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A CRITICAL ANALYSIS ON THE COMPLEX MODULUS PROVIDED BY DMA

Isadora Ruas Henriques
Lavinia Maria Sanabio Alves Borges
Daniel Alves Castello
Department of Mechanical Engineering, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil
ir.henriques@mecanica.coppe.ufrj.br, lavinia@mecanica.ufrj.br, castello@mecanica.ufrj.br

Marysilvia Ferreira da Costa
Department of Metallurgical and Materials Engineering, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil
marysilvia@metalmat.ufrj.br

Bluma Guenther Soares
Instituto de Macromoleculas, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil
bluma@ima.ufrj.br

Abstract. *Dynamic mechanical analysis (DMA) is a widely used technique to characterize viscoelastic materials as function of temperature and also frequency. This work aims to measure the complex modulus in three different operational modes of a DMA to investigate its frequency- and temperature-dependence, and also to compare all results. Even through the test conditions were almost the same, discrepancies were found between the measured complex modulus. However, the thermorheologically simple behavior could be observed in all measurements.*

Keywords: viscoelastic materials, DMA, complex modulus, thermorheologically simple behavior.

1. INTRODUCTION

Dynamic Mechanical Analysis, also known as DMA, is a powerful technique in the field of rheology, especially in the study of viscoelastic materials, in which it is possible to identify and characterize the material's behavior. It is one of the most common methods used to measure viscoelastic properties as a function of temperature and frequency. It can basically be described as applying a sinusoidal force to a test-specimen and measuring its deformation, or as applying a sinusoidal deformation and measuring its force, or even as applying a constant force/deformation and measuring its creep/relaxation modulus (Deng *et al.*, 2007). Different modality tests can be performed in a DMA and also different test conditions can be imposed to the system.

Generally speaking, DMA is in some sense versatile. Through the tests, one can study about the composition, physical and viscoelastic properties of the material. It is possible to have information about the temperature- and time-dependent behaviour, transitions, extent of phase mixing in blends, degree of crosslinking, crystallinity, interfacial adhesion, ageing, degradation (Lacík *et al.*, 2000) depending on the modality test and the parameters chosen.

However, literature indicates that there are discrepancies in DMA results (McAninch *et al.*, 2015; Kazakevičiūtė-Makovska *et al.*, 2013; Swaminathan and Shivakumar, 2008; Deng *et al.*, 2007; Lacík *et al.*, 2000) for the same viscoelastic property and the same test conditions, regardless the DMA machine. Sometimes, even the DMA manual or the DMA software provides incorrect equations (Swaminathan and Shivakumar, 2008). These discrepancies are often caused by: clamp type, test-specimen dimensions, test-specimen alignment, load amplitude, contact stresses, test-specimen span-to-thickness ratio, thermal lag, scanning rate, heat conductivity, instrument design, machine compliance, vibrations near the equipment, human errors, seasonal variations and evaluation of measured data (Sun *et al.*, 2014; Rodríguez-Pérez *et al.*, 2001; Lee-Sullivan and Dykeman, 2000a,b; Lacík *et al.*, 2000).

In the work of (Rodríguez-Pérez *et al.*, 2001), these influential factors were even classified as control factors and noise factors. The control factors correspond to the factors that can be controlled during the experiment, like, for example, frequency and temperature. On the other hand, the noise factors correspond to two types of factors: (1) those that cannot be controlled such as seasonal variations; (2) those that can be controlled but they are not in order to make the experiment easier to measure, such as temperature at which the test-specimen height is measured.

The lack of guidance on the use of DMA is also another reason for these discrepancies found in literature as discussed

by Swaminathan and Shivakumar (2008). Even though there are several ASTM standards about the material characterization using a DMA, they are not so clear, so specific about test conditions and test parameters, especially in terms of the test-specimen dimensions. Some recommendations can be found in DMA manufacturers manuals from different manufacturers, but nothing is said about the differences found when changing parameters or geometries. Divergencies between DMA manufacturers manuals and ASTM standards are also observerd.

