

Influence of the thermal history on the rheological properties of modified bitumens

Cesare Oliviero Rossi¹, Ruggero Angelico², Saltanat Ashimova^{1,3}, Guido Bonin⁴, Giuseppe Loprencipe⁴, Bagdat Teltayev³

(¹ Dept. Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 14/D – 87036 Arcavacata, Italy, cesare.oliviero@unical.it)

(² Dept. Agricultural, Environmental and Food Sciences (DIAAA), University of Molise, 86100 Campobasso (CB), Italy, angelico@unimol.it)

(³ Kazakhstan Highway Research Institute, Nurpeisov 2a, Almaty 050061 Kazakhstan, bagdatbt@yahoo.com)

(⁴ Dipartimento di Ingegneria Civile, Edile e Ambientale, Sapienza Università di Roma Via Eudossiana n° 18, 00184 Roma, giuseppe.loprencipe@uniroma1.it)

ABSTRACT

Due to the wide variation in geographic and climatic conditions, the growing demands of resistant bituminous materials to various environmental conditions have resulted in a search for bitumen modifiers capable to reduce the temperature susceptibility of the binder in the service temperature range. Therefore, in the present contribution, the effects of addition of low molecular weight organic compounds on temperature susceptibility of asphalt binders were investigated by a combination of dynamics oscillatory rheology and Atomic Force Microscopy (AFM). The results analyzed on the basis of weak gel model were found useful to discriminate the selected additives regarding their relative capacity to favor coarse or fine colloidal aggregates, which in turn were responsible for the observed bulk rheological behaviour.

Keywords: complex shear modulus, Atomic Force Microscopy, cooling gradient, additives, asphaltene aggregates.

1. INTRODUCTION

Bitumen, which is the European synonym for asphalt binder in North America, both of natural and industrial origin, is the most employed material in highway paving technologies. From the chemical point of view, it represents a relatively homogeneous and randomly distributed collection of molecules differing in polarity and molecular size [1]. At micrometric scale, there is a general consensus about the fact that bitumen is considered a colloidal dispersion of asphaltenes (A) into a continuous oily phase constituted by saturates (S), aromatics (A) and resins (R), which overall identify the four SARA fractions of bitumen [2,3] Depending on SARA composition, presence of suitable additives and temperature, asphaltenes can lead to the formation of a continuous network giving the entire system a non-Newtonian fluid behavior at high temperatures and an elastic solid at low temperatures; this bitumen is defined as a gel [4]. In practice, most bitumen has intermediate characteristics between these two structures representing limit cases. "Intermediate" bitumen has better elasticity and mechanical properties than sol, while bitumen gels have better mechanical strength but worst elastic properties. From a qualitative point of view, the rheological properties of bitumen depend in some way on the asphaltene

1 content. It can therefore be stated that at low and intermediate temperatures bitumen rheology is
2 strongly influenced by the degree of association of asphaltene and by the presence of other
3 species (e.g. additives) favoring such associations in the system as it will be further illustrated.
4 Therefore, for a good road performance it would be highly desirable that the deformation
5 properties of bitumen remain unchanged under the effect of different cooling rates, and mitigate
6 the susceptibility of asphalt concrete to several drawbacks such as thermal cracking and thermal
7 stress accumulation [5].
8

9 **2. MATERIALS & METHODS**

10 **2.1 Materials**

11
12 The base bitumen was kindly supplied by Loprete Costruzioni Stradali (Italy). It was
13 produced in Italy and the crude oil was from Saudi Arabia. The neat bitumen was modified by
14 adding commercial additives, namely, a) poliphosphoric acid (PPA) provided by Sigma Aldrich
15 (Milano, Italy) and b) phospholipids in form of light yellow powder (hereafter LCS) provided by
16 Somercom srl (Catania (CT), Italy).
17

