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Dynamical Characterization of Propellant using the DMA

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Abstract

The complex response in frequency and temperature of mechanical properties of viscoelastic materials is usually determined in static mechanical tests by performing many tests at different temperatures and rates of load application. This is necessary to have sufficient superimposing conditions to determine shifting factors (a_t), according to the Time-Temperature superposition principle. The aim of this work is to optimize the method for the determination of the shifting factors a_t and the prediction of mechanical properties of propellant specimens using the dynamo-mechanical analysis (DMA).

List of Acronyms:
TTSP: Time-Temperature Superposition Principle
T= Test temperature
T_r= Reference temperature
A_t= shifting factor
c1, c2= constants typical for the material
E': Storage Modulus
E'': Loss Modulus

1. Introduction

Mechanical properties of a viscoelastic materials show complex temperature and frequency dependences. The Time-Temperature superposition principle (TTSP) [1.] allows to describe this complex behaviour with the use of a unique Master Curve of a certain property as a function of frequency at a reference temperature. The construction of master curves of Young Modulus, Strain and Stress, are fundamental to predict properties of a composite propellant grain from storage to firing conditions [2.][3.]. Master Curves are usually determined by performing many static tensile tests at various conditions of temperature and rate of load application. This is necessary to have sufficient superimposing conditions to determine shifting factors (a_t) according to the TTSP. Shifting factors determined from experimental data can be related to temperature variations using the empirical William Landel Ferry equation (WLF) [4.]

$$Log.(a_t) = \frac{-c1(T-T_r)}{c2+(T-T_r)} \tag{1}$$

Where:
T= Test temperature
T_r= Reference temperature
A_t= shifting factor
c1, c2= constants typical for the material

The dynamo-mechanical analysis [5.][6.] is based instead on the measure of the force required to impose oscillation at a defined frequency and amplitude to the specimen. The response of the material to the imposed oscillation can be divided into elastic response (storage modulus) and viscous component (loss modulus). In addition, the tan(δ) - the

DOI: 10.13009/EUCASS2017-326

ratio between the two moduli - is defined. This represents the phase delay between the applied force and the response of the material. Although it is not possible to measure the strength and elongation of the material, the advantage of using the DMA lies in the possibility of performing a large number and type of tests in a wide temperature range using small amounts of material. This is of interest in first stages of propellant development when many different formulation should be tested and compared. In addition, aging tests can be performed on a limited quantity of material reducing the number of total static tensile tests required [7.][8.]. The application of DMA as a tool of product control is also interesting. For instance, specimen, due to their reduced size, could be extracted directly from a propellant grain to measure the elastic modulus and estimate mechanical properties.
Two different clamping schemes have been tested and compared for this work. Tests have been performed in single cantilever and tension mode. For both, optimal temperature, strain and frequency ranges have been optimized. Attention has been dedicated to reproducibility of data and easiness of use. For single cantilever and tension clamps, the major source of non-reproducibility of data, are clamping effects. Clamping effects were carefully evaluated and minimized through the adoption of an optimal specimen shape. Results were compared to one obtained in static tensile tests for a case study.

2. Experimental Part

All measurements were performed using the TA instrument Q800 DMA. Different clamping schemes are available. For this work a tension film clamp and a single cantilever clamp were chosen. In the following paragraphs the optimization of the experimental conditions is described.

2.1. Experimental Conditions

Specimen compositions and preparation:
The composite propellant used for this work is HTPB based and with ammonium perchlorate as active charge.
All the specimens used for this work come from a unique batch of composite propellant cast in a block and cut in slices after curing.
For both clamps it was possible to adopt a dog-bone shaped specimen. Specimens were obtained by die cutting a slice of propellant.

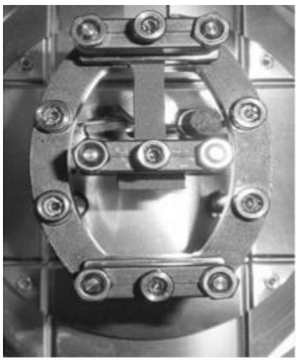


Figure 1: On the left the single cantilever clamp. On the right side the tension film clamp

In both single cantilever and tension configurations specimens are clamped on their wide edges. This allows to partially reduce clamping effects as will be discussed in the following paragraphs. Thickness of the slice of propellant was chosen as a compromise between geometrical constraints of the clamps and the possibility to easily cut a regular slice. The effect of specimen thickness on results was not further investigated. All measurements are therefore valid for specimen thickness between 3 and 4 mm. The use of a die guarantees a constant length and width of specimens leaving their thickness as the only variable. The width of the linear portion of the specimens was measured using a calibrated microscope and then used as a constant value.

DOI: 10.13009/EUCASS2017-326

Specimen Clamping

In both clamping configurations, specimens are held with clamping screws. The torque applied to those screws affects results. This is illustrated in Figure 2 where modulus variations at increasing values of torque are reported. Error bars were determined over three different specimens.

