Influence of the prepolymer molecular weight and free isocyanate content on the rheology of polyurethane modified bitumens

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ABSTRACT

Isocyanate-based modification is lately gaining acceptance as a successful way to give added value to bitumen, a crude oil refining by-product. In order to study the influence of prepolymer type on the rheological properties of the resulting binders, six prepolymers synthesized from polypropylene-glycols (PPG) with varying molecular weight (between 440 and 2425) and different molar excess of a polymeric MDI (4,4'-diphenylmethane diisocyanate) were used. Two modification procedures, either involving or not water addition were followed. The modification achieved depends on both the selected polyol molecular weight and the excess in MDI (i.e., free isocyanate content), although not in a similar extent. Viscous flow and dynamic oscillatory shear tests, at 60 ºC, demonstrated a much higher level of bitumen modification by using the prepolymer prepared with the polyol having a molecular weight of 940 and with a free isocyanate content of 17.4 wt.%, mainly after addition of water. On the other hand, bitumen nature greatly affects the final rheological properties of these bituminous products. In that sense, modification results much more effective when conducted on bitumen with a well-developed colloidal microstructure.

Keywords: bitumen, rheology, isocyanate, polyurethane, product design.

1. INTRODUCTION

Bitumen, by-product from crude oil distillation, is a complex material basically composed of hydrocarbons along with some other molecules which contain small percentages of heteroatoms (sulphur, nitrogen and oxygen). Bitumen compounds can be classified by chromatographic techniques into four different fractions (usually referred to as SARAs): saturates (S), aromatics (A) and resins (R), which make up the maltenes, and asphaltenes (As). The complexity, aromaticity, heteroatom content, and molecular weight increase in the order S<A<R<As [1]. A colloidal model, consisting of asphaltenes being dispersed into an oily matrix of maltenes and peptized by resins, is traditionally used to describe the bitumen behaviour [2,3].

On account of its unique properties, bitumen has found widespread application in the construction of flexible road pavements [4]. Unfortunately, even the best designed and constructed road pavements deteriorate over time under the combined effects of traffic loading and weathering. With this regard, the most common distresses are: rutting, or permanent deformation at high temperatures [5]; thermal cracking, or thermal fracture due to the lack of flexibility at low temperatures [6]; and fatigue cracking, due to the repetitive application of loads [4]. As a consequence, the bitumen performance has been traditionally improved through the addition of synthetic polymers (SBS, SBR, EVA, etc.) and polymer waste (plastics from agriculture, crumb tyre rubber, etc.) [7-10].

Previous studies revealed that isocyanate prepolymers based on polypropylene-glycol (PPG) functionalized with polymeric MDI, 4,4'-diphenylmethane diisocyanate, (i.e. MDI-PPG prepolymers containing –NCO reactive groups) have shown success in the modification of bitumen, resulting in bituminous binders with improved performance at high in-service temperatures. In that sense, Carrera et al. [11,12] evaluated the influence that the type of bitumen (and so, its colloidal nature) and the processing conditions

(curing, addition of water, etc.) exert on the rheological properties of asphaltic bitumen modified with isocyanate prepolymers. On the other hand, Izquierdo et al. [13-15] studied the application of isocyanate prepolymers in the fabrication of stable bituminous foams, and highlighted the influence of bitumen hardness and prepolymer molecular weight.

On these grounds, the chemistry behind this type of reactive modification may help to achieve a better understanding of the experimental results obtained. If water does not take part, bitumen modification is mainly 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) [16]. Hence, the resulting urethane linkages

$$R^1-NCO \;+\; R^2-OH \;\rightarrow\; R^1-NH-COO-R^2 \qquad \text{(reaction 1)}$$

lead to more complex asphaltenic domains which, due to the large -NCO excess used, still have free reactive sites available for further reaction. However, when water is involved, two more series reactions occur. Water is known to react with the remaining isocyanate groups, leading to the formation of carbon dioxide and a highly reactive amine,

$$R^1-NCO \;+\; H_2O \;\rightarrow\; R^1-NH_2 \;+\; CO_2\uparrow \qquad \text{(reaction 2)}$$

which promotes a further reaction with the isocyanate groups left in the large asphaltenic domains previously formed:

$$R^2-NCO \;+\; R^1-NH_2 \;\rightarrow\; R^2-NH-CO-NH-R^1 \qquad \text{(reaction 3)}$$

Consequently, reactions 2 and 3 are expected to build up larger regions, through the formation of urea linkages between two or more smaller units which, as commented,

still had reactive –NCO sites available [16,17].

Based on the above results, interest is now focused on the synthesis of new MDI-PPG prepolymers with different reactivity and physical characteristics, which may be of major relevance in the design of this type of binders. Thus, this work deals with the influence that molecular weight and free –NCO content exert on the rheological behaviour of the resulting MDI-PPG modified binders. With that purpose, various MDI-PPG prepolymers derived from polymeric MDI and a range of di- and tri-functional polyols were synthesized to be used as bitumen modifiers and analyzed by GPC (gel permeation chromatography) and TG (thermogravimetry) tests. The rheological characterization (by means of viscous flow and oscillatory shear tests) provided valuable information about the degree of modification achieved.

2. EXPERIMENTAL

2.1. Materials

Two bitumen samples (A and B), supplied by Repsol S.A. (Spain), were used as base materials. Penetration grade (depth which a needle penetrates a sample of binder under the specified testing conditions stated in EN 1426:2007) and Ring-and-Ball softening temperature (value at which a steel ball deforms the binder contained in a metal ring under the specified testing conditions stated in EN 1427:2007) are presented in Table 1. The Gaestel colloidal index values and definition of this parameter (in terms of bitumen SARAs fractions) have also been included in Table 1.

A set of four NCO-terminated prepolymers (MDI-PPG prepolymers) was synthesized by reaction of polymeric MDI (4,4'-diphenylmethane diisocyanate) and four polypropylene-glycols with different molecular weights and functionalities (see Table 2). Polymeric MDI and polypropylene-glycols were supplied by TH Tecnic S.L. (Spain)

and Repsol YPF (Spain), respectively. Their structural formulae have been included in Figure 1. Regarding polymeric MDI, in general terms it can be defined as a mixture that contains 25-80 wt.% monomeric 4,4'-MDI, as well as oligomers containing between 3 and 6 rings and other minor isomers such as the 2,2'-isomer (so, index "n" in Figure 1 is comprised between 0 and 5). MDI-PPG prepolymers synthesis was carried out for 48 h at 40ºC, in a lab flask equipped with stirrer, thermometer and nitrogen gas inlet. A MDI:PPG molar ratio of 5:1 was always selected. The free –NCO content of the resulting prepolymers (light brownish liquids) was determined by titration with N,N'-dibutylamine, according to ASTM D-2572 (see Table 2). Additionally, and with the aim of establish a comparative analysis between prepolymers with different –NCO excess, two more prepolymers were prepared from the polyol with the largest molecular weight and MDI/PPG ratios of 6:1 and 8:1 (see Table 2).

