The development of polyurethane modified bitumen emulsions for cold mix applications

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Abstract Bitumen emulsions stand for an alternative paving practice to the traditional hot-mix asphalts. In addition, modified bitumen emulsions show a better performance than unmodified ones. This work studies the feasibility of obtaining polyurethane modified bitumen emulsions, in which an isocyanate-functionalized polyol constitutes the bitumen modifier (in varying concentration from 1 to 4 wt%). Storage stability and high in-service performance are evaluated by means of evolution of droplet size distribution (DSD) and rheology tests, respectively. Regarding the emulsion stability, the key factor seems to be the bitumen modifier concentration used to prepare the modified emulsions. Thus, for a selected 50 wt% bitumen fraction, there is a limit concentration (between 1 and 2 wt%) above which the emulsion becomes unstable under storage. Hence, this result limits the modifier content that can be used in the emulsion and the final level of modification achieved if compared to the original non-modified emulsion. On the other hand, the rheological characterization conducted on the emulsion residues at 60 °C has shown an improved resistance to deformation. In terms of applicability, polyurethane modified bitumens allows for the obtaining of modified emulsions which can be prepared at much lower temperatures than those derived from other polymers.

1 Introduction

Bitumen, by-product from crude oil distillation, has been largely used as a binder of mineral aggregates in road paving [21]. Traditionally, the production of the asphalt mixtures (composed of mineral aggregates and bitumen) is always conducted at high temperatures, never below 150 °C, so that the low viscosity of bitumen assures the correct coating of the arids. This practice involves significant consumptions of energy and high levels of emissions to the environment during the road construction and maintenance operations, and increases the risks for the operators' health. Alternatively, different types of reduced-temperature technologies have emerged over the last decades. In this work, we focus on the study of a binder for cold-mix asphalts [11, 13]. This technology consists in coating the mineral aggregates with an emulsion formed by very fine bitumen droplets dispersed in water and stabilized with a surfactant. In that sense, bituminous emulsions present much lower viscosities than bitumen itself and can be applied at temperatures between

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25 and 60 °C. Consequently, bituminous emulsions encompass a reduction in the temperature requirement with respect to traditional hot asphalt mixtures, while increasing flexibility by extending working time for transport and application, and reducing ageing of the binder during the production.

On account of its properties (ductility, waterproofing, adhesiveness, mechanical resistance, etc.), bitumen is used for the construction of flexible pavements. However, these may be severely damaged under the action of traffic when exposed to extreme temperatures. Thus, pavements may undergo one or several of the most common distresses [14, 16, 21]: rutting (permanent deformation under heavy vehicles loading) and fatigue cracking (cracks due to repetitive application of loads) at high in-service temperatures, and thermal cracking (cracks due to the lack of flexibility) at low in-service temperatures. On these grounds, the performance of standard cold-mix asphalts may be improved by using modified bituminous emulsions, that is, by modifying bitumen properties before emulsification. As reported by Bahia et al. [2], bitumen has been traditionally modified by addition of a large list of different types of substances. Illustrative examples are the use of sulphur [23], polyphosphoric acid [18], mineral acids [10] or waxes [25]. However, bitumen modification for paving applications is mostly carried out by means of polymers, both virgin (polyethylenes, EVA, SBS, SBR, etc.) and waste (plastics from agriculture, crumb tyre rubber, etc.) [1, 6, 8, 9].

From a practical point of view, crumb tyre rubber may lead to very heterogeneous systems, with particles well above the micron size, and so it is not used in the preparation of bituminous emulsions. In contrast, it is very common the use of SBS or EVA. However, they may cause serious problems at producing their respective bituminous emulsions (SBS bituminous binders require of high emulsification temperatures, of more than 150 °C, and pressurized tanks may be needed until the emulsion is cooled; EVA/bitumen blends may become highly unstable and phase separation occurs before the emulsion forms). For this reason these emulsions are often prepared by adding latex to the bitumen emulsion. In order to resolve these problems, we propose to conduct a reactive modification with an isocyanate-functionalized polypropylene glycol, a liquid with low viscosity which allows both mixing with bitumen and further emulsification to be

Table 1 Penetration value, R&B softening temperature and Gaestel colloidal index for the neat bitumen studied

	Neat bitumen
Penetration (1/10 mm)	160
R&B softening point (°C)	39.5
Colloidal Index (I_c)[a]	0.44

[a] $I_c =$ (saturates + asphaltenes)/(aromatics + resins)

carried out between 80 and 90 °C in an open vessel. This prepolymer has shown to produce an important increase in the binder viscosity as a consequence of ambient curing once in service [4].

