

Characterization of Regular and Modified Bitumens via Their Complex Modulus

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SYNOPSIS

Rheological methods of characterization of regular and modified bitumens are studied. The fractional model of a complex modulus is inverted to generate the corresponding molecular weight distribution. A possibility to obtain more information about the structure of bitumens via the phase angle is investigated. The problem of a calibration equation is briefly discussed. The presence of polymer additives in modified bitumens is manifested on the molecular weight distribution obtained from the phase angle. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical characterization of bitumens has historically been based on various empirical tests which are difficult to interpret. Moreover, these tests are not able to give sufficient information about the structure of the tested material. A better understanding of the microstructure of bituminous materials can be obtained by combination of classical chemical characterization techniques (e.g., GPC) and the known rheological testing.^{1,2}

From the early days of modern bituminous science, it has been recognized that bitumen is a multiphase colloid system and only the opinions about the internal working of the system have changed with time and the instrumentation available. Because of the extreme complexity of the material, an agreement on the bituminous internal structure has not been fully reached even at the present time. The composition of bitumens varies with the source of the crude oil and the type of manufacturing. By group composition, bitumens are divided to saturates, naphthene aromatics, polar aromatics, and asphaltenes. The first three groups are usually called maltenes. The heaviest parts of maltenes form a group sometimes identified as resins. Resins

and asphaltenes strongly overlap. The lowest molecular weight portion of bitumen has a molecular weight as low as 240 and an H/C ratio as high as 1.76 (per mole). This part resembles and belongs to the highest boiling point fraction of lubricating oils with the structure of condensed cycloalkane and aromatic rings with side chains of varying length. On the other side of the spectrum are asphaltenes. Their molecular weight varies strongly with the method of determination—from about 2000 (by vapor-pressure osmometry or by the ebullioscopic method) up to 10,000 and even 1,000,000 (by the centrifuge method), and their H/C ratio is as low as 1.15 (per mole). Asphaltenes form a loose group identified by their insolubility in the low molecular weight alkanic solvents. The amount of bitumen determined as asphaltenes depends on the selected solvents (usually *n*-pentane, *n*-hexane, or *n*-heptane).

In the late 1930s, scientists started to consider bitumen as a colloid containing micelles—asphaltene surrounded by a protective layer of lower molecular weight hydrocarbons and dispersive oils.³ In recent decades, a considerable amount of research on the chemistry and structure of bitumen was performed using different methods of gel permeation chromatography, ultracentrifugation, X-ray diffraction analysis, and electrical diffraction. Important works in this area were performed by Witherpoon et al.,^{4,5} Altgelt et al.,^{6,7} Yen,⁸ Speight and

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Moschopedis,¹⁰ Maruska and Rao,¹¹ Brule and Migliori,¹² and many others.

One of the current opinions on bitumen's internal structure is that of Yen, who considered asphaltenes as multipolymers: polycondensed substances with different repeating blocks, associated by inter- and intramolecular interactions within the structure. Yen estimated the molecular weight of asphaltenes to be between 800 and 2500. For the macrostructure of asphaltenes, Yen proposed an unisotropic structure of mesomorphic liquid in which many individually oriented clusters are suspended and randomly distributed within lower molecular weight homologs. The individual clusters are ordered and consist of a number of planar aromatic molecules stacked in layers via a π - π association. On the basis of X-ray diffraction, Yen proposed the stacking to occur with five to six layers. He suggested a unit sheet mass of 1000-4000, a cluster or particle mass of 4000-10,000, and a micelle mass of 40,000-40,000,000.

Another point of view is that of Speight and Moschopedis.⁹ These authors considered a micelle in bitumen to consist of a single asphaltene molecule, rather than a stack of asphaltene molecules. According to Speight and Moschopedis, the molecule is surrounded by the resin molecules which act as peptizing and dispersing agents for the asphaltene: the resins associated with asphaltenes in a manner of an electron donor-acceptor. With the concept of hydrogen bonding being one of the means of association between asphaltenes and resins led Speight and Moschopedis to the rejection of asphaltene clusters as parts of the micelle. Resin-asphaltene interactions are preferred to asphaltene-asphaltene interactions. Speight and Moschopedis suggested that it is not possible to compose a model that represents all of the properties of asphaltenes. It is more preferable to design models representing various fractions of an asphaltene.

