

Relationships Between Composition, Structure, and Properties of Road Asphalts: State of Research at the French Public Works Central Laboratory

BERNARD BRÛLÉ, GUY RAMOND, AND CHRISTIAN SUCH

Reviewed is the past and ongoing research conducted at France's Laboratoire Central des Ponts et Chaussées (LCPC) (Public Works Central Laboratory) in the area of asphalt cements. The investigations cover the development of methods for characterizing the physicochemical and rheological properties of such materials, and the establishment of relationships between their composition, colloidal structure, and practical properties. For physicochemical characterization, the research makes use of such techniques as high-pressure liquid chromatography, gel permeation chromatography (GPC), and differential scanning calorimetry. The rheological behavior of materials is studied by the peeling technique, viscoelastisimetry, and viscosimetry on thin films (with specially designed apparatus). Theoretical studies have led to the proposal of a new rheological behavior model better suited to experimental results than conventional models, characterized by its analogy with the laws of chemical kinetics, and allowing the calculation of a structural parameter as well as a parameter dependent on energy per unit volume dissipated and having activation energy characteristics. The foregoing assessment brings out the effectiveness of the facilities set up by the LCPC, and it is important to note that the new characterization methods indicate that asphalt cements with the same specifications have substantially different physicochemical compositions and rheological behaviors. Among the most important results, it is demonstrated that GPC makes it possible to characterize the equilibrium of the colloidal structure of asphalt cement and to obtain information on the ability of asphaltenes to interact to form a more or less developed network responsible for the gel character of the rheological behavior noted. It is also demonstrated that information obtained by GPC on the interaction of asphaltene micelles is closely correlated with certain observed characteristics of rheological behavior.

The Laboratoire Central des Ponts et Chaussées (LCPC) (Public Works Central Laboratory) has long been engaged in research in the area of hydrocarbon binders. Regarding asphalt cements and asphaltic concretes, the observation during the past 10 years of a certain number of disorders related, undoubtedly, to the increase in traffic and to its aggressive action (in France, axle loads of 13 metric tons are authorized) but not entirely explained by these factors, has emphasized the need for research on the relationships between composition and properties.

For asphalt cements, the research has a twofold objective:

- To acquire knowledge on the chemical composition of binders in the generic sense of the term, their microscopic and colloidal structure, and their rheological and practical properties, as well as on the evolution of these properties during mixing and weathering in situ; and
- To establish experimental relationships between composition, structure, and properties and to determine the evolution of these relationships after mixing and weathering.

PHYSICOCHEMICAL CHARACTERIZATION OF ASPHALT CEMENTS

The study of the relationships between composition and properties calls for the use of reliable and fast means of characterization. In this area, the research of the LCPC associated with regional research laboratories involves the use of modern methods of liquid chromatography [high-pressure liquid chromatography (HPLC) and gel permeation chromatography (GPC)] as well as thermal methods [essentially differential scanning calorimetry (DSC)].

High-Pressure Liquid Chromatography

The HPLC technique was used initially for the characterization of asphalt cements and of the fractions composing them (1). The study of operating parameters led to the choice of the following conditions:

- Packing = grafted silica C-18;
- Solvent A = chloroform-methanol-water: 50-40-10 (in volume);
- Solvent B = chloroform-methanol: 85-15 (in volume); and
- Programming:
 - Initial solvent = 80 percent of Solvent A,
 - Final solvent = 100 percent of Solvent B,
 - Gradient = No. 4 of Waters M 660 programmer,
 - Programming time = 10 min,
 - Flow rate = mL/min, and
 - Detection = ultraviolet at 280 nm (nanometers).

Programming is begun 2 min after injection. As an example,

the chromatograms for a road asphalt cement obtained from a residue of blown and acidified Safaniya crude, its maltenes, and its asphaltenes are shown in Figure 1.

The results of this research show that liquid chromatography with reverse phase polarity, on a C-18 grafted silica column, can be used for characterizing asphalt cements and their fractions through the use of a suitable solvent mixture (chloroform-methanol-water). Under these conditions, the chromatograms are clearly differentiated from one fraction to another. On the other hand, unlike what is generally observed with this type of support, the order of elution is not related directly to polarity because the low-polarity fractions are eluted before the higher polarity fractions (maltenes, for example, are eluted before asphaltenes). It is thus difficult to compare elution volume and polarity. The injection of fractions having the same polarity but different molecular weights (for example, aromatic fractions of maltenes and asphaltenes) and chloroformic extracts shows that the separation process is governed essentially by the solubility in chloroform.

During a later phase, the possibilities of applying HPLC to the fast determination of the generic composition of road asphalt cements was examined [it will be recalled that the generic composition is defined by the amount of saturated oils, aromatic oils, resins, and asphaltenes (2)]. The technique adopted consists of eliminating the asphaltenes with *n*-heptane and then injecting the maltenes on an NH_2 grafted microsilica column (3). The saturated oils are eluted at the dead volume and detected by differential refractometry, whereas the aromatic oils, slightly retained, are detected in ultraviolet. Resins, highly absorbed, are eluted by solvent backflushing. Figure 2 shows the type of chromatogram obtained. In this figure, column: μNH_2 ; solvent: heptane; flow rate: 2 mL/min; quantity injected: 160 μg ; and BF: solvent backflush.

A comparison of the results of the fractionation of many samples of asphalt cements, conducted by using traditional methods, with those obtained by HPLC leads to the following conclusions:

- It is possible to characterize in a few minutes a solution of maltenes in heptane. There is a slight correlation between the HPLC results and the aromatic oil content, and a strong cor-

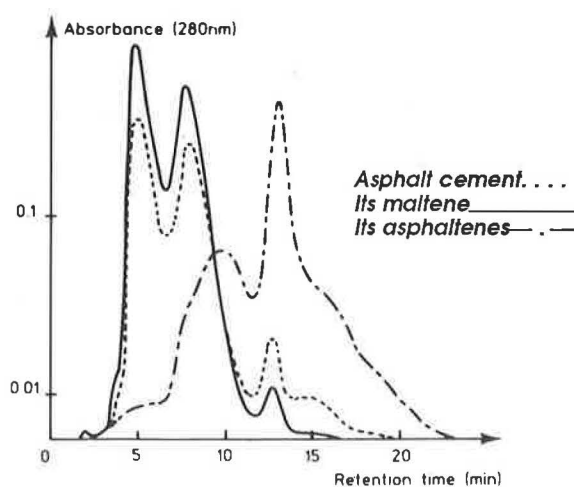


FIGURE 1 HPLC chromatograms.

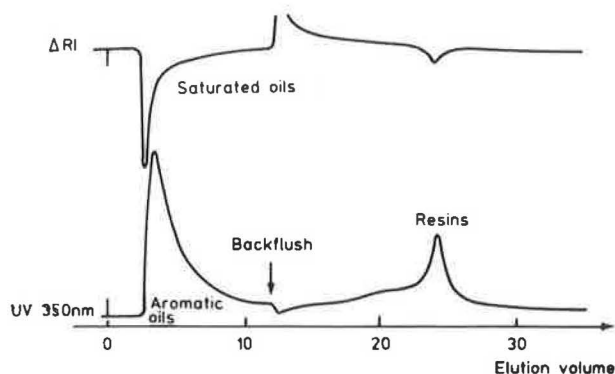


FIGURE 2 HPLC chromatograms of the maltenes of a 40-50 asphalt cement.

relation between the HPLC data and the resin content. There is also a strong correlation between the HPLC results and the sum of the aromatic-oil and resin contents.

