Building Frequency Temperature Superposition Master Curves

Keywords: DMA, master curves, WLF, Arrhenius model, frequency sweep, viscoelasticity

Figure 1. Metravib DMA+1000

Introduction

High frequency needs

Nowadays, a lot of materials are submitted to repetitive mechanical force or solicitation. For example: some joint polymer part in a turbine system, or the surface of a tyre repeatedly crossing the road. In order to characterize this kind of effect on the material, the DMA is one of the best tools. Metravib DMA+ allows the study of specimens from high force range, high displacement and high frequency up to 1000 Hz. While the 1000 Hz range covers up the large majority of direct application from polymer material, studying the viscoelastic properties at higher frequency can bring specific information about the material behavior in certain circumstances. One of the best examples is to evaluate the grip of a tire or a shoe sole on some specific and flat surface. In those cases, the viscoelastic properties over 1000 Hz are of a key characteristic to predict how the car (or the runner in the case of a shoe) will perform on these surfaces.
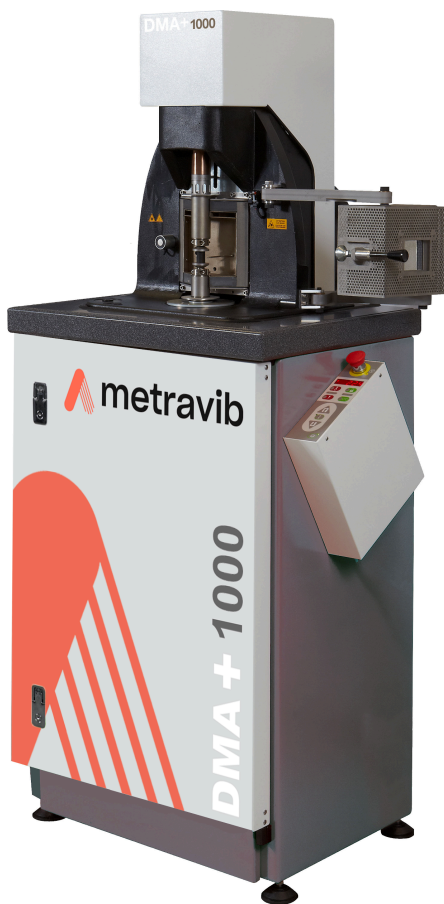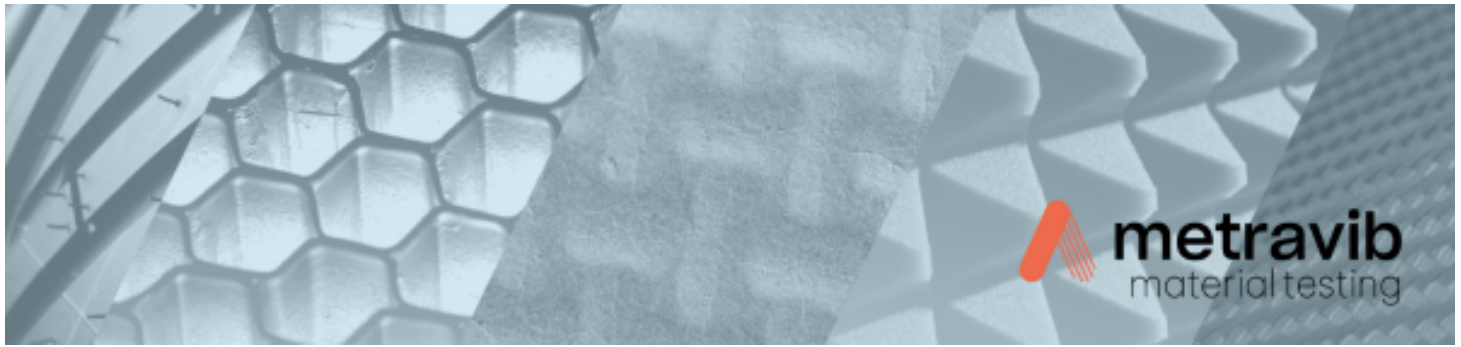
Unfortunately, usual DMA cannot perform tests over 1000 Hz due to mechanical limitations.