18 **2.2 Sample preparations and set up of cooling ramps**

19
20 The additives were mixed separately to hot bitumen (140-160°C) at fixed content of 2 %
21 wt/wt [6,7] by using a mechanical stirrer (IKA RW20, Germany). Firstly, 100 g of bitumen was
22 heated up to 140-160 °C until it flowed fully, then a given amount of additive was added to the
23 melted bitumen under a high-speed shear mixer at 500 - 700 rpm. Furthermore, the mixtures
24 were stirred again at 140-160 °C for 30 min. After mixing, three different cooling ramp rates
25 were applied to bitumen samples modified with PPA and LCS, respectively. Parallel temperature
26 ramp tests were carried out on unmodified bitumen as a reference system. The experimental
27 conditions were isothermal annealing for 10 min at 160°C; then, the samples were allowed to
28 cool to RT at, respectively, 1, 5 and 10 °C/min.
29

30 **2.3 S.A.R.A. determination**

31
32 The Iatroskan MK 5 Thin Layer Chromatography (TLC) was used for the chemical
33 characterization of bitumen by separating it into four fractions: Saturates, Aromatics, Resins and
34 Asphaltenes (S.A.R.A) [8]. During the measurement, the separation took place on the surface of
35 silica-coated rods. The detection of the amount of different groups were according to the flame
36 ionization. The sample was dissolved in peroxide-free tetrahydrofurane solvent to reach a 2 %
37 (w/v) solution. Saturated components of the sample were developed in n-heptane solvent while
38 the aromatics in a 4:1 mixture of toluene and n-heptane. Afterwards, the rods had to be dipped
39 into a third tank, which was a 95 to 5 % mixture of dichloromethane and methanol. That organic
40 medium proved suitable to develop the resin fraction whereas the asphaltene fraction was left on
41 the lower end of the rods.
42

43 **2.4 Empirical Characterization**

1 Penetration tests for bitumens were performed according to the standard procedure
2 (ASTM D946) [9]. The bitumen consistency was evaluated by measuring the penetration depth
3 (531/2-T101, Tecnotest, Italy) of a stainless steel needle of standard dimensions under
4 determinate charge conditions (100 g), time (5 s) and temperature (25 °C).
5

6 **2.5 Atomic Force Microscopy (AFM) analysis**

7

8 An Atomic Force Microscopy equipment (Multimode VIII with a Nanoscope V
9 controller, Bruker) was used to analyse the samples. The AFM has been used in tapping mode,
10 where the cantilever oscillates up and down close to its resonance frequency so that the tip is
11 contacting the sample surface intermittently. When the tip is brought close to the surface, the
12 vibration of the cantilever is influenced by the tip-sample interaction. In particular, shifts in the
13 phase angle of vibration of the cantilever are due to the energy dissipation in the tip-sample
14 ensemble. The phase shift provides information on surface properties such as stiffness,
15 viscoelasticity and adhesion. For measurements, Antimony doped silicon probes (TAP150A,
16 Bruker) with resonance frequency 150 kHz and nominal tip radius of curvature 10 nm were used.
17 All the measurements were performed at room temperature. Phase images were acquired
18 simultaneously with the topographic mode. Materials with different viscoelasticity can be clearly
19 distinguishable. The softer domains appeared dark while the stiffer ones appeared bright in the
20 phase images.
21