- Correlation coefficients are clearly improved if they are calculated for a series of samples belonging to the same specification range.
- The method is applicable to the fast determination of the colloidal instability index (ratio of sum of saturated oils and asphaltenes to sum of aromatic oils and resins).
- Unfortunately, it is difficult to control the reproducibility over a relatively long time period.

Gel Permeation Chromatography

The research activity of the LCPC within the area of GPC was much more extensive than in that of HPLC.

Initially, a simple qualitative characterization of asphaltenes (4) and asphalt cements (5) was sought, and the utility of a comparison between GPC and HPLC was examined (6,7). Then, the desire to use the technique in a more efficient manner for the determination of molecular weight distribution curves led to the observation of the colloidal behavior of asphalt cement solutions (8). The purely analytical aspect was pursued up to the correction of detector response and the experimental determination of a calibration curve in specific molecular weight the equation of which, in relation to traditional polystyrene standards, is as follows (9):

$$\log M (\text{asphalt cement}) = 3.21 - 1.04X + 0.331X^2$$

where X is $\log M$ (polystyrene). However, the use of GPC was especially important in the comparison of the colloidal structure of the binder and the colloidal behavior of the solution.

The most recent work shows that, under well-chosen conditions, GPC makes it possible to obtain an image of the composition of the medium, in the colloidal sense of the term (intermicellar phase and dispersed phase distribution), and to assess the interaction properties of micelles within the colloidal system (10). Conventional GPC (on a set of several columns with usual particle size from 37 to 75 μm on very diluted solutions) leads to molecular weight distributions that are not greatly differentiated. In this case, neither the asphalt cement production method (straight-run distillation or semiblowing)

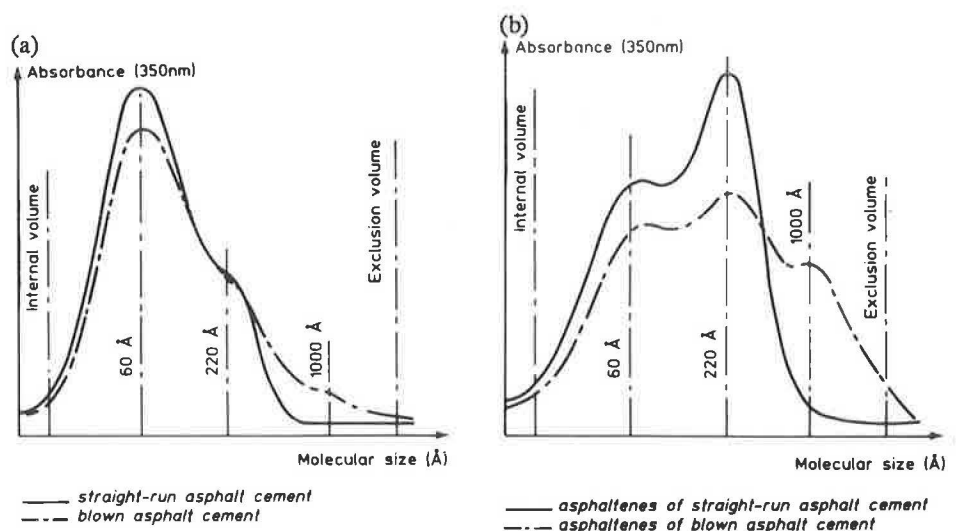


FIGURE 3 Chromatograms of asphalt cements and asphaltenes.

nor the degree of weathering (natural or artificial) has a significant effect on the shape of the chromatograms. This chromatography operates sufficiently slowly so that the dissociation has time to develop and the chromatograms obtained are close to those of ideal solutions.

A fast method is thus proposed, the conditions of which are as follows:

- Columns: dual columns of μ Styragel of 10^3 and 10^4 Å, 30 cm long;
- Solvent: freshly distilled tetrahydrofuran;
- Injected quantity: 1 mg (10 μ L of 10 percent solution);
- Flow rate: 3.5 mL/min; and
- Detection: ultraviolet at 350 nm (nanometers).

Under these conditions, it was possible to demonstrate that straight-run asphalt cements and especially their asphaltenes lead to bimodal distributions, whereas blowing always results

in the appearance, more or less accentuated, of a third population located toward the large molecular sizes. This is shown in Figures 3a and 3b, which give the chromatograms of blown and unblown road asphalt cements (Figure 3a) and of asphaltenes extracted from these asphalt cements (Figure 3b).

Systematic study of the influence of operating conditions on the image of molecular size distribution as obtainable by GPC (and comparison between results obtained on μ Styragel and on traditional Styragel) leads to the following conclusion: the entities eluted at the level of the third population (toward 1000 Å) and, to a lesser degree, at the level of the second population (220 Å) correspond to dissociable entities because their apparent content decreases with the injected solution concentration (8).

The chromatograms of the asphaltenes of 40–50 asphalt cements before and after Rolling Thin Film Oven Test (RTFOT) have been reproduced in Figure 4 (under normalized conditions at 163°C). The signal height for a mass of about

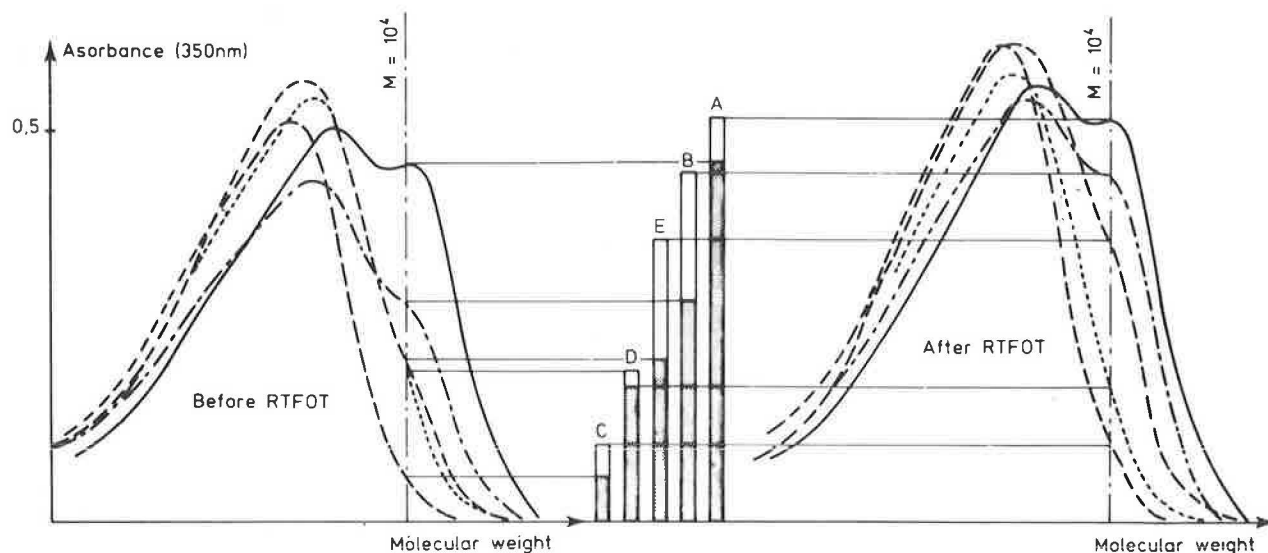


FIGURE 4 GPC chromatograms of asphaltenes before and after RTFOT.