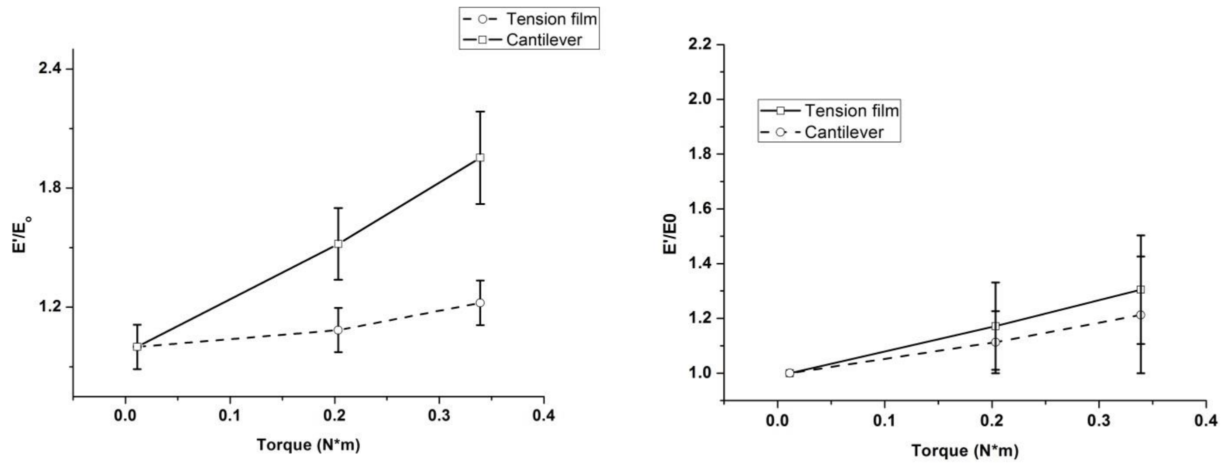


Figure 2: Clamping effects for tension film clamp and single cantilever clamp. On the left measurements at room temperature, on the right measurements at -40°C

Table 1: Clamping effects on modulus values at different temperatures

Modulus increment each 0,1 Nm of torque [%]

TEMPERATURE [°C]	Tension film Clamp	Single Cantilever Clamp
+23	6	28
-40	8	6

Clamping effects represent the major source of error for DMA and if not controlled, they can produce inconsistent results.

Temperature Range

As discussed in the previous paragraph, the tension film clamp seems to be a better choice with respect to the single cantilever clamp, considering reproducibility of data.

However, the tension film clamp is limited by the maximum force applied by the instrument. This limits the range of moduli that can be measured. At lower temperatures, when the material approaches its Tg, the force necessary to attain a certain strain level become closer to the maximum force applied by the instrument and it is not able to maintain a constant deformation. This is shown in Figure 3 where the strain applied to the specimen on a temperature ramp experiment is reported. As can be seen, the tension film clamp is not able to maintain the applied value of strain (0.03%) for temperature lower than -50, -60 °C.

DOI: 10.13009/EUCASS2017-326

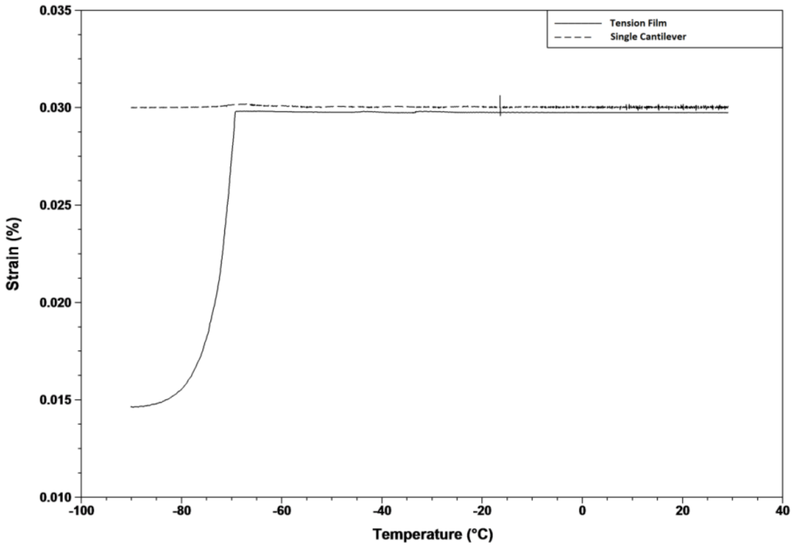


Figure 3: Strain value in a temperature ramp at 1hz and 1°C/min using the single cantilever and the tension film clamp. For temperatures close to the Tg, the elastic modulus of the material approaches the maximum range measurable with the tension film clamp. As a result, the DMA is not able to maintain a constant strain level.

