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Bitumen in colloid science: a chemical, structural and rheological approach

L. Loeber[a,b,*], G. Muller[a], J. Morel[b] and O. Sutton[c]

[a]UMR 6522 CNRS and University of Rouen, 76821 Mt. St. Aignan Cedex, France
[b]University of Le Havre, 76600 Le Havre, France
[c]Mobil Oil France, 76330 Notre Dame de Gravenchon, France

The present study gives a new understanding about bitumen's colloidal behavior, related to its chemical composition, microscopic structure and rheological properties. Bitumens possess a strong temperature dependence of rheological properties, governed by the interaction of the individual constituents. Much importance is given to the colloidal index of the bitumen, based on the ratio of the four main chemical components (asphaltenes, resins, aromatics, saturates). Increasing one of these constituents fundamentally changes the structure and the rheological behavior of bitumen. Therefore, a gel bitumen contains high asphaltene/resin concentrations, leading to a network structure with high rigidity and elasticity (high IG^*I, low δ), whereas a sol bitumen possesses a high resin/asphaltene ratio, forming domains of coherent asphaltene micelles which lead to a good time–temperature equivalence in the Black space but also high viscous behavior. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

What are bitumens? Bitumens are important factors in road construction and roofing systems. They possess strong temperature dependent rheological properties, governed by the chemical–physical interactions of their individual constituents. Another approach is their chemical composition or their fractionating by distillation in narrow molecular weight determination by GPC, Iatroscan or liquid chromatography[1-5,11]. More recently, new approaches were used to define bitumens or bitumen's heavy constituents as RMN, scattering techniques and scanning or tunneling force microscopy[6-10]. In a general way all bitumens are classified in terms of 'grade' by penetration and ring and ball softening point measurements. However, a simple compositional analysis shows that a same grade bitumen does not have the same chemical composition (Table 1) or the same rheological/physico-chemical behavior when in contact with polymers, acids or stones. So the question still remains, what really is bitumen? What is the relationship between the bitumen's rheology, composition and structural arrangement?

Chemical nature of bitumens

A bitumen is a complex system of different constituents, made of hydrocarbons and hetero-atoms. After fractionation of the bitumen by specific solvents, four main chemical families (saturates, aromatics, resins, asphaltenes) are obtained[1,12-14]. The association of asphaltene sheets

(highly polycondensed pseudomonomers of a carbon backbone, chemical functions and hetero-atoms surrounded by aliphatic chains) leads to formation of macrostructures or 'micelles'. They can also form aggregates.

The different constituents in the bitumen follow a colloidal law, expressed by the following relationship[2,15,16]:

$$CI = \frac{\text{dispersed constituents}}{\text{flocculated constituents}} = \frac{\text{aromatics} + \text{resins}}{\text{saturates} + \text{asphaltenes}}$$

A higher colloidal index means that the asphaltenes are more peptized by the resins in the oil based medium.

Structure of bitumen

To obtain structural information about bitumens, microscopy and diffusion techniques can be implemented. However, the presence of an oil phase disturbs normal observation for microscopy and the bitumen has to endure preparation to leak out the oil phase. This can lead to artifacts or destroy the original structure. Diffusion techniques always have to be done in very diluted systems, hence changes of the concentration can change the structure and the structural properties because bitumens are colloidal systems.

To preserve the bitumen structure a freeze-fracturing method can be used[17]. Dickie et al.[18], who used spraying/evaporation techniques of diluted (0.1%) Boscan asphalt, published values between 15 and 30 nm for associated asphaltene particles, or 2–3 nm for individual polyhedral shaped particles. Donnet et al.[19] showed by SEM that pure asphalt consists of a network structure. Loeber et al.[8] compared three different microscopic techniques (SEM,

AFM, fluorescence microscopy) and found comparative results for the bitumen studied and the preparation techniques used: pure gel bitumen forms a network structure, made of small spherical particles, the asphaltenes, with a diameter of about 100–200 nm and a network porosity of about 6 μm.

Bardon and coworkers[6] applied scattering methods (X-ray, neutron) and cryo-scanning microscopy to study asphaltene and resin solutions and vacuum residue. They describe a lamella structural model for asphaltenes and resins with large heterogeneity even in dilute systems which can be related to a network structure. Sheu et al.[4] proposed self-association of asphaltene particles through weaker interactions which are easily overcome by dispersion energy and smaller particles in molecular form or aggregates formed by self association through strong intermolecular attraction forces.

