

Data interpretation and comparison of DMA results from HTPB-IPDI bonded composite elastomer samples used in an international Round Robin Test

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Abstract

Dynamic mechanical analysis (DMA) is a very useful method to characterize elastomers, which consist of a three-dimensional non-thermoplastic network or are built-up by linear polyurethanes resulting in thermoplastic materials. The so-called glass-to-rubber transition is determined by DMA very properly as function of mechanical deformation rate. This makes DMA a more realistic characterization tool than for example DSC (differential scanning calorimetry), NMR (nuclear magnetic resonance), or dielectric relaxation, because these are used in mechanically static mode. The investigated materials comprises two samples from an international RR test: (1) one inert sample manufactured by the US Naval base in China Lake, California, USA, which simulates an HTPB-IPDI bonded PBX (plastic bonded high explosive); (2) one inert sample provided by DGA Techniques Terrestres in Bourges, France, which simulates composite rocket propellants.

The DMA instrument used is an ARESTM (Advanced Rheometric Expansion System) Type A1 manufactured by the former Rheology Unit of Rheometric Scientific Inc., Piscataway, NJ, USA (now belonging to Waters Inc., BU TA Instruments, Newcastle, Delaware, USA). This instrument uses the torsion mode and the complex shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ is obtained. The symbol ω is the angular frequency ($\omega=2\pi\nu$) applied and G' and G'' are storage shear modulus and loss shear modulus, respectively. The sample sizes are typically rectangular with dimension 30 to 50 mm long, 10 mm wide and 4 to 5 mm thick. To measure in the linear viscoelastic range first so named strain sweeps are performed typically at low, ambient and higher temperatures, here at -100°C, about +22°C and +70°C. By this, the strain range is determined, in which the modulus is independent of applied strain, which is the definition of linear viscoelastic behaviour. Then the typical 'production' runs were performed. Discrete temperature sweeps with 1°C or 2°C temperature step and hold (soak) time of 40 sec, and on each temperature step a discrete frequency sweep was made, typically at 0.1 Hz, 1.0 Hz, 10 Hz and 30 or 56 Hz. Further on runs were performed at more frequency steps to calculate the so-called master curves assuming the time-temperature superposition principle is valid. For establishing the master curves the TriosTM or OrchestratorTM software package of TA Instruments was used with only horizontal shifting of the curve parts. A comparison of the data between the sample is made and discussed. As expected, the horizontal shift factors can be well described with WLF (Williams-Landel-Ferry) equation. But a new description called modified Arrhenius works equivalently well and provides with the molecular parameter activation energy.

Keywords: DMA, round robin test, PBX simulant, CRP simulant, master curves on G' and G'' , WLF, modified Arrhenius

1. Introduction

Since about 2007 the re-working of the STANAG 4540, 'Explosives, Procedures for Dynamic Mechanical Analysis (DMA) and Determination of Glass Transition Temperature' was on the agenda which turned into a working part from 2009 on. Very soon, it was recognized that a coordination in applying a DMA instrumentation was necessary, which lead to the need for a round robin (RR) test with dynamic mechanical analysis (DMA). Organized was the RR by the NATO AC/326 Subgroup I, and its working group called Custodian Nations Group (CNG) was commissioned. Later the subgroup structure was changed and a special working group dealing only with mechanical properties of energetic materials was introduced, which establishes the Allied Ordnance Publication (AOP) 4717 on 'Mechanical Analysis of Energetic Materials', This AOP deals not only with DMA. In this paper only DMA is treated and some specialities will be discussed. It is the view of the German member of the working group and will present data obtained in Fraunhofer ICT.

2. Materials

After testing some pre-samples for their suitability two main samples were manufactured and supplied to the working group members from two sites. One producer is the 'Naval Air Warfare Center, Weapons Division, Energetic Materials Research & Processing Branch, China Lake, CA, USA. The other sample supplier is European, the DGA Techniques terrestres, Bourges, France.