Strain Optimization

The DMA approach and the successive analysis based on the WLF equation are only valid for a strain range where the material responds elastically.

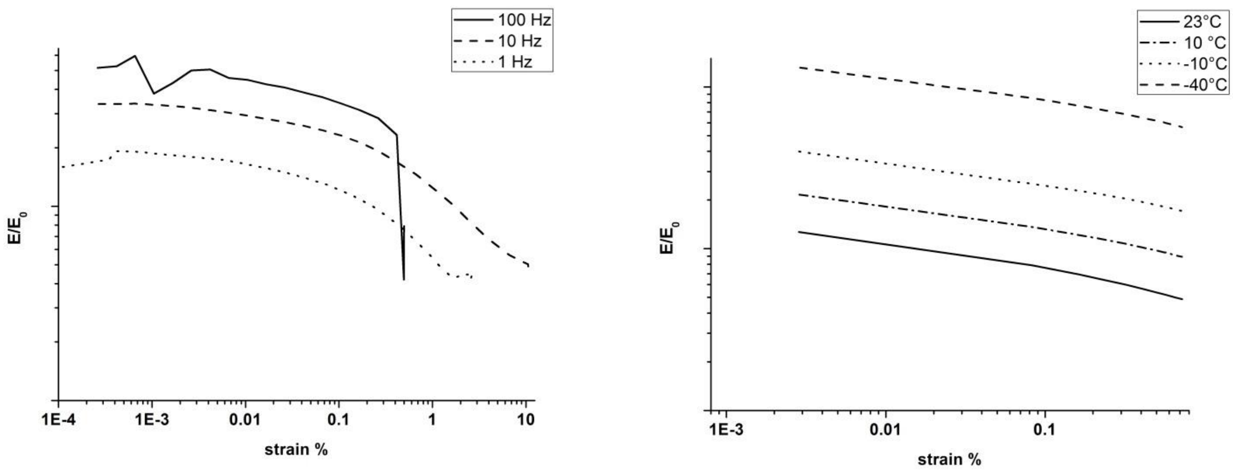


Figure 4: On the left typical strain sweep at different frequencies at room temperature. On the right typical strain sweep at 10 Hz and various temperatures

To determine the optimal value of strain level, strain sweep measurements were performed at 1,10, 100 Hz at temperatures of -40, -10,10 and 35°C.
Typical results for single cantilever and tension film clamps are reported in Figure 4. The analysis of strain sweep measurements showed that for both clamps, a strain level of 0.03% seems to be optimal. The material never shows a true linear range. The 0.03% value was chosen as a compromise between signal level and stability of measurements.

DOI: 10.13009/EUCASS2017-326

Creep Effects and Specimen Degradation

The chosen experimental conditions need to be tested to check whether results are affected by creep effects or specimen degradation. This is particularly important for tensioning clamps where the specimen is subjected to a constant tension generated by oscillating forces superimposed to a constant preload force.
For the film tension clamp, the stability of measurements was evaluated on a 30-minute test, performed at 35°C and 1 Hz on a single specimen with three repetitions. Results are reported in Figure 5. As can be seen the value of modulus does not change over the whole period of stability test.

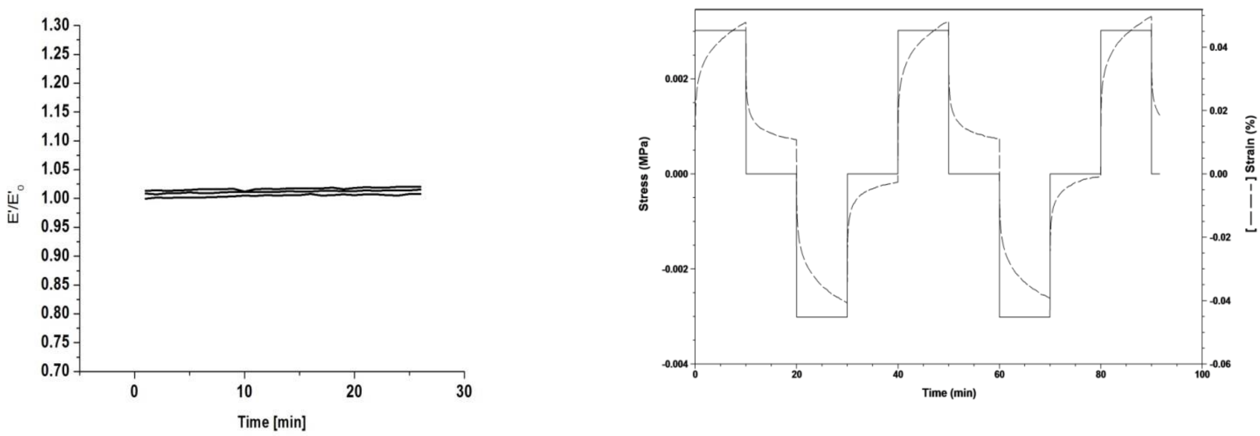


Figure 5: On the left stability test for the tension film clamp. On the right stability test for the single cantilever clamp.

