

## Prediction of Bitumen Molecular Weight Distribution Using Rheological Property

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**Abstract:** There are some problems to find heavy hydrocarbon characteristic such as lack of method or techniques and the special hydrocarbon property. Therefore, it is important to obtain the relation to find heavy hydrocarbon characteristic analytically or by experiment. These relations help us to predict special property in different range or area. In this study tried to predict the bitumen's molecular weight distribution by using its rheological property. This function obtained from the definition of complex modulus and phase angle for polymeric mixtures and investigated by zero relaxation time as rheological property. The result indicate that molecular weight distribution is sharp in low zero relaxation time and it's so wide in high zero relaxation time and this means that the molecular weight of bitumen's mixture increase by increasing the zero relaxation time and the distribution of molecular weight be wider.

**Keywords:** Bitumen, molecular weight, MWD, rheology

### INTRODUCTION

It is important to predict the characterization of heavy hydrocarbon compound in the high carbon number range and Organic geochemistry has been concerned to this area. High molecular weight hydrocarbons have received little attention because of two main reasons (Philp *et al.*, 1995). The first cause is the lack of techniques such as methods and limitation for example gas chromatographic that is limited to species with sufficient volatility. Next cause is the low solubility and mobility at surface temperatures and pressures of high molecular weight hydrocarbons (Del Río and Philp, 1999; Del Rio and Philp, 1992).

It is known that various dynamic material functions can be studied the structure of rheological complex systems (Zanzotto *et al.*, 1999). It is possible to use any measurable property that depends on molecular weight to invert such a relation to predict it. Strong functions of molecular weight are the linear viscoelastic properties of concentrated polymer solutions and melts. As an example, the zero shear rate viscosity of many polymeric materials depends approximately on molecular weight to the 3.4 power and the first normal stress coefficient for monodisperse linear polymers has the power law dependence on molecular weight with exponent 6.8. The reported sensitivity of the rheological properties of polymers to the molecular weight distribution is very high; it may be higher than the sensitivity of gel

permeation chromatography (Eder *et al.*, 1989; Graessley, 1984).

There is also a practical reason for such studies, besides the theoretical interest in developing other methods of characterization of complex materials. Low solubility of some materials in common solvents is cause to restricting the use of the conventional methods of determining molecular weight distributions (Zanzotto *et al.*, 1999). Asphalts are one of the groups of materials that can benefit from the rheological method of determining molecular weight distributions. There is a strong indication that the parts of asphalt with the highest molecular weights associate. Rheological properties should then depend on an apparent molecular weight distribution that includes the associates rather than on the molecular weight distribution of individual molecules alone (Tuminello, 1986; Wu, 1988). The main objective of this research is to predict the bitumens molecular weight distribution by using its rheological property such as relaxation time.

**Molecular weight distribution:** There are four molecular weight averages in common use (Sperling, 1986); the number-average molecular weight,  $M_n$ ; the weight-average molecular weight,  $M_w$ ; the z-average molecular weight,  $M_z$ ; and the viscosity-average molecular weight,  $M_v$ .

The relation between these different molecular weight for general polymer is obvious in Fig. 1 that  $M_n > M_w > M_z$ . These different types of molecular