Moreover, the manufacture of stable emulsions is an important issue. The small bitumen droplets suspended in an emulsifier aqueous solution may eventually become unstable through a variety of physicochemical mechanisms [12, 24, 26]. These phenomena promote changes in the emulsion droplet size distribution which may significantly alter its rheology.

The goal of this work is to study the feasibility of obtaining stable polyurethane modified bitumen emulsions, which can be prepared at temperatures below 100 °C, and which presents enhanced resistance to permanent deformation at high in-service temperatures if compared to standard non-modified bituminous emulsions. This task will be conducted by using isocyanate-functionalized polyols as bitumen modifier. In this sense, the existence of isocyanate-water reactions, and consequent formation of gas bubbles, may imply significant changes in these polyurethane modified emulsions during their storage time. In order to evaluate the emulsion stability and characterize their potential applicability, droplet size distribution and different rheology tests were carried out on both emulsions and their bituminous residues (i.e., the binders that remain after water evaporation).

2 Experimental

2.1 Materials

Bitumen with a penetration grade of 160/220, supplied by Repsol S.A. (Spain), was used as base material for the emulsions preparation. Results of penetration and R&B softening temperature tests (EN 1426:2007 and

EN 1427:2007, respectively), along with the Gaestel colloidal index value [7, 22] are included in Table 1.

A polypropylene-glycol functionalized with –NCO groups by reaction with polymeric MDI (4,4′-diphenylmethane diisocyanate), henceforth MDI-PPG, was used as bitumen modifier. The prepolymer synthesis consisted in the reaction of Alcupol D-0411 (donated by Repsol S.A., Spain), a difunctional polypropylene-glycol with molecular weight of 440 g mol^{-1}, with polymeric MDI (supplied by TH Technic S.L., Spain), which has a –NCO content of 32.4 wt%. The reaction was conducted at 40 °C, for 48 h, under agitation in N_2 atmosphere. A large excess of –NCO (MDI:PPG molar ratio of 5:1) was used in order to assure that the polyol –OH groups had completely reacted. The resulting prepolymer is a liquid which presents an average molecular weight of 925 g mol^{-1} and NCO content of 22.9 wt%.

An alkyltrimethylenediamine derived from N-tallow, with average molecular weight of 340 g mol^{-1} and melting point between 30 and 40 °C (provided by Kao Chemicals, Spain), was used as the emulsifier. This choice is based on using a very common type of emulsifier for the preparation of cationic bituminous emulsions (these are preferred over anionic ones).

In order to better understand the experimental results obtained, it is worth giving some insight into the chemistry behind bitumen modification by isocyanate-based reactive prepolymers. In a first stage, bitumen modification is expected to occur by reaction of the free –NCO groups in the prepolymer with –OH pendant groups present in the most polar molecules of bitumen (asphaltenes and resins) [17]. Hence, the resulting urethane linkages,

$$R^1-NCO + R^2-OH \rightarrow R^1-NH-COO-R^2 \qquad (1)$$
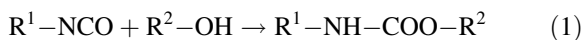
lead to larger and more complex asphaltene/resin-associations which, due to the high excess of polymeric MDI used in the synthesis of the prepolymer, still have free –NCO sites available for further reaction. Nevertheless, if water is present, it is known to react with the remaining isocyanate groups, leading to the formation of an amine and carbon dioxide:

$$R^1-NCO + H_2O \rightarrow R^1-NH_2 + CO_2 \uparrow \qquad (2)$$

Further reactions may occur between the highly reactive amine and the excess of isocyanate groups located in the previous associations:

$$R^2-NCO + R^1-NH_2 \rightarrow R^2-NH-CO-NH-R^1 \qquad (3)$$
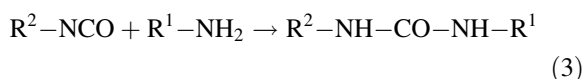
Even though water is not directly added to the formulation, we may expect reactions (2) and (3) to occur during the emulsification process (in aqueous medium). If compared to the original modified bitumen (before this is emulsified), those reactions (2) and (3) favour the formation of urea bonds [22]. As reported by Martín-Alfonso et al. [17], a more complex microstructure develops through the links between two or more smaller colloidal units which, as commented, still had reactive –NCO sites available.