The French (Bourges) sample is an inert simulant for a composite rocket propellant (CRP). The ingredients are:

Binder	HTPB-IPDI (hydroxyl terminated polybutadiene – isophorone diisocyanate)
Plasticizer	Dioctyl azelate (DOZ)
Additive	TEA (triethanol amine), crosslinker in part also bonding agent
Antioxidant	2-2 methylene bis (4 methyl-6 tertiary butyl) phenol (= Vulkanox™ BKF)
Curing catalyst	DBTL (dibutyltin dilaurate)
Solid filler	bimodal aluminium oxide (Al ₂ O ₃), in total about 73 mass-%
Req = NCO/OH = 1.3	

The US (China Lake) sample is an inert simulant for highly filled plastic-bonded high explosive (PBX). The ingredients are:

Binder	HTPB-IPDI
Plasticizer	Dioctyl adipate (DOA)
Additive	Dantocol (N,N'-di(2-hydroxyethyl)-5,5-dimethylhydantoin) or DHE, bonding agent for glass beads and nitramine type high explosives
Antioxidant	2-2 methylene bis (4 methyl-6 tertiary butyl) phenol (= Vulkanox™ BKF)
Curing catalyst	TPB (triphenyl bismuth)
Solid filler	trimodal glass beads, in total about 84 mass-%
Req = NCO/OH = 1	

3. Measurement procedures

The DMA instrument was of type ARES™ (Advanced Rheometric Expansion System) manufactured by former Rheometric Group of company Rheometric Scientific Inc., Piscataway, NJ, USA, now belonging to TA Instruments, Newcastle, Delaware, USA. The deformation mode is in torsion. The applied deformation frequencies have been for standard temperature-frequency sweep 0.1 Hz, 1 Hz, 10 Hz, 30 Hz and 56 Hz. The Measurement temperature range was from -110°C to +80°C. stepwise temperature increase from the lowest temperature on with tempera-

ture step 2°C und soak time 60 sec. To find suitable strain values (means a strain range in which the moduli do not change), strain sweeps have been performed at deformation frequencies 1 Hz, 0.1 Hz, 10Hz at three measurement temperatures -105°C, +21 to 24°C and +70°C. For the establishment of DMA master curves (MC) more data are needed. Table 1 shows the frequencies used to get the data on the storage shear modulus G' , loss shear modulus G'' and loss factor $\tan\delta$. The distance between two values is logarithmic in order to get equidistant data points in the diagrams. The master curves were obtained with Trios™ / Orchestrator™ software from TA Instruments.

Table 1: Data on G' , G'' , $\tan\delta$ at the used deformation frequencies in Hz for MC establishment

Decade 1	Decade 2	Decade 3	Decade 4
0.01	0.1	1	10
0.01259	0.12589	1.25893	12.5893
0.01585	0.15849	1.58489	15.8489
0.01995	0.19953	1.99526	19.9526
0.02512	0.25119	2.51189	25.1189
0.03162	0.31623	3.16228	31.6228
0.03981	0.39811	3.98108	39.8108
0.05012	0.50119	5.01188	50.1188
0.0631	0.63096	6.30958	63.0958
0.07943	0.79433	7.94329	79.4329

4. Results on the RR materials

In the following representative data are shown with diagrams for both sample materials. First some strain sweep data the production runs for the two shear moduli and the loss factor.