For the single cantilever clamp stability was evaluated by applying subsequent cycles of negative and positive loads. As can be seen in Figure 5, in each cycle the specimen reach the same amount of strain testifying a stability of its mechanical properties.

Frequency Range

For the optimized strain level, frequency sweeps were performed at various temperatures to find the optimal frequency range. In Figure 6 we can see frequency sweep scans at 0.03% strain level for the tension film clamp at various temperatures.
As can be noted, the measurements become unstable at frequencies higher than 30 Hz.

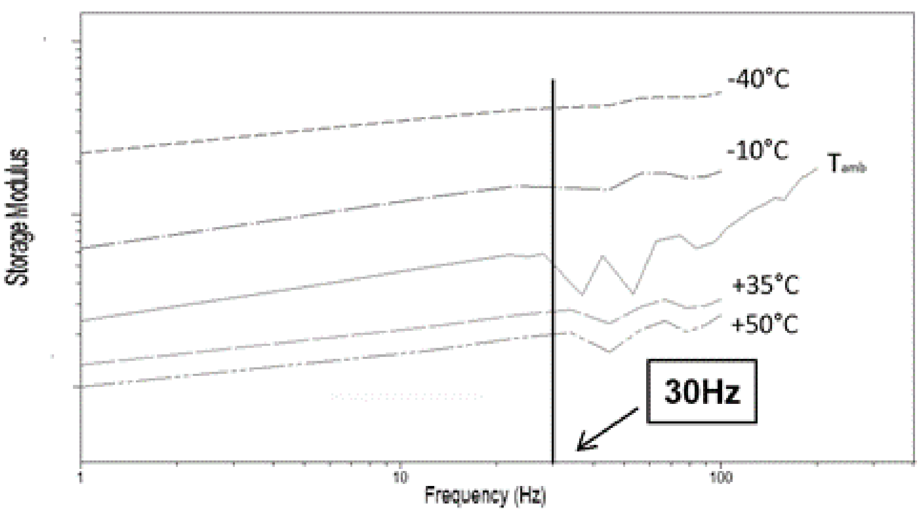


Figure 6: Frequency sweep scans for the single cantilever clamp at 0.3% strain and various temperatures. Measurements are unstable for frequencies higher than 30 Hz

DOI: 10.13009/EUCASS2017-326

All measurements were taken in the frequency range 1-30 Hz. It was chosen not to use frequencies lower than 1 Hz to keep the analysis time short.

Specimen Thermal Equilibration

Tests have been made to determine the minimum thermal equilibration period. This was checked by evaluating storage modulus trend over time after the application of a positive or negative temperature. An example is shown in Figure 7. As can be seen, 20 minutes are the minimum needed to guarantee a constant modulus value over time.

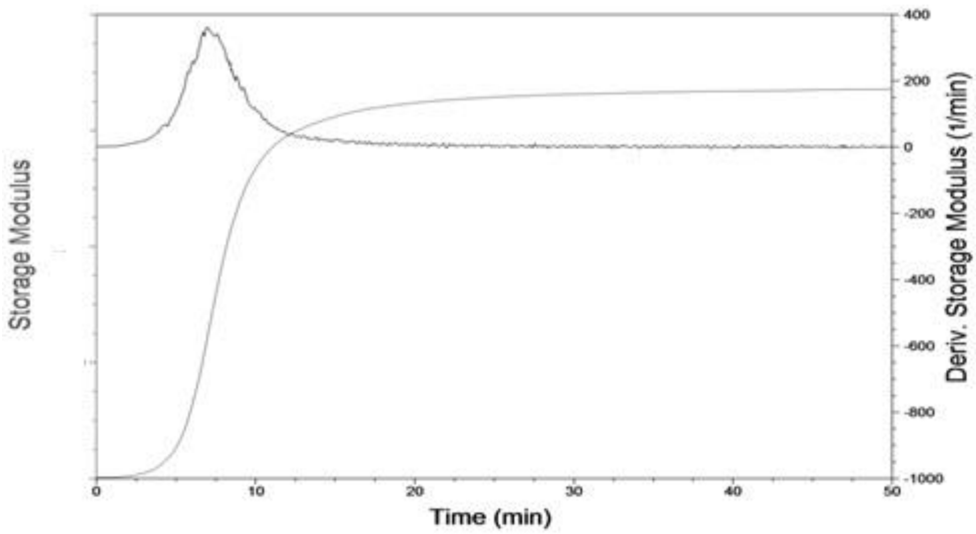


Figure 7: Effect of thermalisation of a specimen in the DMA. At least 20 minutes are needed to obtain a constant value of modulus over time.