The preparation or concentration of bitumens accounts for part of the discrepancy of bitumen molecular weights and particle dimensions. It seems to be important to leave the colloidal structure of the system intact when structural observation investigations are undertaken. Dilution methods will give answer to the smallest particle dimension of asphalt molecules, but this may not be representative of the asphaltene organization at a higher level.

Table 1 Composition of the different bitumens

Bitumen (grade)	Saturates (S)	Aromatics (A)	Resins (R)	Asphaltenes (Ap)
B1 (70/100)	5.2	58.8	23.9	12.2
B2 (70/100)	4.3	61.2	23.5	11.0
B3 (70/100)	4.7	57.8	22.0	15.5
B4 (10/20)	2.7	50.4	27.9	18.9
B5 (10/20)	2.65	48.8	29.3	19.2
B6 (200)	5.3	56.7	22.8	15.2
E1 (70/100)	3.4	71.1	10.8	14.8
E2 (70/100)	5.0	69.8	11.0	14.2
E3 (70/100)	4.8	63.2	15.3	16.7
E4 (70/100)	6.8	69.6	11.6	11.9
E5 (10/20)	3.7	53.1	21.2	22.0
L1 (70/100)	2.1	71.0	9.4	17.6
L2 (70/100)	4.5	59.9	16.7	18.9
L3 (70/100)	2.2	66.3	14.6	16.9
L4 (70/100)	2.4	64.2	15.7	17.7
L5 (10/20)	6.8	59.7	15.1	18.4
L6 (10/20)	1.6	59.4	14.1	24.9
M1 (70/100)	4.0	55.5	15.1	25.4
M2 (70/100)	5.7	54.4	16.2	23.7
M3 65	4.6	53.2	17.5	24.7
M4 45	3.8	51.6	17.0	27.6
M5 200	7.5	57.6	15.1	19.8
N1 (70/100)	13.2	45.1	19.7	22.0
N2 (70/100)	8.9	49.3	18.3	23.5
N3 (70/100)	8.13	49.8	19.4	22.7
G	3.0	45.7	3.8	47.5
R	3.9	95.0	1.1	0

Table 2 The colloidal index of the different bitumens

Bitumen	R/Ap	$\underline{L} = R/(Ap + S)$	A/Ap	$\underline{P} = A/(Ap + S)$	$\underline{Ci}$
B1 (70/100)	2.0	1.4	4.8	3.4	4.75
B2 (70/100)	2.1	1.5	5.55	4.0	5.55
B3 (70/100)	1.4	1.1	3.7	2.85	3.9
B4 (10/20)	1.5	1.3	2.6	2.3	3.7
B5 (10/20)	1.5	1.3	2.5	2.2	3.6
B6 (200)	1.5	1.1	3.7	2.8	3.85
E1 (70/100)	0.7	0.6	4.8	3.9	4.5
E2 (70/100)	0.8	0.6	4.9	3.6	4.2
E3 (70/100)	0.9	0.7	3.8	2.9	3.7
E4 (70/100)	1.0	0.6	5.8	3.7	4.35
E5 (10/20)	1.0	0.8	2.4	2.1	2.9
L1 (70/100)	0.5	0.5	4.0	3.6	4.2
L2 (70/100)	0.9	0.7	3.2	2.6	3.3
L3 (70/100)	0.9	0.8	3.9	3.5	4.25
L4 (70/100)	0.9	0.8	3.6	3.2	4.0
L5 (10/20)	0.8	0.6	3.2	2.4	2.9
L6 (10/20)	0.6	0.5	2.4	2.2	2.8
M1 (70/100)	0.6	0.5	2.2	1.9	2.4
M2 (70/100)	0.7	0.55	2.3	1.85	2.4
M3 65	0.7	0.6	2.15	1.8	2.4
M4 45	0.6	0.5	1.9	1.6	2.2
M5 200	0.8	0.55	2.9	2.1	2.7
N1 (70/100)	0.9	0.6	2.05	1.3	1.8
N2 (70/100)	0.8	0.6	2.1	1.5	2.1
N3 (70/100)	0.85	0.6	2.1	1.6	2.2

Rheological behavior of bitumens

Rheological properties of a bitumen system are determined by measuring its viscosity at different rates of shear for a given temperature, shear stress and time.

To obtain more information about the viscous/elastic balance in binders, dynamic oscillation stress measurements should be undertaken. This provides information about the elastic and inelastic, viscous parts of bitumens when submitted to oscillatory shear stress with varying frequencies and temperatures and enables the determination of fundamental rheological parameters such as the complex modulus G^*, the elastic modulus G', the viscous modulus G'', the phase angle and the viscosity. Representation of master curves such as the Black or the Cole–Cole curves shows the binder's characteristics at different temperatures and frequencies. These master curves express a time–temperature or a time–frequency equivalence (straight line) for bitumen[20–24].

