Generation of isothermal relaxation spectrum for bitumen

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ABSTRACT: The relaxation spectrum is a critical tool for characterising the viscoelastic properties of bitumen. This study investigates the challenges associated with generating an isothermal relaxation spectrum from frequency domain data spanning a short range of frequencies. Experiments were carried out on unmodified VG30 bitumen at 0 °C and 60 °C across a limited frequency range spanning 1.39 decades. This was extended using generalised linear viscoelastic models with an appropriate number of relaxation modes to derive continuous relaxation spectra. The range of the relaxation time is found to be more for 0 °C than for 60 °C and in both the cases, the corresponding frequency range to capture the dominant relaxation modes was found to be too high to be accessed by the testing equipment.

1 INTRODUCTION

A relaxation spectrum (discrete or continuous) offers a distribution of relaxation times (Findley et al. 1976, Ferry 1980) and provides a fundamental representation of the mechanical response of a material. Each relaxation time corresponds to a distinct mode of stress relaxation, with the spectrum quantifying the contribution of each mode to the overall viscoelastic behavior. The distribution of relaxation times can be either discrete or continuous, comprising infinitesimal contributions across an infinite range of relaxation times (Ferry 1980). Studies have highlighted several challenges in determining the discrete relaxation spectrum (DRS), including the non-uniqueness of values and the occurrence of negative spectra (Zhang et al. 2020). Though the continuous relaxation spectrum (CRS) also poses problems due to the inversion of integrals, it is preferred over the DRS as it is said to represent the fundamental nature of the relaxation process in many materials (Bhattacharjee et al. 2012).

For bituminous binders and mixtures, scant data exists related to computing the CRS and DRS. The relaxation spectrum can be obtained from experimental data carried out in the time domain (Nivitha et al. 2023), such as stress relaxation or in the frequency domain, such as frequency sweep experiments (Zhao et al. 2018). When the stress relaxation data is used, the time duration of testing influences the relaxation spectrum. In addition to this, the difficulties associated with generating an instantaneous deformation and tracking the rapid initial decay of stress exist in the case of stress relaxation experiments (Narayan et al. 2012, Yu et al. 2020, Xi et al. 2022). Hence, the frequency domain experiments are usually preferred over the time domain experiments, where the experiments are generally carried out over a range of frequencies in the small amplitude oscillatory shear mode. However, the range of frequencies that could be accessed by the equipment typically spans no more than three decades, owing to the limitations of the equipment (Yu et al. 2020). This short frequency range may be insufficient to fully capture the relaxation characteristics of bitumen.

To overcome this issue, most studies on the relaxation spectrum derived from frequency domain experiments utilise information from the master curve obtained through the time-temperature superposition principle (TTSP), which extends the experimental frequency range (Behera et al. 2024, Medam et al. 2024). However, due to the transitory response of bitumen in the temperature range of 20 to 60 °C (Padmarekha & Krishnan 2013, Nivitha et al. 2020), it is not always possible to construct a unique master curve in this temperature range, in addition to the practical difficulty of collecting data over a large range of decades of frequency. Considering this limitation, alternative methods have to be used to extend the frequency window in such instances, which might be using linear viscoelastic models.

This study focuses on the issues concerning the generation of the isothermal relaxation spectrum using frequency sweep experiments carried out over a short frequency range.

2 EXPERIMENTAL INVESTIGATION

The material used in this study is an unaged unmodified bitumen of Viscosity Grade VG30 as per Indian Standards, IS 73 (2018).

The material was subjected to frequency sweep experiments in the strain-controlled mode at temperatures of 0 and 60 °C in a parallel plate system in a Dynamic Shear Rheometer (DSR). The sample dimensions were 8 mm diameter and 2 mm height when tested at 0 °C and 25 mm diameter and 1 mm height when tested at 60 °C. The following frequencies were applied in a step-wise manner, starting with the highest frequency: 0.1, 0.3, 0.5, 0.7, 0.9, 1.3, 1.5, 1.7, 1.9, 2.1 and 2.5 Hz. Twenty cycles of data were collected for each frequency. The amplitude was kept constant across the frequencies and was chosen such that the material response is linear as per ASTM D7175(2023). This was ensured by carrying out an amplitude sweep experiment at the highest frequency of 2.5 Hz for each temperature. The test matrix is shown in Table 1.

