

POLYMER MODIFIED ASPHALTS RHEOLOGICAL PROPERTIES WAGNER MODELING

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Wagner Model¹ is a modification of the Lodge model², in which the non-linear visco-elastic region is described through a time and strain dependent memory function, $\mu(t, \gamma)$. Wagner modified the Lodge model by representing the memory function as the product of two functions: the linear visco-elastic memory function (strain independent), $\mu(t)$, and the damping function (strain dependent) $h(\gamma)$. The resultant constitutive model, that is the relation between stress and strain, is given by the following equation:

$$\sigma(t) = \int_0^t \mu(t-t') h(t, t') \gamma(t, t') dt' + \gamma(t) h(t) \int_{-\infty}^0 \mu(t-t') dt' \quad \dots\dots(1)$$

donde: $\sigma(t)$ is the stress, $\mu(t-t')$ is the memory function evaluated at $t-t'$

t is the time at which the stress or strain is being evaluated

t' represents all the times previous to time t

$h(\gamma)$ is the damping function γ is the strain, and $\int_{-\infty}^0 \mu(t-t') dt' = G(t) \dots\dots(2)$

where $G(t)$ is the linear visco-elastic relaxation modulus. Analytical solution of equation for the stress or the strain, depends on the functionality of the memory and damping functions, as well as on the functionality of the strain. Memory functions have been typically represented as a serie of exponentials (references) and is the way they will be represented in this study. The functionality of the damping function has been represented in different ways.

$h(I_1, I_2) = 1/[1 + a(I_2 - 3)] \dots\dots(3)$ where $I_2 = \beta I_1 + (1-\beta)I_2$ $h(\gamma) = \exp(-n_1 \gamma)$ by other way, it is possible used a double exponential damping function as suggested by Laun³:

$$h(\gamma) = f_1(\exp(-n_1|\gamma|)) + (1-f_1)(\exp(-n_2|\gamma|)) \dots (4)$$

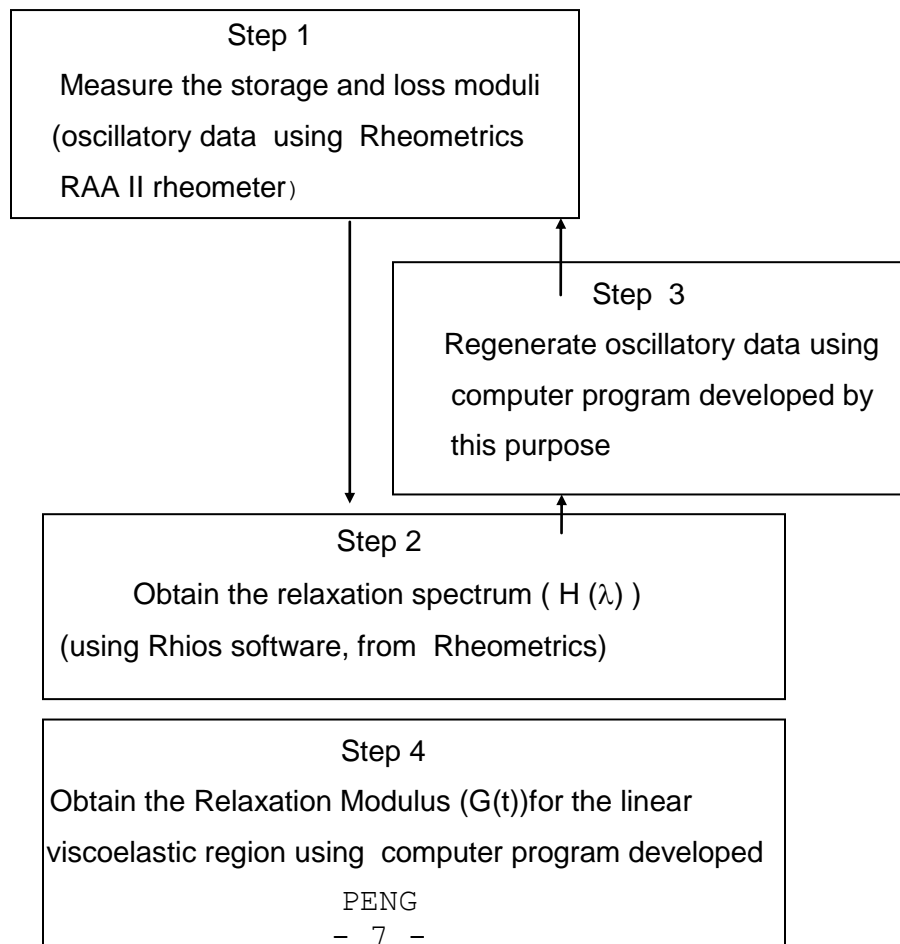
Solution for shear response at constant strain rate