Neumann and Rahimian¹⁰ concluded that resins do not constitute the outside layers of asphaltene micelles but are separate colloid entities. Both of these groups are lyophilic micelloids and do not need protective surrounding layers.

Interesting work was performed by Maruska and Rao¹¹ who hypothesized the mechanism of the intermolecular associations of asphaltenes. Several intermolecular association interactions can be envisioned based on induced and permanent electrical polarization of bonds. These include van der Waals forces, hydrogen bonding, and other polar interactions. The residue contains the highest molecular weight polar compounds in crude oil. These molecules containing heteroatoms exhibit the most pro-

nounced molecular association. The observation suggests that the asphaltene dipoles do participate in the aggregation interaction. Ultimately, high molecular weight oligomers are formed.

Bitumen, according to the majority of authors and experimental evidence, is a multidisperse micellar system. The study of the internal structure of bitumens is difficult because of their high viscosity and the complexity of their components. All studies were done in a solvent, which, depending on its type, inadvertently changes the structure of the part with either the largest molecular weight or the greatest polarity. The results of tests conducted on such diluted bitumens contribute considerably to our knowledge of the material. However, the results are those of the behavior of the material in diluted form (and solvent according to its type either contributes to dissolution or aggregation of the heaviest or the most polar molecules). Thus, if one can find a less invasive method, which does not rely on dissolution of a sample, one can obtain additional information about the real internal structure of bitumens. The possibility to use the rheological characterization of bitumens for a study of their microstructure is discussed in the following paragraphs.

VISCOELASTICITY AND THE MOLECULAR WEIGHT DISTRIBUTION

It is well established¹³ that the linear behavior of bitumens is described by the general linear viscoelastic model, e.g., see Ferry¹⁴ and Bird et al.¹⁵ The response of a viscoelastic fluid to small deformations is usually studied in the small-amplitude oscillatory shear experiment. The material function obtained in such an experiment is the complex modulus $G^*(\omega)$ or the complex viscosity $\eta^*(\omega) = G^*(\omega)/i\omega$.

The complex modulus $G^*(\omega)$ can be written as

$$G^*(\omega) = |G^*(\omega)| \exp[i\delta(\omega)] \quad (1)$$

where ω is the frequency; $|G^*|$, the magnitude of G^* ; δ , the phase angle between the stress and strain; and $i = \sqrt{-1}$.

It has been found that the complex modulus of regular and polymer-modified bitumens can be successfully modeled by the following complex function¹⁶:

$$G^*(\omega) = i\omega\eta_0 \left[\frac{\prod_1^m (1 + i\omega\mu_k)}{\prod_1^n (1 + i\omega\lambda_k)} \right]^{(n-m)-1} \quad (2)$$

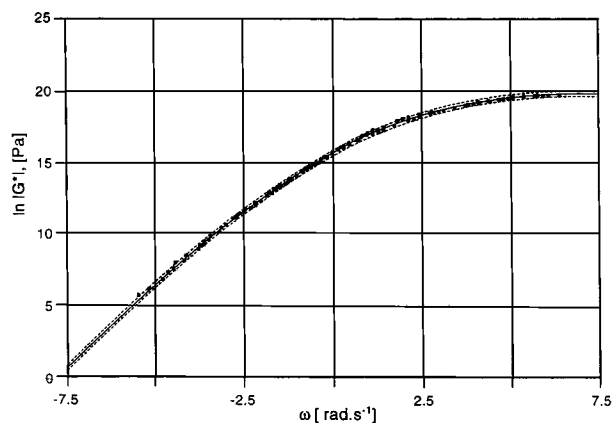


Figure 1 $\ln |G^*| - \log \omega$, sample 200/300—regular bitumen; eq. (9). — 99% confidence intervals.

where relaxation times λ_k and μ_k are positive, $m < n$ (integers), and the zero shear rate viscosity $\eta_0 > 0$.