100 000 gives a first idea of the interaction properties of the asphaltenes.

GPC examination of unfractionated asphalt cements indicates that it is not essential to isolate the asphaltenes to have information on intermicellar interactions, but the evaluation in this case is much less precise (Figure 5). It is important to note that the information obtained on asphalt cements is not rigorously equivalent to that obtained on asphaltenes because to isolate the latter it was necessary to destroy the colloidal equilibrium of the system.

Because the entities eluted at the level of a mass of about 10^5 correspond to aggregates in the process of dissociation, it was decided to highlight the display of this intermicellar interaction property.

To accomplish this, the authors acted on two parameters: the number of columns and the packing porosity. By eliminating one of the two columns, the elution time was divided by two, thereby limiting the dissociation. Moreover, by deliberately reducing the efficiency of the system in the range of large masses, the latter were as obliged to group within a narrow range of elution volumes (in this instance, practically the exclusion volume if only the column of 10^3 Å porosity is maintained).

With these new conditions of ultra-fast GPC, which differ from usual conditions only by the elimination of the 10^4 Å porosity column, the chromatograms shown in Figure 6 are obtained. Under these conditions, the display of what shall be called the interaction index is obtained on unfractionated asphalt cement in a few minutes and in a satisfactory manner. For comparison, and arbitrarily, the interaction index will be marked as being the height of the signal at the exclusion volume for the ultraviolet detector. It is obvious that under these conditions the interaction index varies with all the operating parameters so that the comparisons can be only relative on a series of samples examined under rigorously identical conditions.

It is thus confirmed that ultra-fast GPC is a method of choice for the qualitative characterization of the complex equilibrium existing within the asphalt cement between

Molecule \rightleftharpoons Micelles \rightleftharpoons Aggregates

In such a diagram, the molecules (first population) are representative of the intermicellar phase; the micelles (second population with a mass of about 10 000 are representative of the sol-type dispersed phase; and the interaction peak (entities with a mass exceeding 100 000) is an image of the fraction of the dispersed phase giving the binder its gel character. It is essential to note that there is no relationship between the interaction index and the consistency of the asphalt cement as it can be evaluated by penetrability measurement, for example. (Similarly, there is no relationship between the interaction index and the asphaltene content.)

Differential Scanning Calorimetry

Examples of the application of DSC to the characterization of road asphalt cements are relatively few, and the research was oriented by the desire to use the method to investigate phase transformation kinetics and molecular association aptitude (11).

In Figure 7, the DSC curves of five 40–50 asphalt cements are grouped under helium and oxygen examined between -80°C and $+80^\circ\text{C}$.

Under helium, the existence of exothermic transformations (of the crystallization type) are noted between approximately -30°C and 0°C and endothermic ones (of the fusion type) between approximately -5°C and $+65^\circ\text{C}$. Their number and intensity are different for all the asphalt cements examined.

To better understand the origin of these transformations, Sample A was fractionated into its four generic groups. The thermograms of the fractions are shown in Figure 8.

It can be observed that only the saturated and aromatic derivatives exhibit transformation waves. However, in a mixture in a ratio equivalent to that existing within the unfractionated asphalt cement, these two derivatives yield a thermogram very different from that of the original asphalt cement (Figure 9).

Under oxygen, with the exception of one asphalt cement

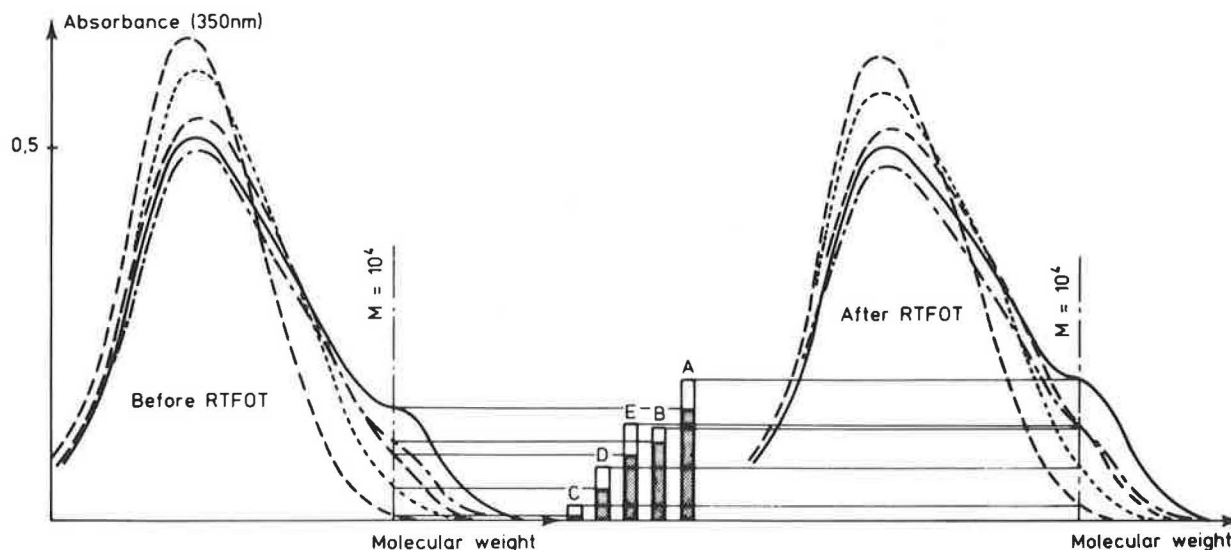


FIGURE 5 GPC chromatograms of asphalt cements before and after RTFOT.