Sol bitumens have high temperature susceptibility but time–temperature equivalence. They contain only small amounts of asphaltenes. The particles or 'asphalt micelles' are free moving in a homogeneous material.

Gel bitumens are characterized by a retarded elastic deformability with considerable elastic deformations. In contrast to sol bitumens, they have small kinetic dependence
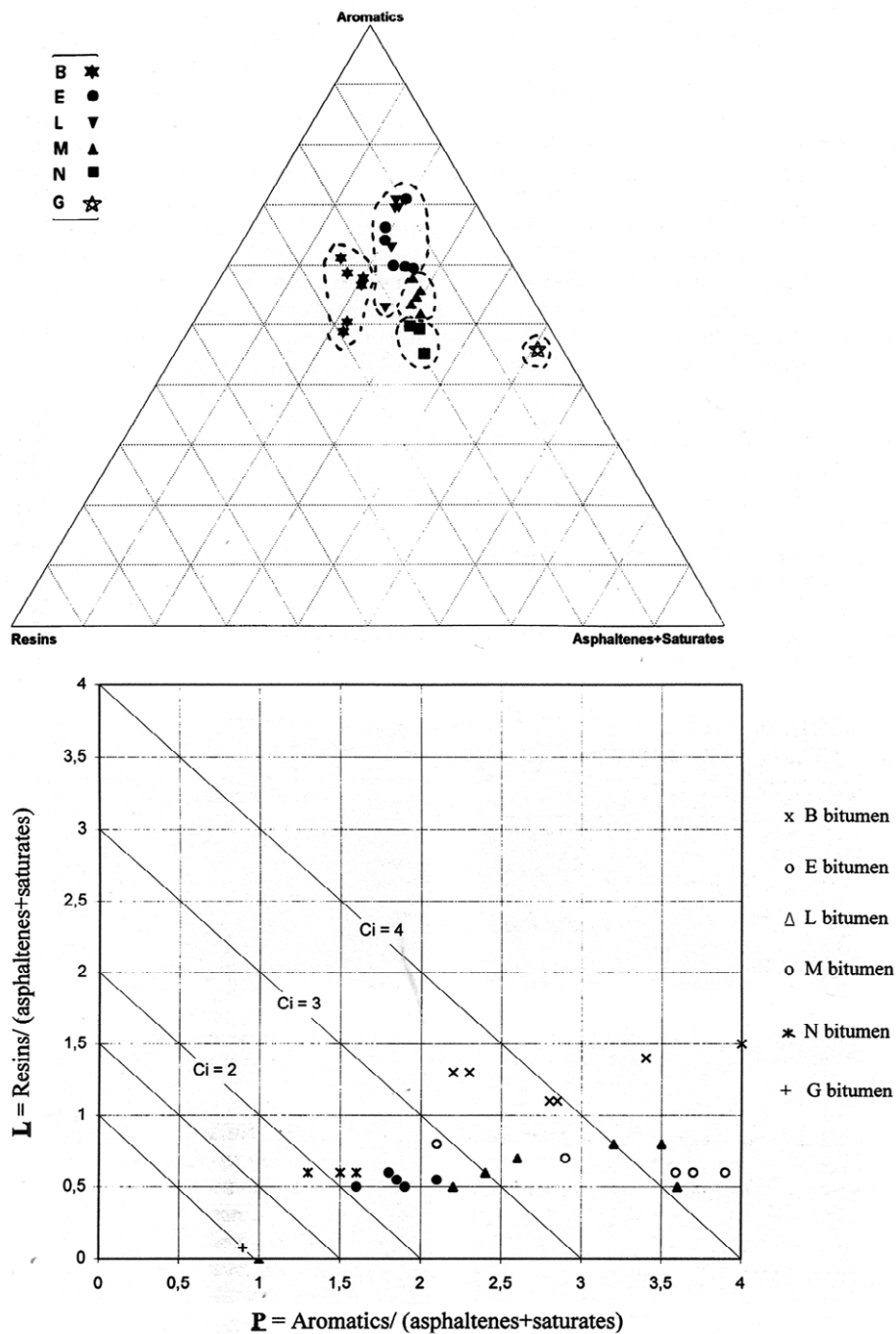

Figure 1   (a) Triangular representation of the different bitumen families. (b) Isolines of the colloidal index

and are structured and correspond to 'gels'. They have a large relaxation spectrum and their phase angle does not vary very much with the moduli. Often, there is no time–temperature equivalence of such bitumen.

