

SLOW MECHANICAL RELAXATION IN ASPHALT

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INTRODUCTION

Asphalt (or bitumen) is one of the earliest construction materials used by mankind. However, despite the long history of its use and the important role it plays at the present time, in the construction of pavements, the composition and especially the structure of asphalt is still not fully understood. It is generally believed that asphalt is a multiphase system in which the large and polar molecules called asphaltenes, or their agglomerates are dispersed in the medium consisting of the smaller molecules with low or no polarity. Opinions on how the asphalt structure is arranged vary (1, 2, 3). The study of asphalt structure is made extremely difficult by the nature of this material. Non-invasive methods such as dynamic mechanical or electric testing, which investigate the asphalt in its original state may greatly contribute to our knowledge of the asphalt internal structure.

STRETCHED EXPONENTIAL RELAXATION

Around 1835, in Gottingen, Wilhelm Weber made the first systematic investigation of elastic "after-effect" in silk and glass threads (4). He noted that a weight suspended from such fibres generates an instantaneous elongation followed by an additional time dependent strain which recovered when the load was removed. For the dependence of displacement x on time t , Weber used a power law. The problem of after effect (creep in modern terminology) has been further studied by Rudolf Kohlrausch. He noticed the analogy with time dependent electric displacements, q , in charged capacitors and proposed for this effect the stretched exponential law: $q(t) = q_0 + \exp(-t/\lambda)^\beta$. In 1863 Frederick Kohlrausch (5) (the son of Rudolf) used the stretched exponential as an empirical fit for creep and relaxation data in silk and glass fibres and in rubber. The stretched exponential law has been revived after more than one hundred years in the study of dielectric relaxation. Usually the analysis of dielectric relaxation in polymers is focused on the complex dielectric "constant" $\epsilon^*(\omega)$ and its deviation from the form derived from a single relaxation time (6). A change of interest from frequency to time, i.e. from ϵ^* to the relaxation function $\phi(t)$ has been generated by the work of G. Williams and D. Watts (7). They found that the stretched exponential can fit data for many glassy and polymeric materials. In the past decade this form has been used to fit a wide variety of experimental data, dielectric, enthalpic, dynamic light scattering, magnetic relaxation, reaction kinetics, etc. (8). The possibility to use the stretched exponential in regular and polymer modified asphalts is discussed in the next paragraph.

STRETCHED EXPONENTIAL AND DYNAMIC MATERIAL FUNCTIONS

As usually we assume that for small deformations, the general linear viscoelastic constitutive equation is valid, i.e.

$$\underline{\tau}(t) = \int_{-\infty}^t -M(t-t') \underline{\dot{\gamma}}(t, t') dt' = \int_{-\infty}^t G(t-t') \underline{\dot{\gamma}}(t, t') dt' \quad 1)$$

Here, $M(t-t') = M(s) = -dG(s)/ds$; M represents the fluid memory, and G is the relaxation modulus (relaxation function). Extra stress tensor $\underline{\tau}$ is related to the strain tensor $\underline{\gamma}$, or to the rate of strain tensor $\underline{\dot{\gamma}}$ via 1). In the case of small amplitude oscillatory shear motion the complex modulus $G^*(\omega)$ is given as (9)

$$G^*(\omega) = i\omega \int_0^{\infty} G(s) \exp(-i\omega s) ds \quad 2)$$

Assume that the relaxation function, $G(s)$ has the form of stretch exponential,

$$G(s) = C \exp(-(s/\lambda)^\beta) \quad 3)$$

where C , λ , and β are constants.

Using the series representation of exponential function, and the definition of gamma function, the complex modulus $G^*(\omega)$ corresponding to the stretched exponential relaxation can be formally written as

$$G'(\omega) = C \sum_{k=0}^{\infty} \frac{\Gamma(\beta k + 1)}{k!} \cos\left(\frac{\pi}{2}(2-\beta)k\right) \left(\frac{1}{\omega\lambda}\right)^{\beta k} + iC \sum_{k=0}^{\infty} \frac{\Gamma(\beta k + 1)}{k!} \sin\left(\frac{\pi}{2}(2-\beta)k\right) \left(\frac{1}{\omega\lambda}\right)^{\beta k} \quad 4)$$

