri-block copolymer SBS and a “reactive” isocyanate-based prepolymer were used as modifying agents in the preparation of the binders. Linear viscoelasticity tests revealed that polymer type exerts, at high temperatures, a significant influence on the binder contribution to the overall rheological properties of the resulting mastic.

Keywords: rheology, bitumen, mastic, polymer, isocyanate, product design.

1. Introduction

Bitumen, by-product from crude oil fractionation, is a colloidal dispersion of asphaltenes into an oily matrix, referred to as maltenes, constituted by saturates, aromatics and resins [1,2]. Bitumen chemical composition depends primarily on its crude source and the refining process involved [3]. The colloidal model of bitumen, first proposed by Nellensteyn [4] and further developed by Pfeiffer and Saal [5], reveals that both temperature and chemical composition greatly affect bitumen microstructure and, consequently, its rheological properties.

Bitumen has been traditionally used as a binder of mineral aggregates in the paving industry, although it has also found many other civil and engineering applications like roofing, flooring, tanking, etc. So, in general, bitumen is demanded to remain flexible enough to withstand sudden stresses without cracking at low temperatures during winter, but must also resist the permanent deformation or viscous flow at high in-service temperatures.

Bitumen modification with polymers may help overcome shortcomings provoked by the combined action of heavy traffic loads and extreme temperatures, that is, rutting and fatigue cracking at high temperature, and thermal fracture at low temperature [6,7]. Polymer modifiers for bitumen can be classified into two general categories, “passive” and “active” polymers [8]. Passive polymers, which are the most common modifiers used, are often further classified into elastomers and plastomers. Among the thermoplastic elastomers, the styrene-butadiene-styrene block copolymer (SBS) has proved to present the greatest potential when blended with bitumen [8].

However, it is well-known that these two classes of polymers usually present a very low compatibility with bitumen [3]. Thus, the addition of active polymers, containing

functional groups which can form chemical bonds with certain bitumen compounds, is being lately envisaged [9,10]. Among them, isocyanate-based prepolymers have shown to be a promising bitumen modifying agent, leading to enhanced mechanical properties, mainly at high service temperatures [11-19].

Although added in a very low concentration (around 5 wt.%), bitumen controls the final properties and the performance of the asphalt mixture, since it is the only deformable component and forms a continuous matrix [20-22]. However, mineral fillers (with a particle size below 75 microns) typically represent from 2 to 12 wt.% of the total mineral matter in a bituminous mix. Hence, a bitumen/filler blend (commonly referred to as mastic) naturally forms when bitumen is mixed with aggregates [2]. In that sense, bitumen/filler mastic is the actual product used to hold coarser aggregate particles together in the asphalt mixtures [23,22]. Consequently, the characterisation of mastics is essential to improve the understanding of the response and performance of asphalt concrete pavements at both high and low temperatures [25], as well as to obtain pertinent information on the mixing and compaction temperatures of the asphalt mixtures [26].

Suspension laws describe very well the behaviour of mastics, as long as particles do not come into close contact. In other applications, rather than paving, mineral filler content in the mastic formulation may be much higher. In this case, the properties of the concentrated mastic become quite different from that of the parent bitumen because of the presence of numerous aggregate-aggregate contacts [2], situation that remains, at the moment, quite difficult to mechanically model.

It is generally recognised that there is a lack of experimental data concerning the behaviour of mastics [27] and so, the need to conduct research on the influence of mineral fillers on the stiffening properties of mastics is a major concern. On the other

hand, not much work has been done on polymer-modified bituminous mastics, and the effect of the polymer nature on the mastic performance.

With the aim of improving knowledge on this subject, this study presents a comparative analysis between mastics containing calcium carbonate as reinforcing filler (from 65 up to 80 wt.%), derived from bituminous binders which were previously modified by addition of either a thermoplastic elastomer SBS or a reactive isocyanate-based prepolymer. Linear viscoelasticity tests, related to the small deformations which the binder is assumed to sustain during service, revealed that polymer type exerts a significant influence on the binder contribution to the overall rheological properties of the mastics.

2. Experimental

2.1. Materials

In order to study the rheological behaviour of polymer-modified bituminous mastics, a bitumen sample with penetration grade between 40/50 has been selected. The results of penetration grade trials and R&B softening temperature tests, according to ASTM D5 and D36, respectively, as well as chemical composition in terms of SARAs fractions are presented in Table 1.

Two different types of polymers have been considered as bitumen modifying agents:

- a) On the one hand, a polyethylene glycol functionalised with isocyanate groups, by its reaction with polymeric MDI (4,4'-diphenylmethane diisocyanate) in N₂ atmosphere, at 40°C, for 48 hour and under agitation. A molar ratio PEG:MDI of 1:5 was selected, assuring an excess of non-reacted MDI molecules in the product. The resulting reactive prepolymer (henceforth MDI-PEG), with an average M_w of 784 g mol⁻¹, presents free –NCO groups available for reaction.

b) On the other hand, a SBS triblock copolymer (trade name “Kraton D-1101”), provided by Shell Chemical Co. (United Kingdom), was used for the sake of comparison, as it leads to physical (instead of chemical) bitumen modification. This copolymer contains 31 wt.% styrene and has an average M_w of $1.5 \cdot 10^5 \text{ g mol}^{-1}$.