4.1 French sample material

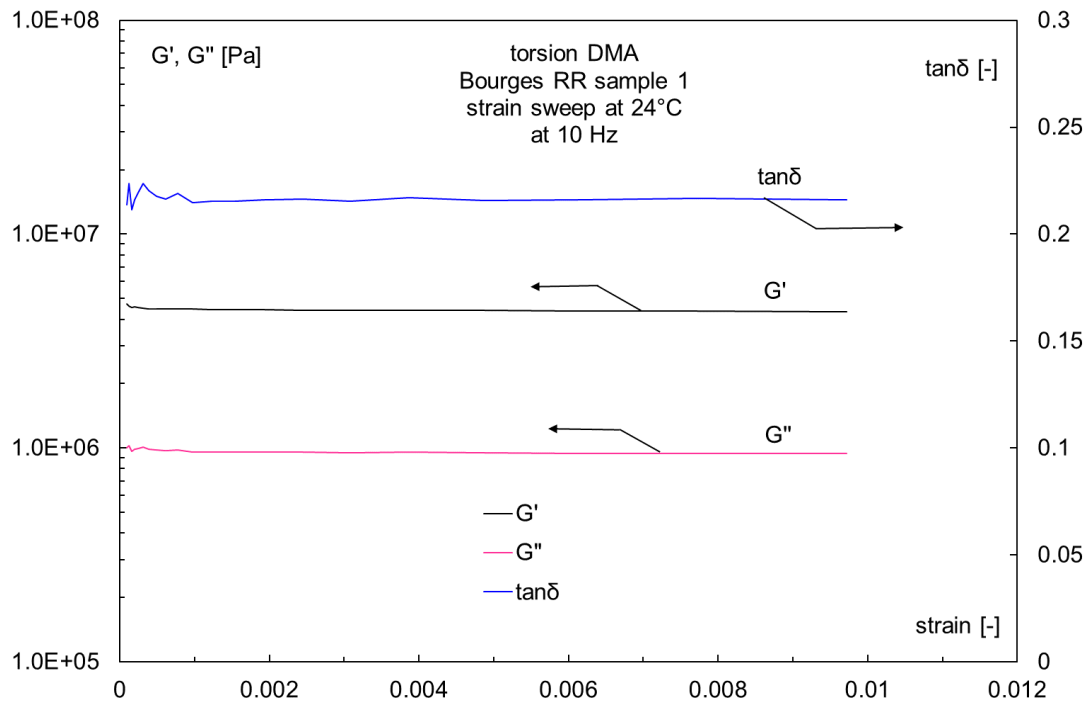


Figure 1: Strain sweep at 24°C and 10 Hz deformation frequency.

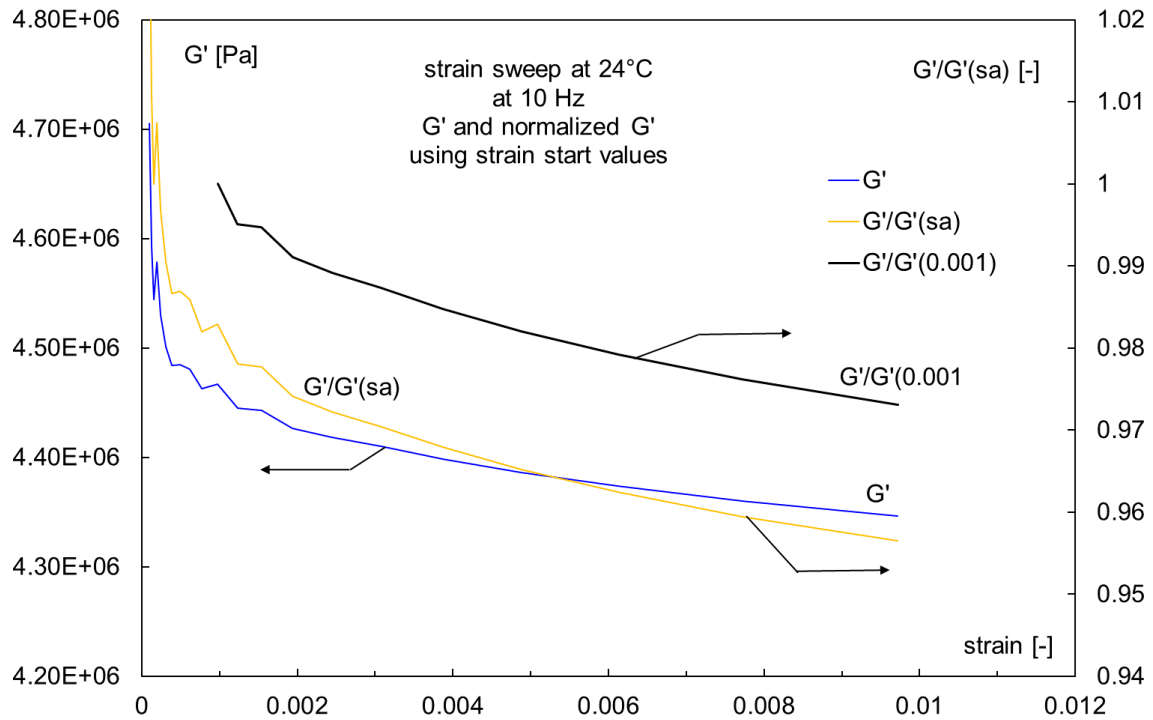


Figure 2: Strain sweep at 24°C and 10 Hz deformation frequency, but with normalized G' to show in enlarged way the drifts.