The purpose of this work is to study and compare the complex modulus, $E^*(\omega)$, of a viscoelastic material obtained through different experiments in a PerkinElmer DMA 8000. Measurements were carried out in three different modality tests: single/dual cantilevers and three-point bending, using the same test conditions. Two DMA temperature scanning techniques were performed, namely: temperature scan and temperature-frequency scan. A critical assessment on how DMA calculates the complex modulus in these modes was done. Furthermore, the thermorheologically simple behaviour was verified through Cole-Cole diagram (Han *et al.*, 1993) and Black space (van Gurp and Palmen, 1998).

The paper is organized as follows. Sections 2 gives the principal aspects of the theory of linear viscoelasticity and how DMA calculates the complex modulus. Section 3 explains the experimental set-up. Section 4 presents the experimental results and analysis, followed by concluding remarks in Section 5.

2. FUNDAMENTALS

2.1 Theory of Linear Viscoelasticity

From the theory of linear viscoelasticity (Christensen, 1982), for an isotropic viscoelastic material under small isothermal and small deformation conditions, the one-dimensional stress-strain relation is based on the Boltzmann superposition integral. This is expressed in Eq. (1).

$$\sigma(t) = \int_0^t E(t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau, \tag{1}$$

where $\sigma(t)$ is the stress at time t, $\varepsilon(t)$ is the strain history and $E(t)$, the relaxation modulus.

Considering that the strain history is an harmonic function of time as expressed in Eq. (2)

$$\tilde{\varepsilon}(t) = \tilde{\varepsilon}_0 e^{j\omega t}, \tag{2}$$

and the stress is also a harmonic function, but no longer in phase with strain, and can be expressed as

$$\tilde{\sigma}(t) = \tilde{\sigma}_0 e^{j(\omega t + \delta)}, \tag{3}$$

where ε_0 is the amplitude of the strain history, σ_0 is the amplitude of the stress, ω is the angular frequency and δ, the phase lag between the stress and strain. The stress-strain relation expressed in Eq. (1) then becomes

$$\sigma(\omega) = E^*(\omega)\varepsilon(\omega) \tag{4}$$

where $E^*(\omega)$ is the complex modulus that can be decomposed as

$$E^*(\omega) = E'(\omega) + jE''(\omega) \tag{5}$$

where $E'(\omega)$ is the real part known as storage modulus and $E''(\omega)$, the imaginary part known as loss modulus. The former corresponds to the elastic response and it represents the material's ability to return or store energy, whereas the latter is related to the viscous response, corresponding to material's ability to dissipate energy. The relation between these two parts is known as tan δ or damping or loss factor, and it is represented in Eq. (6).

$$tan\delta(\omega) = \frac{E''(\omega)}{E'(\omega)} \tag{6}$$

2.2 DMA Principles

In this work, a PerkinElmer DMA 8000 were used to perform all tests. It measures the material's response after an application of a force to a test-specimen in a cyclic manner. From the measurements of the dynamic force (F), the

displacement (d) and the phase lag (δ), it calculates the material's modulus over the test reporting it as a complex quantity as expressed in Eq. (7) (Menard, 2008).

$$E^*(\omega) = \frac{F}{G_F d}(cos\delta + jsin\delta), \tag{7}$$

where G_F is the geometric factor that depends on the modality test chosen due to the different boundary conditions applied.

For the Single Cantilever mode, which the test-specimen is anchored on one end by a stationary clamp and by a moveable clamp on the other, the geometric factor is given by Eq. (8). For the Dual Cantilever mode, which the test-specimen is anchored on both ends by a stationary clamp and by moveable clamp in the middle, the geometric factor is expressed in Eq. (9). Finally, for the Three-point Bending mode, which the test-specimen is supported on both ends by a stationary bar and the moveable clamp is in the middle, Eq. (10) expresses its geometric factor.

$$G_{Fsingle} = \frac{L^3}{4bh^3}, \tag{8}$$

$$G_{Fdual} = \frac{L^3}{16bh^3}, \tag{9}$$

$$G_{F3pt} = \frac{4L^3}{bh^3}, \tag{10}$$

where b is the width, h is the thickness and L is the free length.