2.2. Samples preparation

MDI-PPG/bitumen blends were prepared in a batch mixer (a cylindrical glass vessel of 60 mm diameter and 140 mm height), using an IKA RW-20 stirring device (Germany) equipped with a four-bladed 45º-pitched turbine. Bitumen modification, always with 4 wt.% MDI-PPG, was carried out by following two different procedures, one of which involves addition of water:

1. "Water-free" procedure: Bitumen and MDI-PPG were mixed for 1 h, at 90 ºC and 1200 rpm, after which the resulting binder was set in an oven for 24 h at 90 ºC (referred to as "MDI-PPG 24h" sample, hereinafter).

2. "Water-involved" procedure: 2 wt.% water was added to the "MDI-PPG 24h" sample previously prepared, and the blend was stirred for 45 min, under same conditions (referred to as "MDI-PPG-water 24h" sample, hereinafter).

In order to evaluate the effect of ageing on samples cured during 24 h at 90ºC, a sample of neat bitumen was subjected to the above conditions and then tested on the rheometer. The resulting viscosity curve indicates a non-significant viscosity increase if compared to the original neat bitumen.

2.3. Testing procedures

Viscous flow measurements, at 60 ºC, were carried out in a controlled-stress RS-150 rheometer (Haake, Germany), using a plate-and-plate geometry (20 mm and 35 mm diameter; 1 mm gap).

Different oscillatory shear tests were conducted in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria): a) frequency sweep tests, from 0.03 to 100 rad/s, at 60ºC, within the linear viscoelasticity region; and b) temperature sweep tests between 30 and 90 ºC, using a heating rate of 1 ºC/min, frequency of 10 rad/s and strain of 1%. A plate-and-plate geometry (25 mm diameter; 1 mm gap) was always used. In order to ensure the repeatability of the results, all the tests were carried out at least twice.

The prepolymers molecular weights were determined by GPC (gel permeation chromatography), with the apparatus Waters 2414 Refractive Index Detector, the column Styragel® HR 4E and using THF as solvent. GPC measurements were carried out on 0.1 wt.% solutions in THF. In order to assign a molecular weight to the different prepolymers tested, a calibration curve based on standards of similar molecular architecture and nature was conveniently obtained. Thus, five different polypropylene-glycol standards [18] and pure MDI, supplied by Sigma-Aldrich, were used. The calibration curve was obtained by plotting the molecular weights provided by the supplier versus the retention times determined. The molecular weights calculated by integration of the prepolymers peaks are shown in Table 2.

TGA runs, between 40 and 600 ºC (heating ramp: 10 ºC/min; nitrogen atmosphere), were conducted on 5-10 mg samples of the polymeric MDI, PPGs and the resulting MDI-PPG prepolymers, using a Seiko TG/DTA 6200 (Seiko Instruments Inc., Japan).

3. RESULTS AND DISCUSSION

3.1. NCO-terminated prepolymers characterization

As previously commented, four different NCO-terminated prepolymers were synthesized by reaction between poly(propylene glycol) with different molecular weights and polymeric MDI (in molar excess). GPC and TGA measurements were conducted on them, and the results shown in Figures 2 and 3.

Figure 2A shows the GPC chromatograms corresponding to the raw materials for the prepolymers preparation. On the one hand, every PPG sample presents a single peak from which the molecular weight data in Table 2 were obtained. As can be seen, retention time decreases with increasing molecular weight. On the other hand, the chromatogram for the polymeric MDI reveals various peaks. The first one, located at the highest retention time and which corresponds to the lowest molecular weight component, may be attributed to pure MDI. According to Gurke [19], it stands for 50 wt.% of polymeric MDI, approximately. The second peak observed might be ascribed to tri-isocyanate (about 10 wt.%). Finally, the third peak and the curve left-tail might be related to the components with the highest molecular weights (tetra-isocyanate, penta-isocyanate and higher homologues). From this chromatogram, an average molecular weight (M_w), which considers all the existing components in the polymeric MDI, was calculated (see Table 2).

Furthermore, chromatograms for the different NCO-terminated prepolymers synthesized

can be observed in Figure 2B. All of them present quite similar responses. A large first peak, attributed to non-reacted pure MDI, corroborates the excess of polymeric MDI used. The second peak observed may be associated to components having a higher molecular weight than pure MDI, as well as molecules resulting from the MDI dimerization [20]. Finally, the remaining peaks are assigned to all the different products which may arise from the reaction between the polyols and polymeric MDI [21,22]. Analogously to polymeric MDI, average molecular weights were determined (see Table 2).

Figure 3, which shows the TGA curves obtained at a heating rate of 10ºC/min, can also shed some light on the prepolymers characterization. With regard to the polyols (see Figure 3A), all the curves undergo a rapid and single decay, with the temperature values corresponding to the onset of decomposition increasing as their molecular weight does (212, 295, 317 and 324 ºC). On the other hand, polymeric MDI exhibits two first overlapped decays in the TGA curve (onset temperature of 174ºC), which would be attributed to monomers of MDI. It also shows a latter decay, which may be the consequence of several thermal events (onset temperature of 452ºC), which would correspond to higher homologues. Finally, degradation of the resulting prepolymers is known to be a complex and multistep process, in which three defined stages are involved [23]: a) the first degradation stage is related to the mass loss of isocyanate when the urethane bonds decompose into the original isocyanate and alcohol [24]; b) the second degradation stage can be related to destruction of ether bonds in the soft segment of polyol; c) the third stage is related to degradation of residues produced after the second stage and other segments of the remaining structure. In our case, that first stage may be attributed to the above mass loss after decomposition of urethane bonds, as well as that corresponding to the excess of MDI molecules (and its higher

homologues) in the prepolymer. Thus, for a fixed MDI:PPG ratio of 5:1, a polyol with lower molecular weight would lead to a higher mass fraction of polymeric MDI in the resulting prepolymer. As a consequence, the analysis of data in Figure 3 demonstrates higher degradation rates and mass loss as the polyol (or prepolymer) molecular weight decreases. In addition, the onset temperatures for this first stage would increase with the prepolymer molecular weight as follows: 160, 178, 184 and 195ºC. On the contrary, the mass fraction of the polyol soft phase in the resulting prepolymers increases as the polyol molecular weight does. This provokes a much faster rate of degradation in the second step, associated to the break of ether bonds within the polyol soft phase, for the prepolymers with the highest molecular weights. Finally, the third stage is very similar for all the prepolymers studied.