22 **2.6 Isothermal rheological tests after different cooling ramps**

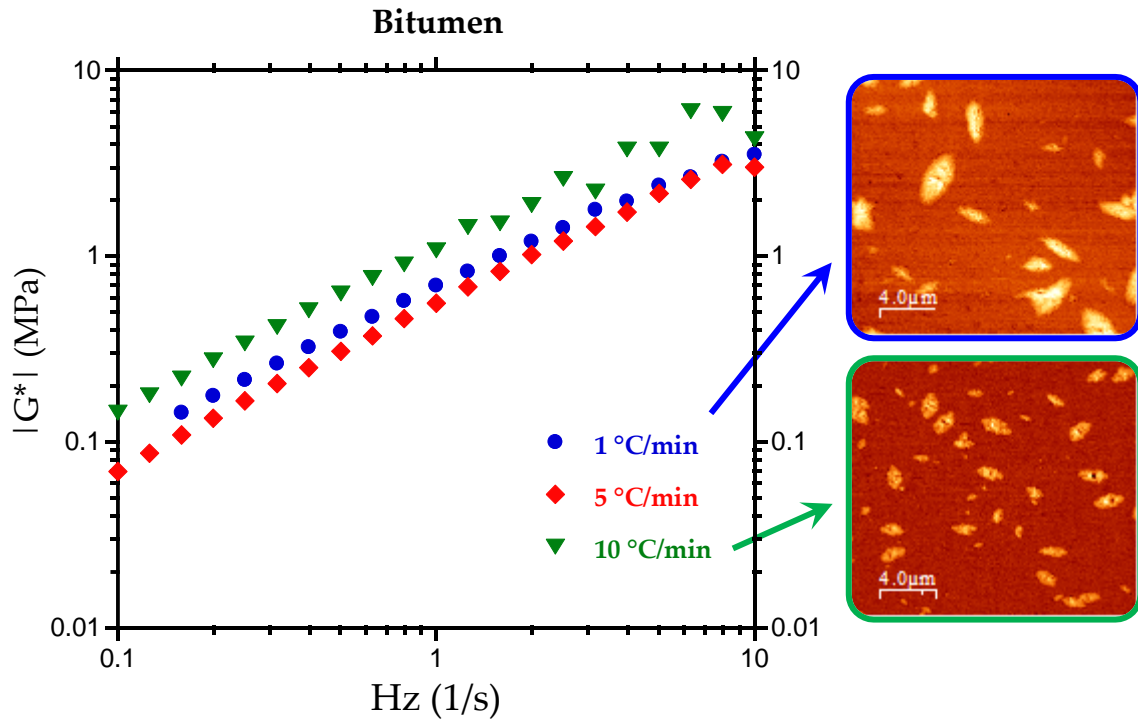
23

24 After each cooling ramp, samples were subjected to oscillatory rheological tests at
25 constant temperature $t = 25^{\circ}\text{C}$, controlled by a Peltier element ($\pm 0.1^{\circ}\text{C}$), using a dynamic stress-
26 controlled rheometer (SR5, Rheometric Scientific, USA) equipped with a parallel plate geometry
27 (gap 2.0 ± 0.1 mm, diameter 25 mm). The linear viscoelastic regime of both neat and modified
28 bitumen was preliminary checked through the determination of the complex shear modulus G^* in
29 the regime of small-amplitude oscillatory shear [10,11]. $|G^*|$ is the magnitude of the complex
30 shear modulus, defined as the ratio of shear stress to shear strain amplitudes in steady state when
31 a sample is subjected to oscillating shear stress at a specific frequency. It is a critical property of
32 the binder that dictates its performance in an asphalt mixture: the higher $|G^*|$ the stiffer the
33 binder.
34

35 **3. RESULTS & DISCUSSION**

36

37 The viscoelastic properties of tested bitumen specimens were analysed by frequency-
38 sweeps experiments at 25°C . The frequency dependence of the experimental complex shear
39 modulus $|G^*|$ for the unmodified bitumen has been illustrated in Figure 1 in correspondence to
40 different thermal cooling gradients of, respectively, $1^{\circ}\text{C}/\text{min}$, $5^{\circ}\text{C}/\text{min}$ and $10^{\circ}\text{C}/\text{min}$. The effect
41 of different thermal treatments on the microstructure is also evident from the comparison of
42 AFM images showing coarse and irregular aggregates (catana-phase, [12]) obtained after slow
43 cooling whereas small crystalline nuclei are favoured if bitumen undergoes to fast cooling rates
44 [13]. Remarkably, the highest gradient provides to increase the stiffness of the binder as it is
45 evidenced by the upward shift of $|G^*|$.



1
2 **FIGURE 1** Complex modulus $|G^*|$ vs frequency at 25°C for neat bitumen subjected to different
3 thermal treatment: 1°C/min (circles), 5°C/min (diamonds), and 10°C/min (triangles). The AFM
4 images acquired after, respectively, slowly and fast cooling are also shown.