A viscoelastic sol–gel bitumen shows both elastic effect and some permanent deformation. Barth[1] indicates that this system contains asphaltenes from 15 to 25%, arranged in micelles which are free flowing in the outer, oily phase. With increasing micelle concentration, elastic deformation increases almost proportionally and the material exhibits pseudoplastic behavior.

EXPERIMENTAL

In order to establish the relationship between the composition, structure and rheological properties of bitumen, the following measurements are undertaken.

Apart from standard measurements such as Ring and Ball softening point and penetration tests, controlled stress measurements using a Carrimed CSL100 rheometer (Peltier effect) have been assessed. Frequencies varied between 0.06 and 10 Hz, temperatures were set between − 5 and 60°C. The hot bitumens were put on a 99°C hot plate, then cooled to − 5°C by Peltier effect. The measuring system was parallel plates geometry, 20 mm in diameter with a plate distance of 1 mm. The 'Black' representation (log G^* versus phase angle) was chosen as this master curve provides information on the viscous/elastic balance and the stiffness of the bitumen.

For chemical analysis, Iatroscan thin film chromatography was chosen as this method gives the main constituents of the bitumen: saturates, aromatics, resins and asphaltenes. Dissolution in various solvents was done as described elsewhere[25].

To obtain structural information of bitumens, scanning electron microscopy (SEM; Leica MK) and atomic force microscopy (AFM; Nanoscope Inc.) were used. In the case of SEM observations the samples are deoiled by a special preparation method[8].

RESULTS

Chemical composition

For this study, standard bitumens from different origins (Persian Golf, North Sea, Venezuela) and different grades (from 10 to 200) were used. The Iatroscan analyses give the following composition of the bitumens (*Table 1*): for bitumens with the same origin but different grade, the total oil content (aromatics, saturates) varies and gets higher with a higher grade, explaining the softness of these bitumens.

Bitumens with the same penetration grade but provided from different origins show variations from each other in the percentage of their individual constituents. Thereupon B bitumens show the lowest asphaltene contents but the highest resin contents, whilst M and N bitumens show the highest asphaltene content and in the case of M bitumens also a low resin concentration. E, L and N bitumens have intermediate resin concentrations. E and L bitumens differ from N bitumens by their total resin and asphaltene concentration which is higher in the case of N bitumens.

A triangular representation of the four constituents of each bitumen (resins, aromatics, asphaltenes + saturates) shows that each bitumen family can be represented by individual regions (cluster) (*Figure 1(a)*). Thus, the Iatroscan analyses allow the main bitumen families to be distinguished.

These observations also lead to the determination of some important ratios: the resin/asphaltene ratio, the aromatic asphaltene ratio and the calculation of the colloidal index, as listed in *Table 2*.

The resin/asphaltene ratio (*R/Ap*) of one bitumen family does not vary with the grade of the bitumen, whereas the aromatic/asphaltene ratio (*A/Ap*) of one bitumen family increases slightly with the penetration grade of the bitumen.

Figure 1(b) represents the different bitumen families by their colloidal index. The resin/(asphaltene + saturate ratio), called the <u>L</u> ratio is plotted versus the aromatic/(asphaltenes + saturates) ratio, called the <u>P</u> ratio. The intermediate straight lines (isolines) give the values of the colloidal index
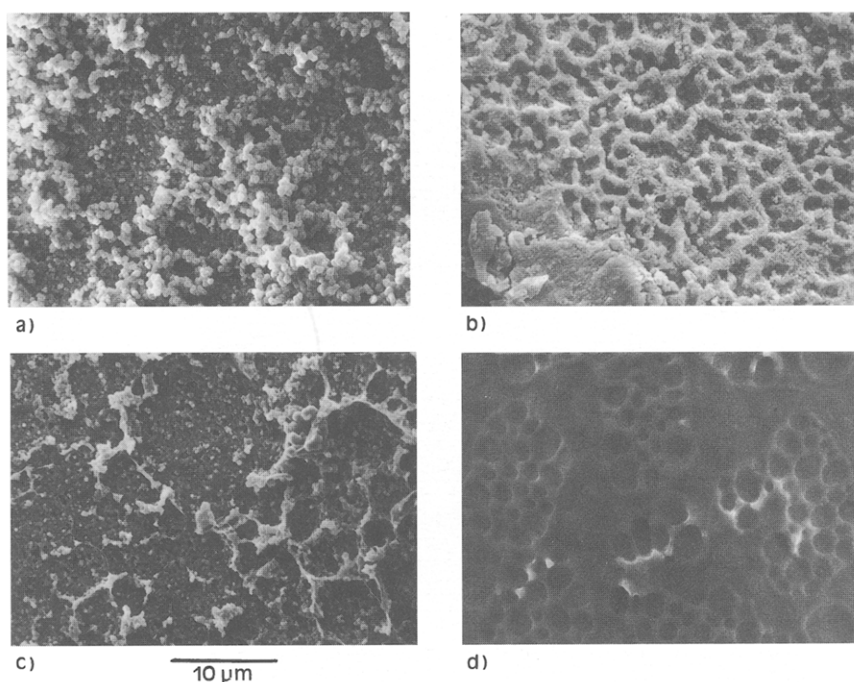

