COMPARISON OF COMPLEX MODULUS PROVIDED BY THREE DIFFERENT DYNAMIC MECHANICAL ANALYZERS

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Abstract

Polymer matrix composites have been used in several applications of engineering and applied sciences. This wide range of applications is due to their distinguished properties. Therefore, the great understanding of their physical and mechanical properties is required to make an efficient use of these materials. Among the experimental techniques, Dynamic mechanical analysis (DMA) is one of the most common methods employed to study the materials' composition and properties. This work presents an investigation on the mathematical formulation for complex modulus determined by this technique and how it is evaluated. Measurements of temperature-dependent complex modulus were performed by three different dynamic mechanical analyzers using three-point bending mode. Test conditions were basically the same in these different machines. Comparisons of the results were made in order to observe the effects of testing equipment and test parameters.

1. INTRODUCTION

Polymer matrix composites (PMCs) have been widely used in many applications of engineering and applied sciences, such as civil engineering structures, aerospace, wind energy and super sport cars [1,2]. This great range of applications is due to their outstanding properties[2]. As the fields of applications have been continuously growing, many efforts have been done to characterize and model these materials in order to predict their mechanical behavior, optimize designs and minimize project risks.

Recently, the time and temperature dependences of PMCs have been pointed out to be related to the matrix properties. Etaati et al. [26] investigated the influence of fiber content in short hemp

polypropylene composites. Results showed that the influence of temperature is independent of the fiber, i.e., that the temperature dependence of this composite is related to the matrix properties. Liu et al. [27] reported that the effects of time and temperature on composites are concerned with the properties of the matrix. If one wants to characterize the thermal and temporal behavior of PMCs, it is essential to characterize their matrix properties.

One of the most common methods used to experimentally characterize materials' properties is the Dynamic Mechanical Analysis, also known as DMA. This technique has become a powerful one in the field of rheology by enabling one to identify and characterize the material's behavior especially as a function of temperature and frequency. It enables more information about the material's properties than techniques involving static tests [4].

Generally speaking, DMA is in some sense versatile. Depending on the operational mode and the parameters chosen, 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 behavior, transitions, extent of phase mixing in blends, degree of crosslinking, crystallinity, interfacial adhesion, ageing, degradation, among others [5].

On this regard, DMA is becoming widely used in several areas to study the various aspects of a material. The traditional applications are concerned with the identification of thermal transitions [6–8] and how some parameters affect the material's properties [9–13]. Recently, the use of DMA as a characterization technique has been expanded to other studies such as crack healing [14], spatial distribution of material's properties [15] and mechanical properties of heterogeneous materials [16].

Despite the great range of DMA applications and its potential, literature indicates that there are some discrepancies in DMA results. The absolute values of the modulus and temperatures related to phase transitions are well-known to show divergences between samples and loading clamps even when the test conditions were essentially the same. Even though the property measured should be the same, regardless the DMA equipment [5,17–25]. However, few researches can be found on the mathematical formulation of the modulus and on the comparative data obtained by different machines.

The purpose of this work is to investigate how the complex modulus is mathematically formulated and measured by three DMA machines in three-point bending tests. Experimental tests were carried out in temperature scans to also evaluate how the temperature dependence of the material is identified by different machines. These tests were performed on an epoxy system which is a common matrix used in several applications [28]. Finally, the measurement results were compared to study the influence of testing equipment.

This work is organized as follows. Section 2 gives the principal aspects of DMA principles and how the complex modulus is formulated. Section 3 explains the experimental set-up. Section 4 presents the experimental results obtained, followed by our conclusions.

2. FUNDAMENTALS

2.1 DMA principles

Basically, DMA consists of applying a sinusoidal force to a sample and measuring the sample's deformation, or applying a sinusoidal deformation and measuring the sample's reaction force, or even as applying a constant force/deformation and measuring the sample's creep/relaxation modulus [19]. This material's response can be characterized as a function of temperature, frequency, time, stress or a combination of these control parameters, depending on the intended

use of the material. Based on these measurements, DMA can determine the material's properties, like modulus and viscosity.