A typical regular bitumen (sample 200/300 Pen grade produced from Lloydminster heavy crude oils) and the fit of eq. (2) are shown in Figures 1 and 2. To improve its service performance, it was modified by a polymer (sample PMA). The complex modulus and the fit of eq. (2) for PMA samples are shown in Figures 3 and 4. As one can see, there is only a little change in $|G^*|$ between the original and the modified bitumen. However, the form of δ (phase angle) is different in the modified material. This difference is also portrayed in Figure 5, where the phase angle of the original and two modified bitumens are shown. In studying various regular and polymer-modified bitumens, we have found that the complex modulus of regular materials is well modeled by eq. (2) if $m = 0$ and $n \leq 10$. For the studied samples of modified bitumens, one has to consider

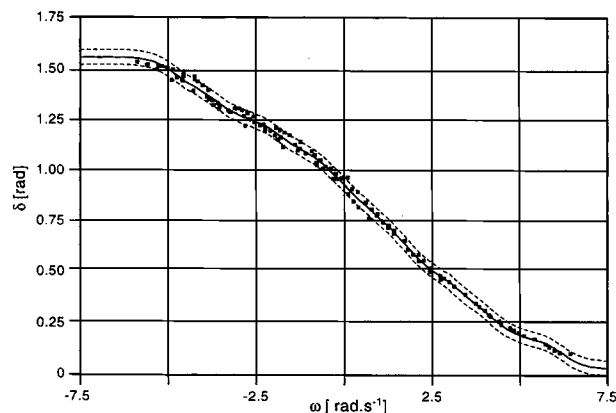


Figure 2 $\delta - \log \omega$, sample 200/300—regular bitumen; eq. (10). — 99% confidence intervals.

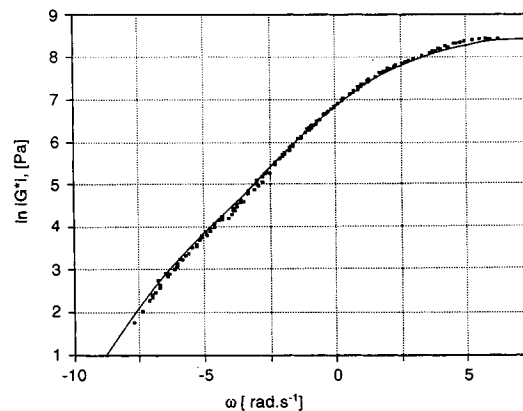


Figure 3 $\ln |G^*| - \log \omega$, sample PMA—modified bitumen; eq. (9).

$m \neq 0$, usually $m \leq 2$. Parameters of model (2), for the portrayed samples, are given in Table I.

It is known that rheological properties of polymers strongly depend on molecular weight. Generally, it should be possible to invert such a relationship and obtain the molecular weight distribution (MWD) from the measured material functions. The inverse problem of obtaining MWD from rheological data is a nonlinear problem. Thus, one has to decide which rheological property is sufficiently sensitive to MWD and also be sure that this property has a broad domain, if the complete MWD is to be recovered. It has been recognized^{2,17} that only the linear viscoelastic region is required for the characterization of polymeric materials. In fact, the needed region covers only the terminal and plateau parts. This is the consequence of the fact that the dynamic behavior of chemically identical polymers is indistinguishable at very high frequencies.¹⁸ Recently, Mead² studied the numerical and analytical methods of inverting the double reptation mixing rule to ob-

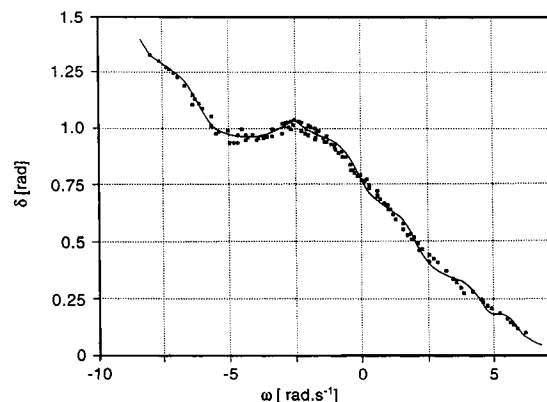


Figure 4 $\delta - \log \omega$, sample PMA—modified bitumen; eq. (10).