Additionally, calcium carbonate powder from marble industry, with an average particle size of 20 microns (measured by laser diffraction analysis), has been used as reinforcing filler in the preparation of the bituminous mastics studied. Moisture was completely removed, as shown by means of TGA tests, by setting the filler in an oven at 130°C overnight.

2.2. Samples processing

Prior to the preparation of the mastics, bitumen was modified by addition of either MDI-PEG prepolymer or SBS. The processing protocol followed depended on the type of modifier selected. Thus, for the reactive polymer, modification was carried out by mixing bitumen and 4 wt.% MDI-PEG, for 1 h, at 90 °C, with a four-bladed turbine rotating at 1200 rpm, and subsequently settling the blend in an oven at 90°C for 24 hours. The resulting modified bitumen was then divided into three parts: a) one was used as such; b) another one was mixed with 2 wt.% water for 45 min at 90 °C; and c) the third part was poured onto aluminium foil, forming a thin layer which was exposed for 35 days to the ambient (under free access of air). Regarding the non-reactive polymer, a sample of bitumen with 3 wt.% of SBS (binder formulation commonly used by the paving industry) was prepared for 1.5 h, at 180 °C, with the same processing device.

The preparation of unmodified and modified bituminous mastics was carried out by manually blending either neat or modified bitumens previously obtained (three from MDI-PEG and one more from SBS) with calcium carbonate at concentrations which ranged from 65 up to 80 wt.%.

2.3. Tests and measurements

Viscous flow measurements, at 60°C, were conducted on neat and modified bitumen samples in a controlled-stress Haake RS-150 rheometer (Germany), using plate-and-plate geometry (20 mm diameter, 1 mm gap). Oscillatory shear temperature sweep tests were also conducted on those samples between 30 and 80°C, by applying a heating rate of 1 °C/min, and a value of deformation within the linear viscoelastic region (henceforth LVR), with the same rheometer and plate geometry.

In addition, dynamic flexural tests were performed on both the unmodified and modified mastics, by means of a Dynamic Mechanical Spectrometer Seiko 6100 (Japan). Thus, frequency sweeps between 10^{-2} and 10^2 Hz, at selected constant temperatures varying from -30 to 70°C (in 20°C-increments) and small values of deformation within the LVR, were carried out on specimens with dimensions 50mm×10mm×2.5mm. All tests were carried out at least twice in order to assure repeatability of the results.

3. Results and discussion

3.1. Viscous flow behaviour and linear viscoelasticity of modified bituminous binders

The viscous flow behaviour, at 60°C, for the 4 different modified bitumens prepared has been studied, and the results are presented in Figure 1. As a reference value, viscosity at

60°C for the neat bitumen used has also been included. It can be observed that neat bitumen, 3 wt.% SBS and 4 wt.% MDI-PEG samples show an almost constant value of viscosity in the entire range of shear rates studied. Instead, addition of 2 wt.% water or curing at room temperature for 35 days lead to a different viscous flow behaviour, with a constant value of viscosity at low shear rates followed by a shear thinning drop once a “critical” shear rate value is reached. On the other hand, bitumen modification with 4 wt.% MDI-PEG yields a very significant increase in viscosity, of nearly 1 decade relative to the neat bitumen. If compared to the 3 wt.% SBS sample, addition of 4 wt.% MDI-PEG also gives rise to binders with clearly higher values of viscosity. As reported by Martín-Alfonso et al. [15,16], these observations are the result of a certain type of reaction between the –NCO groups in the reactive prepolymer and some heavy bitumen fractions with “active” H atoms. It occurs during processing (so, “short-term” modification) and leads to the formation of urethane linkages. However, much higher degrees of modification are observed after 35 days of curing at room temperature and, mainly, after addition of 2 wt.% water, with a viscosity increase of up to 2 decades relative to the base bitumen. According to Martín-Alfonso et al. [15,16] a “long-term” modification occurs if bitumen is exposed to the ambient, during prolonged periods of time (35 days, in our case), after being previously modified with this isocyanate-based prepolymer. Thus, diffusion of moisture into bitumen was seen to promote 2 series reactions involving water, which give rise to a further increase in the binder viscosity. An even greater effect is noticed after direct addition of 2 wt.% water, with modification time being notably shortened [12,15].

For a quantitative analysis of the different degrees of modification achieved, the Carreau model was applied to the viscous flow results:

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

In this model, η_0 is the zero-shear viscosity; $\dot{\gamma}_c$, is the critical shear rate for the onset of the shear-thinning region; and s is a parameter related to the slope of this last region. The values of the Carreau model parameters for the binders showing a shear-thinning region in Figure 1 are shown in Table 2. In other cases, only the values of the Newtonian viscosity, η_0 , are presented. Carreau model parameters confirm that addition of 2 wt.% water after reactive modification of bitumen prompts the largest level of shear-thinning (with lowest and highest values of $\dot{\gamma}_c$ and s , respectively) and suggests the development of a binder with a much higher level of microstructural complexity than the unmodified base bitumen. Moreover, both 2 wt.% water and 35 days curing samples present a very significant degree of modification if compared to the original MDI-modified bitumen. Finally, all of them show values of viscosity higher than the 3 wt.% SBS sample (see Table 2).

A modification index (M.I.), written in terms of the zero-shear viscosity values at 60°C, results very convenient to visualize at a glance the degree of modification achieved.