For a situation where the strain is constant (e.g. constant shear rate at a given time), equation can be solved to determine the viscosity and the first normal stress difference.

Shear Viscosity

$$\eta(t, \dot{\gamma}_o) = f_1 \sum_{i=1}^n g_i \lambda_i^2 / (1 + n_1 \lambda_i \dot{\gamma}_o)^2 \{1 - \exp[-D_1 t] * [1 - n_1 \lambda_i \dot{\gamma}_o D_1 t]\} + (1 - f_1) \sum_{i=1}^n g_i \lambda_i^2 / (1 + n_2 \lambda_i \dot{\gamma}_o)^2 \{1 - \exp[-D_2 t] * [1 - n_2 \lambda_i \dot{\gamma}_o D_2 t]\} \dots (5)$$

The following diagram shows the steps followed to obtain the memory and damping functions:



by the author for this purpose

Step 5

Obtain the Memory function ($\mu(t)$)
for the linear visco-elastic region using
computer program developed by the author
by the author for this purpose

Step 6

Fit the Relaxation Modulus with an eight exponential function:

$$G(t) = \sum_{i=1}^n g_i \exp(-t/\lambda_i) \text{ and obtain the Memory function:}$$

$$\mu(t) = \sum_{i=1}^n g_i \lambda_i \exp(-t/\lambda_i)$$

Step 7

Determine the damping function by
fitting the experimental shear viscosity, using equation at steady state,
setting $f_1=0.57$ and adjusting the values of n_1 and n_2 until agreement :

$$\eta(t, \dot{\gamma}_o) = f_1 \sum_{i=1}^n g_i \lambda_i^2 / (1 + n_1 \lambda_i \dot{\gamma}_o)^2 + (1 - f_1) \sum_{i=1}^n g_i \lambda_i^2 / (1 + n_2 \lambda_i \dot{\gamma}_o)^2$$

Step 8

Calculate the
shear viscosity v.s.

Step 9

Calculate the first
normal stress

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Step 10

Calculate the first
normal stress

versus time at several
shear rates

difference versus time
at steady state

difference versus time
at several shear rates

Flow diagram showing the procedure followed to obtain the memory and damping functions.

Limiting the sums in Eq. (5) to the first three terms, the relation has a total of 9 parameters, which can be used to fit the experimental data. As an example, the fit for the type 3 curve, which is the more “complicated” one, together with the Cox–Merz and Gleissle relations is shown in Fig. 1. The two empirical rules fail to account for the shear-thickening behavior, and, they both seem to indicate a zero shear viscosity coinciding with that of Region II. Eq. (5) is able to describe reasonably well both the shear thickening and thinning regions. It is quite obvious that