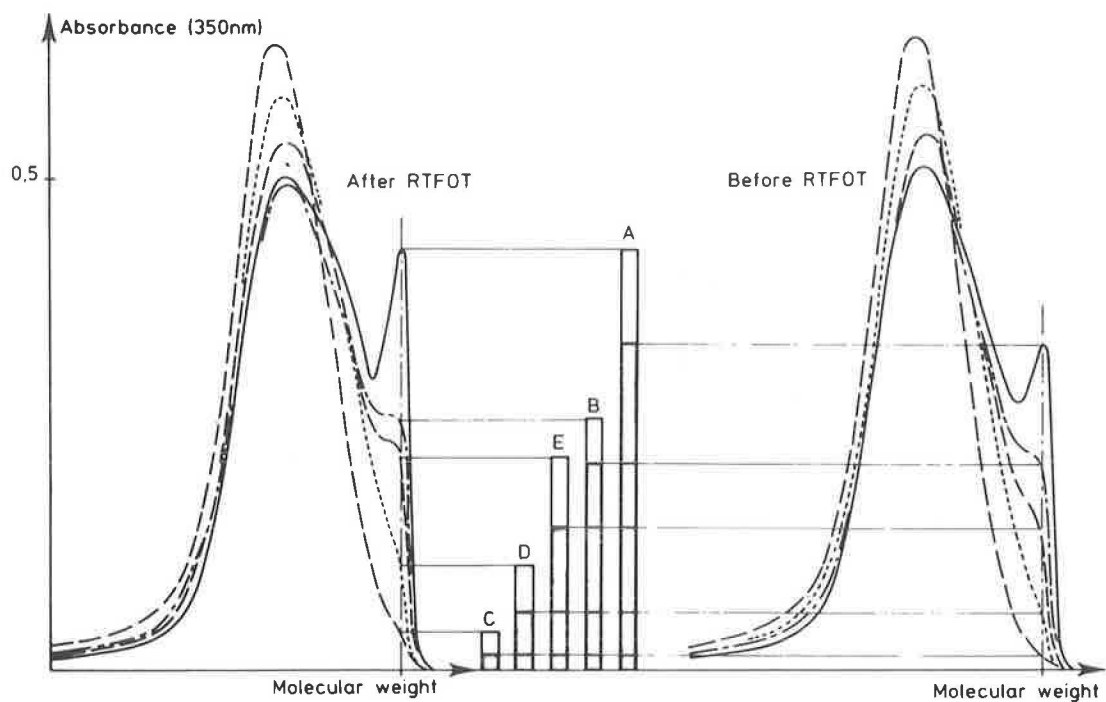


FIGURE 6 Chromatograms of asphalt cements before and after RTFOT under ultra-fast GPC conditions.

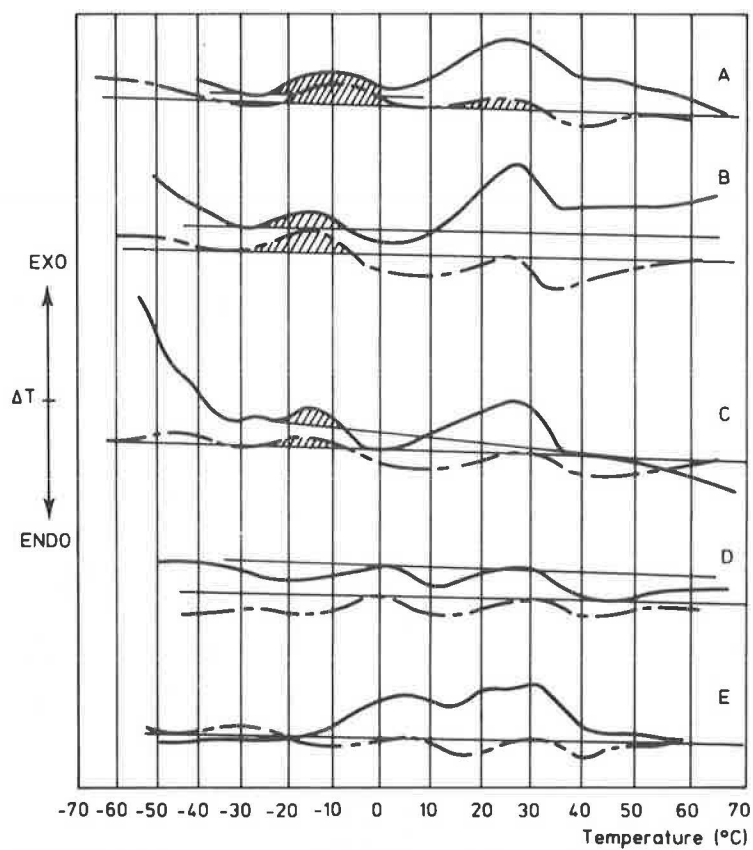


FIGURE 7 Thermograms of five 40-50 asphalt cements: A, B, C, D, E.

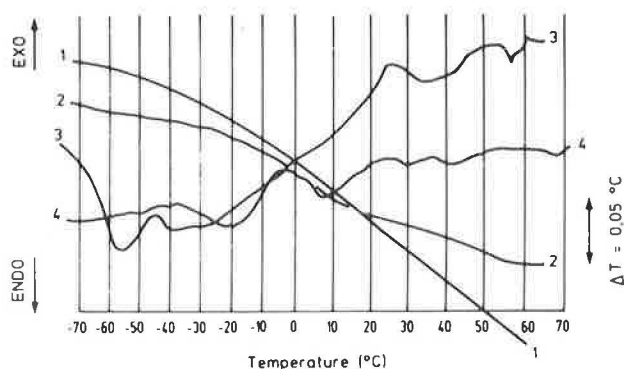


FIGURE 8 Thermograms of fractions of asphalt cement A under helium (1 = asphaltenes, 2 = resins, 3 = saturated, and 4 = aromatic).

(Sample D) for which the DSC curve is little different from that obtained under helium, all of the thermograms are characterized by the existence of one or more exothermic waves between -30°C and $+60^{\circ}\text{C}$.

The exothermic transformation domains at low temperatures (between -20°C and $+5^{\circ}\text{C}$, -25°C and -8°C , and -30°C and -8°C , respectively, for asphalt cements A, B, and C) have the same range and comparable intensities. Changing the scanning gas does not affect the constituents responsible for the crystallization delay.

On the other hand, at positive temperatures, the physiognomy of the thermograms is completely different. The oxygen of the scanning gas appears to disturb substantially the equilibria of the phases and their transformation kinetics.

As in the preceding case, the repeatability of the test can be obtained only after the sample is allowed to rest for a few hours (24 hr). In addition, a return to helium gas after testing under oxygen makes it possible to obtain the same endothermic and exothermic waves again, meaning that under the operating

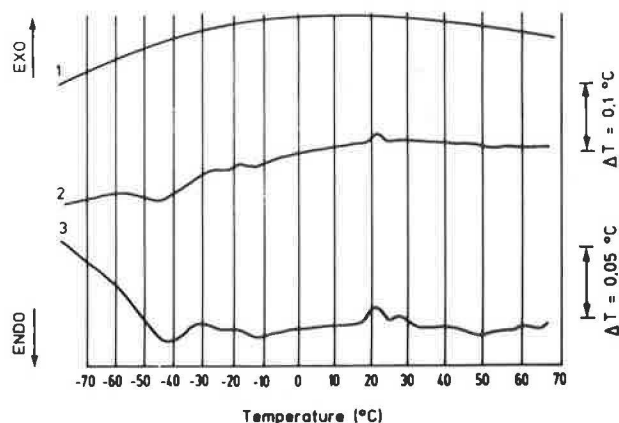


FIGURE 9 Thermograms of mixture (1/1) of saturated and aromatic derivatives of asphalt cement A (1 = derivative, 2 = uncorrected curve, and 3 = corrected curve).

conditions adopted there were no irreversible chemical reactions (oxidation).

The movements observed on these asphalt cements in an oxygen medium could thus be caused by oxygen interference on the aromatic sheets of the products. The aromatic rings are electron acceptors, and the greater the delocalization, the stabler the compound formed.

CHARACTERIZATION OF RHEOLOGICAL BEHAVIOR

Research activity in this area is being pursued along two lines:

- First, the adaptation of existing instrumentation (such as the viscoelastisimeter) and the development of new facilities (peeling, sliding plate viscosimeter for ultra-thin film investigations or very small deformation cone-plane viscosimeter), allowing the experimental characterization of rheological behavior; and
- Second, the adaptation of nonlinear viscoelastic behavior models to experimental results.

Experimental Characterization

Peeling

To evaluate the cohesion of asphalt cements, a method frequently used in the field of polymers was chosen: peeling, which consists of measuring the force required to cause the failure of a film of binder under given speed and temperature conditions (12).