2.2 Preparation of the MDI-PPG modified bitumens and emulsions

Firstly, four blends of bitumen and MDI–PPG at the concentrations of 1, 2, 3 or 4 wt% were prepared. Those were conducted at 90 °C, for 1 h, using a cylindrical vessel (60 mm diameter and 140 mm height) with a four-bladed turbine rotating at 1,200 rpm.

Subsequently, their corresponding oil-in-water (O/W) emulsions were prepared by emulsifying the above polyurethane modified binders into acidic water with the surfactant dissolved. Thus, the emulsifier was dispersed into distilled water in a concentration of 1.4 wt% (so that is reduced to 0.7 wt% in the emulsion), followed by addition of hydrochloric acid until the pH was reduced to 2. At the same time, the modified bitumen was maintained in an oven at 100 °C prior to the emulsification. This temperature ensures that the viscosity of the bituminous phase is low enough so that it can be emulsified. Then, the same quantity of the emulsifier solution was added to the bitumen so that a mass ratio of 50:50 was obtained. In order to reach a final temperature between 80 and 90 °C, the water temperature was conveniently controlled and adjusted. The emulsification process was always carried out for 5 min by using a T-25 Ultra-Turrax homogenizer, with rotation speed of 20,000 rpm. After preparation, the four emulsions were stored in an oven at 40 °C.

In order to evaluate the rheological properties of the actual binders after the emulsion breaking process, asphalt residues for further testing were obtained by following the standard EN13074.

2.3 Testing procedures

Droplet size distribution (DSD) and average Sauter diameter ($D_{3,2}$) were determined by laser diffraction with a Mastersizer 2000 analyzer (Malvern Instruments, UK).

Viscous flow tests, at 25 °C, were conducted on selected bitumen emulsions. Moreover, their residues were characterized, at 60 °C, by viscous flow tests and oscillatory shear frequency sweeps (within the LVE region), from 0.01 and 100 rad/s. They all were carried out with a controlled-stress MARS II rheometer (Thermo Haake, Germany). Serrated plate-and-plate geometries (20 and 35 mm diameter, 1 mm gap) were always used in order to prevent results from being affected by wall slip phenomena. Average values of, at least, two replicates have been used.

Bitumen SARA fractions (used in the calculation of its Gaestel colloidal index) were determined by thin layer chromatography coupled with a flame ionization detector (TLC/FID), using an Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan). Elutions were performed sequentially in hexane, toluene and dichloromethane/methanol (95/5 vol%), following the procedure outlined elsewhere [5].

3 Results and discussion

3.1 Stability and rheology of modified bitumen emulsions

Four different O/W emulsions, containing 50 wt% bitumen phase, were prepared from bitumens previously modified with a MDI-PPG concentration ranging from 1 to 4 wt%. Emulsions stability was analyzed by means of both laser diffraction and visual inspection.