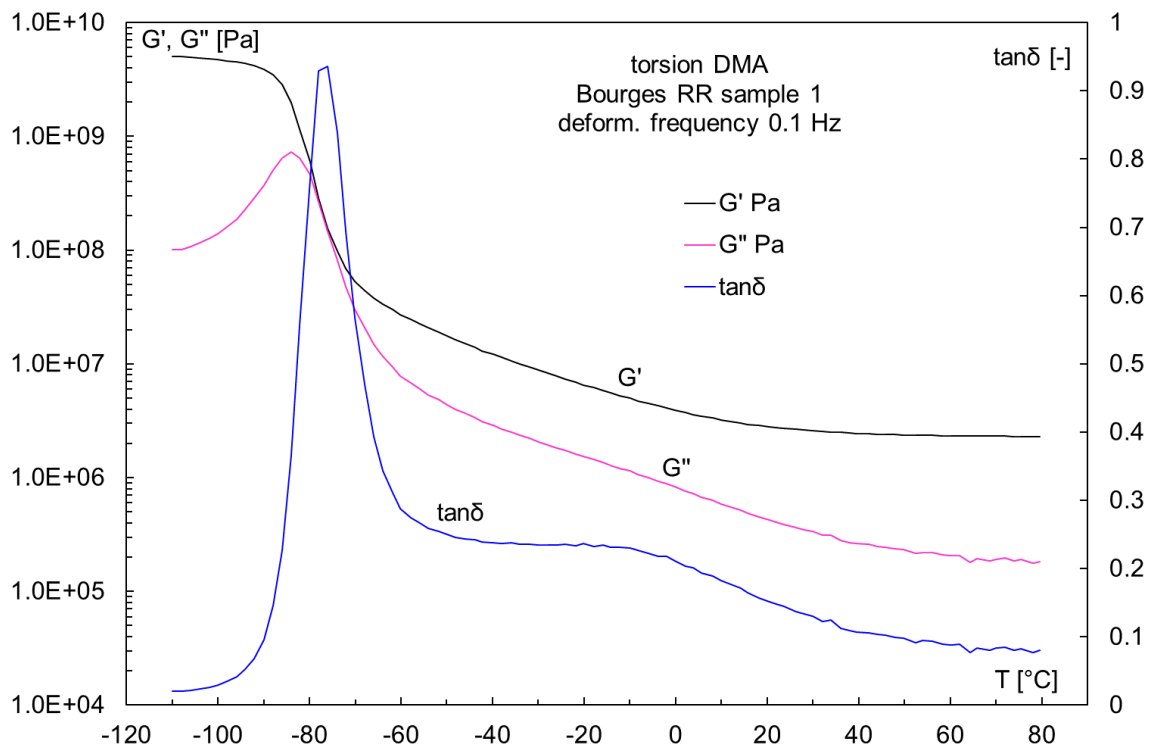


Figure 3: Presentation of the three important measurement results G' , G'' and loss factor $\tan \delta$.