Master Curve Principle

To overcome this limitation, the FTS (Frequency Time Superposition) is used to build Master Curves based on the WLF model (Williams–Landel–Ferry equation) or Arrhenius model. The principle is quite simple, it is based on the fact that there is an equivalence between the frequency of the mechanical sollicitation and the temperature on the viscoelastic properties of material. In other words, increasing the frequency of mechanical sollicitation on a specimen studied by DMA has the same effect on E', E'' and Tan δ as decreasing the temperature. This principle is illustrated in Figure 2 with a fictive representation of two frequency sweeps tests performed at 10°C and 30°C between 1Hz and 100 Hz: the modulus of elasticity shows the same value at 10°C from 1 Hz to 10 Hz than at 30°C from 10 Hz to 100 Hz.
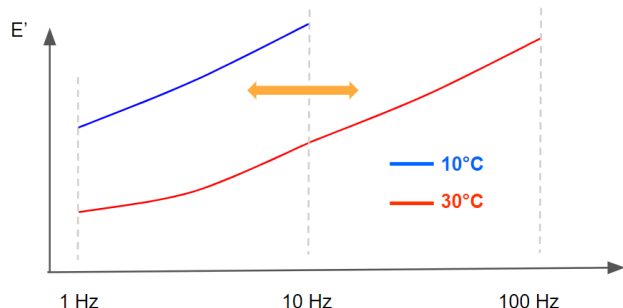

Figure 2. Fictive representation of the equivalence between time and temperature. There is an equivalence for E' values between 1 Hz - 10 Hz at 10°C and 10 Hz - 100 Hz at 30°C.

From a molecular point of view, polymer chains exhibit similar behavior when a deformation or a force is applied, the latter being both temperature and frequency dependent. As an example, for a polymer submitted to a constant load, E' decreases over the time because the polymer rearranges his chains in order to decrease the stresses applied. This explains why the modulus of elasticity is lower at low frequencies. On the other hand, increasing the temperature (which corresponds to providing energy to the system) leads to an acceleration of the chain motions in the polymers and their rearrangement when submitted to a mechanical stimulus. From this, one understands that decreasing frequency leads to similar effects on the viscoelastic properties than increasing the temperature. Of course, the opposite is also true, increasing the frequency corresponds to decreasing the temperature.

A DMA+ from Metravib is able to perform tests up to 1000 Hz and the temperature range is between -150°C and 500°C. **From this specification, in order to study the viscoelastic properties of materials above 1000 Hz, it will be necessary to perform frequency sweeps at different temperatures and use the frequency-temperature equivalence in order to simulate very high and very low frequencies.**

Preliminary tests

Before going further in the parameters setting, there are two very important points (or rules to some extent) to consider before building the master curve.
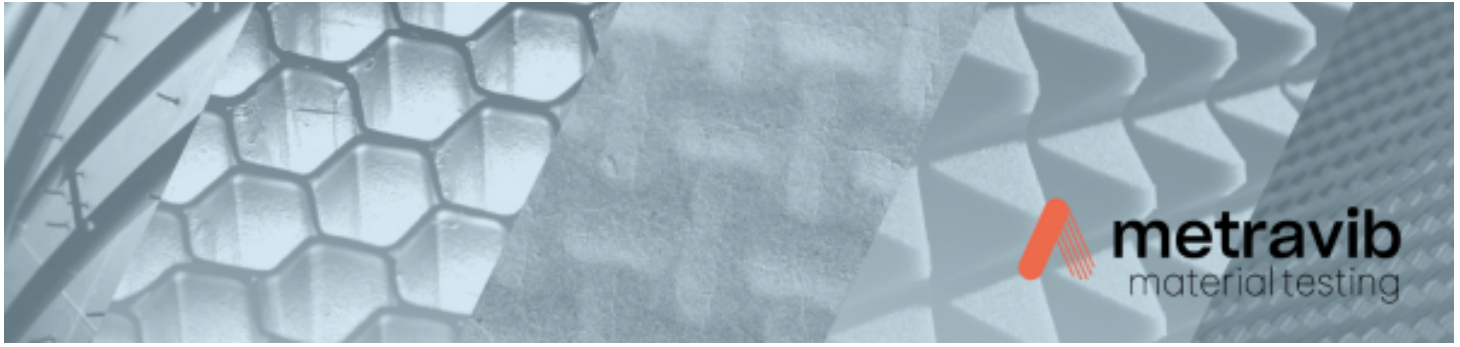
The first one is to stay in the linear domain of the material. As a reminder, the linear domain is a strain amplitude in which the viscoelastic properties are constant with the strain. In other words, the force applied during the test must be low enough to not induce large molecular rearrangements in the polymer matrix. Technically, in order to respect the first point, it is necessary to perform a strain sweep prior to the Master curve (an example is given in the results part, see Figure 5) to define the linear domain.