3.2. Influence of prepolymer type and processing on the rheology performance of MDI-PPG modified binders

Figure 4 shows the steady state viscous behaviour, at 60 ºC, of the different "MDI-PPG 24h" and "MDI-PPG-water 24h" samples. As observed, the degree of modification achieved clearly depends on the type of bitumen employed, being more effective for the bitumen with the highest Gaestel colloidal index (bitumen B). In that sense, Carrera et al. [11] highlights the complex chemistry behind the bitumen modification by MDI-PPG prepolymers. For a selected processing method, the highest modification was obtained for the neat bitumen which exhibited the largest quality of colloidal microstructure and highest reactivity. In that sense, the bitumen colloidal microstructure is directly related with its Gaestel colloidal index. Thus, according to the definition of Gaestel colloidal index, a neat bitumen with a well-developed microstructure and, consequently, with a larger concentration of asphaltene regions, presents a higher Gaestel colloidal index. Consequently, modification becomes more successful as the

base microstructure, over which the new microstructure is built, presents a higher level of organization.

Thus, neat bitumen A and its corresponding modified binders display a nearly Newtonian behaviour in the entire shear rate interval tested, with a moderate increase in viscosity after polymer addition (from 64 to 160 Pa·s, at best). Furthermore, Figure 3A reveals that the above increase is, in most cases, quite insensitive to the prepolymer type used and processing procedure followed. On the contrary, large differences were observed with bitumen B. As shown in Figure 4B, modification may be of up to 3 decades. Moreover, water addition always leads to binders with a much higher viscosity than those derived from the water-free procedure, mainly for the two prepolymers with lowest molecular weights (MDI-PPG^{440} and MDI-PPG^{940}). Surprisingly, MDI-PPG^{940} prepolymer, both before and after water addition, endows bitumen B with a much higher viscosity than any other prepolymers studied in this work. Contrarily, a poor degree of modification was found for the prepolymer with the highest molecular weight (MDI-PPG^{2425}).

The viscous behaviour of bitumen B binders is seen to differ from bitumen A. Hence, a region with nearly constant viscosity (at the lowest values of shear rates) followed by a shear-thinning drop may be observed. The Carreau's model may fit the bitumen B results fairly well:

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

where η_0 (Pa·s) is the zero-shear-limiting viscosity, $\dot{\gamma}_c$ (s^{-1}) is the critical shear rate for the onset of the shear-thinning region and 's' is a parameter related to the slope in that

region. Table 3 gathers the values of the Carreau's model parameters.

In order to emphasize the influence of the prepolymer molecular weight on the degree of modification, an index in terms of η_0 values at 60 ºC will be defined as follows:

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

where $\eta_{0,mod}$ and $\eta_{0,neat}$ are the zero-shear-limiting viscosity values, at 60 ºC, for MDI-PPG modified binders and neat bitumen, respectively. Hence, this parameter will quantify changes due to the type of modifying agent (for "MDI-PPG 24h" samples), or the combined effect of prepolymer type and water addition (for "MDI-PPG-water 24h" samples). Figure 5 illustrates the modification index values, M.I., for the different types of prepolymers. As previously described, the strong influence of the bitumen nature on the degree of modification attained is quite apparent. Thus, bitumen B always leads to binders with much larger M.I. values. On the other hand, Figure 5 reveals that the MDI-PPG^{940} modified binders exhibit, mainly for bitumen B, higher M.I. values than the others.

This result hints at the existence of another parameter which, along with the prepolymer molecular weight, seems to effectively control the binder's rheology. With the goal to find an answer to this issue, Figure 6 presents the evolution of M.I. values with the free –NCO content (corresponding to the four types of prepolymers used), for the different bitumen types and processing protocols. Curves demonstrate a maximum for a free –NCO content of 17.44 wt.%, which corresponds to MDI-PPG^{940}. So, the highest values of the modification index do not correspond to the highest content in free –NCO, revealing that viscosity is controlled by the combined effect of this parameter along with molecular weight. It can be deduced that the highest enhancements in viscosity are

the consequence of a balance between the molecular weight and the concentration of –NCO groups available for reaction with bitumen. However, the contribution of the –NCO content appears to be more important than that of the molecular weight itself, as the highest levels of modification are observed for the two prepolymers with the largest free isocyanate content (MDI-PPG^{440} and MDI-PPG^{940}).

Furthermore, the inset in Figure 6 shows the evolution of the ratio M.I.^{water}/M.I. with the free –NCO content of the above ratio, for bitumens A and B. This ratio compares the overall viscosity increase, due to the combined action of prepolymer and water addition, relative to the single contribution of the prepolymer. It can be appreciated that, for MDI-PPG binders from neat bitumen B, the ratio above increases as the free –NCO content does. It can be concluded that, a high free –NCO content results of major importance in increasing the binders viscosity after water addition, although the prepolymer molecular weight seems to initially contribute (before water addition) and conditions the final modification achieved. However, no significant differences are observed for those binders from neat bitumen A, as this one was shown to be, in general, quite insensitive to the prepolymer type.

With the same regard, Figure 7 shows the viscous flow curves, at 60 ºC, for a set of three different modified bitumens containing MDI-PPG^{2425} prepolymers which were prepared with three MDI/PPG^{2425} molar ratios of 5:1, 6:1 and 8:1, respectively. Both systems, with and without water addition, underwent an increase in viscosity with the free -NCO content (Table 2). Thus, the two prepolymers with largest –NCO concentration (molar ratios of 1:6 and 1:8) present much higher increase than the other one. However, such an increase does not compare to the values exhibited by MDI-PPG^{940} and MDI-PPG^{440} in Figure 4, which have a similar free –NCO content to the binders MDI-PPG^{2425}(6:1) and MDI-PPG^{2425}(8:1), respectively. As modification is

always conducted by adding 4 wt.% prepolymer, the concentration of free –NCO groups is the same, but the number of functionalized-polyol units is very different. Consequently, a higher number of smaller units (in prepolymers MDI-PPG^{940} and MDI-PPG^{440}) results in a more effective contribution to the final modification. This fact again confirms the influence of prepolymer molecular weight on the results obtained.

Moreover, Figure 8 shows the evolution with frequency of the linear storage and loss moduli (G' and G'', respectively) at 60 °C, for neat bitumen B and its corresponding "MDI-PPG 24h" and "MDI-PPG-water 24h" samples. Due to the quite limited degree of modification shown by bitumen A, its viscoelastic behaviour will not be herein considered. 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 and ω^2, respectively, is notably modified by the addition of the prepolymers. Thus, the differences between both moduli are reduced after modification, as G' increases much more than G'' does, what reduces the viscous character of the binders. However, especial attention should be paid to the water-involved procedure, for which the increase observed in the viscoelastic functions results much more evident. Additionally, G' and G'' become parallel in a relatively large frequency interval for the two prepolymers with the lowest molecular weights (and even coincident, for MDI-PPG^{440}), which suggests an important enhancement in the material solid-like features. In accordance with the results in Figures 4 to 6, the highest level of modification (highest values of G' and G'') corresponds to MDI-PPG^{940}.