Figure 1 presents the droplet size distribution (DSD), as a function of the different prepolymer concentrations studied, for emulsions freshly prepared (Fig. 1a) and after 10 days of storage (Fig. 1b). Large differences in the DSD were found among the fresh emulsions (0 days storage) with different MDI-PPG contents. On the one hand, emulsions with 1 or 2 wt% MDI–PPG present one single significant peak, which shifts towards larger diameter values for the highest prepolymer content. Such an increase may be quantified by means of the Sauter mean diameter ($D_{3,2}$)
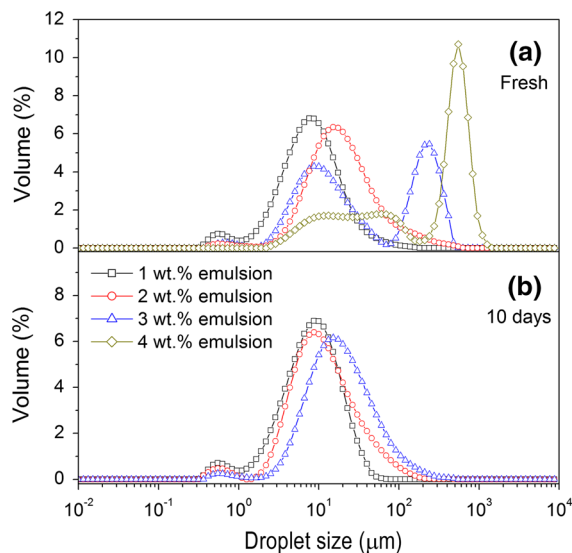

Fig. 1 Droplet size distribution of the four different emulsions studied: **a** freshly prepared; and **b** after 10 days of storage

Table 2 Sauter mean diameters, $D_{3,2}$, for the different emulsions studied

MDI-PPG concentration (wt%)	$D_{3,2}$ values (µm)		
	0 days		10 days
	First peak	Second peak	
1	4.63	–	4.7
2	11.34	–	6.61
3	8.94	228.45	10.8
4	19.98	458.07	Non applicable

[20], which was calculated according to the following expression:

$$D_{3,2} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \tag{1}$$

where n_i is the number of droplets with a diameter d_i.

As can be observed in Table 2, $D_{3,2}$ increases from about 5–11 µm for emulsions having 1 and 2 wt% MDI-PPG, respectively. On the other hand, emulsions with 3 or 4 wt% MDI-PPG exhibit a bimodal distribution, with a second peak appearing at much larger diameters (Table 2). It can also be observed a much wider DSD for the 4 wt% MDI-PPG emulsion.

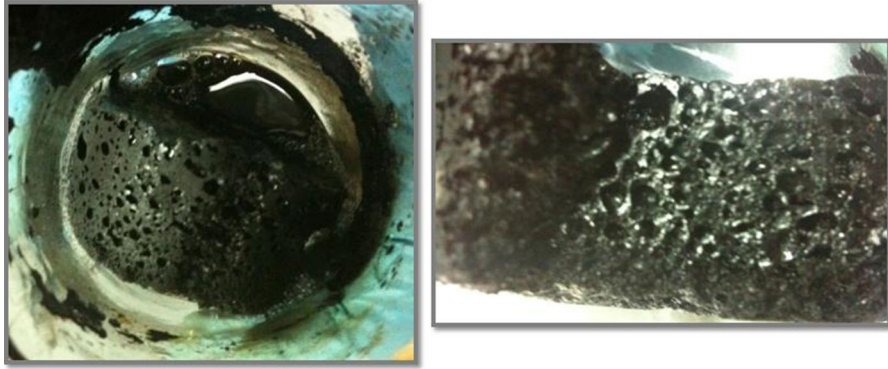With regard to the stored emulsions, no change was observed in the emulsion with 1 wt% MDI-PPG after

Fig. 2 Photograph taken at room temperature on the 4 wt% MDI-PPG modified emulsion after 10 days storage

storage for 10 days. Nevertheless, Fig. 1b makes clear very significant differences in the DSD for higher MDI-PPG concentrations (in fact, the DSD for the 4 wt% could not even be determined, as explained below). Thus, the peak for the 2 wt% emulsion moves down to a slightly smaller mean diameter and the second peak for the 3 wt% emulsion disappears. The eventual flocculation/coalescence processes which seem to occur in the 2 or 3 wt% MDI–PPG emulsions upon storage lead to a decrease in the effective mean diameter (or makes the second peak disappear) as a consequence of the destabilization and precipitation of the largest bitumen droplets (i.e., emulsion phase separation).