The second point is to define the thermal profile of the viscoelastic properties. As said previously, a master curve is built by combining frequency sweeps performed at different temperatures. If there is not enough data, then the master curve construction will be harder and most likely incomplete. Then, from the lowest to the highest temperature, it is important to consider how much the viscoelastic properties change between each temperature step and set the parameters accordingly. In other words, because during the glass transition, E', E'' and Tanδ change a lot, it is important to increase the number of frequency sweeps performed during the transition. That is why it is highly recommended to perform a temperature sweep before the master curve, in order to define the temperature range of the glass transition. As for the first point described above, an example is given in the results section (see Figure 6). The WLF law is applicable for reference temperatures above Tg: Tg < reference temperature < Tg+100˚C.

Building Master Curves

Technically, the first step to build a master curve is to perform successive frequency sweep tests at different stabilized temperatures (details are given in the method part). Then, the frequency sweeps are horizontally shifted towards a reference temperature (usually one of the frequency sweep curves performed). Shifting the curve vertically is also a possibility when building a master curve, but this possibility is not discussed in this article. The Figure 3 below illustrates how to build a full master curve. This process can be done all automatically using the Dyna+ software, or manually using a spreadsheet program.
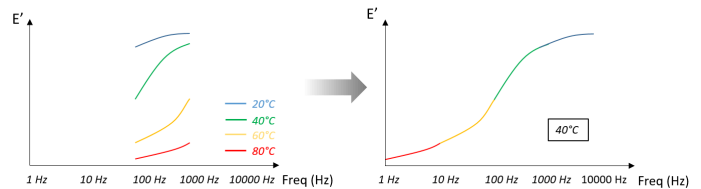

Figure 3. Schematic representation of the master curves creation from frequency sweep performed at different temperatures to a final master curves at 40˚C

WLF Model

The degree of horizontal shifting needed to shift the frequency sweeps around the reference can be determined as a function of the temperature. Generally, two models are used to build the master curve. The relation of Williams-Landel-Ferry applied on the principle of time-temperature superposition, which is
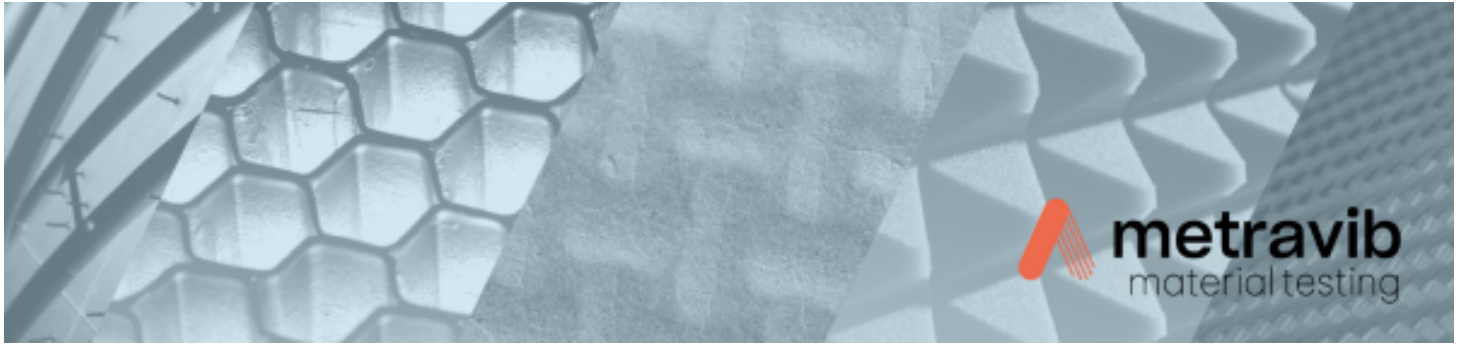
usually the most used, is especially adapted for temperatures close to the glass transition temperature and also for the flexibility of the model. The WLF model expresses the change of the shift factor with the temperature as described below:

$$\log a_{\mathrm{T}} = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)}$$

With a_{T} the shift factor, T the temperature, T_0 the reference temperature, C_1 and C_2 two positive constants that depend on the material and the reference temperature. In other words, the determination of C_1 and C_2 allows the determination of the shift factor (Figure 8 in the results section). Then, any curve at temperature T can be shifted around the reference curve (T_0).

Arrhenius Model

The other model used to determine the shift factors with the temperature is the Arrhenius model The relation between the shift factor and the temperature can also be determined using the following equation :

$$\log(a_{\mathrm{T}}) = -\frac{E_a}{2.303R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

with E_a the activation energy, R is the universal gas constant (8.31), T the temperature and T_0 is the reference temperature. The Arrhenius law is well adapted to describe polymer behavior below the glass transition temperature and applies well to secondary transitions. It is also useful to obtain the activation energy associated with the glass transition.

## Materials & methods

Specimens

Rubber materials were studied with a DMA+1000 in film shear mode. A film of rubber with the following dimensions was prepared:

- Length: 50 mm
- Width: 11,27 mm
- Thickness: 2 mm

Methodes

A sinusoidal waveform is applied on the specimen at different frequencies (see Figure 4) at different temperatures. To study the specimens, the shear film mode was used. A dynamic displacement is applied on the specimen, the shear is applied on the 2 parts of the specimen between the specimen holder jaws. One of the advantages of this method is that no static is necessary to maintain the specimen in the specimen holder. The specimen must have a form factor complying with the dimensioning rules for the excitation mode and must have a stiffness variation range complying with the instrument's measurable stiffness range. Moreover it is important to use a homogeneous (no copolymers), isotropic and amorphous specimen and that no structural

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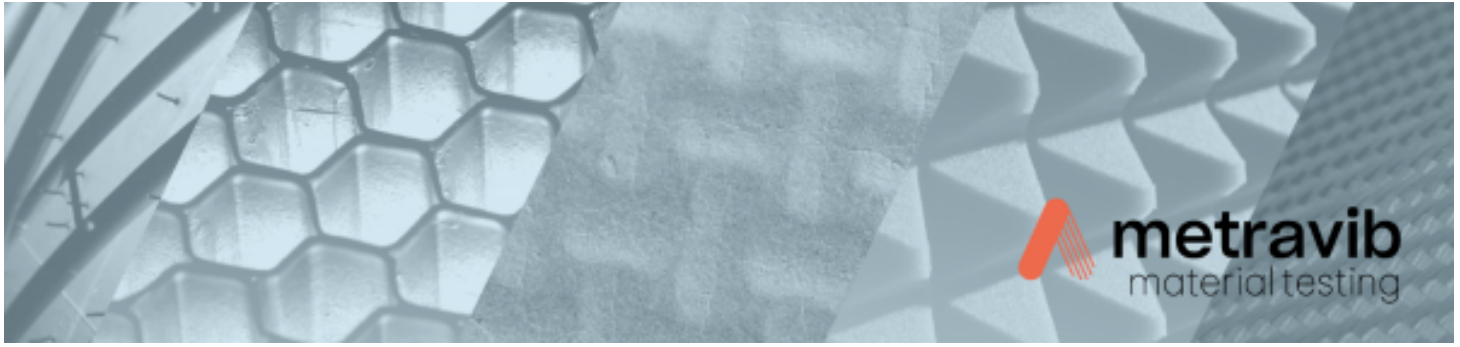
changes over the characterization temperature range (e.g. post-firing or decomposition).
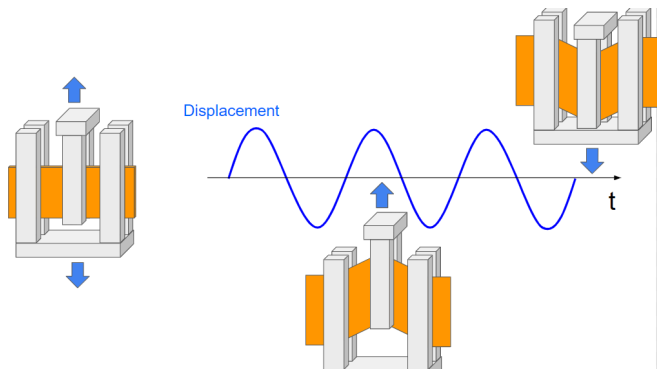