Table 1. Test matrix.

Temperature (°C)	Strain amplitude (%)	Frequency (Hz)
0	0.27	0.1, 0.3, 0.5, 0.7, 0.9,
60	8.6	1.3, 1.5, 1.7, 1.9, 2.1, 2.5

3 ANALYSIS AND RESULTS

The storage and loss modulus values in terms of the CRS are given as,

$$G'(\omega) = \int_{-\infty}^{\infty} \frac{\omega^2\tau^2}{1+\omega^2\tau^2} h(\tau) d\ln\tau \quad (1)$$

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{\omega\tau}{1+\omega^2\tau^2} h(\tau) d\ln\tau. \quad (2)$$

Here, ω is the angular frequency, τ is the relaxation time and $h(\tau)$ is the relaxation spectrum. To construct the CRS, the regularisation method is used and this is achieved with the help of an open-source Python programmed code, pyReSpect (Takeh & Shanbhag 2013). Here, the CRS, $h(\tau) = e^{H(\tau)}$ is obtained by minimising the cost function using the Tikhonov regularisation. This yields the $H(\tau)$ curve, which is a trade-off between the smoothness of the curve and the overfitting of the curve. Following this, this program requires the values of frequency, storage modulus and loss modulus to generate the CRS.

The pyReSpect program yields the relaxation spectrum spanning the range given by $e^{\frac{B\pi}{2}}/\omega_{max} \leq \tau \leq e^{-\frac{B\pi}{2}}/\omega_{min}$ by allowing for the choice of B which takes the values of -1, 0 or 1. The value of $B = 0$ generates the relaxation time range where it is restricted by the experimental frequency range, i.e., $1/\omega_{max} \leq \tau \leq 1/\omega_{min}$. When $B = 1$, the range of the relaxation time gets reduced by 1.36 decades, i.e., 0.68 decades on either side of the range. When the value of $B = -1$, the experimental frequency range is increased by 0.68 decades on either side of the maximum and minimum values of frequency, i.e., the entire frequency range increases by 1.36 decades. In this study, the experiment covers frequencies ranging from 0.1 to 2.5 Hz, which is only 1.39 decades of frequency. Even the choice of $B = -1$ may not be able to yield the necessary frequency window that is required to capture the relaxation characteristics of bitumen, as pointed out by Yu et al. (2020) and hence, the experimental frequency range is extended using a linear viscoelastic model.

3.1 *Choice of the linear viscoelastic model*

Since the material response is obtained at two different temperatures, the same model may not be able to capture the material response across both the test temperatures. In this context, a Generalised Maxwell (GM) model is proposed to capture the response of bitumen at the higher temperature of 60 °C and a Zener model is proposed to capture the response of bitumen at the lower temperature of 0 °C. The GM model consists of several Maxwell models connected in parallel with n relaxation modes and the linear viscoelastic parameters, storage and loss modulus as obtained from the model are given by,

$$G'(\omega) = \sum_{i=1}^{n} \frac{G_i\omega^2\tau_i^2}{1+\omega^2\tau_i^2} \quad (3)$$

$$G''(\omega) = \sum_{i=1}^{n} \frac{G_i\omega\tau_i}{1+\omega^2\tau_i^2}. \quad (4)$$

Here, G_i and τ_i are the relaxation modulus and relaxation time corresponding to the i^{th} relaxation mode. The Zener model is very similar to the GM model but with an additional spring parallel to the Maxwell elements and hence a modulus term G_0 gets added to the storage modulus in Equation (3). The loss modulus remains unchanged. For a given number of modes, the Zener model is found to show better predictions of the linear viscoelastic parameters across the frequencies for the data collected at 0 °C and this is represented as a decrease in the normalised root mean square error (NRMSE) values compared to the GM model as shown in Figure 1.