Figure 2 Micrographs (SEM) of (a) 70/100 grade L bitumen, (b) 10/20 grade L bitumen, (c) 70/100 grade N bitumen and (d) G bitumen
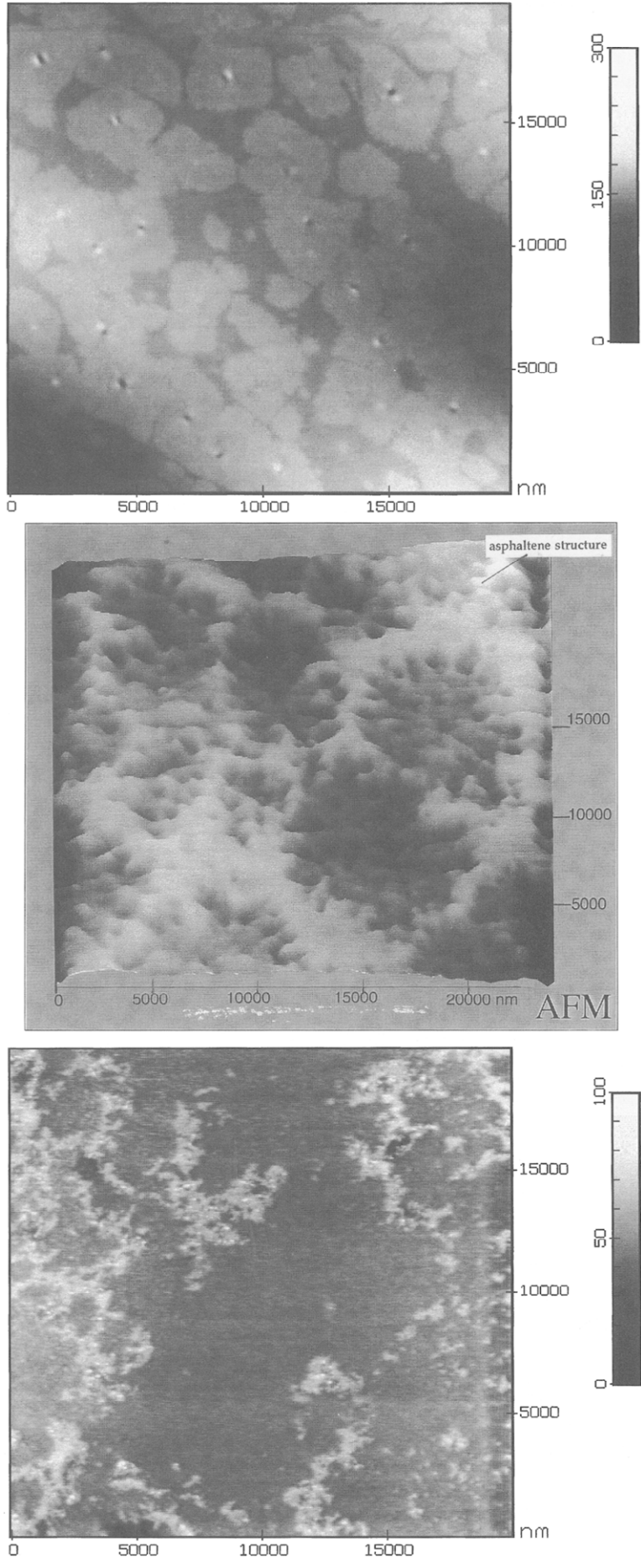
Figure 3 Micrographs (AFM) of (a) 70/100 grade L bitumen, (b) 10/20 grade L bitumen, (c) 70/100 grade N bitumen

Ci. B bitumens have a higher colloidal index than M bitumens. E and L bitumens are intermediate. A higher colloidal index means that the asphaltenes of these bitumens are more peptized in the oil based medium.