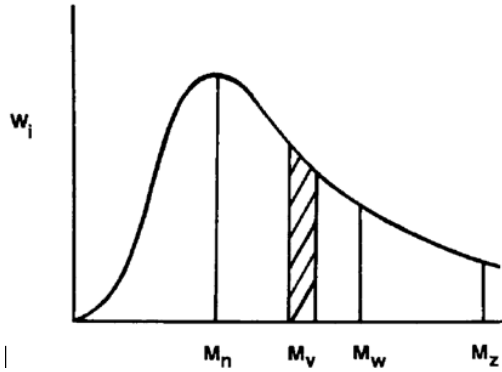


Fig. 1: Molecular weight of species i

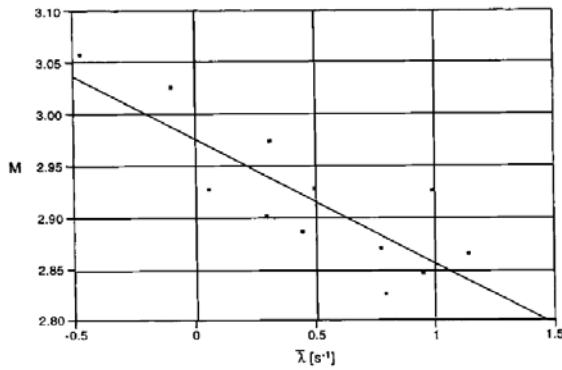


Fig. 2: Correlation of  $M$  and  $\bar{\lambda}$

weight have physical meaning because in different practical methods to predict the molecular weight often measure one of them. For example, number average molar mass obtain from osmometry measures and weight average molar mass obtain by small-angle laser light scattering measures. Also, viscosity-average molecular weight obtains from viscosimetry and intrinsic viscosity experiment and the z-average molecular weight by sedimentation.

**Rheological formulation:** It is known that the linear viscoelastic model is described the linear behavior of bitumen's. The complex modulus  $G^*(\omega)$  is the material function that obtained in such an experiment. It can be written as equation 1 that  $|G^*|$  is the magnitude of  $G^*$ ,  $\delta$  is the phase angle between the strain and stress and  $\omega$  is the frequency. Equation 2 shows the complex function that can be successfully modeled the regular and polymer-modified bitumen's. In this equation  $\eta_0$  is the zero shear rate viscosity and  $\lambda_k, \mu_k$  are positive relaxation times. Also, the phase angle is given as Eq. (3). Equation 4 illustrate a simple power law that can be covered the mass region ( $M$ ).  $K$  and  $\alpha$  in last equation are constants (Zanzotto *et al.*, 1996):

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

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

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

$$M = k\omega^{-\alpha} \quad (4)$$

$$x = \log \omega \quad (5)$$

The transformation obtains in above equation shown the molecular weight is related to the frequency. Tuminello (1986) was shown a good correlation of  $M$  for narrow-distribution polystyrenes. Figure 2 illustrate the correlation of  $M$  function in Eq. (4).

Molecular weight obtained by vapor-pressure osmometry. This figure clearly shown that the data for bitumens follow the Eq. (4), but it is difficult to predict a unique constant for the whole studied samples group. However, the best fit of the constant data reach for  $\alpha = 0.1231$  and  $k = 2.976$ . The phase angle function as molecular weight obtains from Eq. (3, 4 and 5). This function is shown in equation 6. The molecular weight function can be deriving by differentiation of the last Eq. (7). This equation shows that it is possible to find bitumens structure information from the phase angle study.  $|G^*|$  and  $\delta$  in Eq. (8 and 9) are obtained from Eq. (1), respectively:

$$\delta(\omega) = 1 - \int_{M=k10^{-\alpha x}}^\infty W(M') dM' \quad (6)$$

$$W(M) = -\frac{10^{\alpha x}}{\alpha k \ln 10} \frac{d\delta}{dx} \quad (7)$$

$$|G^*(\omega)| = \omega\eta_0 \left[ \frac{\prod_1^m (1+(\omega\mu_k)^2)}{\prod_1^n (1+(\omega\lambda_k)^2)} \right]^{1/2(n-m)} \quad (8)$$

$$\delta(\omega) = \frac{\pi}{2} - \frac{1}{(n-m)} \left[ \sum_1^n a \tan(\omega\lambda_k) - \sum_1^m a \tan(\omega\mu_k) \right] \quad (9)$$

The dependence of the phase angle  $\delta$  on molecular weight is well shown by Zanzotto *et al.* (1999) in Fig. 3. The sample undergoes a series of relaxation processes during dynamic experiments. It is possible to picture the tested material as a mixture of various species with relaxation modes, where each mode is associated with a characteristic monodisperse molecular weight. As the oscillation frequency increases smaller and smaller components of the system will relax and the already relaxed parts of the system will act as a diluents for the unrelaxed components.