In practice, an angle of 90 degrees is most often used, and the failure is obtained by imposing a separation speed and measuring the force generated. The failure may occur in the binder and the cohesion is then measured, or it may occur in the interface, making it possible to evaluate the overall adhesion.

Because peeling resistance depends on the width of the peeling front, it has been expressed by a parameter defined by the formula $\gamma = F/G$, F being the measured force and G the width of the peeling front. This may be represented as a function of speed in the form of isotherms in log-log coordinates (Figure 10). In this form, it is possible to plot a master curve because of the horizontal shift defined by a translation factor, a_T , similar to the Williams, Landel, Ferry (WLF) parameter (13,p.216).

In a study conducted on 12 binders it was demonstrated that (14)

- On all of the asphalt cements tested, the peeling master curves have a parabolic shape in a representation giving a correspondence between the logarithm of the peeling force and the logarithm of the speed; this curve shape corresponds to the data of the literature. At low speed, the peeling force is small, increases with the increase in speed, goes through a maximum, and then drops. As a rule, when cracking propagates in an asphalt cement, the maximum force corresponds approximately

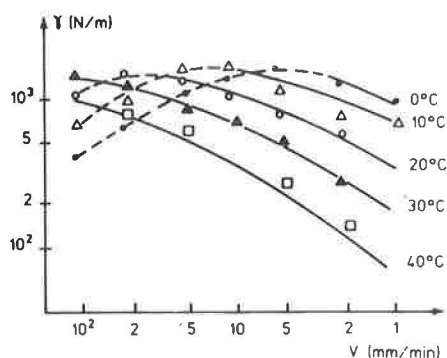


FIGURE 10 Isothermal curves of peeling force.

to the beginning of the slip-stick phenomenon (case of brittle fracture in which the cracking speed is higher than the advancing speed: the force increases; the system stores energy, which is dissipated to cause a sudden advance of the crack; and it is necessary to wait for the strip to tension again).

- The plotting of master curves leads to the adoption of different figures for the value of the constants C_1 and C_2 of the WLF law, depending on the asphalt cements.

- As the peeling fracture energy is related to the complex modulus and hence to the relaxation time spectrum, which can be assimilated with a log-normal curve, it is not surprising that the general shape of the master curves leads to a mathematical formula of the log-normal type (15).

- There is a good correlation between the speed giving the maximum force and the Fraass brittleness temperature.

In a second series of tests, an attempt was made to specify the relationship between the peeling resistance and the complex module. Figure 11 shows, for two asphalt cements (H and I), the variations of the loss modulus E_2 as a function of frequency (master curve at 10°C) and those of the peeling force as a function of traction speed, under the same temperature conditions.

Within the range of temperatures and speeds (or frequencies) tested, it is possible to assimilate them as a first approximation

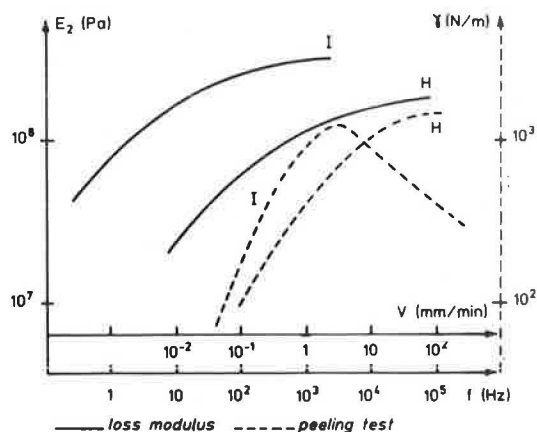


FIGURE 11 Comparison of master curves of loss modulus as a function of frequency and of the peeling resistance as a function of traction speed.

with a log-normal curve arc. This simplification is not absolutely rigorous, but allows them to be characterized more conveniently by two parameters: the median and the average peak width ($\log f_m$ and σ_f for the loss modulus, and $\log V_m$ and σ_v for peeling).

In Table 1 the calculated values of the medians and the average widths of the loss-modulus and peeling curves are grouped for the six asphalt cements investigated, along with their conventional characteristics. It can be observed immediately that the characteristics are related:

- The parameters σ_v of the peeling curves represent about 50 percent of those of the complex modulus curves σ_f , and
- The smaller the medians of E_2 , the smaller the medians of the peeling curves.

The application of Grosch's formula ($V_m = \lambda_m f_m$) would thus give, for the parameter λ_m (defined as the average distance between two consecutive molecules), values on the order of 10^{-8} m for the asphalt cements G, H, I, and K, and on the order of 10^{-9} for the less sensitive asphalt cements F and J (16, p. 21). The parameter λ_m decreases as the penetration index (PI) increases, which was expected because an increase in molecular interlacing is accompanied by a decrease in thermal susceptibility.

Consequently, the peeling test appears to allow, with relatively simple equipment and operating procedures, a good discrimination of the binders from the viewpoint of cohesion and brittleness. Because the peeling force depends on the viscoelastic properties and in particular on the complex modulus, it may indirectly provide precious qualitative information on the rheological behavior of the products tested.

This test can provide valuable information on the relationship between the energy restitution rate and the cracking speed, until a theoretical study permits their direct calculation from the complex modulus. Carried out under slightly different conditions, this test should be utilizable for testing overall adhesion on mineral supports with or without the presence of water.

Thin-Film Viscosimetry

Regarding thin-film viscosimetric experiments, the authors wished to check whether the rheological behavior of asphalt cements between two solid surfaces separated by a few microns was the same as in the case of a large thickness. It appeared of interest to investigate the creeping of thin films to determine the behavior of the binder located at the interface. For this purpose it was necessary to design and build equipment specifically suited to this problem (17).

Thus a creep apparatus was designed based on the principle of simple shearing between two sliding parallel planes. The load is applied and the relative displacement of one of the planes as a function of time is measured. This original prototype is distinguished by the following:

- The imposed thickness of the examined film; a gluing bench makes it possible to obtain a rectangular film with an area of 18 cm² and a few microns thick (approximately 10 μ m);
- The range of the authorized loads (1 to 10 000 g), which

TABLE 1 COMPARISON BETWEEN PEELING AND COMPLEX MODULUS FOR SIX ASPHALT CEMENTS

	Pen ₂₅ (0.1 mm)	R & B (°C)	P.I. (Pen.)	log f_m (Hz)	σ_f	log V_m (mm/min)	σ_v	σ_v/σ_f	λ_m (10 ⁻⁹ m)
F	88	54	1.2	≈ 7	≈ 2.5	≈ 2.6	≈ 1.3	0.52	0.01
G	88	46	-1.1	4.1	1.6	1.3	0.9	0.56	0.26
H	82	48	0.1	5.1	2.1	1.8	1.25	0.60	0.083
I	82	44	-1.7	3.0	1.5	0.5	0.8	0.53	0.53
J	38	60	1.1	5.5	2.5	1.3	1.3	0.52	0.01
K	54	53	-0.3	4.0	1.9	0.65	1.2	0.63	0.7

was obtainable by adequate dimensioning and a sliding system design that cancels all of the undesired movements;

- The loading system, which allows loading and unloading without disturbing the asphalt cement film, and tensioning is almost instantaneous;

- Finally, depending on the thickness chosen, the range of measurable speeds, which is between 10⁻⁴ μm/sec and 10 μm/sec: the corresponding gradients range from 10⁻⁶ sec⁻¹ to 1 sec⁻¹.