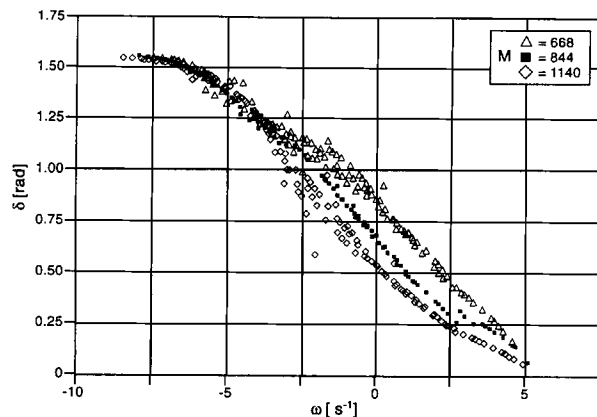


Figure 5 $\delta - \log \omega$, three regular bitumens; M , from vapor-pressure osmometry.

tain the MWD of polybutadiene and polypropylene. He found the MWDs calculated from rheological data are in good agreement with the corresponding GPC data.

For the studied samples of regular and two polymer-modified bitumens, we found that the dependence on molecular weight is more pronounced in $\delta(\omega)$ than in the magnitude $|G^*|$. This can be seen in Figure 5, where $\delta(\omega)$ for regular bitumens are shown. Assuming that in accordance with the double reptation mixing rule (Tsenoglu¹⁹ and Wasserman and Greasley²⁰) and also with the earlier work of Tuminello,¹⁷ the phase angle is given as

$$\delta(\omega) = \int_0^{\infty} W(M')c(M', \omega) dM' \quad (3)$$

where $c(M, \omega)$ represents the “monodisperse” phase angle and $W(M)$ is the weight distribution function. Consider the following step form of $c(M, W)$:

$$c(M', \omega) = [1 - H(M' - M)] \quad (4)$$

where H represents the Heaviside function and the frequency region (ω) is related to the mass region (M) by a simple power law:

$$M = k\omega^{-\alpha} \quad (5)$$

where k and α are constants.

Denoting

$$x = \log \omega \quad (6)$$

it follows from eqs. (3), (4), and (5) that

$$\delta(x) = 1 - \int_{M=k10^{-\alpha x}}^{\infty} W(M')dM' \quad (7)$$

for normalized W . Differentiation of the last equation yields

$$W(M) = -\frac{10^{\alpha x}}{\alpha k \ln 10} \frac{d\delta}{dx} \quad (8)$$

where $M = k10^{-\alpha x}$. Thus, in principle, one should be able to obtain additional information about the structure of bitumens from the study of the phase angle $\delta(\omega)$.

Table I Parameters of the Model (2)

Sample	λ_k [s]	μ_k [s]	η_0 [Pa·s]
200/300	4.34789 e-04		5.79091 e+07
	8.013198 e-03		
	2.262382986		
	2888.50961		
	4.4691 e-05		
	6.0422 e-07		
	0.03470017		
	5.263316264 e+04		
	54.1177568		
	0.433125175		
PMA	1.21459 e-05	467.612631	5.30373 e+09
	1.06215 e-06	3.902 e-06	
	1.083945076		
	193.3113949		
	1.46153 e+06		
	0.00571852		
	2.55244 e+08		

EXPERIMENTAL AND NUMERIC RESULTS

The following forms of $|G^*|$ and δ are generated by eq. (2):

$$|G^*(\omega)| = \eta_0 \omega \left[\frac{\prod_1^n (1 + (\omega \mu_k)^2)}{\prod_1^n (1 + (\omega \lambda_k)^2)} \right]^{1/2(n-m)} \quad (9)$$

$$\delta(\omega) = \frac{\pi}{2} - \frac{1}{(n-m)} \left[\sum_1^n a \tan(\omega \lambda_k) - \sum_1^m a \tan(\omega \sum \mu_k) \right] \quad (10)$$

Calculating the limit of eq. (9) at infinity, one obtains

$$\lim_{\omega \rightarrow \infty} |G^*(\omega)| \equiv G_N = \eta_0 \left[\frac{\mu_1 \mu_2 \cdots \mu_m}{\lambda_1 \lambda_2 \cdots \lambda_n} \right]^{1/(n-m)} \quad (11)$$