Figure 4. Graphical representation of the dynamic mechanical displacement applied to the specimen

The following tables show the different parameters used for the 2 preliminary tests and for the Master Curve itself.

Strain Sweep Setting Parameters	
Dynamic	Force from 0.01 to 50 N
Frequency	1 Hz
Static	-
Temperature	Room temperature

Table. 1: The setting Parameters of the strain sweep preliminary test

Temperature Sweep Setting Parameters	
Dynamic	5 µm
Frequency	1 Hz
Static	-
Temperature	From –100°C to 80°C, 2°C/min

Table. 2: The setting Parameters of the temperature sweep preliminary test. The dynamic displacement has been defined following the results of the strain sweep test.

Temperature Sweep Setting Parameters	
Dynamic	5 µm
Frequency	from 1 Hz to 100 Hz
Static	-
Temperature	15 minutes stabilization at –75°C, then a frequency sweep. The process is repeated at –70°C, –65°C, –60°C, –55°C, –50°C, –45°C, –40°C, –35°C, –30°C, –25°C, –20°C, –15°C, –10°C, –5°C, 0°C and 10°C

Table. 3: The setting Parameters of the temperature sweep preliminary test. The dynamic displacement has been defined following the results of the strain sweep test.
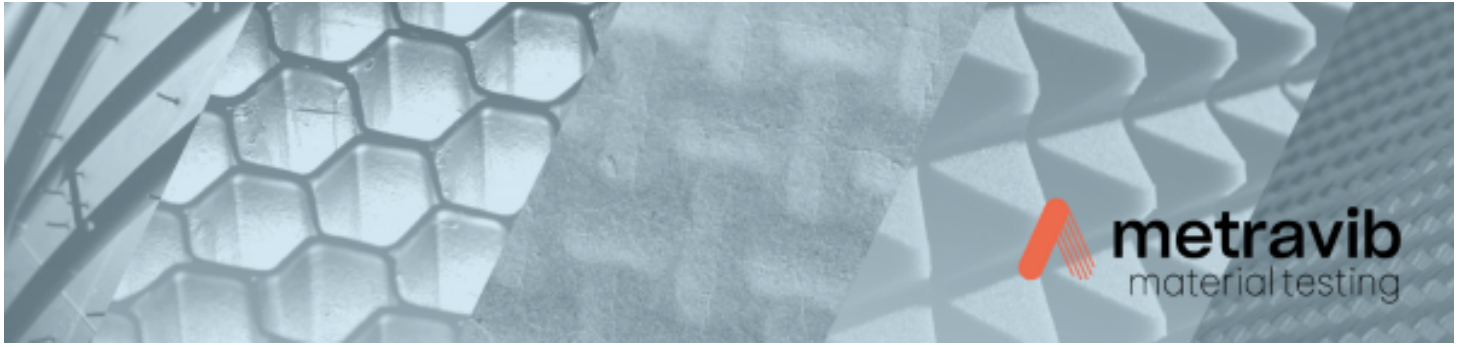
Results