Further, temperature sweep tests in oscillatory shear, from 30 to 90 ºC, were carried out on neat bitumen B and their corresponding "MDI-PPG-water 24h" modified bitumen samples. Figure 9 shows the evolution with temperature of the loss tangent (ratio G''/G'), as a function of the type of prepolymer. As expected, prevailing viscous

features, characterised by values of tanδ>1 which increase as temperature does, are noticed for the neat bitumen B. Prepolymer addition provoked a notable decrease in the tanδ values, as the differences between the viscous and elastic moduli were significantly reduced (and so, the elastic response enhanced). The most important elastic response was found for the prepolymer with the highest free –NCO content (or lowest molecular weight). Hence, values of tanδ of around 1 may be found at the lowest temperatures (in accordance with the mechanical spectrum in Figure 8, with coincident curves of G'' and G' at the highest frequencies). This fact reveals that the free –NCO content, but also the reactivity derived from the size of the molecules, may be the key parameters at controlling the enhancement in the binder elastic features. Furthermore, it also seems to lead to an outstanding decrease in the binder thermal susceptibility, as shown by a nearly constant value of tanδ in a broad interval of temperatures. This result would suggest an improved thermal resistance for these binders [25,26].

4. CONCLUDING REMARKS

With the aim of assessing the influence of the molecular weight and free isocyanate content on the rheology of polyurethane bituminous binders, a total of six MDI-PPG prepolymers, derived from different polypropylene-glycols and MDI:PPG ratios, were used.

Firstly, the results demonstrate that the degree of modification achieved by this type of MDI-PPG prepolymers clearly depends on the bitumen nature and modification protocol followed. Thus, for a selected processing method, the highest modification was obtained for the neat bitumen which exhibited the largest quality of colloidal microstructure (represented by larger value of its Gaestel colloidal index). However, no significant differences are observed between the binders prepared from bitumen A, as

this one was shown to be, in general, quite insensitive to the prepolymer type and to modification itself. With regard to the processing protocol, water addition leads to binders with a much higher viscosity than those derived from the "free-water" procedure, mainly for the two prepolymers with the lowest molecular weights.

On the other hand, if the overall viscosity increase is compared to the single contribution of the prepolymer addition, it can be concluded that a high free –NCO content appears to be more important than the molecular weight itself in increasing the binders viscosity after water addition. However, the prepolymer molecular weight seems to initially contribute and to condition the final modification achieved. Thus, in this case, the highest modification observed corresponds to the MDI-PPG^{940} prepolymer. This fact reveals that the viscosity increase is controlled by the combined effect of the free –NCO content along with the molecular weight.

Finally, if prepolymers with similar free –NCO contents are used, the results demonstrate that, for fixed prepolymer and water concentrations (4 and 2 wt.%, respectively, in this study), a higher number of smaller functionalized-polyol units (prepolymers MDI-PPG^{940} and MDI-PPG^{440}, in this study) results in a more effective contribution to the final modification.

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Table 1. Penetration grades, R&B softening temperatures and Gaestel colloidal index values (in terms of SARAs fractions) for neat bitumens A and B.

	Bitumen A	**Bitumen B**
Penetration (1/10 mm)	145	160
R&B softening point (ºC)	41.5	39.5
Colloidal index*	0.26	0.44

* Colloidal index=(asphaltenes+saturates)/(resins+aromatics)

Table 2. Molecular weight and architecture, and free –NCO contents of polyols, polymeric MDI and prepolymers synthesized.

Designation	**Molecular architecture**	**M_w[a] (g/mol)**	**Free –NCO content (wt.%)[b]**
Polymeric MDI	--	364	32.40
PPG^{440}	Linear	440	--
PPG^{940}	Linear	940	--
PPG^{1850}	Linear	1850	--
PPG^{2425}	Branched	2425	--
MDI-PPG^{440}	Linear	925	22.9
MDI-PPG^{940}	Linear	1390	17.4
MDI-PPG^{1850}	Linear	2372	12.1
MDI-PPG^{2425}(5:1)	Branched	5682	10.7
MDI-PPG^{2425}(6:1)	Branched	--	17.5
MDI-PPG^{2425}(8:1)	Branched	--	21.5

[a]Molecular weights determined by GPC measurements.

[b]According to ASTM D-2572.

Table 3. Carreau's model parameters for the different "MDI-PPG 24h" and "MDI-PPG-water 24h" samples studied.

			Carreau's model parameters		
		Binders	**η_0 (Pa·s)**	**$\dot{\gamma}_c$ (s^{-1})**	**s**
Bitumen A	**Prepolymers**	Neat bitumen	$6.4 \cdot 10^1$	--	--
	$MDI\text{-}PPG^{440}$	MDI-PPG 24h	$9.3 \cdot 10^1$	--	--
		MDI-PPG-water 24h	$1.6 \cdot 10^2$	--	--
	$MDI\text{-}PPG^{940}$	MDI-PPG 24h	$1.1 \cdot 10^2$	--	--
		MDI-PPG-water 24h	$1.6 \cdot 10^2$	--	--
	$MDI\text{-}PPG^{1850}$	MDI-PPG 24h	$1.0 \cdot 10^2$	--	--
		MDI-PPG-water 24h	$1.3 \cdot 10^2$	--	--
	$MDI\text{-}PPG^{2425}$	MDI-PPG 24h	$9.7 \cdot 10^1$	--	--
		MDI-PPG-water 24h	$1.1 \cdot 10^2$	--	--
Bitumen B	**Prepolymers**	Neat bitumen	$8.5 \cdot 10^1$	--	--
	$MDI\text{-}PPG^{440}$	MDI-PPG 24h	$1.0 \cdot 10^3$	$8.2 \cdot 10^{-2}$	$8.7 \cdot 10^{-2}$
		MDI-PPG-water 24h	$2.4 \cdot 10^4$	$4.9 \cdot 10^{-2}$	$5.0 \cdot 10^{-1}$
	$MDI\text{-}PPG^{940}$	MDI-PPG 24h	$5.8 \cdot 10^3$	--	--
		MDI-PPG-water 24h	$6.3 \cdot 10^4$	$3.0 \cdot 10^{-2}$	$4.3 \cdot 10^{-1}$
	$MDI\text{-}PPG^{1850}$	MDI-PPG 24h	$5.2 \cdot 10^2$	$6.5 \cdot 10^{-1}$	$1.7 \cdot 10^{-1}$
		MDI-PPG-water 24h	$1.7 \cdot 10^3$	$1.0 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$
	$MDI\text{-}PPG^{2425}$	MDI-PPG 24h	$3.3 \cdot 10^2$	$2.6 \cdot 10^{-1}$	$6.1 \cdot 10^{-2}$
		MDI-PPG-water 24h	$9.5 \cdot 10^2$	$2.6 \cdot 10^{-1}$	$9.1 \cdot 10^{-2}$

Figure captions

Figure 1. Structural formulae of: (A) polymeric MDI; (B) poly(propylene glycol).

Figure 2. GPC chromatograms for: a) polyols and polymeric MDI; b) different prepolymers studied.

Figure 3. TGA curves for: a) polyols and polymeric MDI; b) different prepolymers studied.

Figure 4. Viscous flow curves, at 60 ºC, for neat bitumens A and B, and their corresponding modified binders (derived from prepolymers with different molecular weights).