Introducing

$$\lambda^{-\beta} \equiv \alpha \quad 5)$$

the storage and the loss moduli generated by the stretched exponential relaxation function 3) are given as follows:

$$G'(\omega) = C \sum_{k=0}^{\infty} \frac{\Gamma(\beta k + 1)}{k!} \left(\frac{\alpha}{\omega\beta}\right)^k \cos\left(\frac{\pi}{2}(2-\beta)k\right) \quad 6)$$

$$G''(\omega) = C \sum_{k=0}^{\infty} \frac{\Gamma(\beta k + 1)}{k!} \left(\frac{\alpha}{\omega\beta}\right)^k \sin\left(\frac{\pi}{2}(2-\beta)k\right) \quad 7)$$

It is clear that these series representations of the components of the complex modulus do not converge for all $\omega \in (0, \infty)$. However, by choosing a finite frequency subinterval $\omega \in (a, b)$ one can always find the values of parameters λ , β , and C in such a way that the series in 6) and 7) will approximate, with the prescribed precision, G' and G'' on (a, b) . This idea is applied in the next paragraph to one regular and one polymer modified asphalt.

REGULAR ASPHALT MODIFIED BY SBS POLYMER

Dynamic material functions of a regular asphalt 200/300 Pen grade have been dynamically tested at different temperatures and the master curves of G' and G'' (ref. $T=0^\circ\text{C}$) prepared by the time temperature shifting. The mentioned regular asphalt has been modified by SBS copolymer. It is known (10) that SBS copolymer exhibits a rheological transition from Newtonian to non-Newtonian behavior at a region of higher temperature. In the low temperatures the SBS system is plastic with a yield stress. It is believed (10) that such a transition is generated by a transition of the structure from microphase-separated state to the homogeneous state.

Again the dynamic material functions of this PMA (polymer modified asphalt) have been measured and the master curves of G' and G'' prepared. The shift factor a_T for these master curves was fitted to Arrhenius and WLF forms.

The domain of experimental master curves G' and G'' for the regular 200/300 Pen grade asphalt, is $\log \omega \in [-5.6, 7]$ and we have found that the series representations 6) and 7) can be used for this sample if the domain is subdivided into three subdomains. These subdomains are: $A = \{\log \omega \in [-5.6, 1]\}$, $B = \{\log \omega \in [-1, 2.5]\}$, $C = \{\log \omega \in [2.5, 7]\}$. The given subdomains represent a minimum number of subintervals covering the domain of the master curve for regular asphalt 200/300 Pen grade, in the sense that minimally three stretched exponential; relaxation functions 3) are necessary for the description of the whole master curves G' and G'' . The parameters of the stretched exponentials in all three subdomains are: in A, $\alpha = 7.479$, $\beta = 0.0857$, $C = 4.075e+09$; in B, $\alpha = 6.1826$, $\beta = 0.1346$, $C = 9.4056e+08$; in C, $\alpha = 10.0824$, $\beta = 0.237$, $C = 4.231e+08$

The storage, G' , and the loss, G'' , moduli were calculated according to Equations 6) and 7). In these calculations the sums of series were terminated when the absolute value of the next term was less than 10^{-9} , thus strictly speaking the calculated values of G' and G'' are approximations. The compositions of calculated G' and G'' are compared with the experimental data (master curves at reference $T = 0^\circ\text{C}$) in Figs. 1, 2. The high frequency (low temperature) behavior is better seen in Fig. 2. The graph of G'' clearly shows the maximum of G'' . The high frequency behavior of G' is probably overestimated by the series approximation in the subdomain C. However, it is also possible that the last three experimental points of Fig. 1 represent the region which is difficult to access experimentally - these points are measured at $T = -30^\circ\text{C}$, i.e. roughly around the glass transition temperature ($T_g = -27^\circ\text{C}$).