The first experiments conducted were aimed at verifying and specifying the performance of this equipment. It was thus possible to obtain homogeneous asphalt cement films with a constant thickness to within ±0.5 μm and a minimum value of 6.5 μm with road asphalt cements of the 60 to 70 class, that is, having an average viscosity of 10⁶ to 10⁷ Pa · sec (Pascal multiplied by second) at 20°C. The deviation sensitivity tests under a light load demonstrated that, in the presence of an asphalt cement film more than 50 μm thick, the balance of the beam should be obtained within less than 500 mg to avoid any significant creep in the specimens (a few microns in 2 or 3 hr). The dynamic range of the possible loads is thus wide.

The minimum displacement speed depends on the system for regulating the temperature, which causes viscosity fluctuations. The tolerable fluctuation has been estimated within the limit of 1/10 of a degree. The curves determined for the smallest loads (between 1 and 5 g) and for the transducer used show that the steady flow established as of the first instants remains stable throughout the test (about 18 hr). These speeds are on the order of 10⁻⁴ μm/sec. On the other hand, the highest speeds measurable are deliberately limited to 10 μm/sec for practical recording reasons.

Theoretical Aspect: Adaptation of Nonlinear Viscoelastic Behavior Models to Experimental Results

It has been shown, based on cone-plane viscosimetry experiments on model asphalt cements (in which the maltenes have been replaced by tetraline), that the equations governing the kinetics of the process are not linear and can be likened to those that govern the advance of chemical reactions (18). It will be recalled that in chemical kinetics, during a reaction, the variation in the concentration $|A|$ of the reagents follows a law of the type

$$d|A|/dt = k|A|^n$$

where $d|A|/dt$ is the time derivative of A concentration, k is related to the activation energy, and n is related to the order of the reaction.

It is thus possible to transpose to rheology the two basic notions of activation energy and order. The application of these principles makes it possible to differentiate, by their orders, the behavior of asphaltenes extracted respectively from a straight-run asphalt and from a blown asphalt.

The continuation of experimentation by studying the evolution of shearing stress with time at a constant shearing rate followed by relaxation tests leads to curves that all have the shape shown in Figure 12 (19).

It is noted that the stress increases regularly with time up to a maximum value that corresponds to a steady flow of the material and that depends on both the shearing rate and temperature. The representation in bilogarithmic coordinates of σ_{\max} as a function of $\dot{\epsilon}$ gives a line with an excellent correlation ($r^2 \geq 0.999$) for the different temperatures. Figure 13 shows the lines obtained for 20°C, 40.5°C, and 60°C. Further, it has been noted that the experimental relaxation curves all confirm, with a good correlation, an equation of the type

$$d\sigma/dt = -k\sigma^n$$

Several experiments were carried out for different deformation values (after relaxation) and it was observed that the results were independent of these values. This led to the adoption of rheological model of the Maxwell-Norton type (20). It is governed by the differential equation

$$\dot{\epsilon} = J\dot{\sigma} + \alpha\sigma^n$$

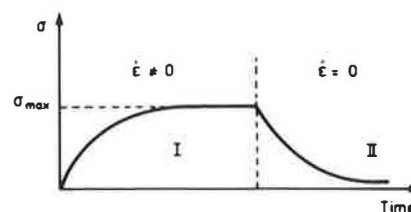


FIGURE 12 Typical curves of isothermal evolution of stresses (I = test at constant shearing rate, and II = relaxation test).

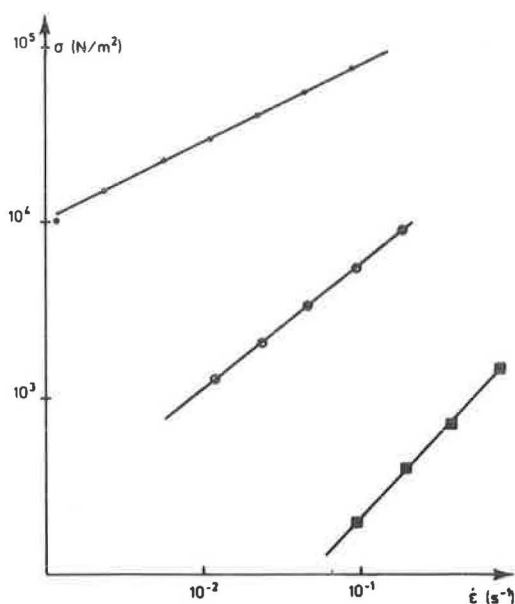


FIGURE 13 $\sigma_{\max} - \dot{\epsilon}$ curves for three temperatures (\bullet = 20°C, \circ = 40.5°C, and \blacksquare = 60°C).

The values of the parameters α and n were determined from the line $(\log \sigma_{\max} - \log \dot{\epsilon})$ and the value of J from the relaxation curves. These values are given in Table 2 for the different temperatures. The relative errors are estimated at about 5 percent for α and n , and 10 to 15 percent for J , at 20°C. These errors are smaller for high temperatures.

The rheological model is a great interest for two reasons. First, it allows, for relaxation investigations, an analogy with models that are well known in chemical kinetics (see previous discussion). Second, it is easily applicable to the case of multi-axial stresses because of the generalized Norton-Hoff law, which lends itself readily to numerical calculation (by finite elements, for example) (21). In the model, n is a structural coefficient that reveals the importance of the spatial distribution of intermicellar interactions: the higher the value of this coefficient, the larger the order because the material then has the properties of a gel; on the other hand, the closer the order to unity, the more numerous and dispersed will be the asphaltene micelles without any strong interactions between them. The coefficient α is a function of the energy per unit volume dissipated and has the characteristics of an activation energy.

TABLE 2 NUMERICAL VALUES OF DIFFERENT PARAMETERS AS A FUNCTION OF TEMPERATURE

T °C	20	30	40.5	49	60
n	2.28	1.47	1.415	1.12	1.05
J (M K S)	$8.5 \cdot 10^{-4}$	$9.0 \cdot 10^{-4}$	$9.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$
α (M K S)	$6.56 \cdot 10^{-13}$	$6.18 \cdot 10^{-9}$	$4.85 \cdot 10^{-7}$	$3.92 \cdot 10^{-5}$	$3.90 \cdot 10^{-4}$

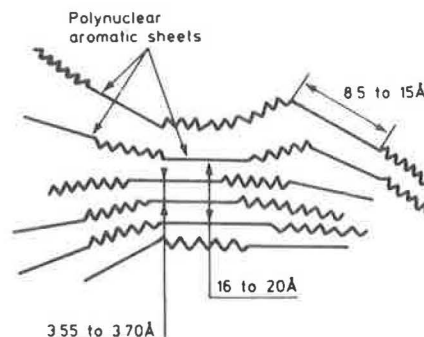


FIGURE 14 Section of an asphaltene micelle model according to Yen.

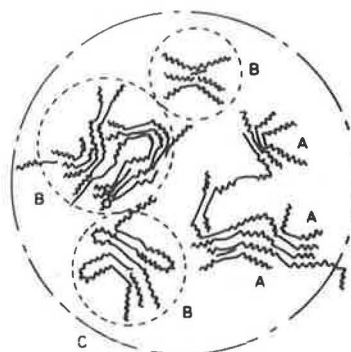
RELATIONSHIPS BETWEEN COMPOSITION, STRUCTURE, AND PROPERTIES

Review of Colloidal Structure of Asphalt Cements

The comparison of composition criteria, in the chemical sense of the term, with rheological behavior properties necessarily requires a schematic but realistic description of the colloidal structure of asphalt cements for proper understanding of the relationships.