For all three geometric factors, the free length and the test-specimen thickness are the parameters with the highest influence as shown in Eqs. (8)-(10). They are both cubic terms.

3. EXPERIMENTAL PROCEDURE

3.1 Material and Test-specimen Preparation

An epoxy system was used in the current work. The epoxy resin was Araldite LY 1564 and the hardener for the curing process was Aradur 2963. All reagents were purchased from Maxepoxi (São Paulo, Brazil).

A mixture of epoxy resin and curing agent in a proportion of 48 phr was thoroughly mixed, then it was put on an ultrasonic bath for 15 minutes to avoid the presence of air bubbles. Afterwards, the resin was poured into a silicone rubber molds with appropriate dimensions for the tests. Finally, the curing process was done at room temperature for 24h, followed by a post-curing cycle at 60°C for 8h. In order to eliminate variations in material properties caused by processing, test-specimens from only one batch were used in all tests.

3.2 Dynamic Tests by DMA

Dynamic tests were performed in a PerkinElmer DMA 8000 to measure the complex modulus $E^*(\omega)$. Three operational modes were used, namely: single and dual cantilever, and three-point bending modes. They were all carried out in similar conditions in order to obtain reliable results.

Firstly, temperature scans were performed from 298 to 363 K with a heating rate of 2 K/min and a constant frequency of 1 Hz. The real and imaginary components of the complex modulus were obtained as a function of temperature. The regions of material's behaviour were identified so as the glass transition temperature.

Afterwards, in order to verify the thermorheologically simple behaviour, temperature-frequency scans were performed from 1 to 100 Hz at several temperatures from 298 to 363 K. Isotherms were maintained for 5 minutes every 5 K and the heating rate was 2 K/min. This technique was only performed in Single and Dual cantilever modes.

Following recommendations to reduce experimental errors in (Menard, 2008), each modality test and temperature scan technique was performed on three different test-specimens. For Single cantilever mode, their dimensions were approximately 25 mm x 7 mm x 2 mm. For Dual cantilever and Three-point Bending modes, on the other hand, their dimensions were approximately 50 mm x 7 mm x 2 mm.

4. RESULTS AND DISCUSSION

4.1 Temperature Scans Results

Figure 1 shows the results obtained in temperature scans for all three operational modes. Storage modulus presented the same pattern in all modes: it decreased with the increase in temperature, indicating the regions of material's behaviour and also the glass transition. This trend is coherent with the classical behaviour of polymeric materials (Shaw

and MacKnight, 2005). However, it had different values for all three test modes, especially before the glass transition. These differences reached 65 percent of the highest modulus which indicates a precision only on order of magnitude. Temperatures related to the onset point were also different. Focusing on loss modulus and loss factor, one can identify the same descrepancies between each test, but Single and Dual cantilevers tests presented a reasonable accordance in some temperatures. Temperatures related to their peaks differed from one another up to 20 K.