Preliminary Strain Sweep Results

Figure 5 shows the modulus of elasticity G' and Tan δ as a function of the displacement at 1 Hz and room temperature. The graph clearly shows that the domain of linearity is obtained for strain below 0,05% (which corresponds to a 5 μm displacement), the modulus decreases and those changes are correlated with the nonlinearity domain. To build a proper master curve, the experiment must be performed in the linearity domain otherwise the curve superpositions are meaningless.
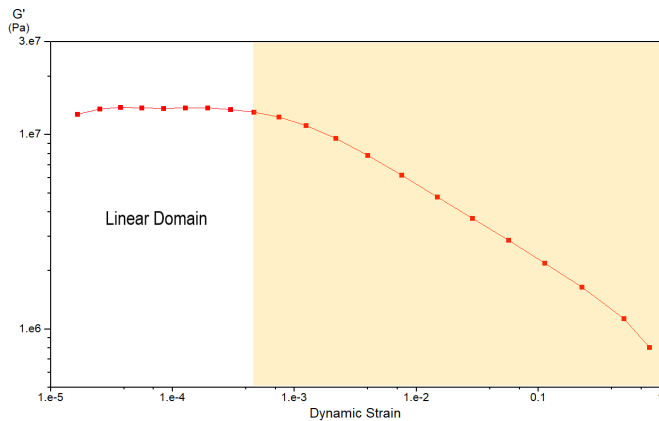

Figure 5. G' and Tan δ as a function of the dynamic displacement at 1 Hz and room temperature. The linear domain is highlighted

Preliminary Temperature Sweep Results

Figure 6 below presents G' and Tan δ as a function of the temperature. The decrease of the modulus with the temperature and the Tan δ peak at –41.17°C are characteristic of a glass transition in the rubber. During this transition, a gradual and reversible change in amorphous materials occurs, from a hard and relatively brittle "glassy" state into a viscous or rubbery state as the temperature is increased. Knowing this is important for the master curve experiment setting, because more data are needed around the glass transition temperature. In other words, around the glass transition temperature, more frequency sweeps need to be performed in order to obtain enough data to compile the master curve.
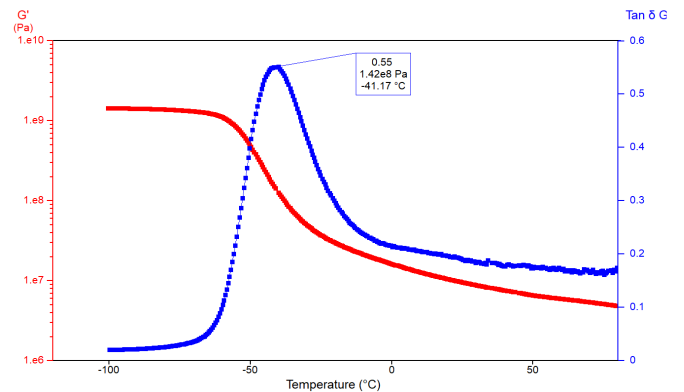