This index is defined as follows:

$$\text{M.I.} = \frac{\eta_{0,\text{mod}} - \eta_{0,\text{neat}}}{\eta_{0,\text{neat}}} \quad (2)$$

where $\eta_{0,\text{mod}}$ and $\eta_{0,\text{neat}}$ are the zero-shear viscosity values at 60°C for modified and neat bitumen samples, respectively.

Figure 2 shows the values of the modification index (M.I.) for the 4 different samples studied. The binder with 2 wt.% water presents, by far, the highest degree of

modification (its viscosity is 110 times higher than neat bitumen's). The binder cured for 35 days exhibits a lower value of M.I. (about 72), but still being much higher than that for 4 wt.% MDI-PEG and 3 wt.% SBS samples. This fact confirms that, on the one hand, water (either added or absorbed from air) promotes reactions with free –NCO groups which significantly alter binder microstructure [15] and, on the other hand, “reactive” modification by this isocyanate-based prepolymer brings about much higher viscosity enhancements than physical modification by the thermoplastic elastomer SBS.

On the basis of the previous flow behaviour study, 2 samples, belonging to “physical” and “chemical” modification categories, respectively, were selected for the remaining study: 3 wt.% SBS sample and 4 wt.% MDI-PEG/2 wt.% water sample (which showed highest level of modification than the other 2 MDI-PEG-modified binders). Thus, dynamic temperature sweep tests, within the linear viscoelastic interval, were performed between 30 and 80°C, and results are shown in Figure 3. Neat bitumen, which has been included as a reference, presents a monotonous decrease in G' and G'' as temperature increases, with the viscous features prevailing over the elastic ones in the entire temperature range tested. Moreover, viscous flow zone appears at the highest temperatures. A similar behaviour can be observed for the 3 wt.% SBS sample, although significantly higher values of the elastic and viscous moduli are found. However, 4 wt.% MDI-PEG/2 wt.% water sample present outstanding differences if compared to those samples. On the one hand, G'' only prevails over G' for temperatures higher than 47°C. On the other hand, as previously reported, water addition leads to a stiffer binding material for which the terminal zone does not even appear at the highest temperature value reached in this study (80°C).

3.2. Linear viscoelasticity of unmodified bituminous mastics

In order to determine the linear viscoelastic behaviour of the bituminous mastics studied, frequency sweep tests at 30°C (with flexural deformation values within the LVR) were performed on samples prepared by blending neat bitumen with different contents of calcium carbonate, varying from 65 to 80 wt.%. As can be observed in Figure 4, neat bitumen shows, at 30°C, values of the elastic and viscous moduli which monotonously decrease as frequency does. Moreover, at this testing temperature, viscous features prevail over the elastic ones, as deduced from values of E'' higher than E' in the entire interval of frequencies studied. The addition of filler has pronounced effects on the viscoelastic properties of the resulting materials. On the one hand, it leads to an increase in both viscoelastic moduli, of more than one decade for the highest calcium carbonate concentration (80 wt.%). On the other hand, it reduces the differences found between the elastic and viscous moduli, if compared to the base bitumen, which is related to an enhancement in the material elasticity. However, at this temperature, the viscoelastic response of the unmodified mastics still remains mainly viscous, even at the highest calcium carbonate content. In that sense, the strength of the bituminous matrix at 30°C is high enough so that it still controls the material linear rheology.

With the aim of looking further into the behaviour of the unmodified mastics, Figure 5 presents the effect of temperature on the viscoelastic behaviour of a selected unmodified mastic containing 80 wt.% calcium carbonate. It can be appreciated that increasing temperature from 30 up to 50°C merely decreases the values of the elastic and viscous moduli, although viscous features still prevail over the elastic ones. If temperature is further increased up to 70°C, significant differences in the material viscoelastic behaviour arise. Thus, at this temperature, viscoelastic properties of the continuous bitumen phase would decrease to an extent that interactions among filler particles yield

a notable enhancement in the mastic elastic characteristics, as demonstrated by E' prevailing over E'' nearly in the whole interval of frequencies studied. Moreover, it is worth noting the trend to an apparent plateau at low frequencies (where E' is expected to level off) is characteristic of complex materials in which important interactions among discrete particles may occur. Such a plateau has elsewhere been described in terms of an equilibrium modulus, hardly dependent on frequency and temperature, that reflects the microstructure at rest as well as the interparticle forces [28]. Consequently, results in Figures 4 and 5 demonstrate that, at the lowest frequency values tested, an unmodified mastic with 80 wt.% filler presents much higher stiffness at 70°C than neat bitumen does at 30°C.

3.3. Linear viscoelasticity of modified bituminous mastics

Analysis of the viscoelastic properties of modified bituminous mastics was further carried out. In that sense, Figures 6 and 7 present the evolution with frequency, at 30 and 70°C, respectively, of the complex flexural modulus (a) and loss tangent (b), for 2 selected modified mastics with a fixed calcium carbonate content of 80 wt.%: “physically” 3 wt.% SBS-modified mastic and “chemically” 4 wt.% MDI-PEG/2 wt.% water-modified mastic. Results at 30°C for the neat bitumen, and for the unmodified mastic at 30 and 70°C, have also been included as reference values. It can be observed that, at any of the two temperatures studied, binder modification prompts mastics with improved viscoelastic properties, with higher values of the flexural complex modulus than the 80 wt.% filler unmodified mastic. In addition, the 4 wt.% MDI-PEG/2 wt.% water-modified mastic shows the highest flexural stiffness, as expected from results of level of modification presented in Figure 2. However, Figures 6 and 7 make evident that temperature is seen to produce outstanding differences in the rheological behaviour observed.