If, in bitumens as in polymers, the zero shear rate viscosity is proportional to a power of M , then from (11)

$$G_N = AM^b \left[\frac{\mu_1 \mu_2 \cdots \mu_m}{\lambda_1 \lambda_2 \cdots \lambda_n} \right]^{1/(n-m)} \quad (12)$$

where A and b are constants. Introducing a characteristic time

$$\bar{\lambda} = \left[\frac{\lambda_1 \lambda_2 \cdots \lambda_n}{\mu_1 \mu_2 \cdots \mu_m} \right]^{1/(n-m)} \quad (13)$$

with the corresponding characteristic frequency $\tilde{\omega} = 2\pi/\bar{\lambda}$, one can write

$$M = \left[\frac{2\pi G_N}{A} \right]^{1/b} \omega^{-1/b} \equiv k \tilde{\omega}^{-\alpha} \quad (14)$$

Thus, the molecular weight domain (M) is related to the frequency domain (ω) via the transformation given in eq. (5). This form of dependence ($M \sim \omega^{-\alpha}$) has frequently been used.^{14,17} A very good correlation of M with frequency, [eq. (5)] for narrow-distribution polystyrenes was shown by Tuminello.¹⁷ Note that eq. (5) leads to the known relation $\eta_0 \sim M^b$, which is also applicable to polydisperse systems.^{14,15,17} The correlation of M and $\tilde{\omega}$ for regular bitumens is shown in Figure 6. Here, M is the weight obtained by vapor-pressure osmometry. It is clear

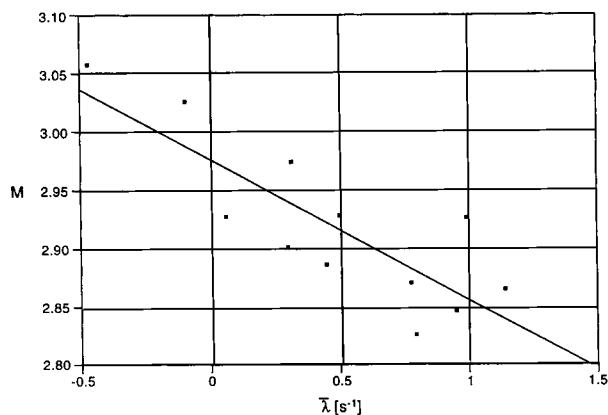


Figure 6 Correlation of M and $\bar{\lambda}$; eq. (14).

from this figure that the data for regular bitumens follow the trend of eq. (5). However, it is difficult to find a unique constant K for the whole group of the studied samples (about 10 samples have been investigated). The best fit of the shown data yields $\alpha = 0.1231$ and $k = 2.976$. Thus, using eq. (8), one can calculate W from the derivative of the phase angle, and using the transformation (5), the MWD can be obtained. The position of MWD is given by constant K , and since, as mentioned above, it is possible to find only an average value of K for regular bitumens, one will obtain MWDs placed slightly off their real positions. Such a drawback is, on the other hand, balanced by the high resolution of the obtained MWDs. This can be seen in Figure 7, where the MWD for one regular bitumen (200/300 Pen grade) is shown. Here, the differential distribution obtained from GPC and from $\delta(\omega)$ are compared. A slight shift in the position of MWD from $\delta(\omega)$ is visible; however, the components with higher weight are visible only on this MWD and not on the one obtained from GPC. Similarly, for sample PMA (Fig. 8), the presence of high molecular weight components is clearly visible. Note the existence of a small negative peak. This feature will be discussed later.

The procedure used for $\delta(\omega)$ can also be repeated for the second component of the complex modulus, $|G^*|$. Assuming, in accordance with Tuminello,¹⁷ that

$$\left[\frac{|G^*(x)|}{G_N} \right]^{1/2} = 1 - \int_0^M W(M') dM' \quad (15)$$

$$M = k10^{-\alpha x}$$

one can again simply calculate the weight distribution function as follows:

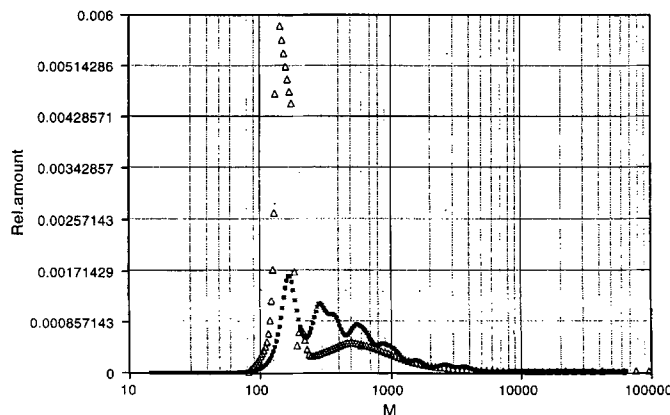


Figure 7 MWD—sample 200/300: (Δ) GPC; (\blacksquare) δ method; eq. (8).

$$W(M) = \frac{10^{\alpha x}}{\alpha k \ln 10} \frac{d}{dx} \left[\left(\frac{|G^*|}{G_N} \right)^{1/2} \right] \quad (16)$$

$$M = k10^{-\alpha x}$$

MWDs for the sample 200/300 Pen grade, obtained from $\delta(\omega)$ and from $(|G^*|/G_N)^{1/2}$, are shown in Figure 9. The higher resolution of the method using $\delta(\omega)$ is demonstrated.

DISCUSSION

To see more clearly how both rheological methods of characterization resolve the distribution of various components of the studied samples, one can analyze the derivatives of $\delta(x)$ and $(|G^*|/G_N)^{1/2}$ for the used model (2). It follows from (11) that

$$\frac{d\delta}{dx} = -\frac{\ln 10}{(n-m)} \left\{ \sum_1^n \frac{10^x \lambda_k}{1 + (10^x \lambda_k)^2} - \sum_1^m \frac{10^x \mu_k}{1 + (10^x \mu_k)^2} \right\} \quad (17)$$

The first derivative of $\delta(x)$ is a superposition of pulselike functions, each positioned at $x = -\log \lambda_k$ or $x = -\log \mu_k$.

The height, h , of these “pulses” is constant: $h = \ln 10/2(n-m)$. On the other hand, for the derivative of $(|G^*|/G_N)^{1/2}$, it is possible to write

$$\frac{d}{dx} \sqrt{\frac{|G^*|}{G_N}} = \frac{1}{2} \sqrt{\frac{|G^*|}{G_N}} \frac{d}{dx} \ln \left[\frac{|G^*|}{G_N} \right] \quad (18)$$

The use of (18) and (9) yields

$$\frac{d}{dx} \sqrt{\frac{|G^*|}{G_N}} = \frac{1}{2} \sqrt{\frac{|G^*|}{G_N}} \left\{ \sum_1^n \frac{1}{1 + (10^x \lambda_k)^2} - \sum_1^m \frac{1}{1 + (10^x \mu_k)^2} \right\} \frac{\ln 10}{(n-m)} \quad (19)$$

Terms in the brackets are again pulselike functions, now positioned at $x = 0$, with different heights, each given by the appropriate relaxation time. These “pulses” are multiplied by a sigmoidal function $(|G^*|/G_N)^{1/2}$; thus, the resolution $W(M)$ obtained with the help of (19) cannot be as high as is the resolution of $W(M)$ obtained from $\delta(\omega)$.

In their study of the Kramers–Kronig relations between viscoelastic quantities, Booij and Thoonen²¹ found the following approximation:

$$\delta(\omega) = \frac{\pi}{2} \frac{d \ln |G^*|}{d \ln \omega} \quad (20)$$

Using this approximation in calculating MWD from $(|G^*|/G_N)^{1/2}$, one obtains an interesting relation. Combining eqs. (15), (17), and (19), the following expression for MWD is obtained:

$$W(M) = \frac{10^{\alpha x}}{\alpha k \pi} \delta(x) \sqrt{\frac{|G^*(x)|}{G_N}} \quad (21)$$

$$M = k10^{-\alpha x}, \quad x = \log \omega$$

Thus, an approximate MWD could be obtained simply by multiplying the phase angle and the square root of the magnitude of the complex modulus. There are two problems with such an approximation. Generally, the functions $\delta(\omega)$ and $|G^*(\omega)|$ are master curves obtained by a time–temperature superposi-