(a) Storage Modulus

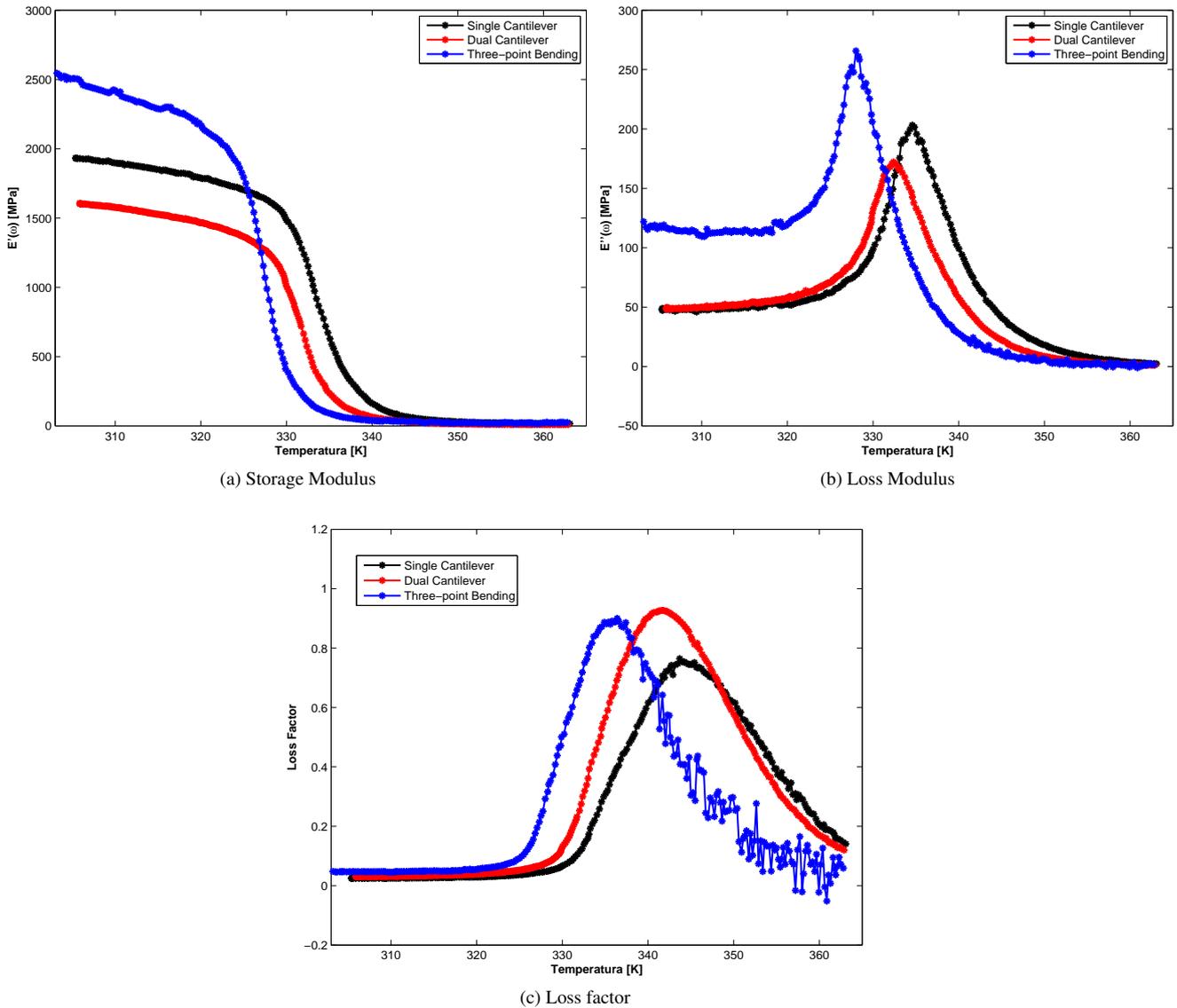

(b) Loss Modulus

(c) Loss factor

Figure 1: Temperature Scan Results

The observed differences can be explained in several ways.

Differences in temperatures related to glass transition may be correlated to the position of the sensor in relation to the test-specimen. The sensor is fixed in the apparatus, near to the moveable clamp of the system, and so, when one varies the modality test, the position of the sensor in relation to the test-specimen is different. In Single Cantilever, the sensor is near to the end of the test-specimen. In Dual Cantilever and Three-point Bending, on the other hand, the sensor is near to the middle of the test-specimen. The heat radiation in the furnace is also another influential factor (Sun *et al.*, 2014; Lacík *et al.*, 2000; Hagen *et al.*, 1994).