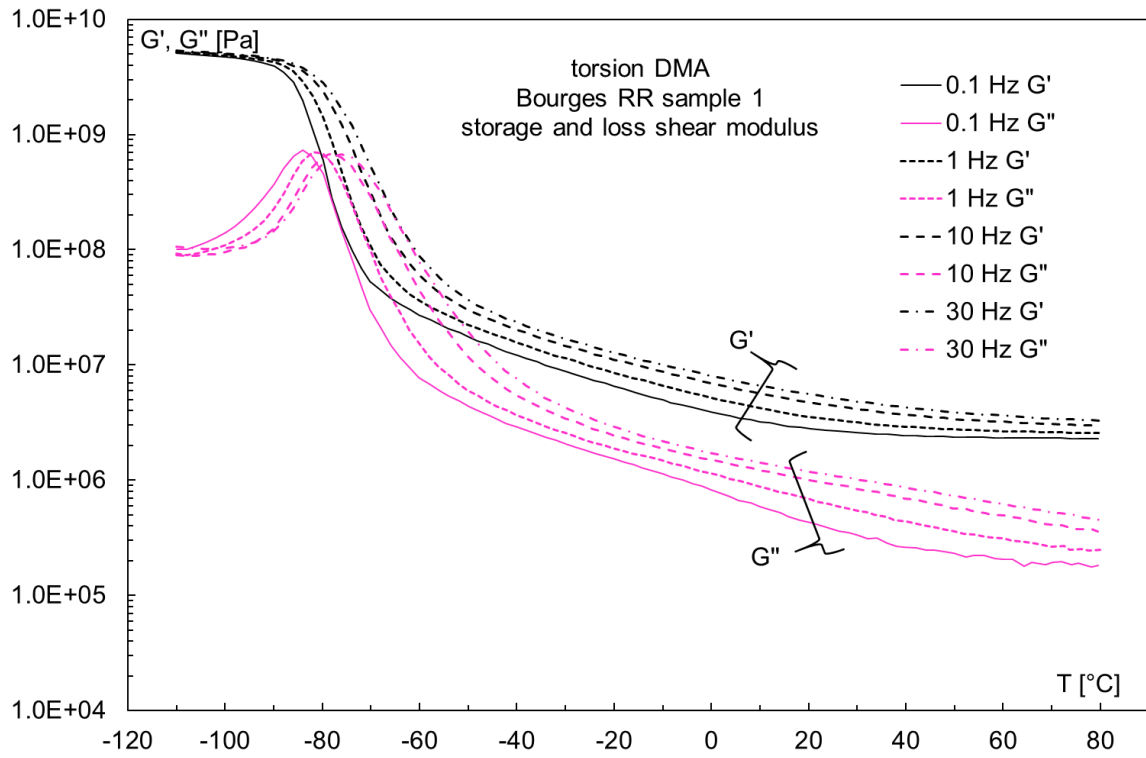


Figure 4: Storage and shear modulus as function of measurement temperature at four deformation frequencies.

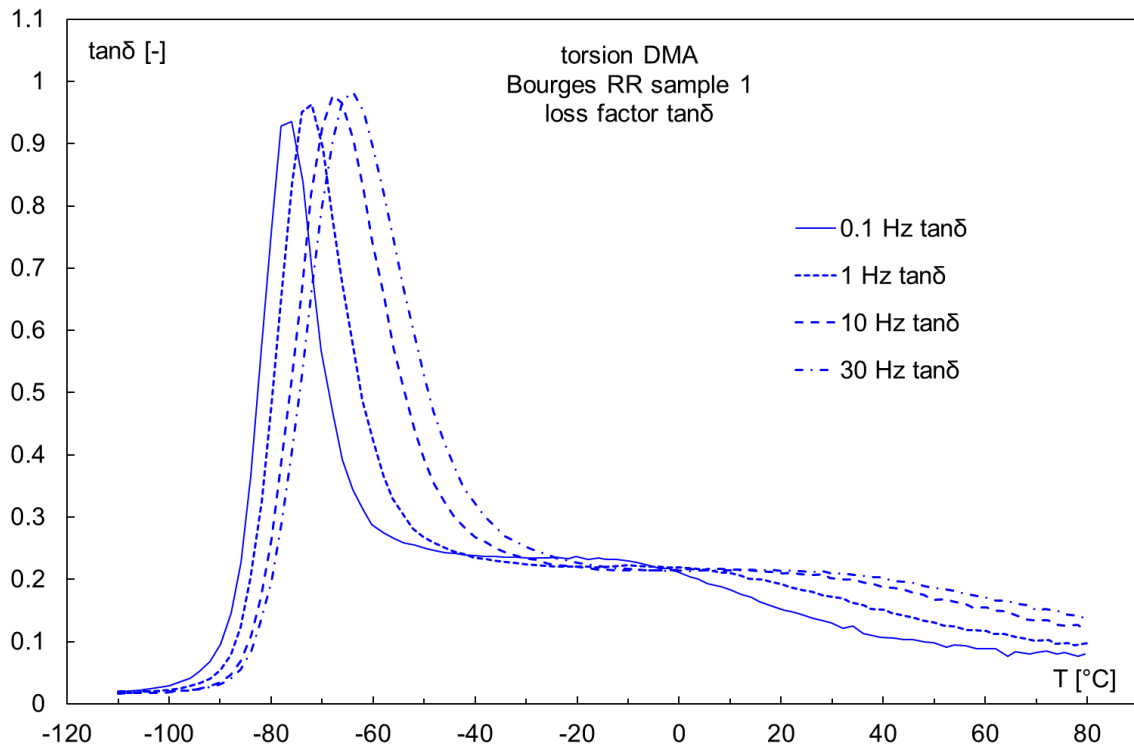


Figure 5: Loss factor $\tan\delta = G''/G'$ as function of measurement temperature at four deformation frequencies.