The domain of experimental master curves G' and G'' , for the PMA is $\log \omega \in [-8, 7.4]$. The minimum number of subdomains, covering this domain in the sense of data fit to the least number of stretched exponentials, is four. The subdomains are: $\bar{A} = \{\log \omega \in [-8, -2.8]\}$; $\bar{B} = \{\log \omega \in [-2.8, 3.5]\}$, $\bar{C} = \{\log \omega \in [3.5, 5.4]\}$; $\bar{D} = \{\log \omega > 5.4\}$. The last subdomain, \bar{D} , covers the interval of low temperatures (again around the T_g of the base asphalt 200/300) Pen grade, and the caution is in place in considering the experimental data in this region. Experimental data were

again fitted to the stretched exponential relaxation, i.e. the series representation 6) and 7) were used in each subdomain. Parameters of the stretched exponentials in these subdomains are: in \bar{A} , $\alpha = 4.369$, $\beta = 0.0792$, $C = 3.76e+07$; in \bar{B} , $\alpha = 7.931$, $\beta = 0.081$, $C = 4.186e+09$; in \bar{C} , $\alpha = 11.112$, $\beta = 0.2174$, $C = 3.92e+08$; in \bar{D} , $\alpha = 27.03$, $\beta = 0.3034$, $C = 3.02e+08$. The compositions of calculated G' and G'' are compared with the experimental data (master curves) in Figs. 3, 4. It is clear that at highest frequencies (lowest temperatures) the fit is not as good as in frequencies $\log \omega \leq 6$. Again one has to stress the experimental difficulties in this region of temperatures.

DISCUSSION

The stretched exponential relaxation function seems to be able to generate reasonably accurate storage and loss moduli for both regular and polymer modified asphalts. The series representation 6) and 7) can be used for the estimates of $G'(\omega)$ and $G''(\omega)$ on any finite subinterval of frequencies. It is clear from the results obtained in the previous paragraph that the parameters of the stretched exponential relaxation function depend on the temperature. Not surprisingly the "relaxation" time λ is very low (order 10^{-11} for regular asphalt, and order 10^{-9} for PMA) at the lowest reduced frequencies (highest temperatures) where asphalts have a Newtonian behavior. On the other hand, at high reduced frequencies (temperatures around T_g in the studied case) the value of λ , in both neat and modified asphalts is of order 10^{-5} .

There are now several mechanisms proposed for the stretched exponential (6), one of the most interesting is the defect diffusion model (7). According to this model, mobile defects move randomly through the medium and generate local conformal abnormalities in the system. On leaving the site of such a local disturbance the defect will cause a disturbance at some other site of the medium. After some time, the neighbourhood of the disturbed "particle" will relax, as the system returns to equilibrium. Thus the migration of defects may cause a mechanical relaxation. If there is a finite concentration (c) of defects, the probability that the "particle" will be reached at time t by one of the N defects in a volume N/c is given as (12).

$$\phi(t) = \exp(-cI(t)) \quad 8)$$

Here $I(t)$ is the number of distinct "particles" attacked by a defect at time t . If each defect undergoes a random walk with the pausing-time distribution $\psi(t)$ there are two important classes of $\psi(t)$. In the first case the form of ψ is exponential

$$\psi(t) \sim \exp(-\lambda t), \quad \lambda = \text{const.} \quad 9)$$

After some time this becomes a classical diffusion which leads to Debye's result (6), $\phi(t) = \exp(-t/\lambda)$, in three-dimensional case. The second case are distributions with an inverse-power tail

$$\psi(t) \sim t^{-(1+\alpha)}, \quad 0 < \alpha < 1 \quad 10)$$

In this case

$$I(t) \sim \begin{cases} t^\alpha & \text{in 3 dimensions} \\ t^{\alpha/2} & \text{in 1 dimension} \end{cases} \quad 11)$$

Substituting 11) into 8) one obtains the stretched exponential form. The defect diffusion model is based on the movement of defects. However, the nature of defects is not known, and many possibilities have been suggested. For example, it has been suggested that a mobile carbonate (CO_3) bond is the "defect" in some high-impact resins, (13). In the case of studied asphalts one can see that the exponent β is of order 10^{-2} at higher temperatures and almost four times larger at low temperatures (around T_g of the base asphalt). Thus the "defect" seems to move in a quasi-one-dimensional motion at higher temperatures and perform a three-dimensional walk at temperatures close to T_g .

In conclusion, it appears that the stretched exponential is important not only in theoretical analysis of complex systems, but can also be successfully used in direct modelling of the stress relaxation in such systems. Such modelling in crack sealants will be discussed elsewhere.