5
6
7
8 A more distinct influence of different cooling ramps on both the mechanical response and
9 microstructure of bitumen has been recorded when the binder was pre-blended with
10 polyphosphoric acid (PPA) 2 % wt/wt. Indeed, the tendency to increase the binder stiffness after
11 10°C/min ramp is more pronounced compared to the base bitumen as it has been illustrated in
12 Figure 2 for various $|G^*|$ vs frequency series. Similarly, large pseudo-spherical or lenticular
13 domains have been imaged after a slow cooling rate (1°C/min) whereas smaller crystallites with
14 irregular or ellipsoidal shapes are formed after subjecting the bitumen modified with
15 polyphosphoric acid PPA to a rapid cooling treatment (10°C/min).

16
17

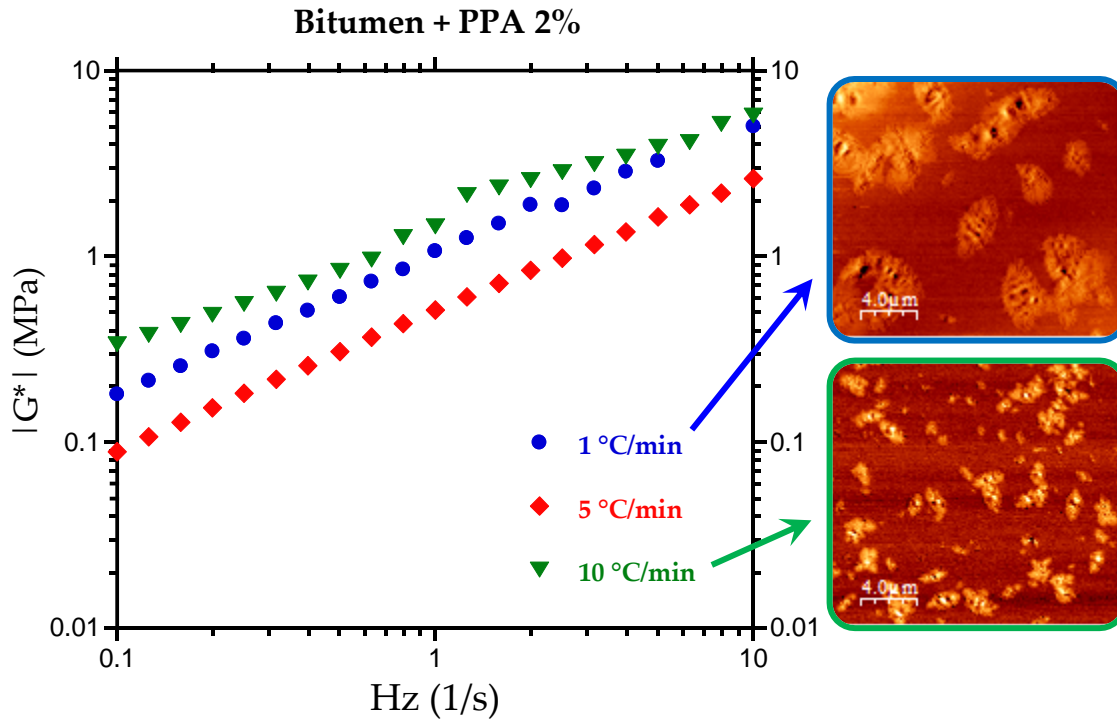


FIGURE 2 Complex modulus $|G^*|$ vs frequency at 25°C of bitumen modified with PPA 2% after different cooling ramps: 1°C/min (circles), 5°C/min (diamonds), and 10°C/min (triangles). The AFM images acquired after, respectively, slowly and fast cooling are also shown.

A complete different behaviour has been found for bitumen modified with addition of 2 % wt/wt of phospholipids (LCS) to the base bitumen. Indeed, the bulk complex shear modulus $|G^*|$ looks almost unaffected by the thermal history as illustrated in Figure 3, which also shows typical high-resolution AFM images highlighting feature-less small aggregates independently of applied cooling rates. According to the colloidal model for the bitumen microstructure, asphaltene manifests the tendency to self-associate and form aggregates through noncovalent interactions between aromatic cores, such as π - π stacking and hydrogen bonding [4]. Therefore, the presence of phospholipids dispersed into the bituminous matrix would enhance the formation of noncovalent interactions between asphaltene aggregates, mediated also by resins that represent the polar fraction of the bituminous material. In this context, LCS exerts his amphiphilic character by stabilizing the resulting supramolecular networks, which in turn is responsible for a better resistance against the action of different cooling rates in the range 1-10°C/min. Other types of additives have been also tested to check their effect on the thermal history of the corresponding modified bituminous specimens as it has been detailed elsewhere [14].