Regarding the 4 wt% emulsion, visual inspection shown in Fig. 2 reveals the formation of a continuous bitumen phase (in the form of a bituminous flexible foam) after 10 days of storage. These observations suggest a notable expansion of the bitumen phase, whose density significantly decreases as a consequence of the CO_2 derived from the above reaction (2). Something similar happens at 2 and 3 wt%, although in a much lesser extent. In that sense, this highest MDI–PPG concentration of 4 wt% leads to the formation of a multiphasic material, in which growing modified bitumen droplets coalescence and eventually produce phase inversion (i.e., a bituminous foam with water droplets embedded).

Consequently, this study demonstrates, firstly, the slow kinetics of reaction (2) and, secondly, the existence of a threshold MDI–PPG concentration over which this type of emulsion cannot be considered as storage-stable. Results reveal that the limit lies, for a bituminous phase fraction of 50 wt%, between 1 and 2 wt% MDI–PPG.
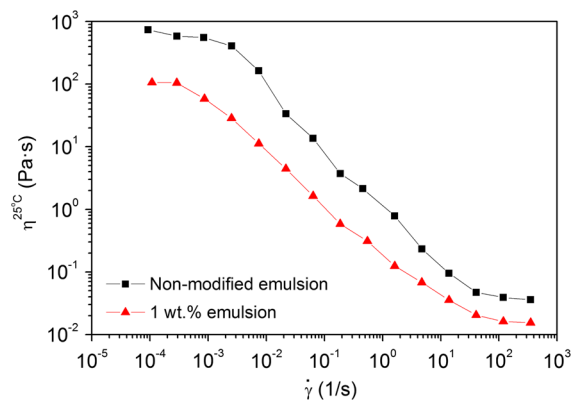

Fig. 3 Viscous flow curves, at 25 °C, for the fresh 1 wt% MDI-PPG modified emulsion and its corresponding fresh non-modified emulsion

However, we may assume that this limit depends on the dispersed phase volume fraction, and should be determined for any other particular bitumen fraction used. Moreover, for very high prepolymer concentrations (4 wt%) the volume increase can be such that a phase inversion may occur, if the maximum packing density is exceeded [3].

In order to ascertain the influence that modification exerts on the viscosity of final emulsion, steady state viscosity curves, at 25 °C, were performed on the selected storage-stable fresh 1 wt% emulsion and compared with its corresponding fresh non-modified emulsion. As can be seen in Fig. 3, both emulsions presented a viscous flow behavior typical from structured fluids, characterized by constant values of viscosity at the lowest and highest shear rates tested, as well as a pseudoplastic drop at the intermediate values.
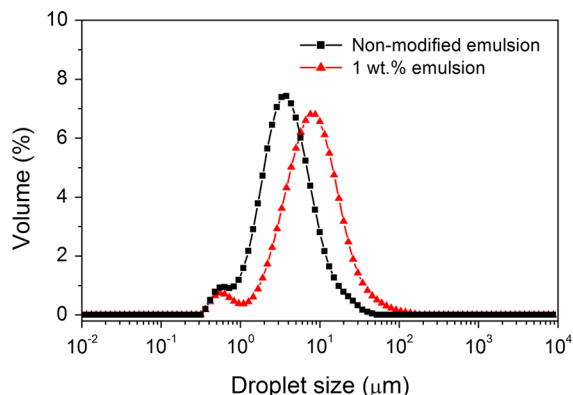
Fig. 4 Droplet size distribution of the fresh 1 wt% MDI-PPG modified emulsion and its corresponding fresh non-modified emulsion

Fig. 5 Viscous flow curves, at 60 °C, for neat bitumen, 4 wt%"MDI-PPG-water" binder and emulsion residues with different MDI-PPG concentration

At the lowest shear rates, the modified emulsion presented viscosity values one order of magnitude lower than the non-modified one. However, differences become less significant with increasing shear rate.