Figure 5. Modification index values for "MDI-PPG 24h" and "MDI-PPG-water 24h" samples.

Figure 6. Evolution of the modification index values with the free –NCO content.

Figure 7. Viscous flow curves, at 60 ºC, for neat bitumen B, and their corresponding MDI-PPG^{2425} modified binders (with 3 different MDI:PPG^{2425} molar ratios).

Figure 8. Frequency dependence, at 60 ºC, of the storage and loss moduli for neat bitumen B and its "MDI-PPG 24h" and "MDI-PPG-water 24h" samples.

Figure 9. Evolution with temperature of loss tangent for neat bitumen B and its corresponding "MDI-PPG-water 24h" samples.

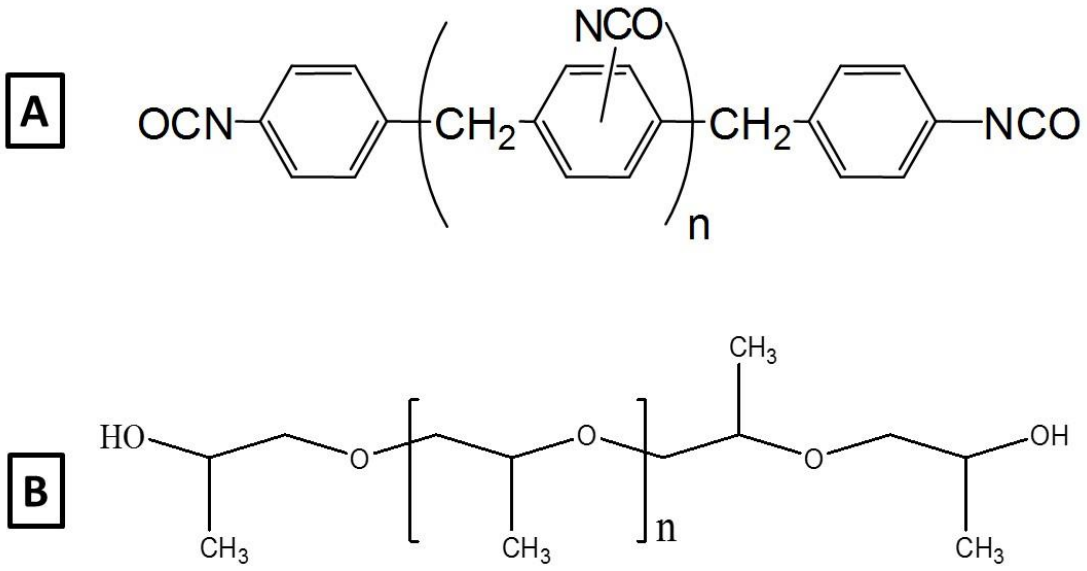

Figure 1

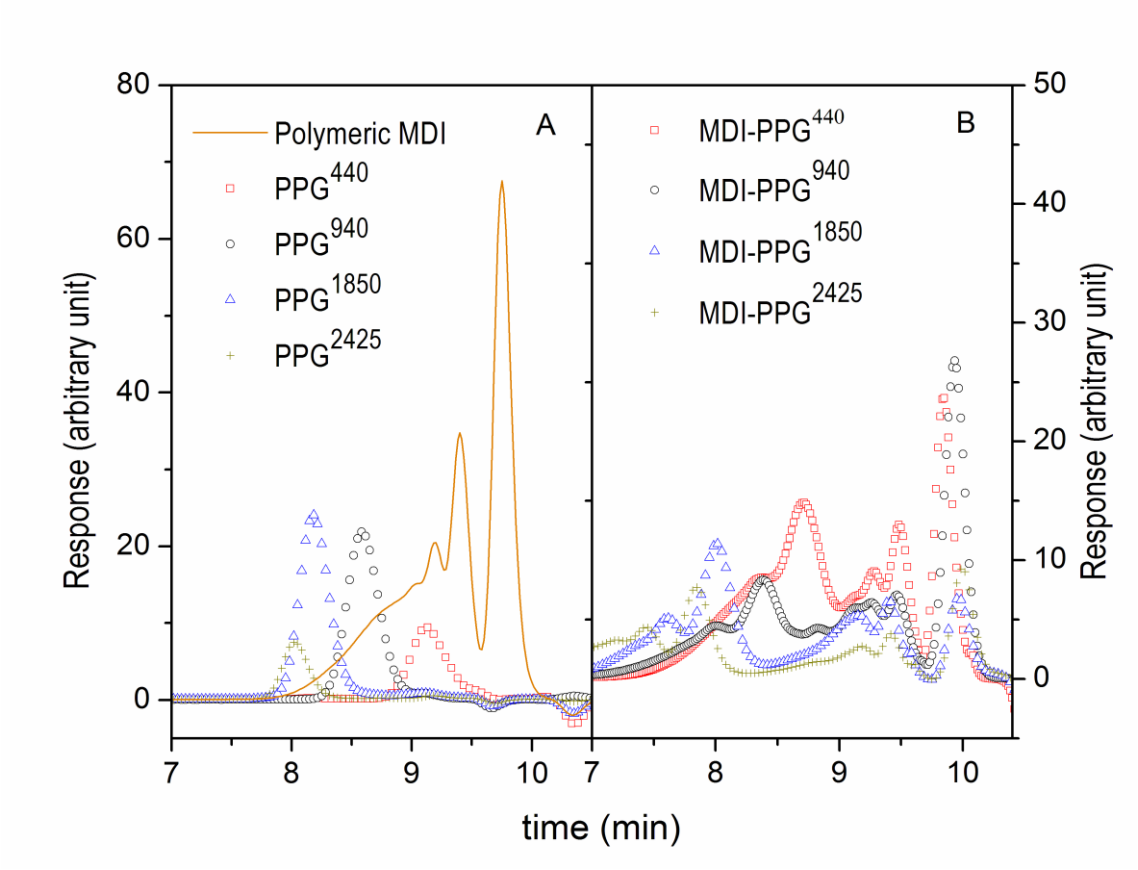
Polymeric MDI
PPG440
PPG940
PPG1850
PPG2425
A
MDI-PPG440
MDI-PPG940
MDI-PPG1850
MDI-PPG2425
B
Response (arbitrary unit)
Response (arbitrary unit)
time (min)