Structural observations of bitumen

Two different techniques were used to observe the bitumen structure: SEM and AFM. The first one gives more details but needs a deoiling preparation method which could introduce artifacts; the second shows the association of the bitumen 'particles' in the oil based medium without any preparation techniques but with lower resolution. Both techniques correlated give very good structural information. *Figure 2(a)* and *(b)* and *Figure 3(a)* and *(b)*, which refer to SEM and AFM respectively, show the structure of a 70/100 and

a 10/20 grade bitumen from the Persian Golf (L bitumen). For both bitumens, the smallest visible particles have round spherical forms, corresponding to the asphaltene particles.

The 70/100 grade bitumen which has a lower asphaltene content and a higher colloidal index, shows large domains of associated round asphaltene particles (*Figure 2(a)*, SEM) surrounded by a smooth phase which corresponds to the oil phase (*Figure 3(a)*, AFM). The domains are not or poorly connected to each other.

In contrast, the 10/20 grade bitumen with a higher asphaltene content and a lower colloidal index, shows associated spherical particles connected to a network structure (*Figure 2(b)*, SEM). Inside this structure is the smooth oil phase (*Figure 3(b)*, AFM).

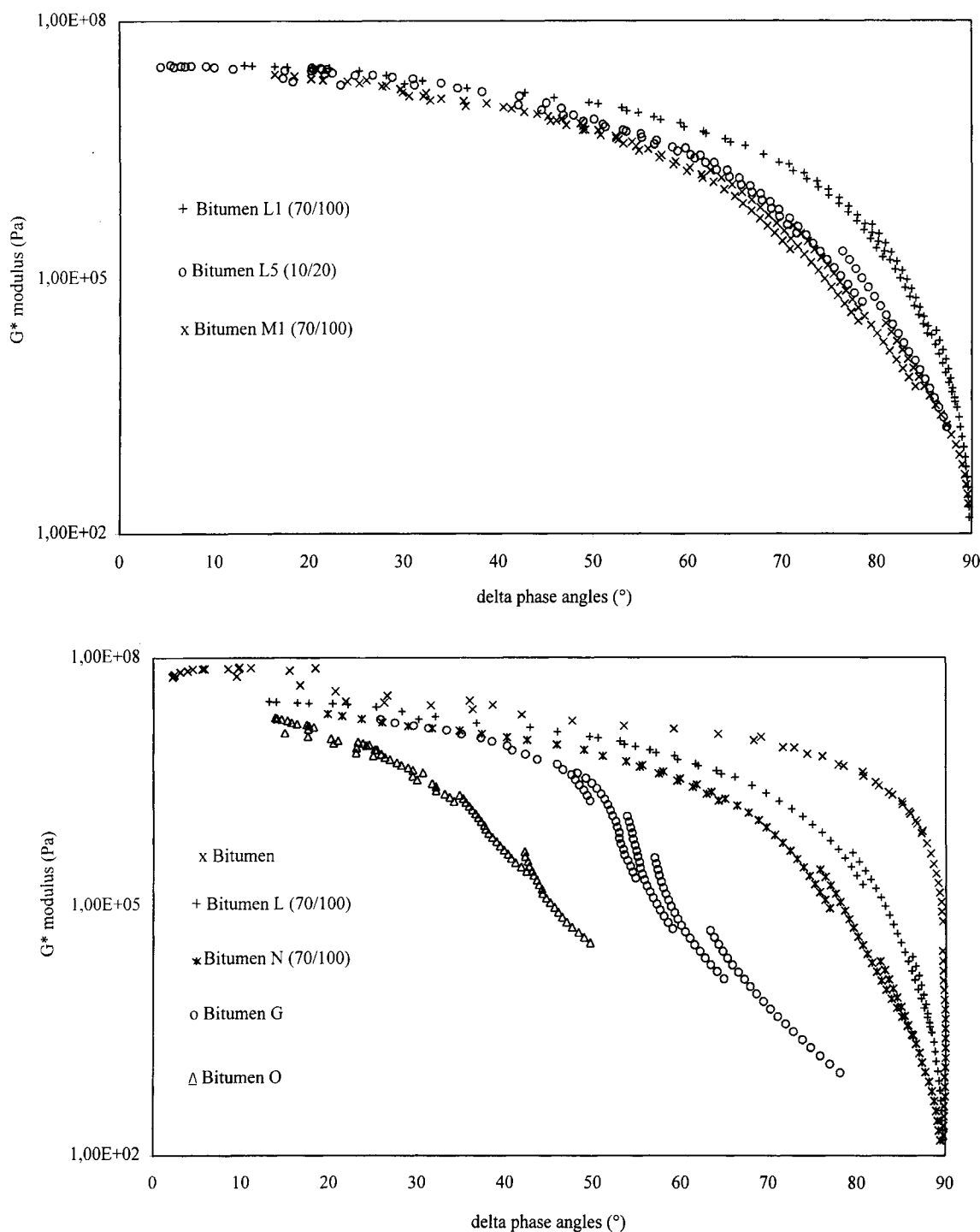The natural acid bitumen (N bitumen, *Figure 2(c)* and