In conventional diagrams, it is generally assumed that asphalt cements are colloidal systems made up of a suspension of asphaltene micelles peptized by resins in an oily medium. Concerning the macrostructure of asphaltenes, research conducted by Yen has led to the proposal of the model shown in Figure 14 for the asphaltene micelle (22). In this model, the overall cohesion of the micelle is provided by interactions between the π electrons of the pericondensed polynuclear aromatic sheets.

However, the Yen model is not limited to the formation of micelles. It also offers the possibility of creating complex edifices formed by the association of several micelles into real aggregates, as shown in Figure 15. The formation of these



A = molecule, B = micelle, C = aggregate

FIGURE 15 Macrostructure of asphaltenes according to Yen (A = molecule, B = micelle, and C = aggregate).

aggregates is considered to be related to intermolecular interactions, the nature of which is not indicated.

It is easily understood that one of the key parameters governing such a colloidal structure equilibrium is the chemical composition of its constituents. It is also easily observed that any modification in this equilibrium (notably, under the action of a temperature variation) leads to a modification in rheological behavior.

Comparison of Composition and Structure

Many authors have attempted to characterize the stability of the colloidal state of asphalt cements at ordinary temperature on the basis of chemical analysis in generic groups. Gaestel, for example, has defined a colloidal instability index as the ratio of the sum of the amounts in asphaltenes and flocculants (saturated oils) to the sum of the amounts in peptizers (resins) and solvents [aromatic oils (23)]:

$$I_c = (\text{Asphaltenes} + \text{Saturated oils})/(\text{Resins} + \text{Aromatic oils})$$

The higher the ratio, the more will the asphalt cement be of the gel type and the lower will be its colloidal stability. Gaestel also notes that all the properties of the binder (softening point, ductility, embrittlement temperature, thermal susceptibility, elastic recovery, shearing susceptibility, etc.) vary significantly with the colloidal instability index and hence with composition.

These different investigations represent a major contribution to the understanding of relationships between composition and properties. However it may be noted that they take into account only the asphaltene concentration parameter, independently of any quality criterion for them. A certain number of experiments have demonstrated that a distinction should be made between asphaltenes coming from straight-run asphalts and those coming from blown asphalts.

Because of the arbitrary nature of the fractionation into generic groups and the lack of methods allowing direct observation of the colloidal structure of asphalt cements, it was considered of interest to develop a fast and reproducible analytical technique making it possible to work on the binder as is, without prior fractionation. This technique is GPC, discussed earlier in the paper. Figure 16 shows the comparison that can be made between the structure of the binder characterized by the equilibrium

Oils \rightleftharpoons Micelles \rightleftharpoons Aggregates

and the GPC chromatogram obtained in a few minutes under the previously proposed ultra-fast conditions. (It should be noted that, in this specific example, the asphalt cements A and B have practically the same asphaltene content, 15 and 15.2 percent, respectively, showing that the GPC interaction peak is independent of this content.)

The diagram just presented offers two advantages, while complying with the models proposed in the past:

- It accounts for the results obtained with respect to the influence of the nature of asphaltenes on the viscosity of model asphalt cements and with regard to the application of GPC to the characterization of asphalt cements, and
- It introduces an additional property of the asphaltenes, namely, their ability to interact in order to yield a more or less complex network, responsible for the gel-type behavior.

The hypothesis set forth to explain the formation of aggregates specific to blowing (or weathering) is that the latter creates a certain number of active centers (polar functions) responsible for the intermicellar interactions (hydrogen bonding). The more severe the blowing, the more numerous these interactions would be. It is hence easily observed that a straight-run asphalt cement is a colloidal system made up of

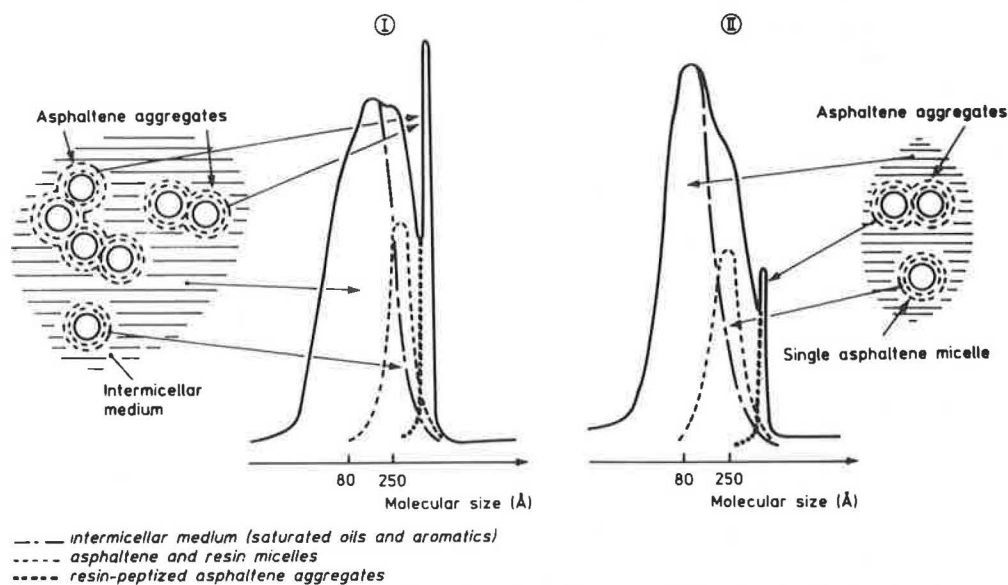


FIGURE 16 GPC chromatograms (broken down into three populations) and colloidal structure of road asphalt cements (I = blown asphalt cement and II = straight-run asphalt cement).

individual micelles, hence of the sol type, as shown in the right part of Figure 16. During blowing, not only does the asphaltene content increase but an increasing amount of micelles interacts to form aggregates that give the material an intermediate sol-gel structure with a viscoelastic behavior, the elastic component of which (or the structural viscosity) varies with the number of micelles engaged in the form of aggregates, and hence with the blowing rate. In the extreme case, for oxydized asphalt cements, the perfect gel structure is reached (left part of Figure 16) in which the asphaltenes are organized in a three-dimensional network, giving the medium its elasticity.

This complement to colloidal structural models already established makes it possible to state that one of the major parameters of the colloidal behavior is the interaction capability of the micelles, more than the asphaltene content. It thus accounts for the experimental results regarding a modification of the origin of asphaltenes in the model asphalt cements.

Discussion of Relationships Between Composition, Structure, and Properties

It was seen previously that GPC makes it possible to obtain an image of the colloidal structure of asphalt cements (ratio of intermicellar and dispersed phases and, especially, quantitative information on sol \rightleftharpoons gel equilibrium). Because the latter has a direct influence on rheological properties, it was logical to examine more closely the relationship that could be established between the characterization of asphalt cements by GPC and their rheological behavior. A first illustration of this relationship is shown in Figure 17.