4.2 China Lake RR sample CL-7

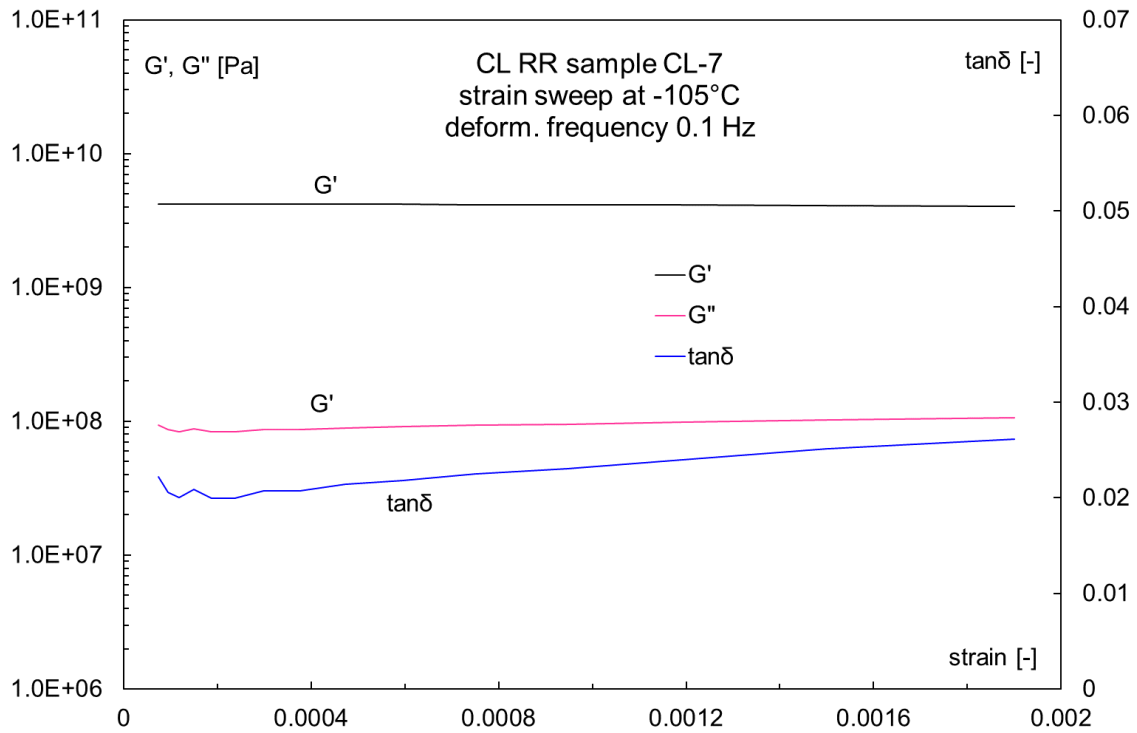


Figure 6: Strain sweep at -105°C and 0.1 Hz deformation frequency.