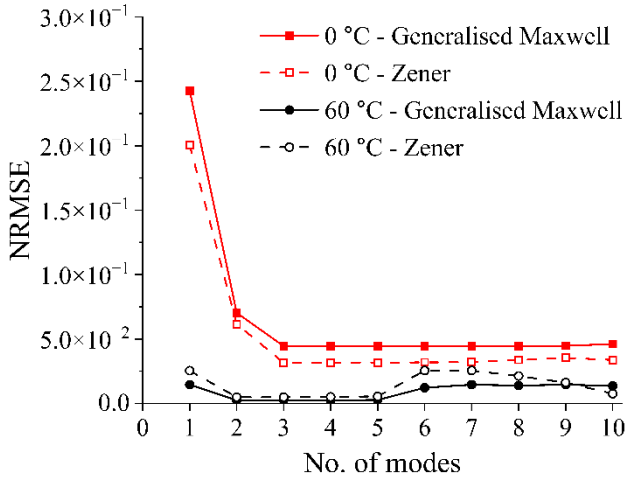


Figure 1. Variation of NRMSE against number of modes for different models.

3.2 *Choice of the number of modes*

It is observed that the NRMSE value decreases significantly with an increase in the number of modes up to a certain value of n and beyond this, there is no significant change or there is an increase in the NRMSE values (Fig. 1). The value of n beyond which there is no further significant decrease in the number of modes is identified as the number of modes for the respective models to predict the material response at the corresponding temperatures. In this context, the number of modes required to predict the material response at 0 and 60 °C are 3 and 2, respectively. The parameters (G_i) associated with the number of modes indicate the DRS of bitumen against the relaxation times (τ_i). An increase in the number of modes beyond the ones identified at the given test temperature was found to yield similar values of the relaxation times, thereby showing redundancy, meaning they do not provide additional insight into the relaxation characteristics of bitumen. Table 2 shows the relaxation moduli and times for different number of modes for 60 °C. It can be observed that beyond $n = 2$, some of the relaxation times are similar and the total distinct values of relaxation time for any number of modes are only 2.

Table 2. Model parameters for different modes for 60 °C

n	G_i (kPa)	τ_i (s)
2	328.33, 0.48	0.001, 0.080
3	131.8 148.20, 0.45	0.001, 0.001, 0.083
4	69.27, 112.99, 96.39, 0.44	0.001, 0.001, 0.001, 0.083

Having identified the suitable model and the number of modes, the frequency range is extended beyond the experimental frequency window and a representative plot is shown in Figure 2.

The CRS is generated using the storage and loss modulus values corresponding to the extended frequency range using the pyReSpect program. The CRS determined for the material at 0 and 60 °C are shown in Figure 3. From the figure, it can be observed that the distribution of relaxation times is greater for 0 °C than for 60 °C.