In Figure 17, the chromatograms of four asphalt cements belonging to the same penetrability class (80–100) are compared with their parameter λ_m as it may be estimated by the interpretation of peeling curves. (λ_m is defined as the average distance between two constituent entities of the medium; in the case of gel systems, it corresponds to a distance between nodes (see the section on Experimental Characterization).

Regarding the parameter n of the Maxwell–Norton model, it is interesting to compare the numerical values at 20°C of the interaction parameter evaluated by GPC for the five 40 to 50 asphalt cements shown in Figure 6. As discussed previously, the Maxwell–Norton model is an order parameter defining the degree of medium organization (n is little different from unity for the sol system and increases with gel properties; see the section on Theoretical Aspect). If these asphalt cements are classified by increasing order of interaction index, the results obtained are those given in the following table (24).

Sample	n
C	1.8
D	1.8
E	2.0
B	2.2
A	2.5

A more systematic study of 22 road asphalt cements of different origins (origin of crude and production process), including a certain number of naturally and artificially weathered samples, indicated that the standard deviation of the relaxation spectrum (as it may be estimated by measuring the

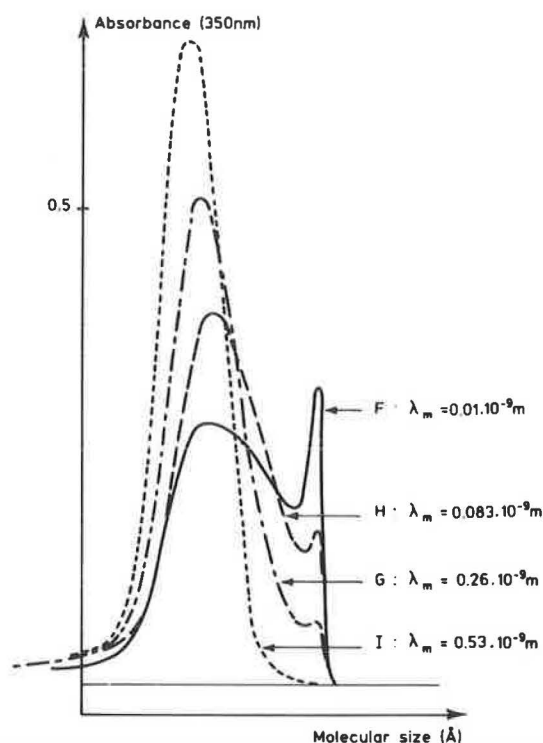


FIGURE 17 Relationship between λ_m and the interaction index.

complex modulus at variable temperatures and frequencies) depends both on the amount of asphaltenes and on the intensity of their interactions (25). A detailed statistical analysis has made it possible to determine the coefficients of a multiple regression with two variables and to select two models:

$$K\sigma = 2.08 + (0.899 I/200) + 0.0348 A$$

and

$$K\sigma = 2.305 + 0.0428[1 + (I/200)]A$$

where

K = proportionality constant,
 σ = standard deviation of relaxation spectrum,
 I = GPC interaction index (height in mm of interaction peak under given operating conditions), and
 A = asphaltene content.

With the first model, a correlation coefficient of 0.952 and a residual variance of 0.0208 are obtained, and with the second a correlation coefficient of 0.944 and a residual variance of 0.0227 are obtained.

Figure 18 allows a comparison of the values of $K\sigma$ measured and estimated on the basis of the first model. The results of this comparison, confirming the significance of interactions between asphaltenes and showing their assessment by means of the interaction index, are already of significant practical value because they allow (a) an a priori classification of asphalt cements of a given category, and (b) follow-up of natural or artificial weathering by two simple tests that are rapid and that

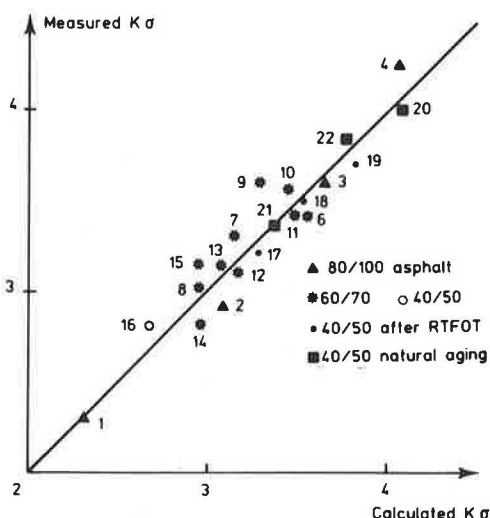


FIGURE 18 Comparison of calculated and measured standard deviations.

do not require much binder. Thus it is possible to limit the number of technological (or rheological) tests, which are clearly more difficult to carry out.

Ongoing, as yet unpublished, research in the area of the rheological behavior of ultra-thin films appears to be promising. It covers six 40–50 road asphalt cements of different origins, for which the viscosimetric behavior of films of different thickness ranges (6 to 8 μm , on the order of 25 μm , and on the order of 50 μm) has been investigated.

The results indicate the following:

- The viscosimetric behavior of the binder varies, for certain asphaltic cements, with the film thickness (Newtonian behavior for films of 50 and 25 μm becoming non-Newtonian for films of 6 to 8 μm);
- The apparent viscosity, for a given shearing rate, can be multiplied by a factor of more than 10 by simply decreasing the film thickness;
- Certain samples exhibit, in small thicknesses, a plastic flow threshold; it is to be noted that this flow threshold is observed only for asphalts exhibiting, in GPC, a clearly marked interaction peak, which is a new means of comparing composition and properties; and
- Behavior depends on the recent thermal history of the sample, and the method permits the study of structural hardening.

SUMMARY

In this paper the facilities acquired by the LCPC road research laboratories in the area of physicochemical characterization (HPLC and GPC) and investigations on the rheological behavior of materials (peeling, viscoelasticity, viscosity of ultra-thin films) have been pointed out. It is important to note that these new characterization methods show that asphalt cements with the same specifications have substantially different chemical compositions and rheological behaviors. In the authors' view, emphasis should now be placed on the practical application of physicochemical methods such as GPC and also

on the experimental relationships between the composition, structure, and properties of these materials.

Regarding the first point, it has been demonstrated that GPC enables a characterization of the complex colloidal equilibrium of asphalt cement:

Molecules \rightleftharpoons Micelles \rightleftharpoons Aggregates
(intermicellar phase)

As the equilibrium is shifted to the right by blowing during manufacture and by low-temperature oxidation during in situ weathering, GPC can be used beneficially to evaluate the blowing rate of new asphalt cements and the degree of evolution of in situ weathered asphalt cements.

Regarding the second point, tests in progress indicate that the shifting of colloidal equilibrium to the right (as a result of blowing and weathering) is accompanied by an evolution of rheological properties from those of a sol system toward those of a gel system.

Research projects are concentrated essentially on the prediction of the behavior of materials during mixing and in-place weathering (experimental research on composition parameters capable of being associated with weathering susceptibility). Current investigations cover the relationship between the RTFOT and the evolution of properties during mixing for different types of asphalt cements, aggregates, and mixing plants. For the simulation of in situ weathering, it appears to be important to look for an artificial weathering technique enabling the oxidation of asphalt cement at a temperature substantially lower than 160°C, which is the temperature of the RTFOT.

From the practical viewpoint, there is the problem of the calibration of artificial weathering tests; a research program is under way for characterizing the evolution of well-selected binders on experimental road sections.

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