Besides, a difficulty in placing the test-specimen in the correct position is another important factor. The alignment and the symmetry of the test-specimen in the apparatus both depend on the operator; it is a manual operation. This is critical on the Three-point Bending mode, which the test-specimen is only supported on both ends.

In Single and Dual Cantilevers, the test-specimen can present a thermal stress in the clamped ends, emerging in erroneous modulus results, as pointed out by (Duncan, 2008). The model to calculate the Complex Modulus, expressed in Eq. (7), does not take into account this thermal stress.

4.2 Temperature-Frequency Scans Results

The results obtained in temperature-frequency scans are shown in Figures 2-4. The storage modulus behaviour in respect to changes in frequency was found the same in both single and dual cantilever modes. For temperatures below 333 K, it did not vary with frequency, whereas for temperatures above 333 K, it increased with the increase in frequency. The influence of the frequency is high in temperatures related to the glass transition region. As the previous analysis, there are discrepancies in the order of magnitude between these modes, indicating that there is possibly a scale factor associated to them.

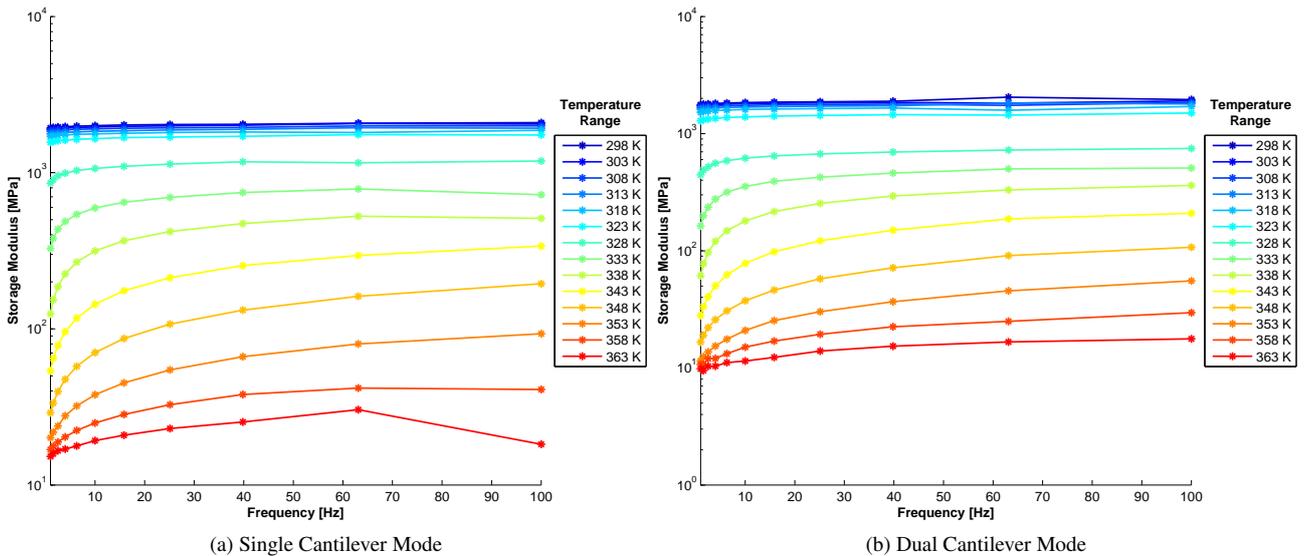(a) Single Cantilever Mode   (b) Dual Cantilever Mode
Figure 2: Temperature-Frequency Scan -Storage Modulus versus Frequency