Figure 6. G' and Tan δ as a function of the temperature at 1 Hz

Building the MasterCurve

From the results obtained, Frequency sweeps were performed between –75°C and 10°C, and from 1 Hz to 100 Hz at each temperature step. The Fig. 7 below shows E' as a function of the frequency at different temperature steps; each curve can be shifted in order to build a master curve. As expected, the
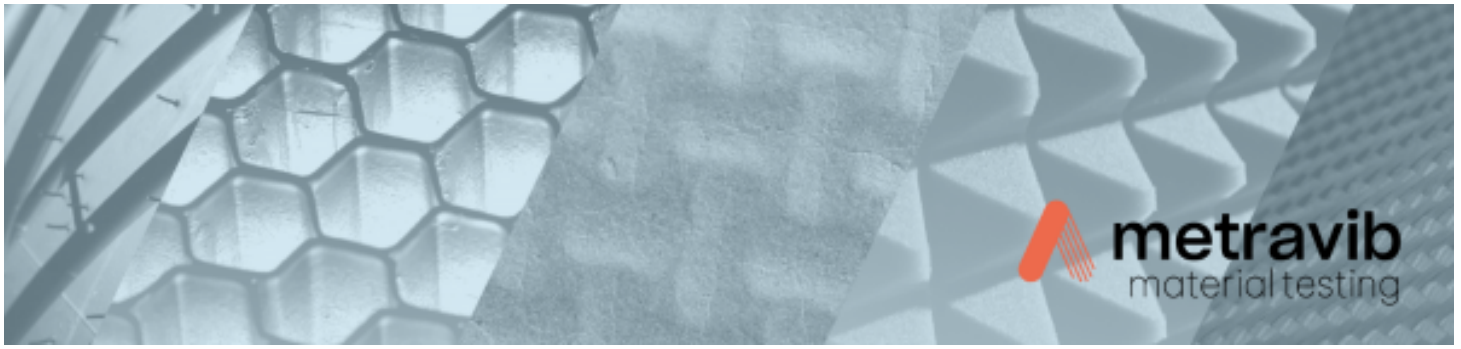
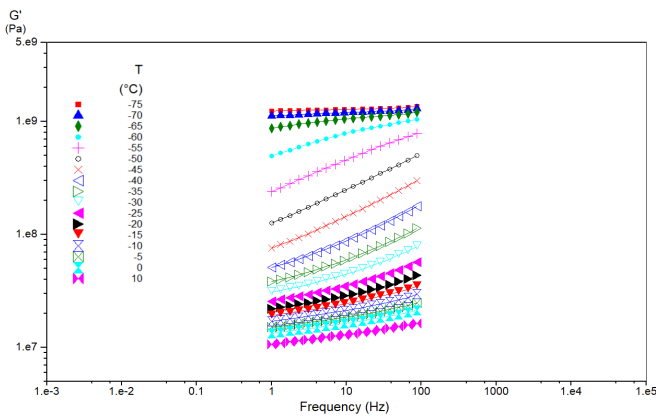Modulus increases a little with frequency and decreases with temperature.

Figure 7. G' a as a function of the frequency at different stabilized temperatures from –75˚C to 10˚C

The computation performed by the DMA+ software allows us to obtain the shift factor versus temperature (Figure 8, at -30˚C, the reference temperature). A shift factor of 1 means that there is no shift at this temperature (which makes sense for -30˚C because it is the reference). Then, the more the shift value differs from 1, the more the shift value is important. As it can be seen on the graph, both WLF and Arrhenius models are used to fit results (see equations in the previous part). The values C1 and C2 for the WLF model and A for the Arrhenius model are not only given as mere information but above all to allow the user to rebuild the master curve on a spreadsheet program.
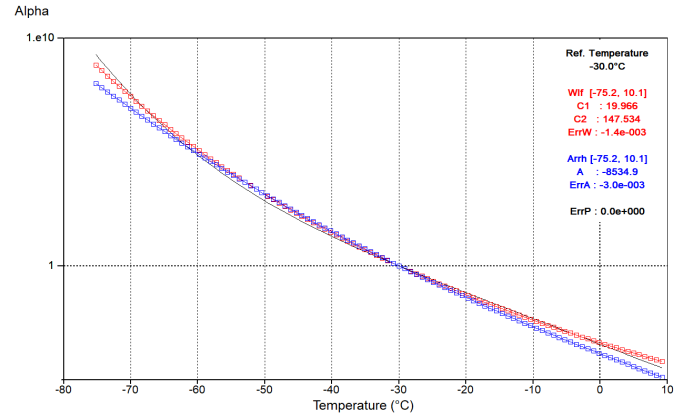

Figure 8 : The shift factor versus temperature, for a temperature of reference equal at –30˚C. Both WLF and Arrhenius are illustrated, in red and blue respectively.