Figure 2

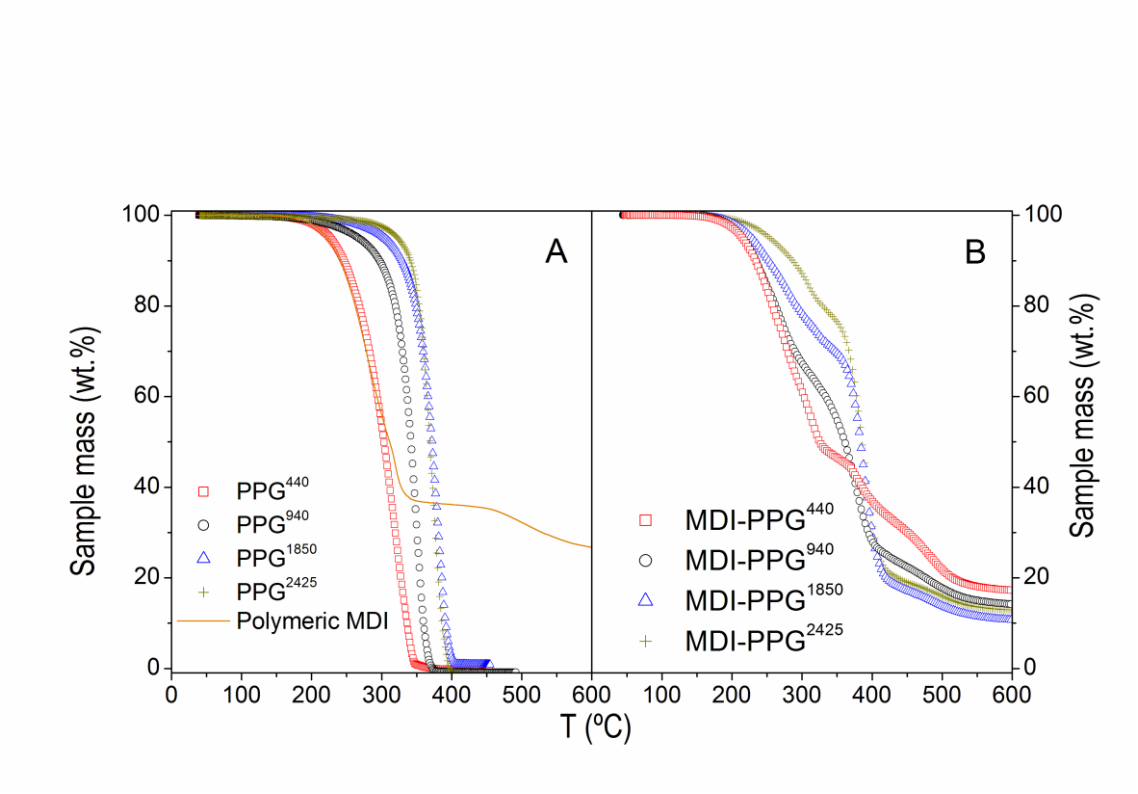
A
B
Sample mass (wt.%)
Sample mass (wt.%)
T (ºC)
PPG440
PPG940
PPG1850
PPG2425
Polymeric MDI
MDI-PPG440
MDI-PPG940
MDI-PPG1850
MDI-PPG2425

Figure 3

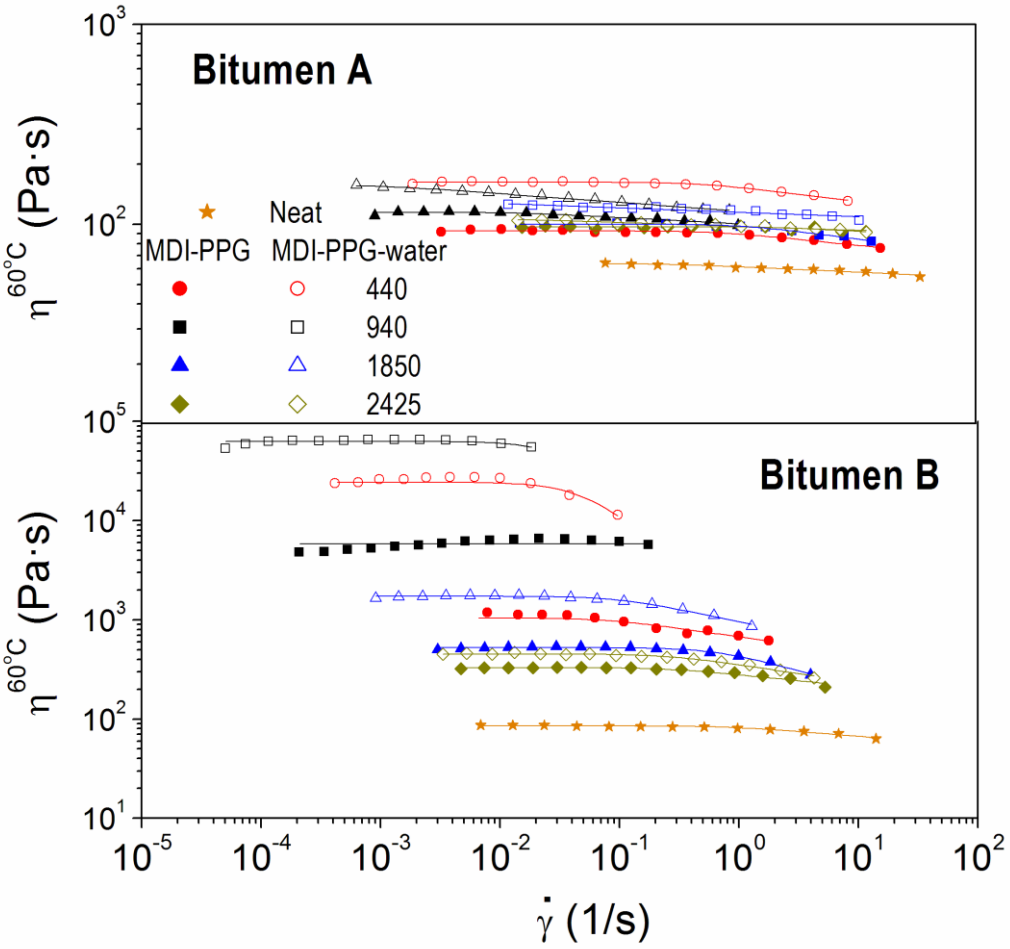
Bitumen A
Neat
MDI-PPG
MDI-PPG-water
440
940
1850
2425
Bitumen B
$\eta^{60°C}$ (Pa·s)
$\dot{\gamma}$ (1/s)