Figure 5 Black representation of different bitumens, varying in composition (from 5 to 60°C)

Figure 3(c)), which possesses a lower colloidal index, shows connected asphaltene particles as in the case of the 10/20 bitumen although it is a 70/100 grade bitumen. Hence the smoother phase (*Figure 3(c)*, AFM) is more important and explains the soft grade (70/100) of this bitumen. The reason could be the acidity of this bitumen, creating more connections or a higher asphaltene and resin concentration which is nearly the same as the 10/20 grade L bitumen.

The G bitumen (*Figure 2(d)*) with the lowest colloidal index shows a very dense structure which possesses only few round clusters made of a network association, resembling the network structure of a hard grade bitumen. The high amount of asphaltene particles leads to a quasi-solid arrangement of this bitumen.

Conclusion. AFM and SEM observations clarify the structural arrangement of different bitumens. An attempt can be made to relate the structure to the chemical composition and the colloidal index. This shows that a low colloidal bitumen has a connected network structure, whereas a higher colloidal bitumen is made of individual domains of asphaltene particles. Increasing the asphaltene concentration of the bitumen leads to a more dense and gel-like structure.

Rheological measurements—oscillation tests

The rheological characteristics of the different bitumens have been assessed by means of oscillation stress measurements with varying frequencies and temperatures. Bitumen from the North Sea (B), the Persian Golf (E, L, M) and Venezuela (N) were analyzed by this method. To obtain more information on the influence of the different constituents in bitumens, two laboratory-reconstituted bitumens and a high asphaltene containing bitumen (O bitumen) were also analyzed. The first (R bitumen) is a bitumen without asphaltenes and the second (G bitumen) a bitumen containing no or only insignificant amounts of resins.

For all current bitumens in general, single curves are obtained at any frequency, expressing a time–temperature equivalence in the Black's representation. All bitumens undergo the following behavior: (a) they exhibit high rigidity (high *IG*I* moduli) and elastic behavior (low delta phase angle) at low temperatures, then, (b) a viscoelastic behavior with decreasing *IG*I* moduli for intermediate temperatures (10–30°C) and finally, (c) they tend to be completely viscous with low rigidity at high temperatures. No significant difference of the Black curves or the *IG*I* modules can be observed between bitumens of similar chemical composition.

The influence of the oil content can be seen by comparing a 10/20 (L5 bitumen) and 70/100 (L1 bitumen) penetration grade bitumen from the same origin (*Figure 4*). With increasing oil concentration a slight shift of the Black curves to higher delta phase angles can be noted. The master curve of the hardener bitumen is moved to smaller phase angles, indicating more elasticity. Therefore, the *IG*I* moduli of the 10/20 grade bitumen are slightly higher at intermediate and high temperatures, indicating a better stiffness of the 10/20 grade bitumen at these temperatures.

When comparing same grade bitumens, but provided from different origins (L and M), the bitumen M which has a higher asphaltene content, exhibits lower delta phase angles and its *IG*I* moduli are also slightly higher than the L bitumen at higher temperatures.