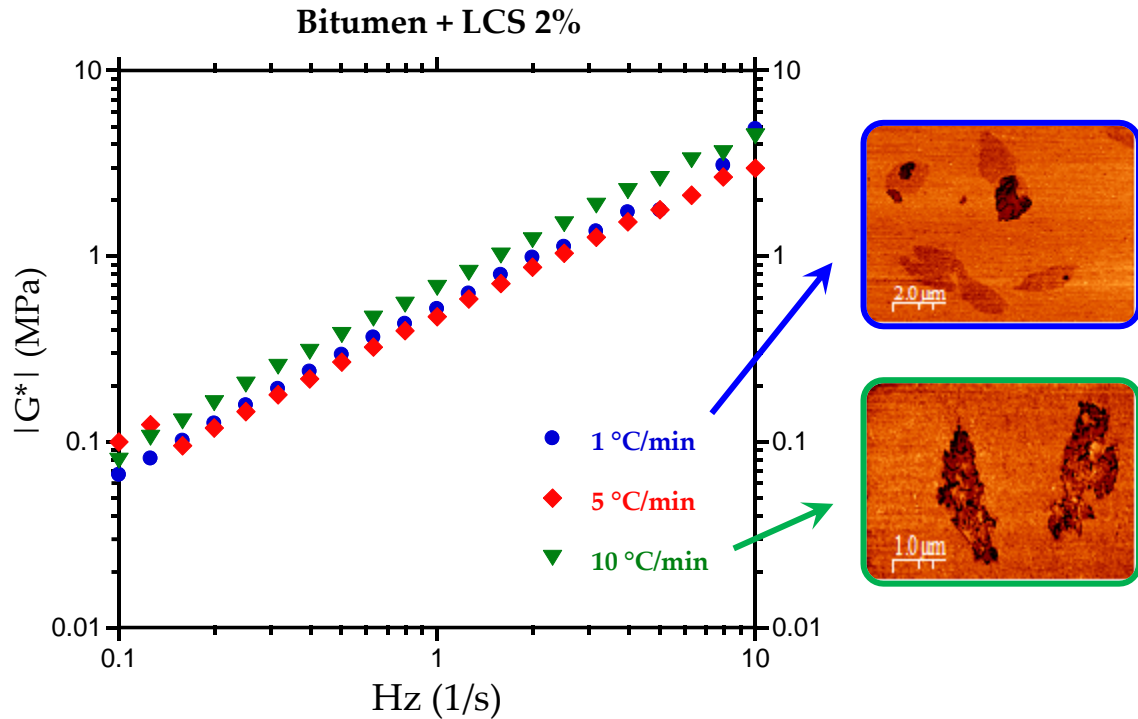


FIGURE 3 Complex modulus $|G^*|$ vs frequency at 25°C of bitumen modified with LCS 2% after different cooling ramps: 1°C/min (circles), 5°C/min (diamonds), and 10°C/min (triangles). The AFM images acquired after, respectively, slowly and fast cooling are also shown.

4. CONCLUSIONS

A comparative investigation of the mechanical responses manifested by bitumen modified with polyphosphoric acid (PPA) and a raw mixture of natural phospholipids (LCS) has been performed at 25°C, after the corresponding specimens have been subjected to different cooling treatments. Aimed at searching for microstructural differences between various types of modified bitumens when they have undergone the action of several thermal ramps, a parallel morphological investigation has been also carried out by using Atomic Force Microscopy (AFM). A remarkable result has been recorded for bitumen incorporating the LCS additive compared to both PPA modified and unmodified bitumen, capable to leave the asphaltene aggregates fairly unaltered after the hot material was either slowly (1°C/min) or rapidly (10°C/min) cooled to the final reference temperature of 25°C. The complex modulus of the correspondent LCS-modified bitumen was found almost independent of cooling rate as well. The addition of LCS to bitumen should prove extremely fruitful in increase the mechanical resistance of bitumen to thermal shocks and provide an attempt to substitute polymer-based rheology modifiers with additives derived from renewable bio-resources.