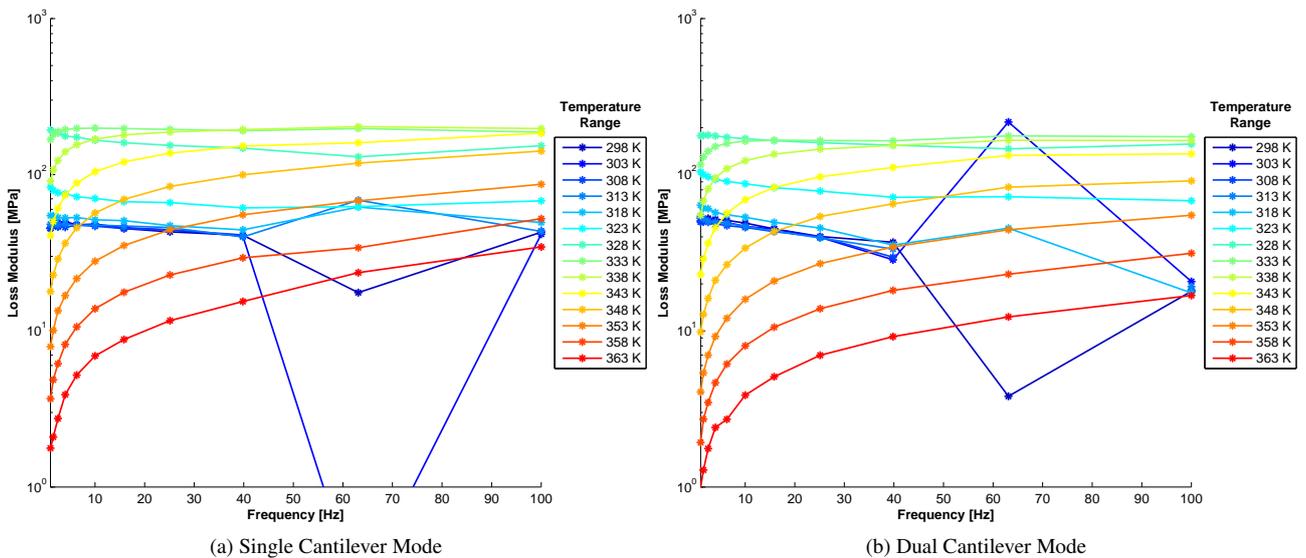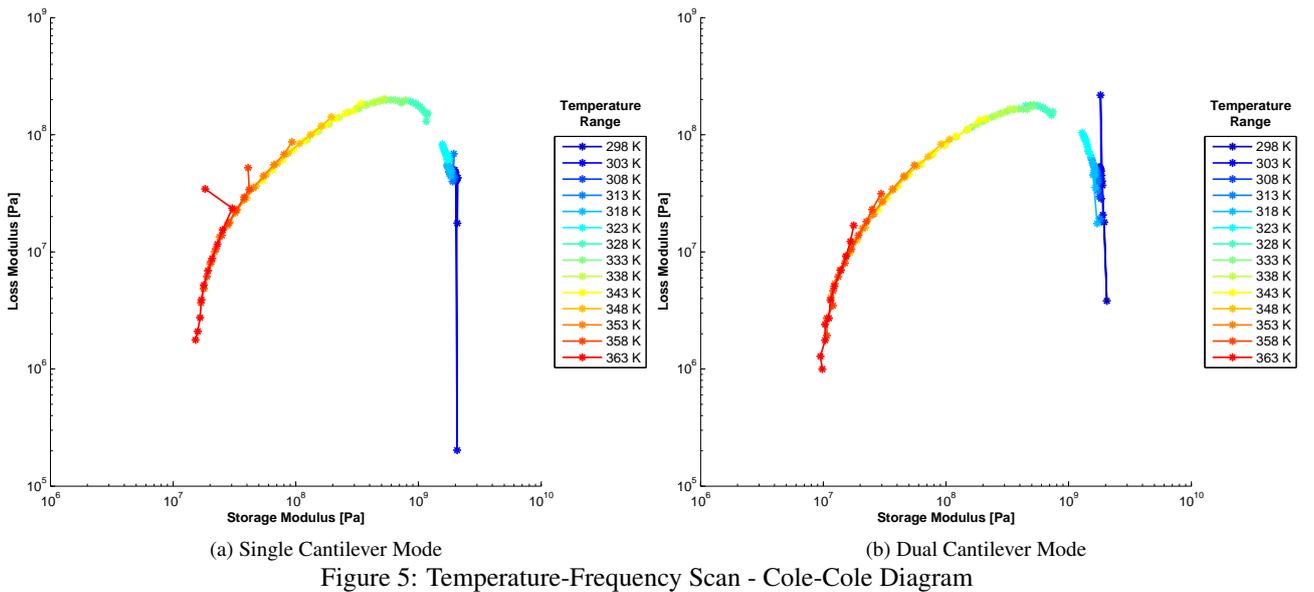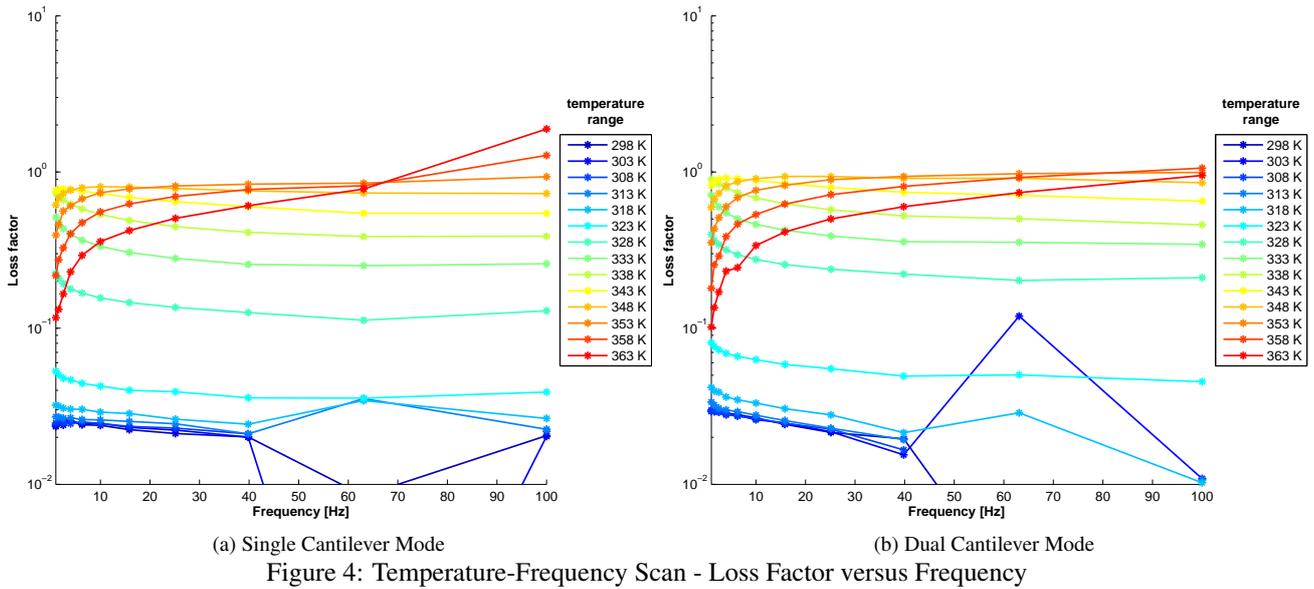(a) Single Cantilever Mode   (b) Dual Cantilever Mode
Figure 3: Temperature-Frequency Scan - Loss Modulus versus Frequency