In particular, the material's modulus is reported over the test as a complex quantity that enables one to better analyze the material's behavior. The real part is usually called as storage modulus and corresponds to the material's ability to return or store energy. It may represent shear, tensile or flexural modulus, depending on the operational mode. On the other hand, the imaginary part is commonly known as loss modulus and corresponds to material's ability to dissipate energy. Further, the ratio between the real and imaginary parts is called tan δ or damping or even loss factor, and represents how quickly the material loses energy.

2.2 Mathematical formulation for complex modulus

Let consider the use of a dynamic stress to deform a sample, i.e., DMA is applying a sinusoidal stress to a sample and measuring its deformation. This oscillatory stress is expressed as

$$\sigma(t) = \sigma_0 \sin \omega t \tag{1}$$

with σ_0 as the amplitude, *t* as the time and ω as angular frequency. The strain history ε(t) can be given by

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t + \delta) \tag{2}$$

with ε_0 as the amplitude of the strain history and δ as the phase angle between the applied stress and the response.

The one-dimensional stress-strain relation in the frequency domain [29] is expressed as

$$\sigma(t) = E^*(\omega)\,\varepsilon(t) = [E'(\omega) + jE''(\omega)]\,\varepsilon(t) = E'(\omega)\,[1 + j\,\eta(\omega)]\,\varepsilon(t), \tag{3}$$

where $E^*(\omega)$ is the complex modulus, $E'(\omega)$ is the storage modulus, $E''(\omega)$ is the loss modulus, and $\eta(\omega)$ is the loss factor given by

$$\eta(\omega) = \frac{E''(\omega)}{E'(\omega)} = \tan\delta. \tag{4}$$

From the measurements of the force, the displacement and the phase angle, DMA determines each component of complex modulus. This estimate also depends on sample geometry, operational mode and boundary conditions.

In this work, we performed three-point bending tests in three DMA machines, namely Netzsch 242 E Artemis, PerkinElmer 8000 and TA Q800. The mechanism of this test and the mathematical formulation provided by each DMA performed in this work are described below.

Three-point (3PT) bending mode consists of a sample being only supported on both ends by stationary clamps. The controlled force is applied in the middle through the moveable clamp. In this mode, the sample is free to move and there is no clamping effect, being considered as a pure mode of deformation.

As for the mathematical formulation of this mode, each DMA has its own considerations. Equations (5), (6) and (7) show how the absolute value of complex modulus is calculated, respectively, in PerkinElmer 8000, TA Q800 and Netzsch 242 E Artemis.

$$|E^*_{3PT}(\omega)|_{PerkinElmer} = \frac{F}{a}\frac{L^3}{48I}\left[1 + 2.9\left(\frac{t}{L}\right)^2\right] \tag{5}$$

$$|E^*_{3PT}(\omega)|_{TA} = \frac{F}{a}\frac{L^3}{6I}\left[1 + 0.6(1+\nu)\left(\frac{t}{L}\right)^2\right] \quad (6)$$

$$|E^*_{3PT}(\omega)|_{Netzsch} = \frac{F}{a}\frac{L^3}{48I} \quad (7)$$

where F is the force applied, a is the displacement amplitude, L is the span between the two supports, t is the sample's thickness, I is the inertia moment and ν is the Poisson's ratio.

Note that both PerkinElmer and TA assume small shear deformation as they both consider the influence of Poisson's ratio on the modulus formulation. PerkinElmer's assumption is based on a constant Poisson's ratio of 0.33 for glassy polymers and 0.5 for rubbers, namely 0.35. On the other hand, TA's assumption depends on the material.

3. EXPERIMENTAL SET-UP

3.1 Description of the testing equipments

Three different DMA machines from different manufacturers were used to perform dynamic tests to measure the complex modulus: DMA Netzsch 242 E Artemis, DMA PerkinElmer 8000 and DMA TA Q800.

These DMA machines are all made of four basic components: force motor, displacement sensor, sample holder and furnace. Force motor provides the control of all forces required to the sample. It has low compliance and is thermostatic. Displacement sensor is the detection system and it tracks any changes in the sample. Sample holders, in turn, enable one to perform different modes of operation. The clamps have a high stiffness to minimize the compliance and they also have low mass for a fast temperature equilibration. Finally, furnace provides a temperature control during the tests.