DSD measurements corresponding to fresh 1 wt% modified and fresh non-modified emulsions shown in Fig. 4 help explain the above viscosity curves. Results reveal smaller droplets for the non-modified emulsion, which would bring about stronger droplet–droplet interactions, and so, increased resistance to flow (higher viscosity). This effect is reduced at the highest shear rates, when interactions are strongly weakened. As reported by Lesueur [15], emulsions of polymer modified bitumens (PMBs) are generally coarser than their corresponding neat bitumen emulsions, as the droplet-breaking step is more difficult. In fact, the size of the polymer-rich inclusions are larger than the final droplet size, which generally limits the choice to PMBs with polymer content of the order of 3 wt%. In our case, we also obtain larger droplets for the modified emulsion. However, this observation is a consequence of the reactive nature of the prepolymer used, rather than the difficulty at the droplet-breaking step. In any case, we compare two types of "monophase" modified emulsions, as opposed to latex modified emulsions ("biphasic"), where latex would have a much larger well-defined particle size of the order of 200 microns. Consequently, a significant decrease in viscosity, at 25 °C, was observed for the 1 wt% modified emulsion, if compared to the non-modified one. However, this was at the expense of a higher average droplet size, but interestingly, the new
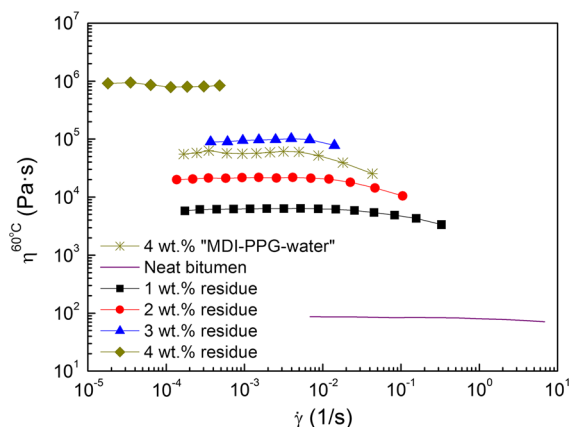
droplets formed have lower density due to CO_2 retained into the bitumen (i.e., foamed bitumen droplets). This fact would prevent such droplets from settling.

3.2 Rheology of the emulsion residues

A viscous and viscoelastic rheological characterization has been conducted on the different emulsion residues. Figure 5 shows viscous flow curves, at 60 °C, for the different residues from emulsions with prepolymers contents from 1 to 4 wt%. However, as previously detailed, the presence of water during the emulsification process may lead to reactions which significantly alter the residues rheological response. Thus, for the sake of comparison, the viscous flow curve corresponding to a modified binder prepared by adding 4 wt% MDI-PPG and 2 wt% water, referred to as "MDI–PPG-water" binder, has been included. All the samples present a Newtonian or nearly Newtonian behavior in the whole range of shear rates tested. With regard to the viscosity increase observed for the "MDI–PPG-water" binder relative to its parent neat bitumen, this can be explained according to the isocyanate chemistry. Thus, blending of bitumen and prepolymer for 1 h provokes a first viscosity increase due to reaction (1), which is further enhanced by addition of 2 wt% water (reactions 2 and 3). Moreover, it can be observed that the viscosities of the residues increase as the MDI-PPG prepolymer content does. However, the result for the residue of the 4 wt% emulsion evidences a highly enhanced viscosity at
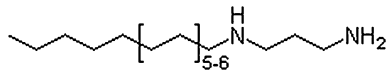
Fig. 6 Structure of the emulsifier used

Fig. 7 Frequency dependence of the linear viscoelasticity functions (G′ and G″), at 60 °C, for neat bitumen, 4 wt% "MDI–PPG-water" binder and emulsion residues with different MDI–PPG concentration

60 °C, if compared to the 4 wt% "MDI-PPG-water" binder (from 6×10^4 up to 10^6 Pa s).

The surfactant used, a *N*-Tallow alkyltrimethylenediamine, presents the molecular structure showed in Fig. 6. Amines are well-known to rapidly react with the –NCO group, leading to urea bonds, according to the reaction (3) above. In this case, the surfactant is a diamine which may act as a chain extender of the MDI-PPG present in the bitumen, with the consequent increase in the length and molecular weight of the resulting products. Moreover, the hydrochloric acid used in the previous preparation of the emulsifier can make the isocyanate-water reactions proceed faster [19]. These contributions may even endow the 3 wt% residue with a higher viscosity than the 4 wt% "MDI-PPG-water" modified binder (Fig. 5).