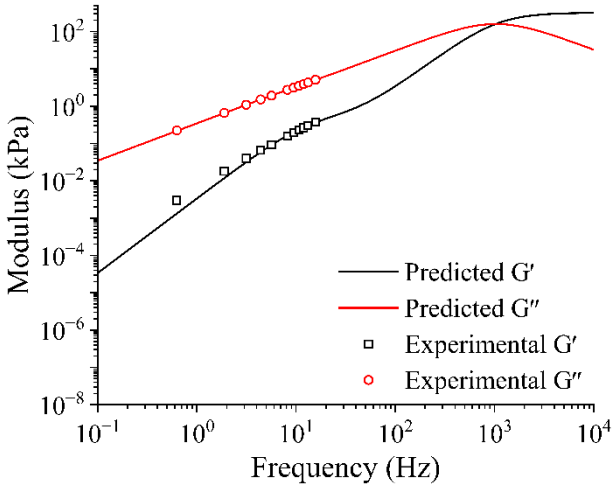
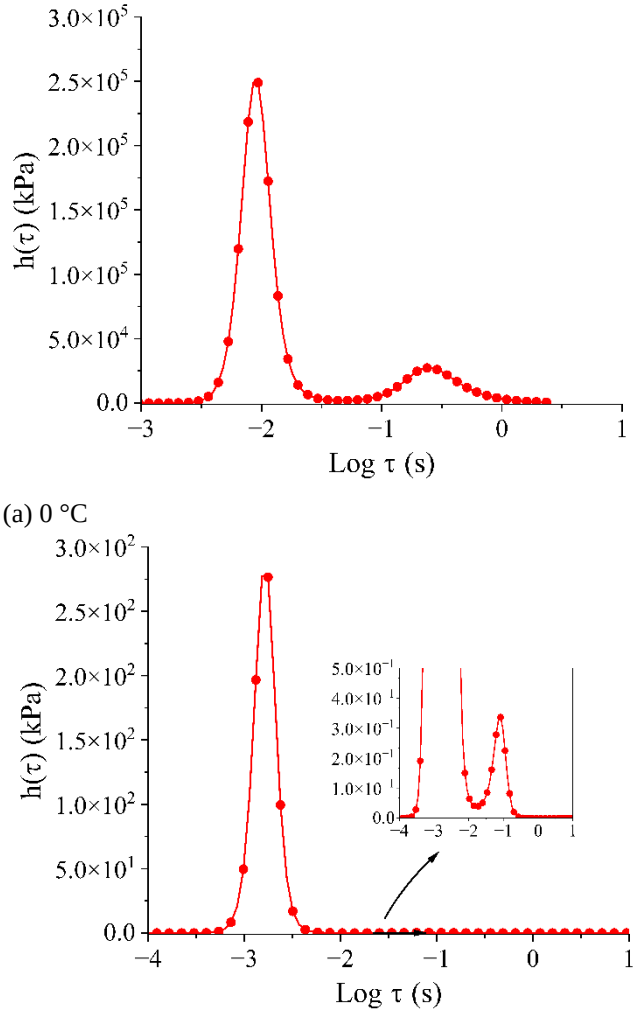


Figure 2. Predicted moduli for extended frequency window at 60 °C.



(a) 0 °C

(b) 60 °C

Figure 3. Continuous relaxation spectrum.

The position and intensity of the peaks observed in all the cases were found to be almost similar to those obtained from the linear viscoelastic model (DRS). In

this context, ideally, the CRS at 0 °C should show three peaks, with the third peak occurring at higher relaxation times. However, it was observed that the model predictions were poor at lower frequencies and hence, were not included in the generation of the CRS for this temperature.

From Figure 3a, it can be observed that the relaxation time required to capture the dominant relaxation characteristics of bitumen spans approximately 3.5 decades at 0 °C, ranging from $\tau_{min} = 10^{-3}$ s to $\tau_{max} = 10^{0.5}$ s. The corresponding frequency range for this relaxation time is ω_{min} = 0.32 rad/s to ω_{max} = 1000 rad/s. Similarly, as shown in Figure 3b, at 60 °C, the frequency range spans approximately 1.5 decades (ignoring the second peak, which is insignificant), extending from ω_{min} = 100 rad/s to ω_{max} = 3162 rad/s. These high frequencies exceed the capabilities of the equipment due to its limitations. Therefore, extending the experimental frequency range is crucial to capture the relaxation characteristics of bitumen. However, it is to be noted that this extrapolated data for a wider frequency range cannot be verified considering the equipment limitations.

In this study, the DRS of bitumen is determined first to extend the frequency range required for generating the CRS. This approach contrasts with methodologies in some existing literature, where the CRS is determined first, and the DRS is subsequently derived to overcome the limitations of the DRS (Bae & Cho 2016). However, such methodologies can be applied only when the experimental frequency range can be extended using the TTSP. In cases where TTSP is not applicable, the DRS must be determined first, followed by the CRS.

4 CONCLUSION

The relaxation spectrum is a crucial parameter in understanding the viscoelastic behavior of materials, particularly bitumen. This study highlights the challenges in generating isothermal relaxation spectra when the frequency range is short. An unmodified VG30 bitumen is subjected to frequency sweep experiment at 0 and 60 °C at 11 frequencies spanning 1.39 decades. The experimental frequency range is extended by appropriate generalised linear viscoelastic models with a suitable number of modes and continuous relaxation spectra were obtained. It was observed that the frequencies required to capture the relaxation behavior of bitumen are much larger than that could be accessed by the equipment.

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