Summary of Experimental Conditions

In Table 2 experimental conditions used for the two clamps are reported.

Table 2: Summary of experimental conditions

TEMPERATURE [°C]	CLAMP TYPE	PRELOAD FORCE [N]	FORCE TRACK [%]	CLAMPING TORQUE [N*m]	FREQUENCY RANGE [Hz]	STRAIN LEVEL [%]
-40+50	Tension film	0.01	125	0.01	1-30	0.03
<-40	Single Cantilever	n.a.	n.a.	0.01	1-30	0.03

DOI: 10.13009/EUCASS2017-326

3. Experimental Results

3.1. Temperature Ramp

A preliminary temperature ramp experiment has been performed in temperature range [-100, 0] °C using the single cantilever clamp. Resulting curves of Storage Modulus, Loss modulus and Tan(δ) are reported in Figure 8.

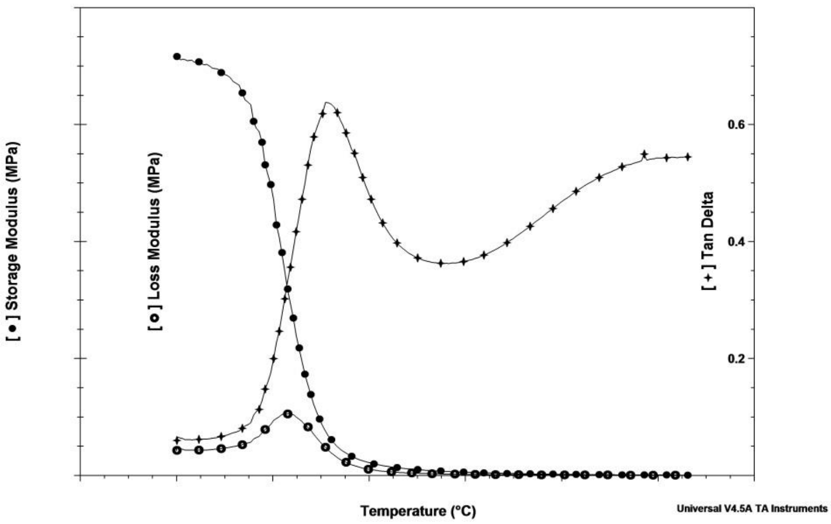


Figure 8 Temperature scan at 1°C/min and 1Hz with single cantilever clamp

At higher temperatures, a broad peak in the tan(δ) curves corresponding to beta transitions of the polymeric matrix is noted.

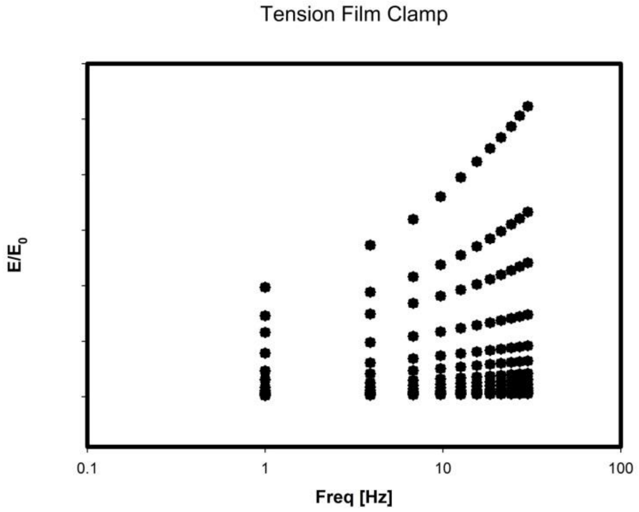
3.2. Frequency Sweeps

Frequency sweep measurements were taken in isothermal conditions with both tension film clamp and single cantilever clamp. Results are summarized in the following paragraphs.

Tension Film Clamp

In Figure 9 we can see the results obtained in frequency sweep mode for 13 different temperatures in the interval [-65°C, + 50°C] with the tension film clamp. In the same figure the master curve obtained using the WLF approach and a reference temperature of -40°C is reported.