Thus, at 30°C, modification yields an important increase in the value of $|E^*|$ relative to the unmodified mastic, with a slight reduction in the average slope of the curve within the frequency interval studied (see Figure 6a). However, a monotonous decrease in the values of $|E^*|$ can always be observed as frequency decreases, which indicates the lack of a plateau or equilibrium modulus, as particle-particle interactions are poorly developed at this temperature. On the other hand, Figure 6b shows that modification enhances material elastic features, mainly for the “chemically”-modified mastic, for which the loss tangent remains below 1 (prevailing elastic modulus over viscous one) from the lowest to the highest frequencies tested. The modified mastic containing 3 wt.% SBS, with an almost constant value of $\tan\delta$ close to 1, would present comparable values of its storage and loss moduli in the whole frequency range.

Figure 7a, which displays results from dynamic bending tests at 70°C, demonstrate that an increase in temperature causes significant effects on the mastic rheology. On the one hand, for each of the mastics studied, it reduces the values of the complex modulus. On the other hand, for the modified mastic prepared from the binder with the lowest viscosity, that is, 3 wt.% SBS-modified mastic, reduction in the matrix viscoelastic moduli with increasing temperature would lead to a notable increase in the interaction among solid particles of filler. As previously commented, this situation brings about the existence of a plateau or equilibrium modulus (with E' values becoming nearly constant as frequency decreases), and the consequent enhancement in the elastic features of the resulting material. Yet, it can be noticed that this plateau is not as evident as in the unmodified mastic. On the contrary, this observation is not found for the bituminous mastic modified by addition of MDI-PEG/water. Reactive modification, instead of physical bonds within polystyrene domains in SBS, produces important changes in the bitumen colloidal nature which results in a highly viscous continuous matrix which

controls the linear rheology of the material even at 70°C. So, in that case, modification prevents the elastic response induced by particle-particle interactions from becoming apparent. Hence, differences found between “physical” and “chemical” modification become much more important at this temperature. Figure 7b, which displays the evolution of $\tan\delta$ with frequency at 70°C for the mastics considered, again reveals a very significant increase in the elastic behaviour of the unmodified mastic as frequency decreases, when the particle-particle interactions become more pronounced. On the contrary, the “chemically”-modified mastic demonstrates a very low level of frequency susceptibility, as $\tan\delta$ remains almost constant.

The most important aspect of the rheological properties of bituminous binders and mastics is their dependence on temperature. In that sense, bitumen thermorheological simplicity, reported by different authors, has become quite controversial. Several authors have claimed that the time-temperature superposition principle (TTSP) fails at high temperature, especially for high asphaltene and/or high crystalline content materials [1] and is, therefore, very unlikely to apply to most PMB's [29]. In contrast, some others sustain that the mechanical spectrum of many modified bituminous products can be represented, reasonably well, by master curves of their linear viscoelastic material functions [30]. Anyway, the TTSP has been widely applied to both neat and polymer-modified bitumens, and synthetic binders [3,6,9,31,32], as well as asphalt mastics [33,34].

Hence, dynamic flexural tests within the LVR were performed on the 2 selected modified mastics with 80 wt.% filler, as well as unmodified mastic (taken as a reference), at fixed values of temperatures between -30 and 70°C (in 20°C-increments). Frequency sweep tests results were combined in the form of “Black” diagrams, by

plotting the phase angle (δ) vs. complex flexural modulus ($|E^*|$). These plots (not shown here) demonstrated that the mastics studied do not conform to TTSP and that, at least strictly, master curves could not be obtained. However, examination of the master curves provides a convenient method for comparison of the elastic and viscous behaviour of the mastics over a wide range of applied loading frequencies (or temperatures, by inverse equivalence). Thus, isothermal elastic and viscous moduli curves were “empirically” superposed onto a master curve by using a shift-factor, a_T , with 10°C as the reference temperature. Within the temperature range studied in this work, the temperature-dependence of the shift factor is described by the Williams-Landel-Ferry (WLF) equation [35] reasonably well:

$$\log a_T = \frac{-C_1 \cdot (T - T_0)}{C_2 + T - T_0} \quad (3)$$

where T_0 is the reference temperature (10°C, in our case), and C_1 and C_2 are two fitting parameters of this model.

According to that, Figure 8a shows the evolution of the elastic and viscous moduli with reduced frequency, $f \cdot a_T$, for the “physically” 3 wt.% SBS- and the “chemically” 4 wt.% MDI-PEG/2 wt.% water-modified mastics. The rheological behaviour shown in Figure 8a is, at least in part, quite similar to that found in unmodified and polymer modified binders (see, for instance, [9,36,37,38]. Transition to the glassy region (delimited by a maximum in the E'' curves) appears at high frequencies, and a crossover point between E' and E'' , at intermediate frequencies, is also observed. Moreover, no plateau at intermediate frequency values (like that which characterises polymer melts and solutions) was detected, which demonstrates the non existence of polymer entanglements [35]. However, major differences are noted at the lowest values of

frequency (or equivalently, highest values of temperatures).