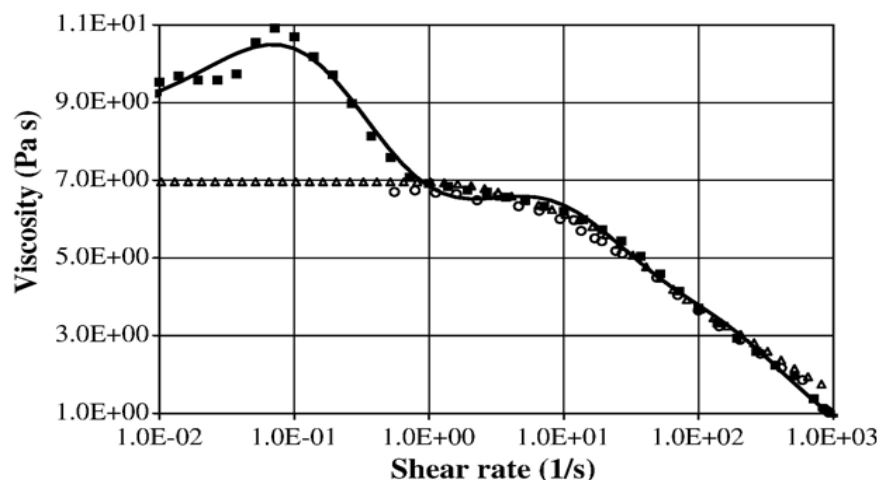


Fig. 1. Viscosity function for a 70/100 BA from vacuum distillation modified with 7% of radial SBS. Temperature = 130 °C. Experimental and calculated data: ■=experimental; ○=Cox-Merz; △=Gleissle; solid line=fit from Eq. (5).

Eq.(5) with a large number of parameters, could be intrinsically able to fit the curve, but with little physical meaning. In this sense, it is interesting to show Fig. 2 where the “short-spectrum”, given by the moduli g_i and relaxation times λ_i calculated during the fitting procedure, is positioned with respect to the linear viscoelastic relaxation spectrum. It can be seen how the spectrum from the fit of the viscosity function falls quite precisely over the linear viscoelastic spectrum, exactly in the zone corresponding to the largest relaxation times. Further fitting examples are reported in ^[4,5].

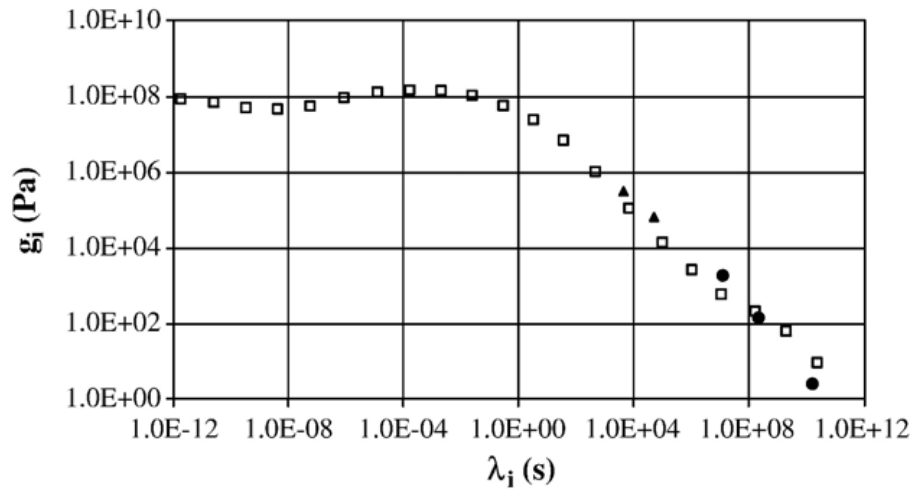


Fig. 2. Comparison between linear viscoelastic spectrum (\square), short-spectrum from Eq. (5) (\bullet) Material and conditions as described in Fig.1; the values are reported to the reference temperature of 0 °C by means of the WLF shifting parameters.

Conclusions

It is well known that all rheologists desire to correlate the knowledge of a material structure at the molecular level with its viscoelastic properties. At best then, a phenomenological model, based only on physical and measurable parameters, would be closely related to the structure of the material, thus providing a tool with general and predictive capabilities. Researchers working on the well-defined polymers still have a long way ahead to reach this goal, but this is a far better situation than that of scientist working on asphalts. Polymer modified asphalts are blends of these two materials and their study and comprehension are very important for the prediction of the “in life” service. When the blending leads to the formation of a polymeric network, swelled by the asphalt components but still maintaining the main features of its original architecture, the overall rheological properties basically reflect those of the polymer. During the last few decades, attention has primarily been paid to the linear properties of these materials. However, the disregarded nonlinear properties actually appear to be the most promising and prone to reveal the “secrets” of polymer modified asphalts.

References:

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