Figure 4

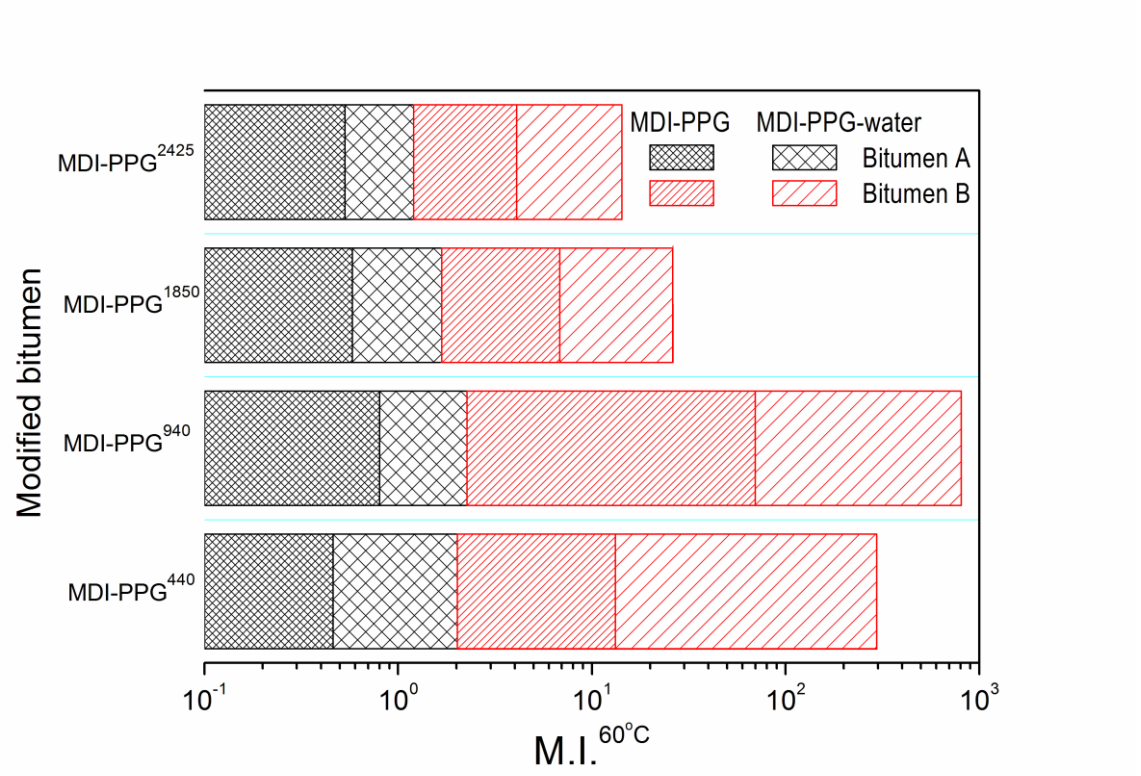
MDI-PPG
MDI-PPG-water
Bitumen A
Bitumen B
MDI-PPG2425
MDI-PPG1850
MDI-PPG940
MDI-PPG440
Modified bitumen
10-1
100
101
102
103
M.I.60°C

Figure 5

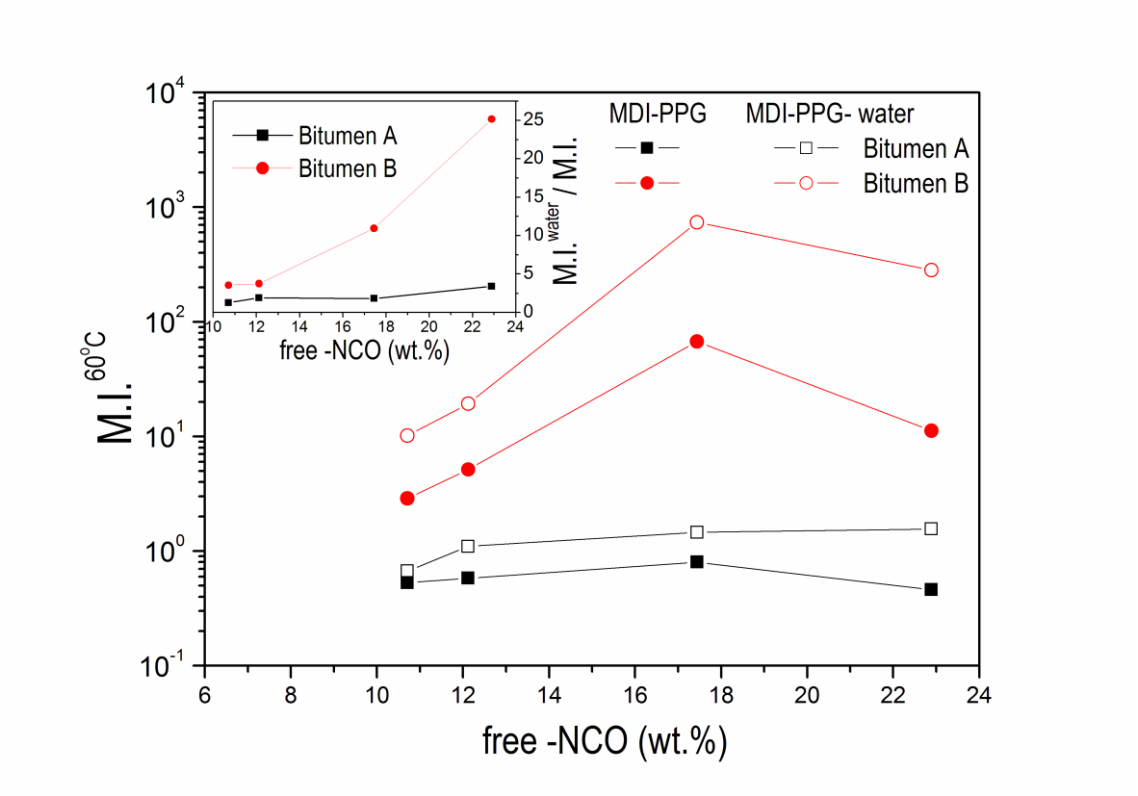
M.I. 60°C
free -NCO (wt.%)
MDI-PPG
MDI-PPG- water
Bitumen A
Bitumen B
M.I.water / M.I.
free -NCO (wt.%)
Bitumen A
Bitumen B