In order to compare the viscoelastic behaviour of the mastics with that shown in Figure 3 for their corresponding base binders, temperature-dependence of the linear E' and E'' moduli, at a fixed frequency value of 1 Hz, was obtained from frequency sweep tests by following the procedure described by Martinez-Boza et al. [39]. However, shift factors were assumed to follow the WLF (instead of Arrhenius) equation in the present work. Figure 8b reveals that the rheological behaviour observed in the “chemically”-modified mastic is not too different from that found for its corresponding binder (in Figure 3). From the crossover point between $E'(G')$ and $E''(G'')$, both moduli remain very close each other (almost coincident in the case of the mastic) and monotonously decrease as temperature increases. However, E' and E'' are notably higher than G' and G'' due to the presence of a high content in solid particles of filler. With relation to the “physically”-modified and unmodified mastics, the behaviour observed at high temperatures is markedly different from that shown in Figure 3 for their corresponding binders. As commented above, interactions between particles aggregates become very important at high temperature for those samples containing bituminous binders with the lowest viscosities, above all the unmodified bitumen (see Figure 1). The dispersed solid phase begins controlling the overall rheological response of the mastic and, consequently, the elastic modulus (which becomes frequency-independent) prevails over the viscous one at temperatures above 70°C. Contrarily, neat bitumen and 3 wt.% SBS-modified bitumen in Figure 3 present, at high temperature, curves of G'' and G' with slopes which are typical from the terminal or viscous flow region of the mechanical spectrum.

On the other hand, a “mechanical” (and so, frequency-dependent) glass transition

temperature, calculated from the maximum value of E'' curve, may result a suitable parameter to establish a comparative analysis between the low temperature performance of unmodified and modified bituminous mastics. However, compared to neat bitumen, inter-particle interactions lead to broader and flatter E'' peaks in mastics (Figure 8b). As a result, significant differences among the 3 samples studied were not found in the low temperature region. In fact, the low temperature behaviour of asphalts is known to be less influenced by polymer modification than the high temperature one [15]. In that sense, from results in Figure 8b, it is hard to conclude if modification leads to any type of efficient improvement on the thermal fracture resistance of the samples.

4. Conclusions

The effect of selected “physical” and “chemical” polymer modifications, by a tri-block copolymer SBS and a “reactive” MDI-based prepolymer, respectively, on bituminous mastics with high concentration of calcium carbonate has been investigated.

Addition of 4 wt.% MDI-PEG and 2 wt.% water was seen to produce the highest enhancement in binders viscosity at 60°C, as proved by the flow viscous results. This outcome has been reported to be the result of the combined effect of “free-water” modification during mixing bitumen/prepolymer, and further modification involving water.

Moreover, dynamic bending tests conducted on unmodified mastics with a high reinforcing particles content of 80 wt.% revealed the significant contribution of interactions among particles aggregates at temperatures for which the bituminous matrix stops controlling the overall rheological response. This fact is shown by the existence of a plateau or equilibrium modulus in E' as temperature is increased up to 70°C, with the material exhibiting enhanced elastic properties.

Finally, Black diagrams demonstrated that the bituminous mastics studied must be considered as thermorheologically complex materials and, at least strictly, they do not conform to the TTSP. Anyway, for comparison of the elastic and viscous behaviour of the mastics over a wide range of applied loading frequencies, the TTSP was applied and E' - E'' curves were “empirically” superposed onto a master curve. Major differences were found in the high temperature region, with the polymer type greatly influencing the binder contribution to the overall rheological properties of the mastics. Hence, the plateau value commented above still remains for the unmodified mastic and, in a lesser extent, “physically”-modified mastic, which contain the binders with lowest viscosities in their formulations. On the contrary, the “chemically”-modified mastic behaviour resembles that shown for its corresponding base modified binder.

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Table 1. Penetration, R&B softening temperature and SARAs fractions for the neat bitumen used.

Neat bitumen properties	
Penetration (dmm)	49
R&B softening point (°C)	53.5
Saturates (wt.%)	6.2
Aromatics (wt.%)	50.3
Resins (wt.%)	24.5
Asphaltenes (wt.%)	19.0

Table 2. Carreau model parameters for the neat bitumen used and its corresponding SBS and MDI-PEG-modified samples (shown in Figure 1)

Binders	Carreau model parameters		
	η_0 (Pa·s)	$\dot{\gamma}_c$ (1/s)	s
Neat bitumen	$7.1 \cdot 10^2$	---	---
3 wt.% SBS	$1.9 \cdot 10^3$	---	---
4 wt.% MDI-PEG	$4.6 \cdot 10^3$	---	---
4 wt.% MDI-PEG + 2 wt.% H ₂ O	$7.9 \cdot 10^4$	$2.2 \cdot 10^{-2}$	$2.1 \cdot 10^{-1}$
4 wt.% MDI-PEG, cured for 35 days	$5.2 \cdot 10^4$	$2.8 \cdot 10^{-2}$	$1.7 \cdot 10^{-1}$

Figure captions

Figure 1. Viscous flow curves, at 60°C, for neat bitumen and different polymer modified binders studied.

Figure 2. Modification index values, at 60°C, for different polymer modified binders studied.

Figure 3. Evolution with temperature of the elastic and viscous moduli in oscillatory shear for neat bitumen and selected polymer modified binders.