Because the error between Arrhenius and the WLF model is in favor of the WLF model (see Figure 8), the fit is based on the empirical relationship of Williams–Landel–Ferry (WLF Model).
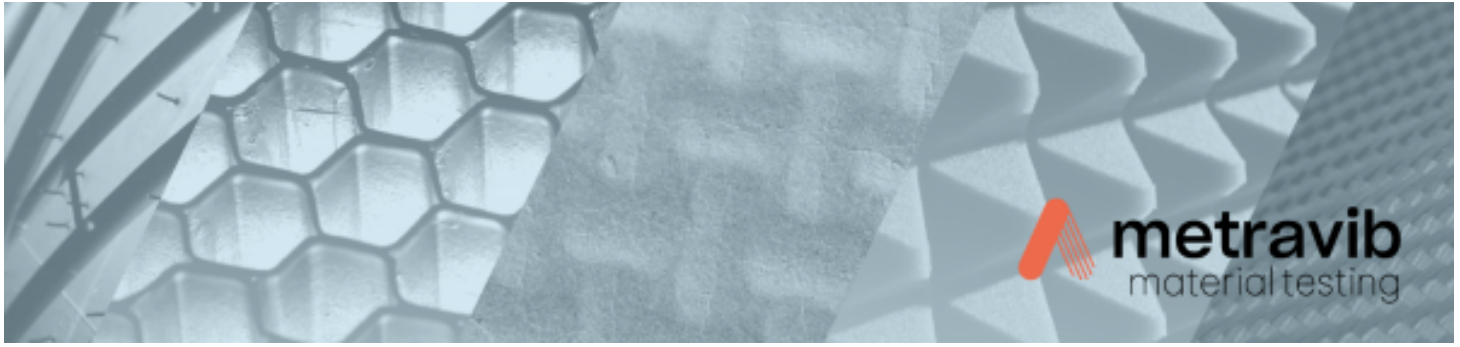
$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)}$$

with the following parameters (obtained from the DMA+ software):

- C_1 = 19.966
- C_2 = 147.534
- Error = $2 * 10^{-3}$

Figure 9 is the master curve built from the combination of all the frequency sweeps (Figure 7) shifted with the a_T values depicted in Figure 8. Figure 9 shows the extrapolated

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viscoelastic properties G'(red square), G''(blue square) and the polynomial fit (black line) as a function of the frequency. The changes in G' and G''as a function of the frequency are similar to ones observed during a temperature sweep (see section preliminary tests) and the G'' are correlated to relaxation times. Moreover, these results highlight the capability of the master curve to predict properties on a large frequency range (in this example, the frequency range goes from 10^{-5} and 10^{10} Hz). In Figure 9, all curves shifting were automatically performed with the Dyna+ software from Metravib Material testing.

Figure 9 : Master Curve of G' (red square), G'' (blue square) and the polynomial fit (black line) as a function of the reduced frequency at -30˚C. The WLF model fit is indicated by a thin black line for G' and Tan δ

Conclusions

The viscoelastic properties of polymers measured at high frequency are a key characteristic to predict the behavior of some final product, such as the grip of tires on wet surfaces. In order to overcome DMA physical limitations at very high and very low frequency, Master curves are used. The scope of this paper was to present the FTS Master curve, a methodology that simulates the viscoelastic properties of polymer material at very high and very low frequencies. The whole process to make a master curve from frequency sweeps at different temperatures was described with details, from the preliminary tests to the different models used to build the final curve.

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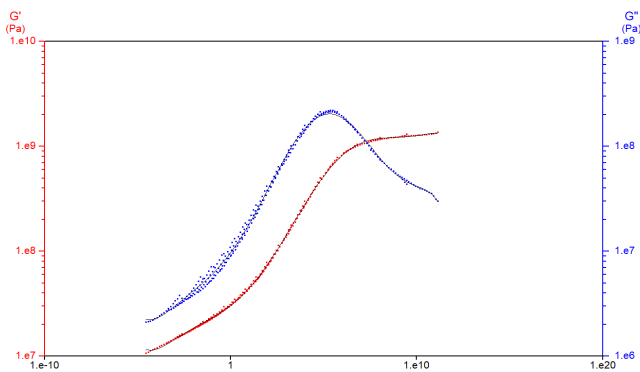
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