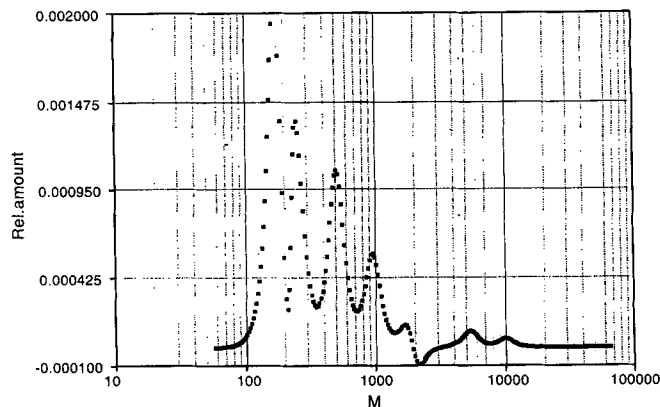


Figure 8 MWD—sample PMA, δ method; eq. (8).

tion.¹⁴ Thus, the values of $|G^*(\omega)|$ and $\delta(\omega)$ are not known at the same frequency ω and one has to use interpolation to obtain these functions at identical values. The second problem is related to a limited length of domains of functions $\delta(\omega)$ and $|G^*(\omega)|$ obtained experimentally. Then, without an extrapolation (i.e., a realistic model of complex modulus), one is not able to obtain a complete MWD. The latter problem was discussed by Tuminello.¹⁷ Approximation (20) is well supported by our experimental data. Experimental values of $\delta(\omega)$ and the calculated derivative $d \ln |G^*|/dx$ for model (2) are shown in Figure 10. The obtained approximate MWD is shown in Figure 11.

Finally, the problem of relaxation times μ_k has to be discussed. The presence of these relaxation times is reflected by the existence of m negative terms in the derivatives $-d\delta/dx$ and $(d\sqrt{|G^*|/G_N})/(dx)$. This may result in negative peaks of MWD, as is seen in Figure 12, where the distribution of a modified sample is shown. The presence of negative peaks probably reflects the interfacial tension be-

tween the original material and the added polymer. It is clear from Figure 4 that the negative peaks are not the artifacts of the used mathematical method. The “strong” local minimum of $\delta(\omega)$, at low frequencies, leads to the presence of these peaks and such a minimum has been observed only in modified bitumens. Here, again, the δ method is more sensitive than is the $\sqrt{|G^*|}$ method. The highest components (highest M) of the regular bitumen are probably associated with the added polymer. Such an association is manifested by additional peaks in the far region of M . The interactive forces of this association are responsible for a small and short-lived increase of the phase angle $\delta(\omega)$, and this phenomenon is represented by a small negative peak around $M \sim 2000$, i.e., in the region of asphaltenes. Unfortunately, bitumens are not “clean” systems and no equivalent of monodisperse polymers is available in this group of materials. However, the $|G^*|^{1/2}$ method was successfully tested for a variety of polymers, e.g., in McGrory and Tuminello,¹ Mead,² and Tuminello.¹⁷ More “clean” polymeric

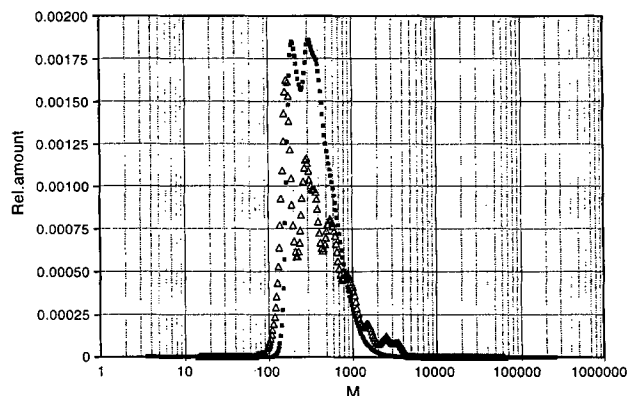


Figure 9 MWD—sample 200/300: (■) $\sqrt{|G^*|}$ method; eq. (16); (Δ) δ method; eq. (8).