Figure 4. Evolution with frequency, at 30°C, of the elastic and viscous moduli in dynamic bending, as a function of filler content, for neat bitumen and unmodified bituminous mastics.

Figure 5. Evolution with frequency of the elastic and viscous moduli in dynamic bending, as a function of temperature, for an unmodified bituminous mastic with 80 wt.% filler.

Figure 6. Evolution with frequency, at 30°C, of: (a) flexural complex modulus, and (b) loss tangent, for neat bitumen, as well as unmodified and selected polymer modified mastics with 80 wt.% filler.

Figure 7. Evolution with frequency, at 70°C, of: (a) flexural complex modulus, and (b) loss tangent, for neat bitumen, as well as unmodified and selected polymer modified mastics with 80 wt.% filler.

Figure 8. (a) Empirical master curves of storage (E') and loss (E'') moduli vs. reduced frequency, $f \cdot a_T$, for neat bitumen, as well as unmodified and selected polymer modified mastics with 80 wt.% filler. (b) Evolution of the linear viscoelasticity functions obtained from frequency sweep tests.

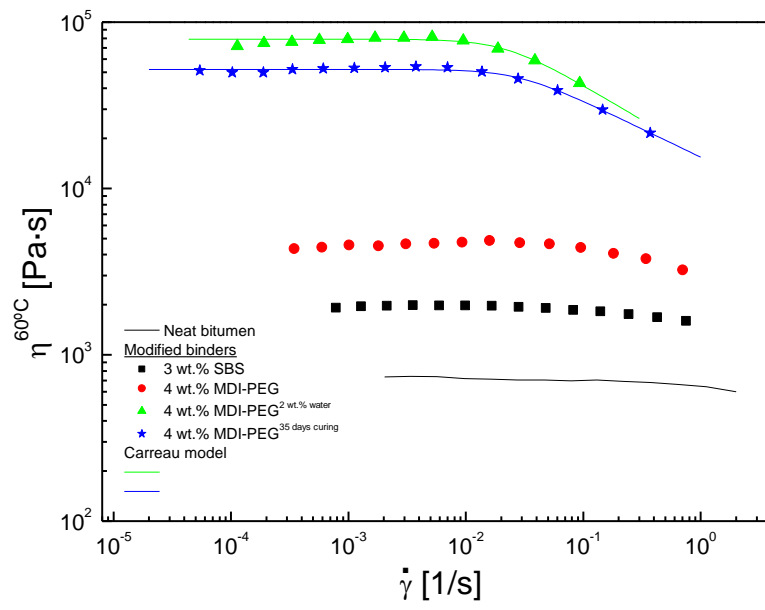


Figure 1.

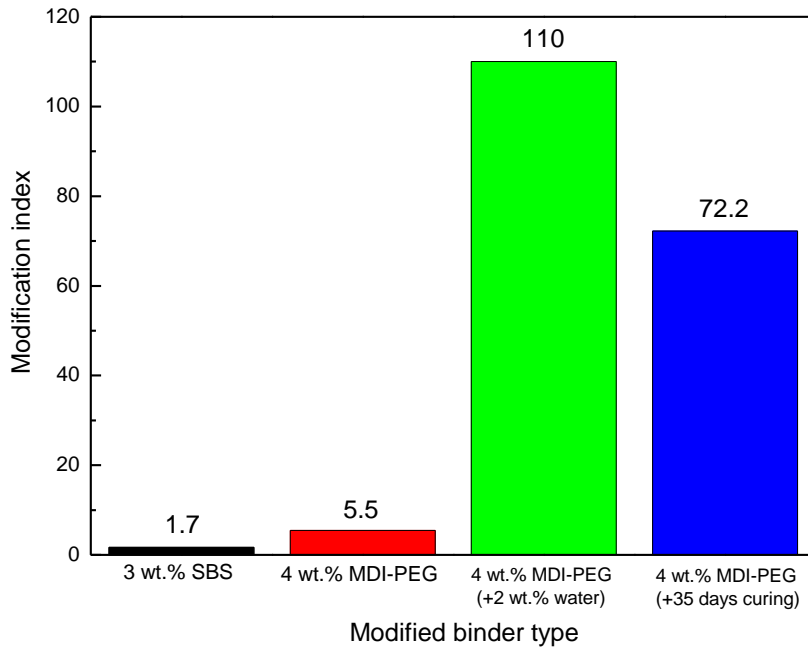


Figure 2.

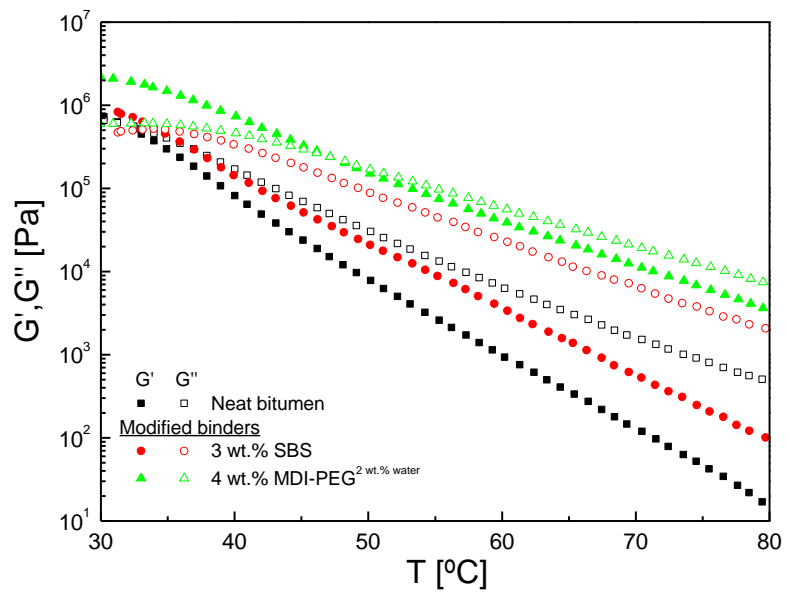


Figure 3.