Figure 6

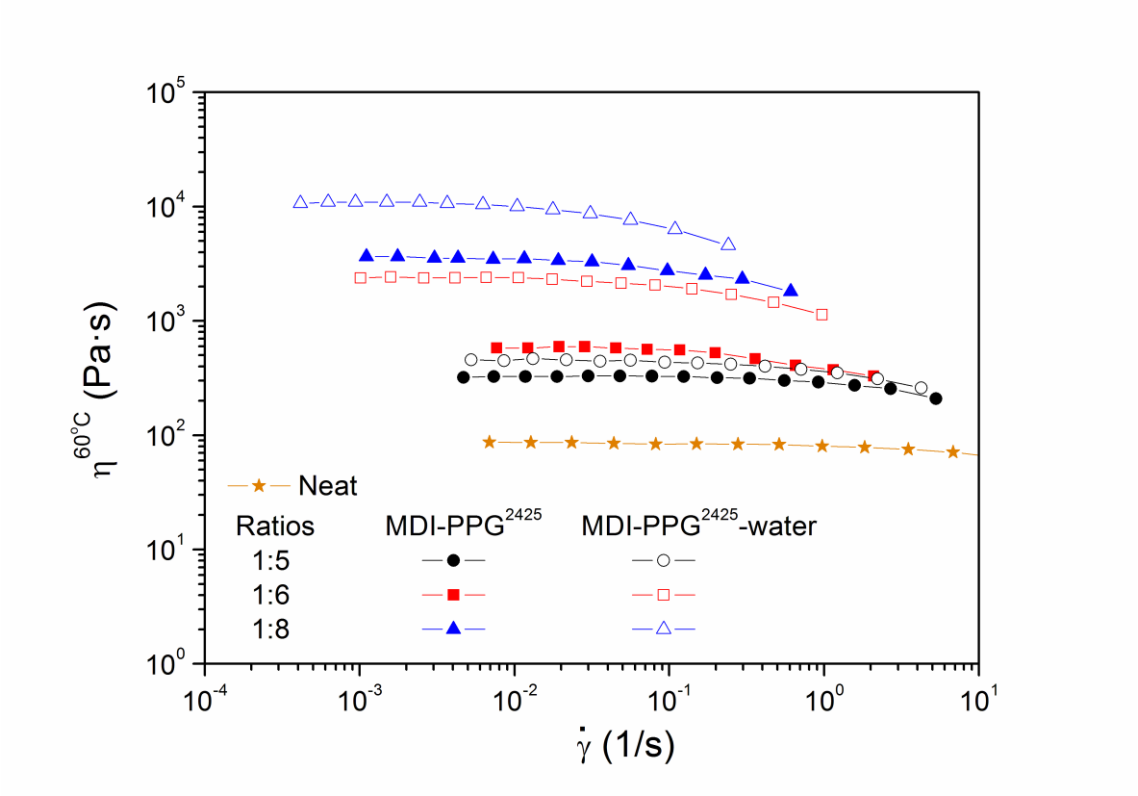
10^5
10^4
10^3
10^2
10^1
10^0
η^{60^oC} (Pa·s)
Neat
Ratios
MDI-PPG^{2425}
MDI-PPG^{2425}-water
1:5
1:6
1:8
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
$\dot{\gamma}$ (1/s)

Figure 7

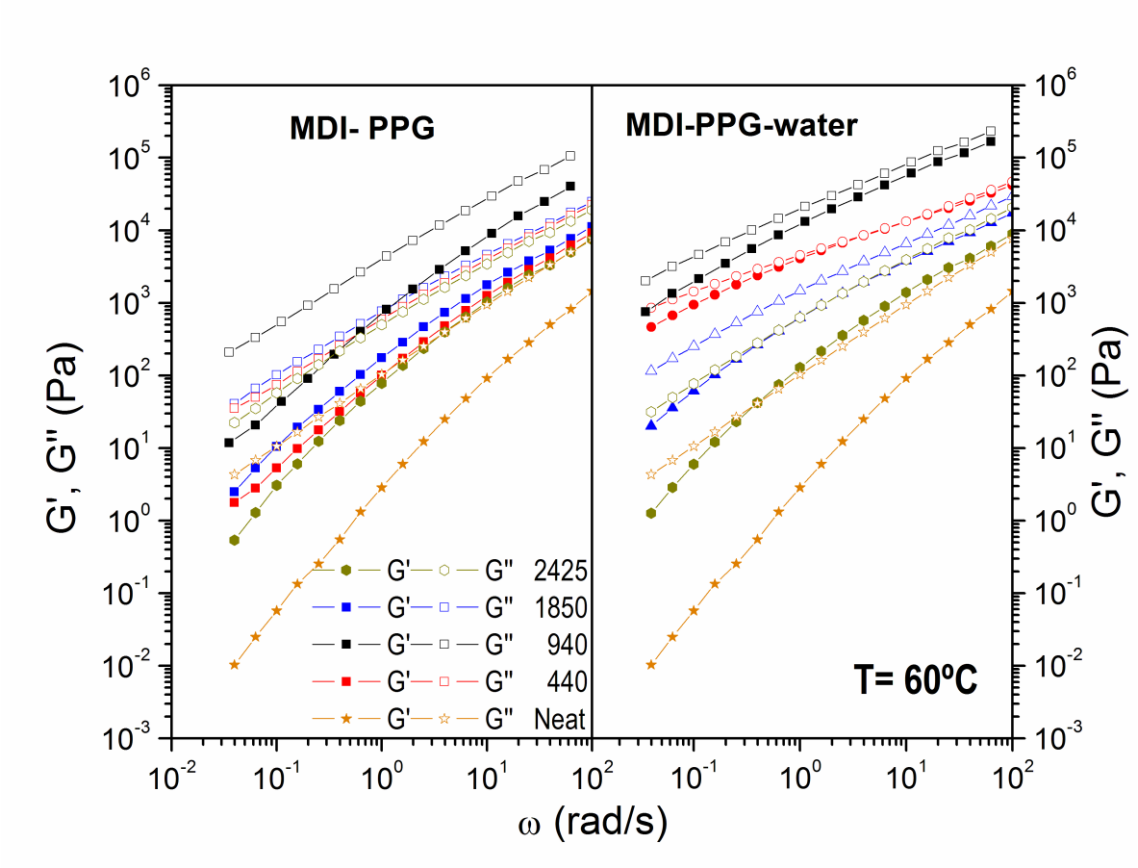
MDI- PPG
MDI-PPG-water
T= 60ºC
G', G" (Pa)
ω (rad/s)
G' G" 2425
G' G" 1850
G' G" 940
G' G" 440
G' G" Neat

Figure 8

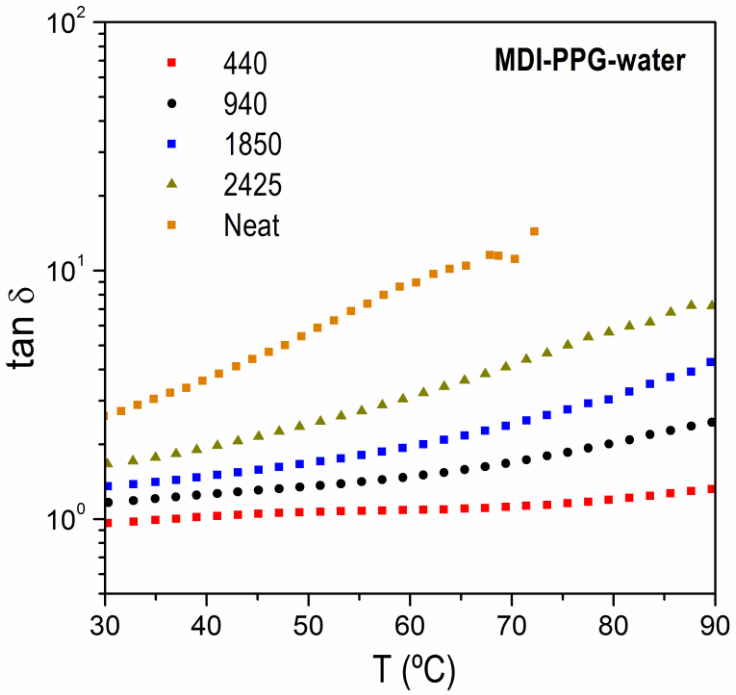
MDI-PPG-water
440
940
1850
2425
Neat
tan δ
T (ºC)
10^2
10^1
10^0
30
40
50
60
70
80
90

Figure 9