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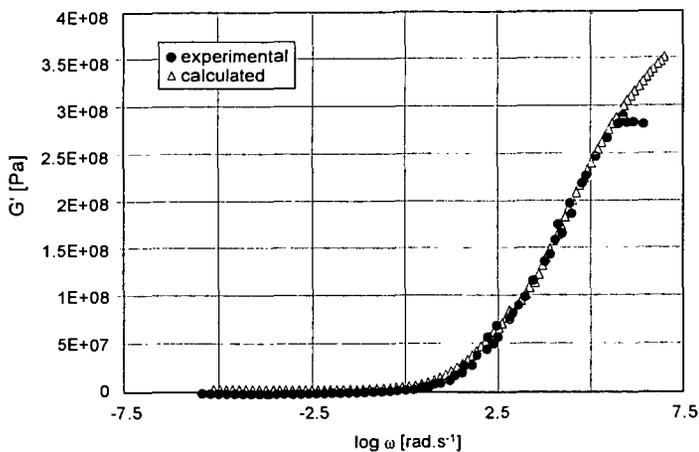


Figure 1. Regular asphalt, G' .

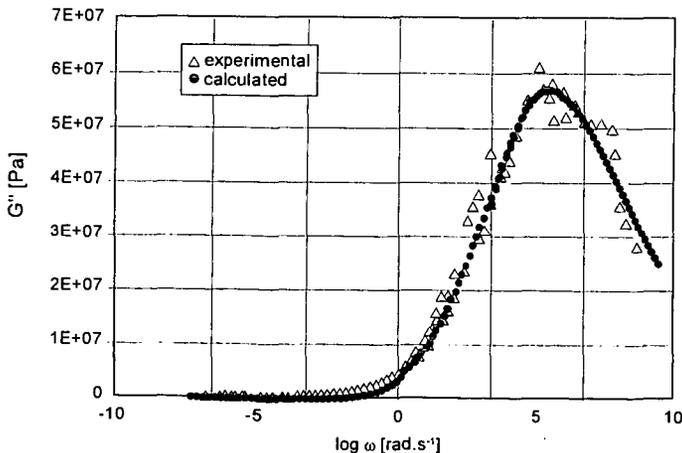


Figure 2. Regular asphalt, G'' .

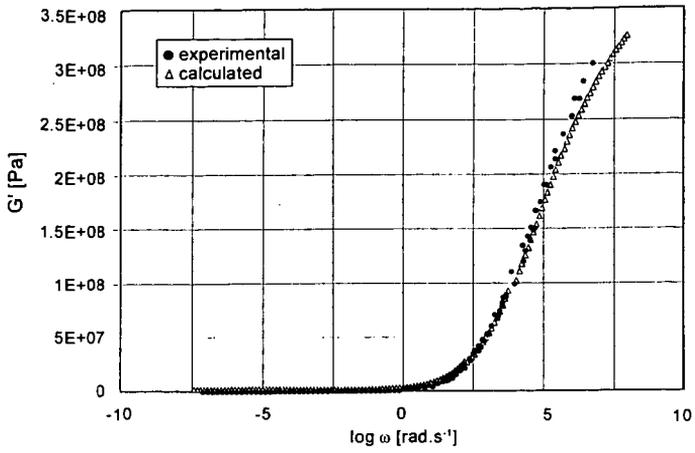


Figure 3. Polymer modified asphalt, G' .

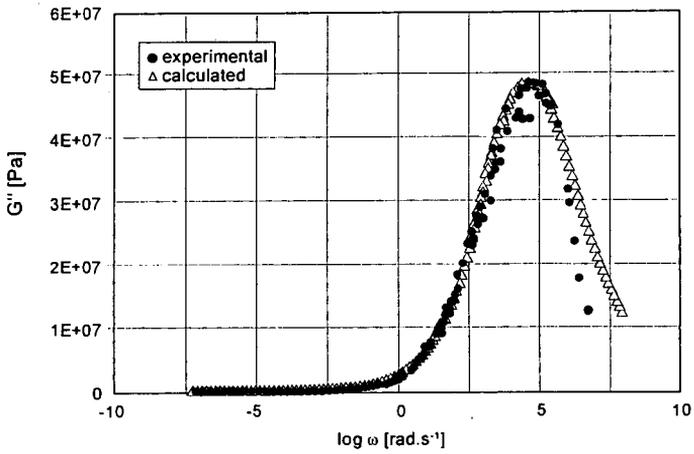


Figure 4. Polymer modified asphalt, G'' .