DOI: 10.13009/EUCASS2017-326



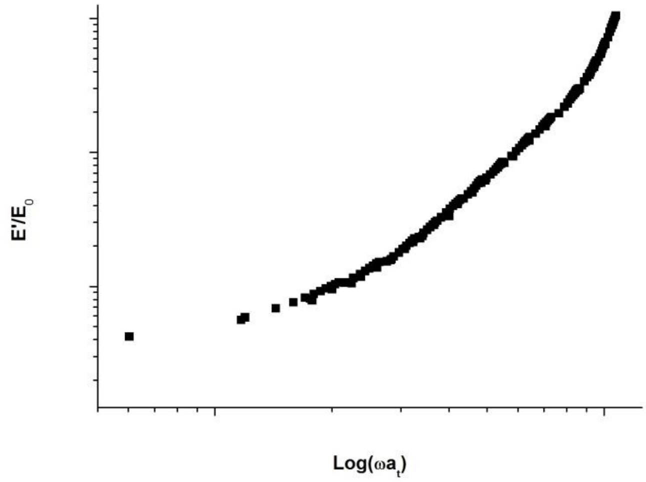
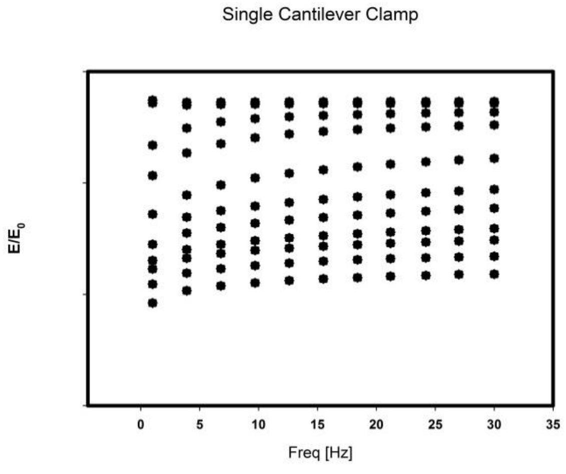


Figure 9: On the left isothermal strain sweeps in the temperature range [-65, +50] °C. On the left the resulting Master Curve

Single Cantilever Clamp

As discussed in the previous paragraphs, the single cantilever clamp was used only for the lower temperatures, in a range less affected by clamping effects.

Figure 10 shows frequency sweep measurements in the range [-90, -40] °C and the resulting master curve obtained using -40°C as reference temperature.



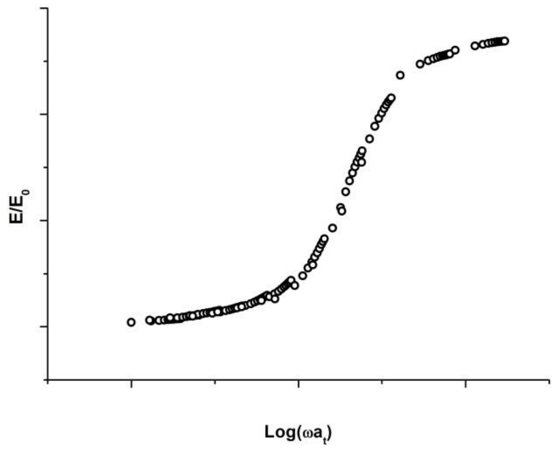


Figure 10: On the left isothermal frequency sweeps in the temperature range [-90, -40] °C with the single cantilever clamp. On the right the resulting master curve.

DOI: 10.13009/EUCASS2017-326

All the shifting factors used for both single cantilever clamp and tension clamp belong to the same WLF equation. The a_t for the temperature range [-90, +50] °C are shown in Figure 11.

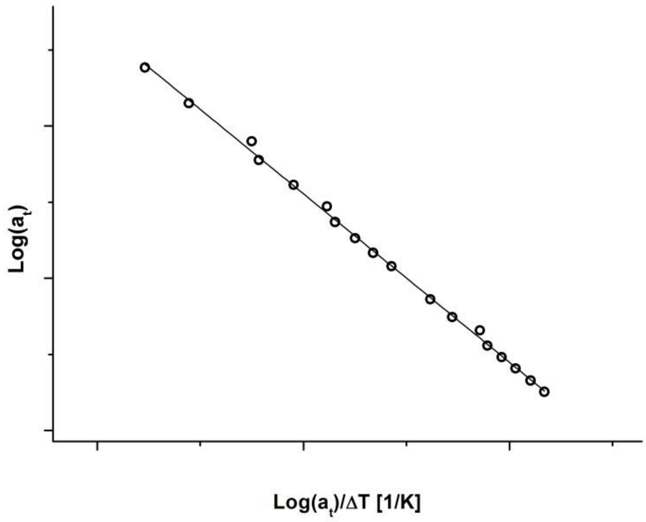


Figure 11: Shifting factors dereived from DMA data

Mechanical Characterization

The same batch of propellant was mechanically characterized with static tensile measurements in the temperature range [-20, +60] °C.
Results are shown in Figure 12. These results can be used to benchmark results obtained with the DMA approach.