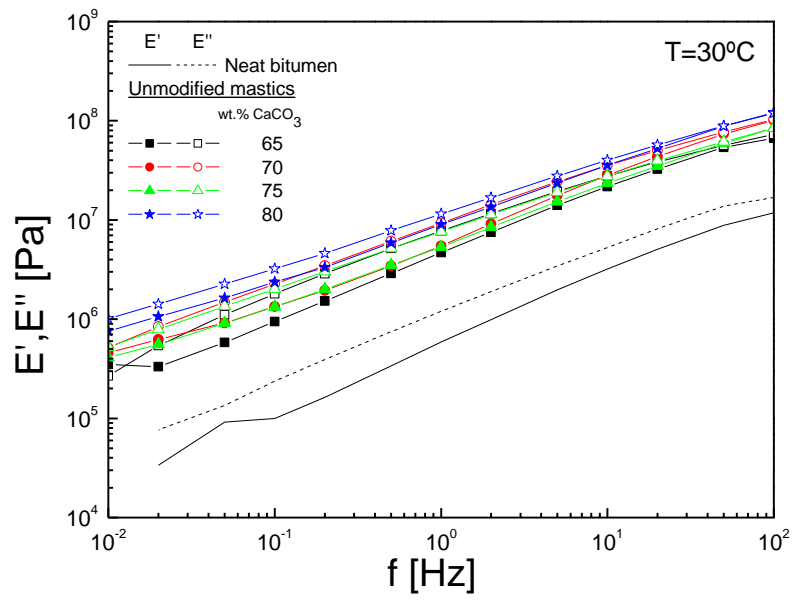


Figure 4.

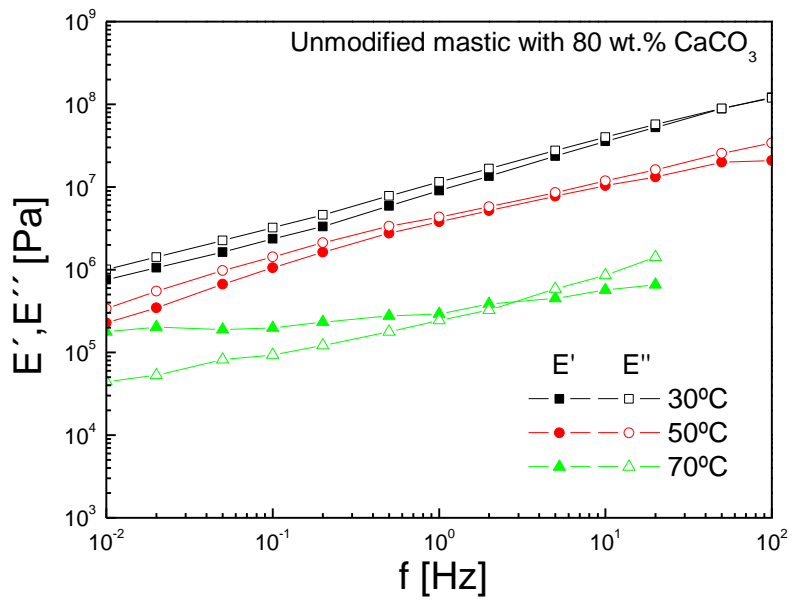


Figure 5.

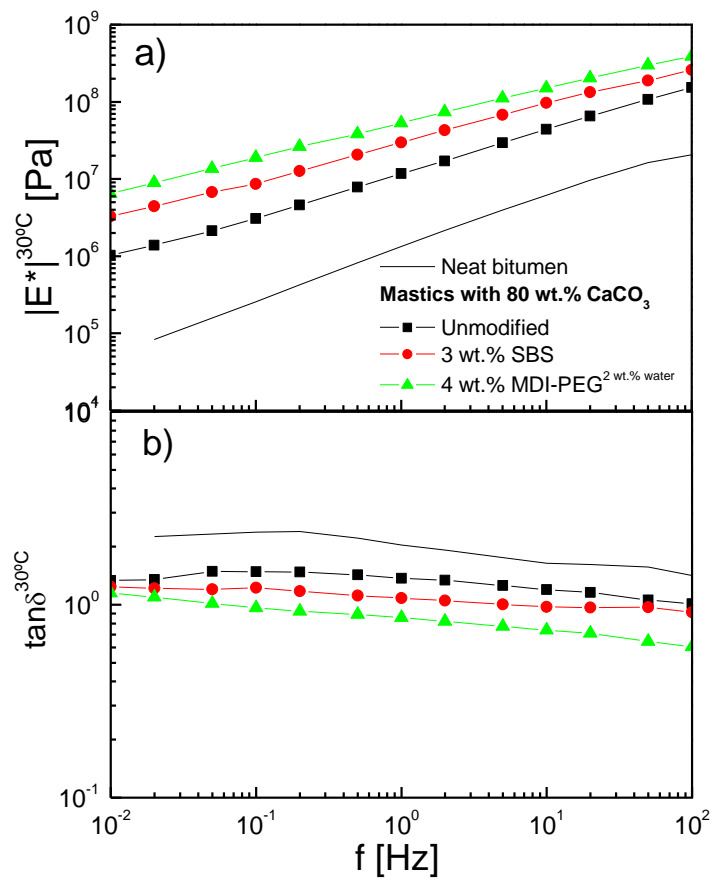


Figure 6.