Influence of the composition on Black curves. To study the influence of the individual constituents in the bitumen on rheology, three bitumens containing large amounts of resins or asphaltenes were analyzed: an artificial reconstituted bitumen containing no asphaltenes (R), an oxidized bitumen (O) and a natural asphaltene bitumen, mixed with oil to obtain a 70/100 grade (G). *Figure 5* shows the Black curves from normal bitumen, compared with this bitumen. The R bitumen has the most uniform master curve, hence it is also the bitumen with the highest delta angles starting at about 20°C. G bitumen is the only one which does not show uniformity of the master curve. This bitumen and the oxidized bitumen exhibit low delta phase angles. Both bitumens are characterized by a very high asphaltene concentration (about 50%). The normal
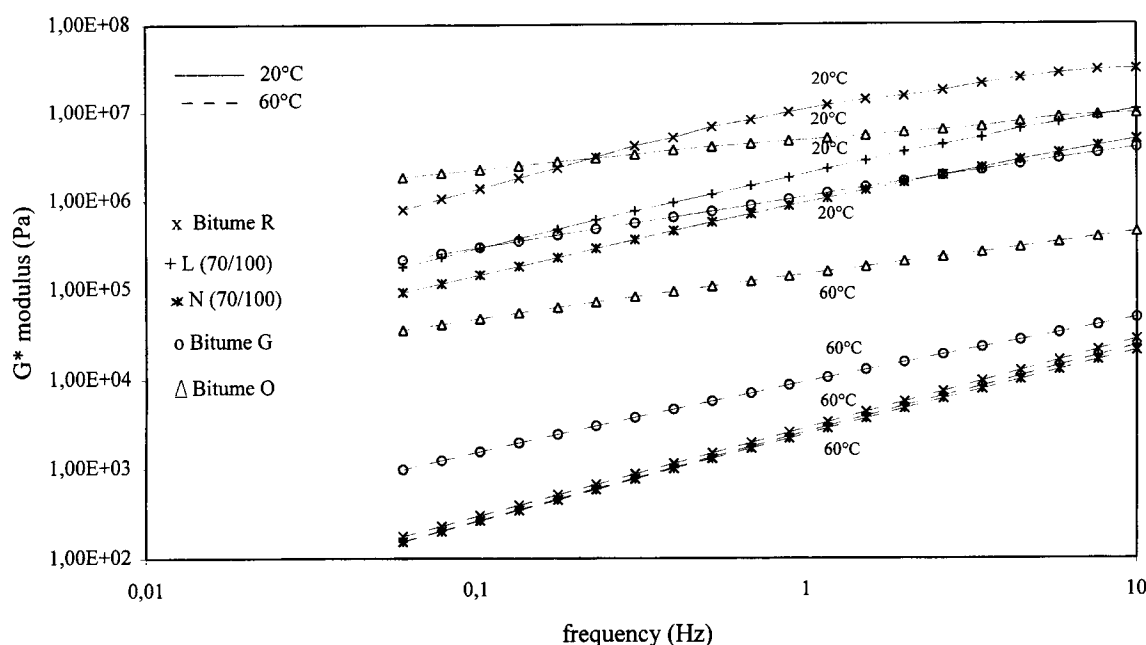

Figure 6 Frequency dependence of *IG*I* for different bitumens at 20° and 60°C

grade bitumens with intermediate asphaltene and resin concentrations have master curves between R and G bitumen.

Figure 6 shows the frequency dependence of the $IG*I$ modulus for the different bitumens at 20 and 60°. For high temperature, the $IG*I$ modulus increases with the asphaltene content of the bitumen.

Relating the rheological oscillation properties of these bitumens to their chemical composition, the following conclusions can be given.

- The higher the asphaltene concentration in the bitumen, the lower will be the delta phase angle (for the same temperature, strain, frequency). For higher temperatures, they retain also more stiffness than the lower asphaltene content bitumen. The total length of their Black curves (for the same domain of frequency analyzed) is reduced, indicating less temperature sensitivity, but also less uniformity and therefore less structural homogeneity.

- In contrast, the higher the resin concentration in the bitumen, the higher the delta phase angle (for the same temperature, strain, frequency). But, in comparison with normal grade bitumen, the $IG*I$ modulus is also greater for the resin bitumen than for the normal bitumen at all temperatures studied. The resins in the bitumen are also responsible for the unity of the Black curves. The presence of resins could be necessary to obtain well dispersed suspensions, whereas if absent, flocculation takes place and leads to heterogeneity. Increasing amounts of resins lead to more homogeneous Black curves (bitumen B, E, R) whereas G bitumen with very low resin concentrations has a discontinued curve.

GENERAL CONCLUSIONS AND DISCUSSION

This study shows the relationship between the rheological properties, structure and chemical composition of bitumens. In fact, the interacting forces in the bitumen systems are governed by a colloidal law, expressed by the colloidal index. This index can be designed in a representation which distinguishes well the different bitumen families.

Increasing the asphaltene concentration (lower part of the equation) leads to a more flocculated system and increasing bonds between particles. A network structure will be formed with more elastic behavior and higher stiffness (large $IG*I$).

Increasing the aromatic oil content (upper part of the colloidal equation) leads to more dispersed and viscous systems (higher δ phase angle). Addition of resins homogenize bitumens because they peptize the asphaltenes by forming smaller asphaltene micelles.

This can be seen by SEM and AFM observations which show the different structures of bitumens with different chemical composition. The outer limits of such systems are on the one hand pure resin bitumen and on the other hand strongly oxidized bitumen or natural asphaltene bitumen.

Special attention should be made to acids which could also increase bonds between particles.

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