3.2 Test conditions

Dynamics tests were performed in three-point bending (3PT) mode in different DMA machines using similar conditions in order to obtain reliable results. Temperature scans were performed after an isotherm of 30 minutes at 25°C. Temperature varied from 25°C to 90°C with a heating rate of 2°C/min at a constant frequency of 1Hz. For all tests, strain mode was used and so, the amplitude was set to 50㎜. Furthermore, a force track was set to 120%, which means that the static force is 120% of the dynamic force.

3.3 Material and Samples' Manufacture

The material used in this work was an epoxy system which the epoxy resin was Araldite LY 1564 and the hardener, Aradur 2963. Specimens were prepared by casting at room temperature for 24h in silicone rubber molds with appropriate dimensions and then post-curing at 60°C for 8h.

Samples dimensions varied a little according to DMA machine. For Netzsch 242 E Artemis, samples were machined to approximately 60 mm x 10 mm x 3.2 mm. For TA Q800, they were approximately 60 mm x 12.7 mm x 3.2 mm. Finally, for PerkinElmer800, since it was possible to vary the span, two sets of samples were studied. In Set 1, they were 50 mm x 7 mm x 2 mm. In Set 2, on the other hand, they were 52.5 mm x 10 mm x 3.2 mm.

4. RESULTS AND DISCUSSION

Three-point bending mode was performed in three DMA machines, PerkinElmer 8000, TA Q800 and Netzsch 242 E Artemis using the same test conditions. In PerkinElmer 8000, tests were carried out for two sets of samples. The measurement results for storage and loss moduli are shown in Figure 1.

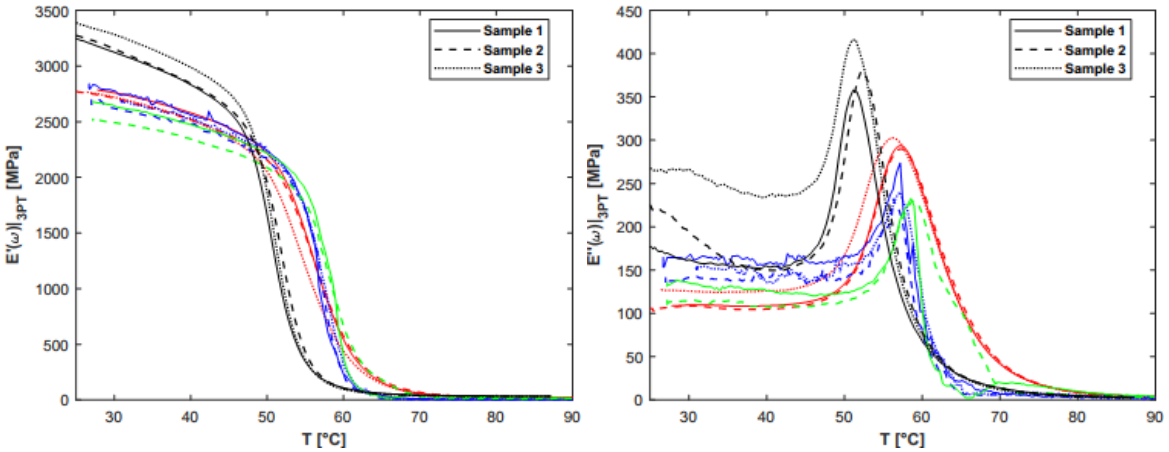

Figure 1 : Three-point bending results. (a) Storage modulus, (b) loss modulus. (Black lines: Netzsch 242 E Artemis, red lines: TA Q800, blue lines: PerkinElmer 8000 Set 1, and green lines: PerkinElmer 8000 Set 2)

The classical behavior of polymers [30] can be observed in all DMAs results. Storage modulus decreased with temperature. This decrease was even more rapid as the material approached its glass transition due to its morphological softening. Loss modulus increased slightly up to a certain temperature and from there, it suddenly decreased with temperature.

It can be observed that, when one performs tests using the same test conditions and testing parameters, all DMA provide good results. In other words, the repeatability and reproducibility is quite good. There is no great variability between the three samples from the same set.