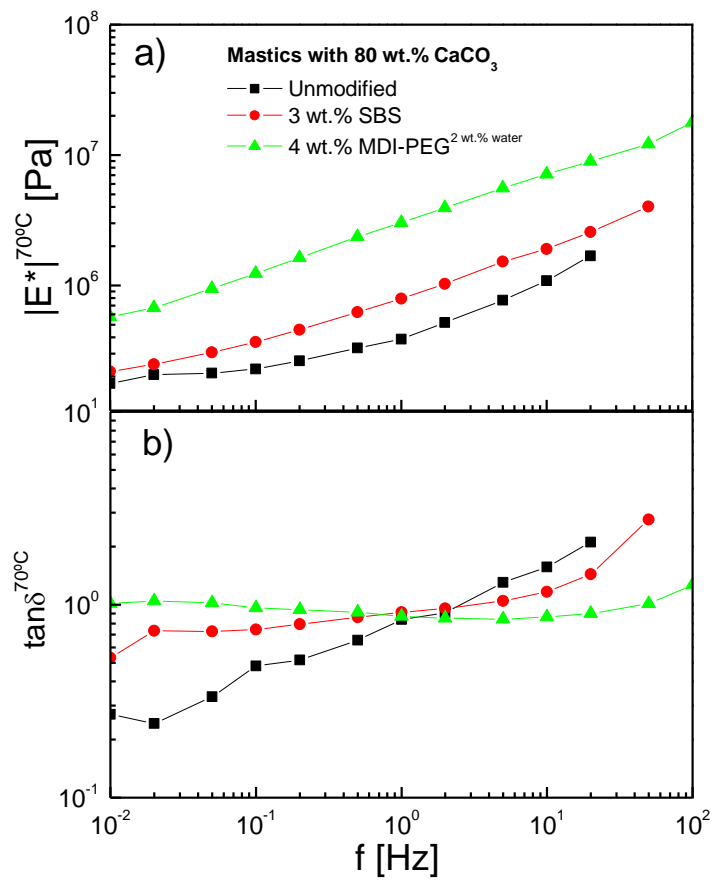


Figure 7.

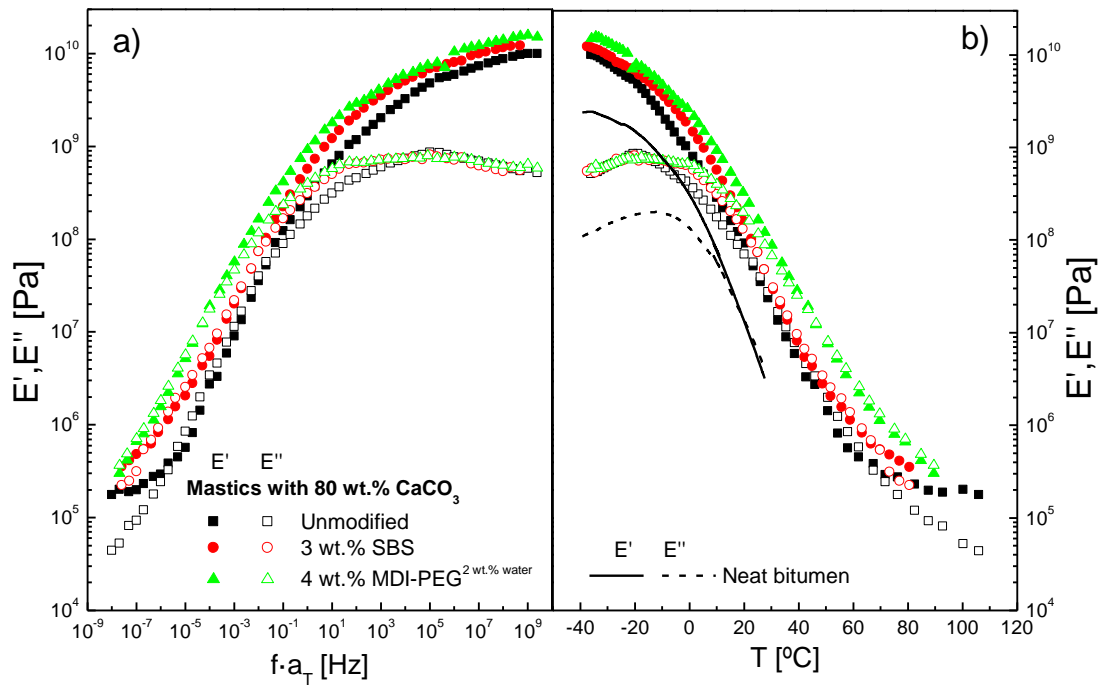


Figure 8.