1 **References**

- 2 [1] Petersen C., Robertson R.E., Branthaver J.F., Harnsberger P.M., Duvall J.J. and Kim
3 S.S. Binder characterization and evaluation. Vol. 1, SHRP-A-367. 1994.
- 4 [2] Yen T.F. and Chilingarian G.V. *Asphalthenes and Asphalts*, Elsevier, New York.
5 1994.
- 6 [3] Rozeveld S., Shin E., Bhurke A., France L. and Drzal L. Network morphology of
7 straight and polymer modified asphalt cements. *Microscopy Res. Techn.*, 38, pp. 529-543. 1997.
- 8 [4] Lesueur D. The colloidal structure of bitumen: Consequences on the rheology and on
9 the mechanisms of bitumen modification. *Adv. Colloid Inter. Sci.*, 145, pp. 42-82. 2009.
- 10 [5] Apeagyei A.K., Dave E.V. and Buttlar W.G. Effect of Cooling Rate on Thermal
11 Cracking of Asphalt Concrete Pavements. *J. Assoc. Asph. Paving. Technol.*, 77, pp. 709-738.
12 2008.
- 13 [6] Oliviero Rossi C., Caputo P., Baldino N., Lupi F.R., Miriello D. and Angelico R.
14 Effects of adhesion promoters on the contact angle of bitumen-aggregate interface. *Int. J. Adhe.*
15 *Adhes.*, 70, pp. 297-303. 2016.
- 16 [7] Oliviero Rossi C., Caputo P., Baldino N., Szerb E.I. and Teltayev B. Quantitative
17 evaluation of organosilane-based adhesion promoter effect on bitumen-aggregate bond by
18 contact angle test. *Int. J. Adhe. Adhes.*, 72, pp. 117-122. 2017.
- 19 [8] Yoon S., Durgashanker Bhatt S., Lee W., Lee H.Y., Jeong S.Y., Baeg J.-O. and Wee
20 Lee C. Separation and characterization of bitumen from Athabasca oil sand. *Korean J. Chem.*
21 *Eng.*, 26, pp. 64-71. 2009.
- 22 [9] ASTM Standard for Penetration-Graded Asphalt Cement for Use in Pavement
23 Construction, D946-82, ASTM International, West Conshohocken, PA. 2005.
- 24 [10] Coppola L., Gianferri R., Oliviero Rossi C., Nicotera I. and Ranieri G.A. Structural
25 changes in CTAB/H₂O mixtures using a rheological approach. *Phys. Chem. Chem. Phys.*, 6, pp.
26 2364-2372. 2004.
- 27 [11] Angelico R., Carboni M., Lampis S., Schmidt J., Talmon Y., Monduzzi M. and
28 Murgia S. Physicochemical and rheological properties of a novel monoolein-based vesicle gel.
29 *Soft Matter*, 9, pp. 921-928. 2013.
- 30 [12] Masson J-F., Leblond V., Margeson J. and Bundalo-Perc S. Low – temperature
31 bitumen stiffness and viscous paraffinic nano- and micro-domains by cryogenic AFM and PDM.
32 *J. Microsc.*, 227, pp. 191-202. 2007.
- 33 [13] Fischer H.R., Dillingh B. and Ingenhut B. Fast solidification kinetics of parts of
34 bituminous binders. *Mater. Struct.*, 49, pp. 3335–3340. 2016.
- 35 [14] Oliviero Rossi C., Ashimova S., Calandra P., De Santo M.P. and Angelico R.
36 Mechanical Resilience of Modified Bitumen at Different Cooling Rates: A Rheological and
37 Atomic Force Microscopy Investigation. *Appl. Sci.*, 7, pp.779-789. 2017.

38
39