•  $M_{vpo} = 610, \Delta M_{vpo} = 844, \square M_{vpo} = 1123$

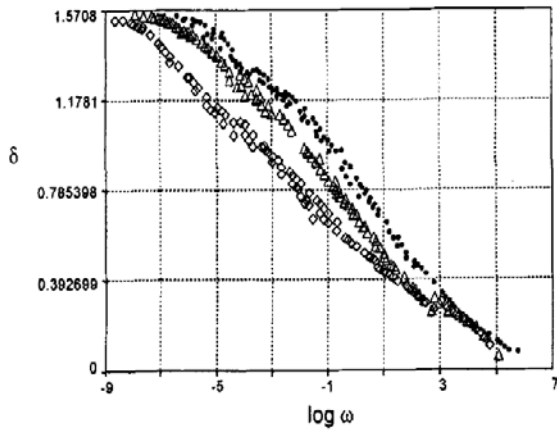


Fig. 3: Phase angle of regular asphalts with different vapor pressure osmometry molecular weight (Mvpo)

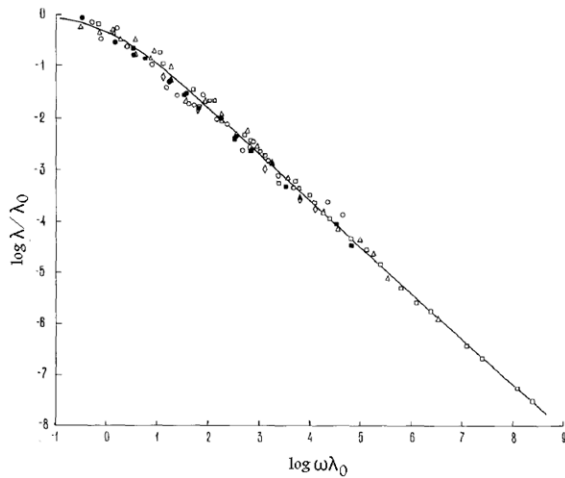


Fig. 4: Generalized characteristic of relaxation properties of bitumens at 25°C

Bitumens have a wide range of relaxation times. Therefore on the basis of their relaxation properties, generalized characteristics of viscoelastic properties must be obtained. In this case it may be suitable to use of dimensionless parameters. The relaxation time of bitumen's can be written as equation 10 by analogy with polymer systems. Also, the initial relaxation time at a frequency tending to zero is shown in equation 11. The initial relaxation time may be obtained from the logarithm of the characteristic relaxation time depending on frequency by extrapolating their values when frequency tending to the zero. The empirical equation shows in equation 12 that illustrate the dependence for bitumen's obtained by Vinogradov *et al.* (1977). This equation shows graphically in Fig. 4. With Eq. (7 and 9), one can calculate the Molecular Weight Distribution (MWD) that shown in Eq. (13):

$$\lambda = \frac{2G'(\omega)}{\omega G''(\omega)} \quad (10)$$

$$\lambda_0 = \lim_{\omega \rightarrow 0} \frac{2G'(\omega)}{\omega G''(\omega)} \quad (11)$$

$$\lambda/\lambda_0 = \frac{2G'(\omega)}{\omega \lambda_0 G''(\omega)} = \frac{1}{1+(\omega \lambda_0)^{0.9}} \quad (12)$$

$$W(M) = \frac{10^{\alpha x + x}}{ak(n-m)} \left( \sum_{h=1}^n \frac{\lambda_h}{1+(10^x \lambda_h)^2} + \sum_{h=1}^m \frac{\mu_h}{1+(10^x \mu_h)^2} \right) \quad (13)$$

### RESULT AND DISCUSSION

There are some rheological relations obtained in previous section to describe molecular weight distribution. Relaxation time is one of the important characteristic in bitumen's rheological functions and it is so different in conventional and polymer modified bitumen's and its amount is related to the type of polymer use in modified bitumen's. The molecular weight of such polymer used in modified bitumen is more than base bitumen and this cause to increase the molecular weight of bitumen mixture and its relaxation times. There is a well studied done by Yousefi *et al.* (2000) in molecular distribution of base and modified bitumen. In this section, we tried to predict the effect of relaxation time of bitumen mixture in different range on molecular weight distribution function. First of all, their obtained from zero relaxation time in a wide range by using Eq. (12). The change of this rheological property is shown in Fig. 5 in a wide range of frequency. It's so clear that the relaxation times  $\lambda_i$  tending to zero relaxation time in low frequency and its tending to zero in high frequency. It's show that its goes to single line for frequency more than 10 cycle/s by different zero relaxation time.