However, Netzsch 242 E Artemis provided a higher storage and loss moduli in the glassy state than the other DMAs. The onset point of storage modulus and the peak point of loss modulus were identified in a lower temperature, indicating that the glass transition happened first in this DMA machine. While Netzsch identified this event in a temperature approximately 50°C, both PerkinElmer and TA measured it at around 60°C. This discrepancy in temperature may be correlated to the position of the sensor in relation to the sample, heat radiation in the furnace and a consequently thermal lag in the sample.

Nonetheless, it was surprising that the results of PerkinElmer 8000 and TA Q800 showed a good agreement, especially for storage modulus, regardless of the sample's dimensions. Although literature [19,23] suggested that instrumentation compliance, sample's stiffness and dimensions, and span-to-thickness ratio may influence DMA results, it is possible to observe that when performing tests in different machines, they can be correlated if the test conditions are the same.

When comparing DMA results from different machines, one should keep in mind that each DMA has its own mathematical formulation for complex modulus as explained earlier. Therefore, small variations in the measurements from different DMAs are quite expected to happen.

It is interesting to investigate how the parameters related to the modulus formulation, force and the displacement amplitude, were measured along each test by each machine. Figure 2 shows the results as function of temperature.

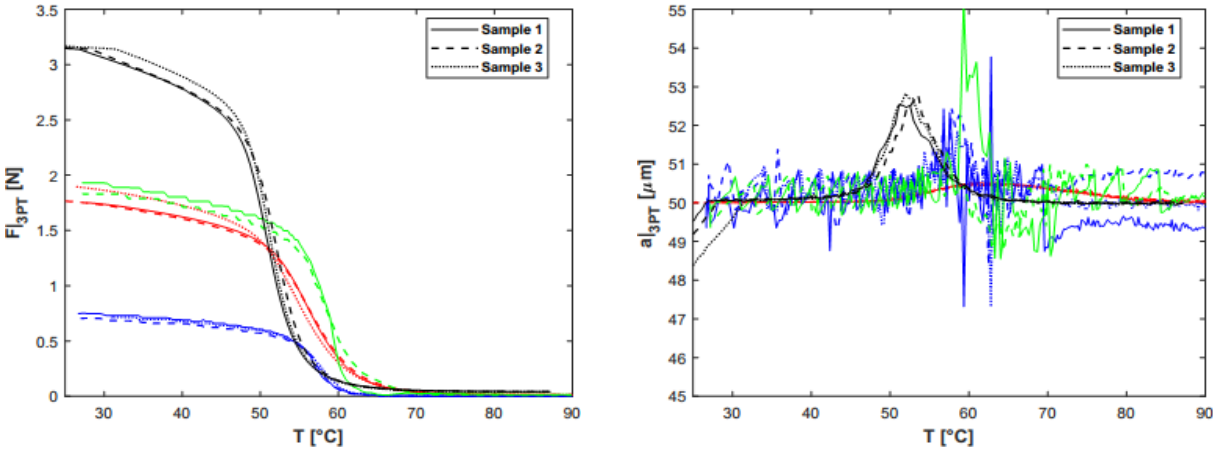

Figure 2: Three-point bending parameters. (a) Force, (b) displacement amplitude. (Black lines: Netzsch 242 E Artemis, red lines: TA Q800, blue lines: PerkinElmer 8000 Set 1, and green lines: PerkinElmer 8000 Set 2)

Note that, for each set of samples in each DMA machine, it was necessary the application of a specific force due to the sample's stiffness and the machine compliance. This applied force decreased with temperature because of the material's softening. It can also be noted that Netzsch applied a greater force than the others. In addition, TA applied almost the same force as PerkinElmer did for the second set of samples. It is worthwhile remind that the second set of samples of PerkinElmer had dimensions close to the ones of the samples of TA.

5. CONCLUSION

To summarize, it was found that each DMA has its own mathematical formulation for the same operational mode and as a consequence, some discrepancies between the measurement results from different DMA machines are somewhat expected to be observed even if the test conditions and testing parameters are the same. Nonetheless, it was possible to find some good agreement in the results, especially for storage modulus. In addition, it was shown that the effects of sample's geometry are not noticeable in this mode. A natural progression is to verify how DMA formulates the complex modulus in other operational modes and compare the measurements from different machines to observe both the effects of testing equipment and the effects of testing parameters into the results.

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