In consequence, the modifier proposed is adequate for the preparation of PMBs which can be emulsified at temperatures between 80 and 90 °C. However, the material hardens with time. Even though "fresh" emulsions can satisfactorily perform as such from the very first moment (compare the large differences in viscosities, at 60 °C, for neat bitumen and residues in Fig. 5), Carrera et al. [4] demonstrated that in-service curing makes these binders evolve towards a better performance against the permanent deformation. In contrast, manufacturing of emulsions with other PMBs may be especially delicate, as processing temperature has to be very high for the PMBs to have a viscosity of about 200 mPa s [15].

Finally, Fig. 7 shows the variation with frequency of the linear storage and loss moduli (G′ and G″, respectively), at 60 °C, for the different residues and for the 4 wt% "MDI–PPG-water" binder. As can be noted, the prevailing viscous behaviour of the neat bitumen, with values of G′ and G″ in the low frequency region being proportional to ω^2 and ω, respectively, is notably modified by the addition of 4 wt % MDI-PPG. Thus, the differences between both moduli are reduced after modification, as G′ increases much more than G″ does (decreasing binders viscous character). Regarding the emulsion bitumen residues, their viscoelastic behaviour
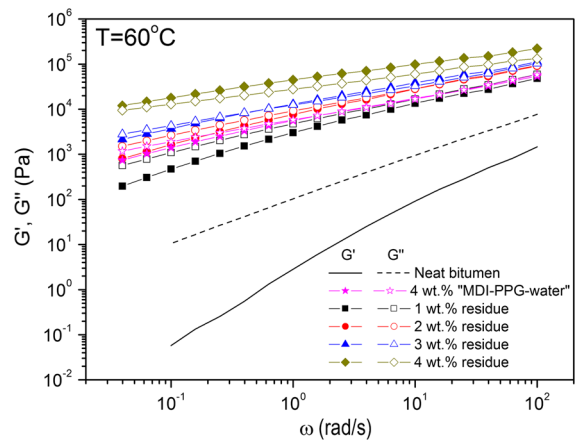
strongly depends on the MDI-PPG concentration. Thus, for the 1 wt% emulsion, G″ prevails over G′ at 60 °C, which demonstrates that, although in a much lesser extent, the viscous behaviour of the neat bitumen still remains. However, an increase in the prepolymer content makes G′ increase faster than G″, reversing the behaviour for the highest MDI–PPG concentration (G′ > G″ for the residue from 4 wt% MDI-PPG emulsion). This suggests an important enhancement in the material solid-like features.

Finally, frequency sweep tests again confirm a much higher degree of modification for the 4 wt% residue, when compared to its counterpart "MDI–PPG-water" binder.

4 Concluding remarks

The feasibility of obtaining stable polyurethane modified bitumen emulsions, from isocyanate-functionalized polyols, has been evaluated. A study of droplet size distribution (DSD) conducted on emulsions with four different prepolymer concentrations revealed that, for a selected bituminous phase fraction of 50 wt%, storage stability may be prolonged for more than 10 days if the prepolymer concentration does not exceed a limit value which lies between 1 and 2 wt%. If a higher concentration is used, the CO_2 due to the

reactions (2) and (3) makes droplets grow to such an extent that phase inversion may eventually occur.

On the other hand, a significant decrease in viscosity, at 25 °C, was observed for the fresh 1 wt% modified emulsion, if compared to the fresh non-modified one, since the former presents a higher mean droplet size.

Finally, residues from the unstable 4 wt% emulsion present significantly higher viscosity and linear viscoelastic moduli, at 60 °C, than its counterpart 4 wt % binder, to which 2 wt% water was added. Hence, the combined action of an acidic (pH 2) aqueous solution (hydrochloric acid, may act as a catalyst) of a diamine-based surfactant (which may act as a chain extender) is seen to further enhance the effect of the polyurethane modification.

To sum up, polyurethane modified bitumens allows for the obtaining of modified emulsions which can be prepared at much lower temperatures than those derived from other polymers. Also, they present a better performance against the permanent deformation than a non-modified emulsion. Although low temperature performance has not been studied, it is not expected to obtain comparable results to SBS modified bitumen emulsions. In any case, it may represent an alternative technology in warm climates.

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