It is need to obtain relaxation times in different range of frequency to predicting the molecular weight distribution by Eq. (9). These data collected in Table 1 for different zero relaxation time. The molecular weight distribution was shown in Fig. 6 by using relaxation time and Eq. (9). The constant in this equation obtained from the correlation between the molecular weight and average relaxation time that shown in Fig. 2. It's clear in Fig. 6 that molecular weight distribution is sharp in low zero relaxation time and it's so wide in high zero relaxation time and this means that the molecular weight of bitumen's mixture increase by increasing the zero relaxation time and the distribution of molecular weight be wider.

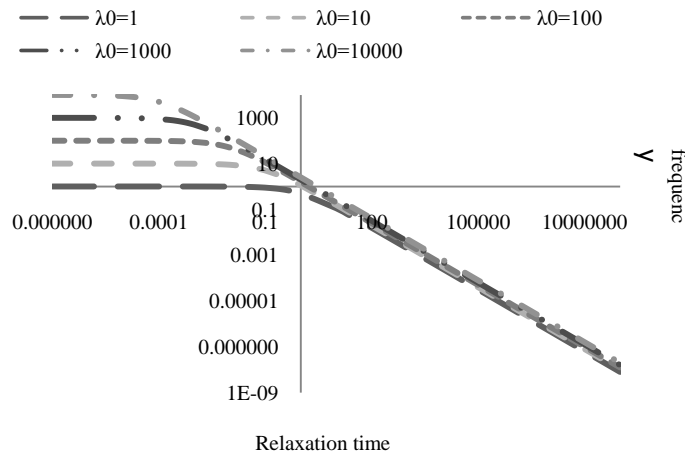


Fig. 5: Relaxation time instead frequency

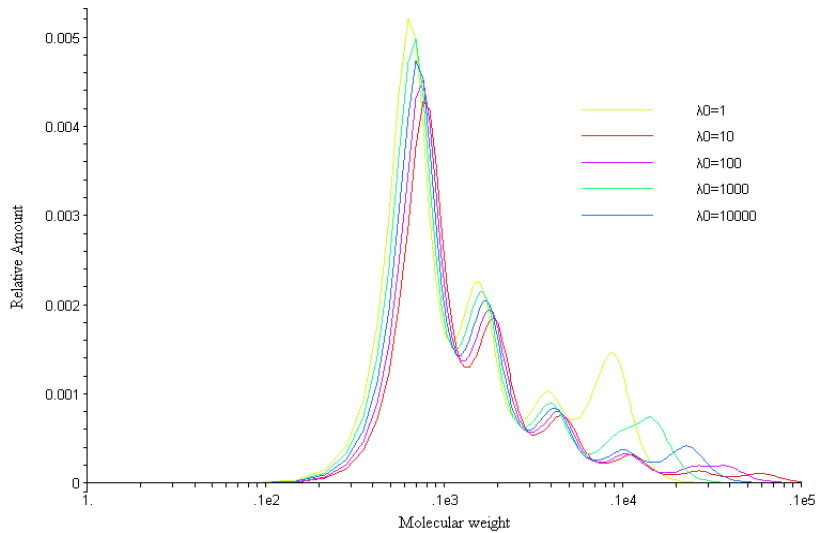


Fig. 6: Molecular weight distribution

Table 1: Relaxation times from different zero relaxation times amount

$\lambda_i$ (1)	$\lambda_i$ (2)	$\lambda_i$ (3)	$\lambda_i$ (4)	$\lambda_i$ (5)
1	10	100	1000	10000
0.999749	9.980087	98.43983	888.1842	5000
0.984398	8.881842	50	111.8158	156.0166
0.5	1.118158	1.560166	1.991289	2.511256
0.015602	0.019913	0.025113	0.031622	0.039811
0.000251	0.000316	0.000398	0.000501	0.000631
3.98E-06	5.01E-06	6.31E-06	7.94E-06	1E-05

### CONCLUSION

A method to calculate the molecular weight distribution of asphalts based on the measurement of their dynamic mechanical properties has been developed. Asphalt molecular weight distribution related to the phase angle of the complex modulus appears to be the dynamic mechanical material function. Also, it is possible to predict the molecular weight distribution by using the zero relaxation time.

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