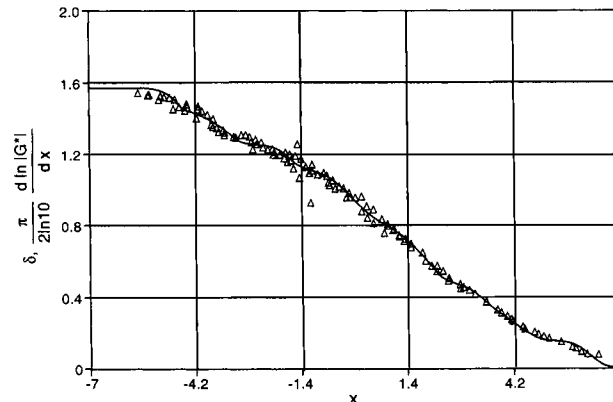


Figure 10 Booiij and Thoone²¹ approximation; eq. (20). Sample 200/300, $x = \log \omega$.

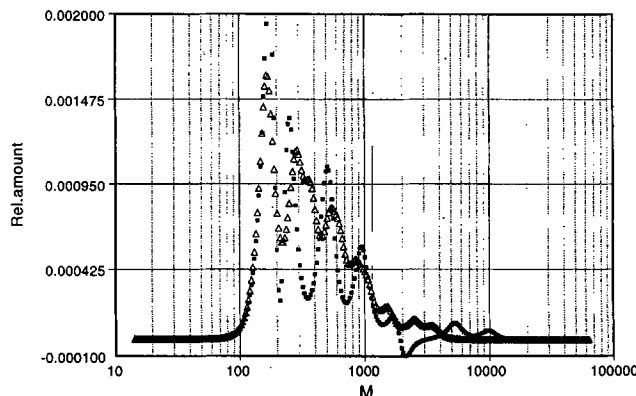


Figure 11 MWD from Booi and Thooe²¹ approximation, sample 200/300.

systems will be tested for calibration purposes in the next part of the study. It should be stressed that the rheological methods of obtaining MWDs depend on the known “calibration equation,” i.e., the relation $M = KW^{-\alpha}$, which relates the mass and the frequency domains. However, one can characterize the tested samples simply by $-d\delta/dx$ or by $d\sqrt{|G^*|}/dx$, thus avoiding the uncertainties generated by the “calibration equation.”

CONCLUSION

By analyzing the polar components of the complex modulus $G^*(\omega)$, we observed that these two functions can be used for the characterization of regular and modified bitumens. The additional information about the size of various components of bitumens is obtained mainly from the derivative of the phase angle $\delta(\omega)$. It has been found that the method using the phase angle yields the higher resolution of MWD than does the method based on the square root of the magnitude $|G^*(\omega)|$. The transformation of the

frequency domain onto the weight domain may have the generic form of a simple power law. However, such a simple transformation is not quite satisfactory, because it is not a unique one. The power law exponent seems to be unique for the regular bitumens. On the other hand, the proportionality constant is not unique for the group of studied regular bitumens (about 12 different samples were studied). The consequence of this fact is that the obtained MWDs are slightly shifted on the M -axis. Regardless of this problem, one is able to detect more components of bituminous materials via the δ method. The present analysis is based on a successful model of the complex modulus. This model is general enough to describe regular as well as modified bitumens. The structure of this model is such that the presence of a polymer additive is manifested by an appearance of small negative peaks in the δ -generated MWDs. We believe that the outlined rheological method of characterization of bituminous materials is promising. The mentioned problem of the “calibration” equation requires further study because a simple power-law probably oversimplifies the real situation.

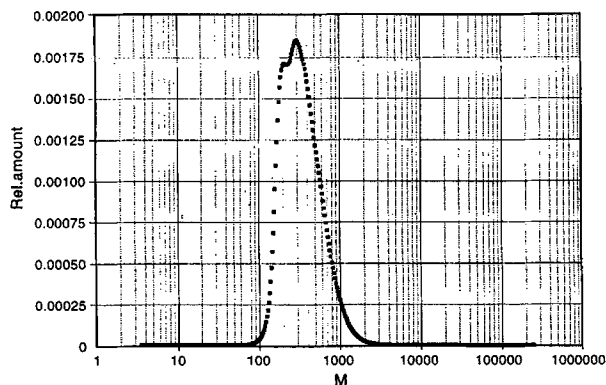


Figure 12 MWD— δ method: (■) 200/300; (Δ) PMA.

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