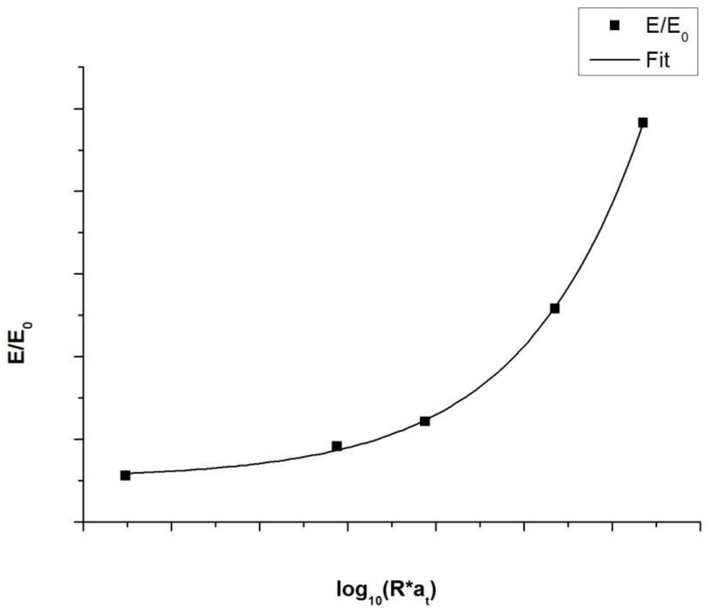


Figure 12: Master Curve obtained with static tensile tests

DOI: 10.13009/EUCASS2017-326

4. Analysis and Discussion

4.1. WLF analysis of DMA data

The DMA is a versatile instrument that allows to quickly perform many different experiments in different clamping configuration, using small amounts of material.
However, in the analysis of composite propellant, different clamp types show a limited range of applicability with respect to the range of temperatures that are needed to analyse.
For this work two different clamps, the single cantilever clamp and the tension film clamp were compared to check if they can be used together to extend the range of applicability of each of them.
Data with the two clamps were recorded in temperature ranges that intersect in the interval [-65, -40] °C.
In Figure 13 data obtained with the tension film clamp and the single cantilever clamp are shown together for the same frequency range in the temperature range [-65, -40] °C.

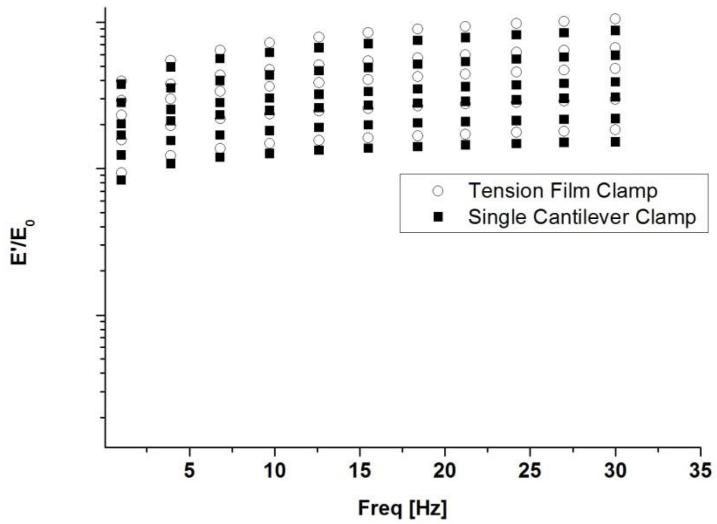


Figure 13: data obtained with the single cantilever clamp and the tension film clamp are shown together for the same temperature range. The two set of data are parallel and scaled by a constant factor

As can be seen the two set of data are parallel to each other and a unique scaling factor between modulus values can be obtained and is equal to 1.16±0.05.
The using of a unique scaling factor implies that the same set of a_t can be used. Data obtained with the tension film clamp and the single cantilever clamp can be analysed together extending in this way the range of applicability of each of them.
To operate to the WLF analysis of the two sets of data, the reference temperature was set at -40 °C.
Shifting factors (a_t) were firstly optimized in the intersecting temperature range. Starting from this first set of a_t, all the other shifting factors were iteratively optimized to obtain the optimal superposition between different curves.
Optimal shifting factors were evaluated in a graph of log(a_t) vs log(a_t)/ΔT that, in the WLF approach, must be linear.
This comes directly from rearranging the WLF equation to obtain:

$$Log.(a_t) = -c2 - c1 * \frac{Log.(a_t)}{(T - T_r)} \quad (2)$$

DOI: 10.13009/EUCASS2017-326

The same set of shifting factors can be used to build master curves of loss modulus and tan (δ). The overall results are reported in Figure 14.