Despite the discrepancies between the results, Cole-Cole diagram and Black space were then build in order to verify if the thermorheologically simple behaviour can be observed in all measurements. The results are shown in Figures 5 and 6. In all diagrams, most points lied close to one single curve, validating this hypothesis. Points that deviate from the curves are related to measurements at high frequencies and they may be related to resonance phenomena in the DMA (Placet and Foltête, 2010).

(a) Single Cantilever Mode   (b) Dual Cantilever Mode

Figure 4: Temperature-Frequency Scan - Loss Factor versus Frequency

(a) Single Cantilever Mode   (b) Dual Cantilever Mode

Figure 5: Temperature-Frequency Scan - Cole-Cole Diagram

5. CONCLUSION

Different tests were performed in a PerkinElmer DMA 8000 to measure the complex modulus of a viscoelastic material. It was observed that when one performs tests using the same operational mode at the same conditions, DMA provides good results, that is, the repeatability and reproducibility is quite good. However, changes on the operational mode lead to discrepancies in terms of magnitude and regions of material's behaviour between the results even though they should be the same. Despite this, the thermorheologically simple behaviour could be observed in all modes. This indicated that there is a scale factor problem in DMA calculus. A natural progression is to verify if this scale factor problem happens with other viscoelastic materials and in other DMA machines, and if there are any correlation between them. Also, investigate how to take into account the effects of the clamped ends in Single and Fual cantilevers modes.

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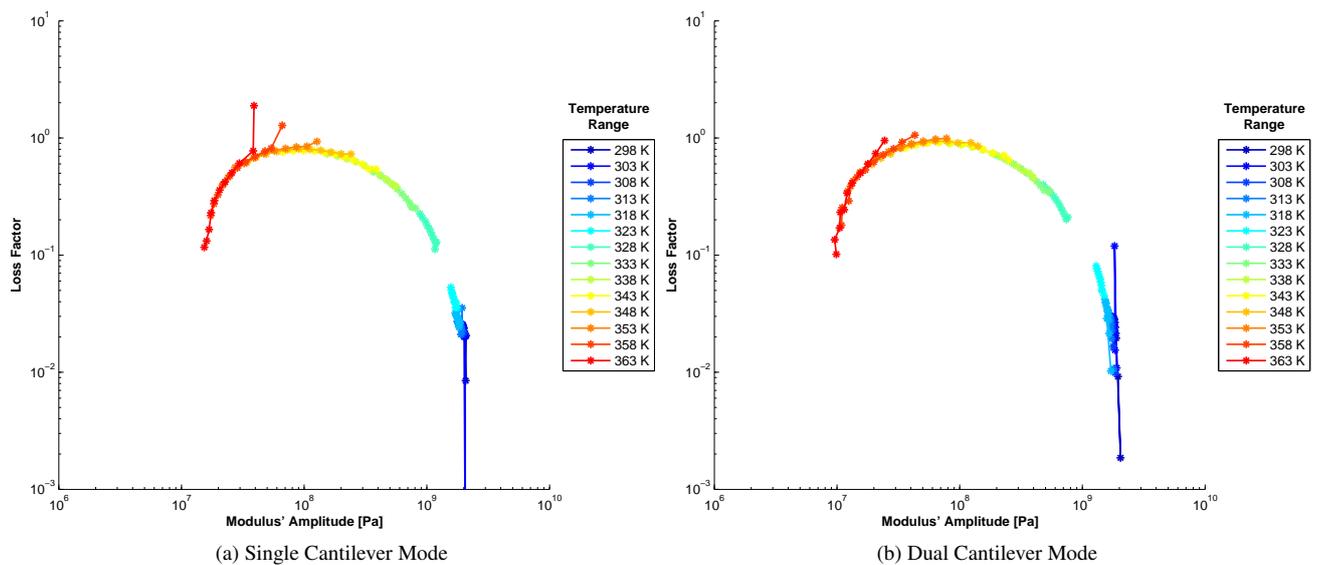(a) Single Cantilever Mode   (b) Dual Cantilever Mode

Figure 6: Temperature-Frequency Scan - Black Space

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