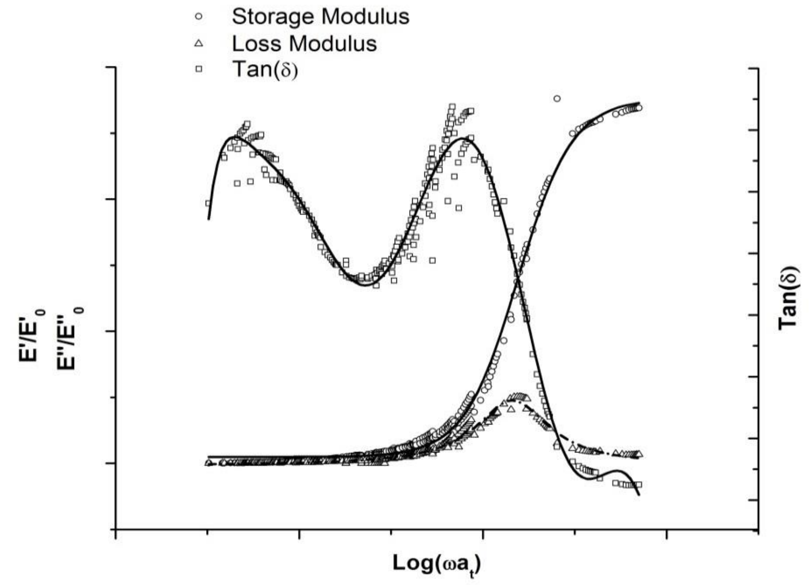


Figure 14: Master Curve of Storage Modulus, Loss Modulus and Tan(δ)

Even if the construction of the tan(δ) master curve is less efficient, the trend reflects the one observed in the temperature ramp experiment. It also shows a double peak in the tan(δ) curve, corresponding to alpha and beta transition of the polymeric matrix.
To check if the DMA can be correlated to static mechanical tensile tests, results were compared to available static tensile tests.
The comparison between master curves is shown in Figure 15. As can be noted, the two curves are parallel for a range of Log(ωa_t). The two curves can be scaled by a factor of 1.1 ± 0.1 with an average 10% difference on the modulus value.

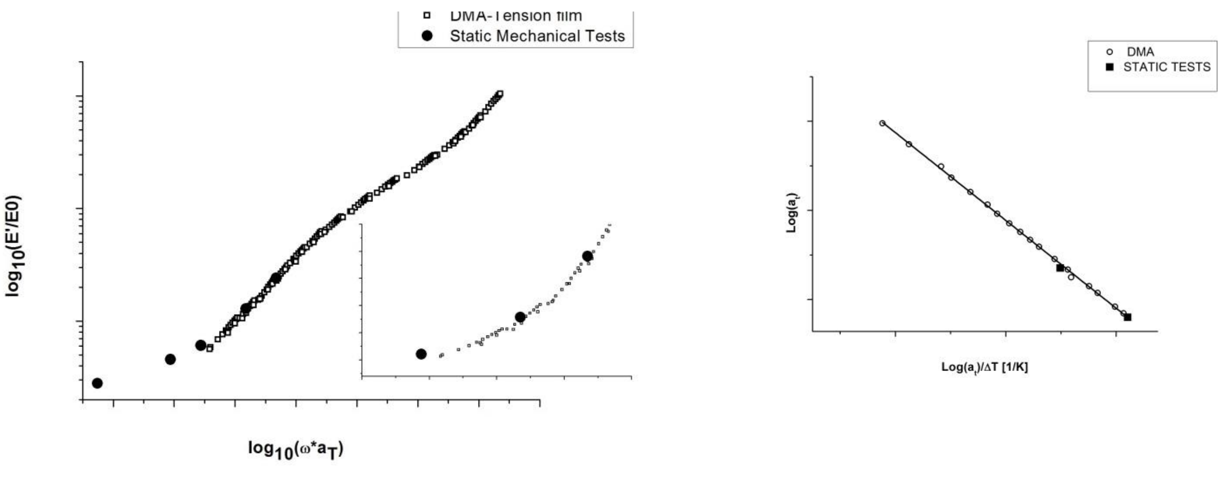


Figure 15 Comparison between DMA and static tensile test results.

DOI: 10.13009/EUCASS2017-326

In the same figure, a_t obtained with the DMA, and shifting factors obtained analysing static tensile tests are compared. As can be seen both data sets belong to the same WLF equations.
From These observations, we can conclude that DMA can be considered a valid method to give an evaluation and prevision of mechanical properties of composite propellants.

5. Conclusions

A method to perform a dynamic characterization of composite propellant was implemented. Two different clamping schemes, the tensions film clamp and the single cantilever clamp were tested in different conditions. The two clamps have limited range of applicability with respect to the range of temperatures that are needed to fully characterize the propellant master curve. The single cantilever clamp is affected by low reproducibility at high temperatures while the tension film clamp is not efficient for low temperatures due to the low maximum force applicable by the DMA. Data obtained with the two clamps are parallel to each other and the same set of shifting factors can be applied. In this way data obtained with the two clamps can be correlated extending the temperature range measurable.
Overall data were compared to available static tensile tests for the same batch of propellant. Same set of a_t can be used and a constant ratio between results obtained with static tests and dynamic test can be found.

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