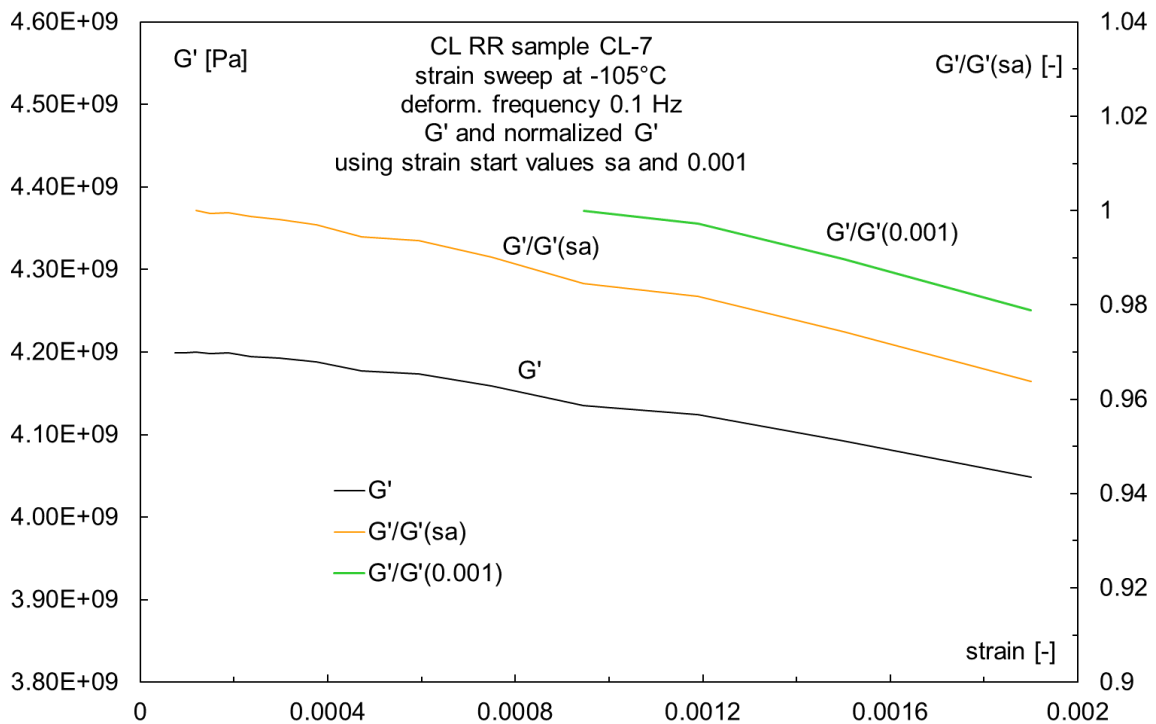


Figure 7: Strain sweep at -105°C and 0.1 Hz deformation frequency, but with normalized G' to show in enlarged way the drifts.

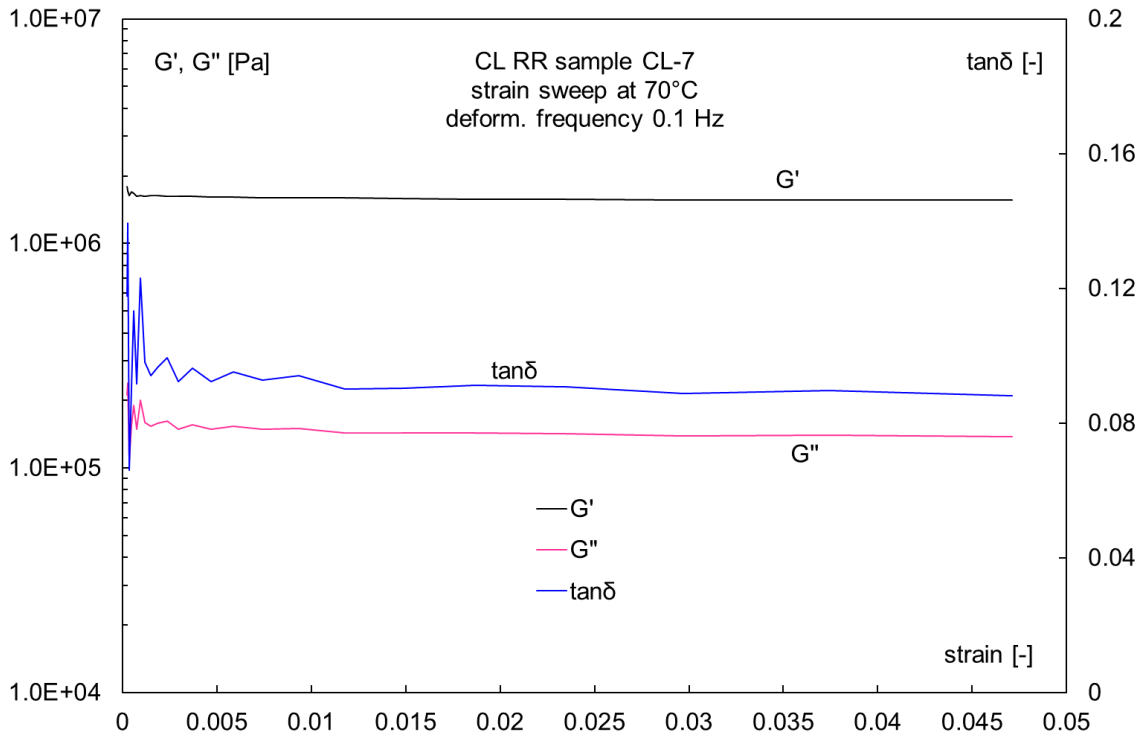


Figure 8: Strain sweep at 70°C and 0.1 Hz deformation frequency.

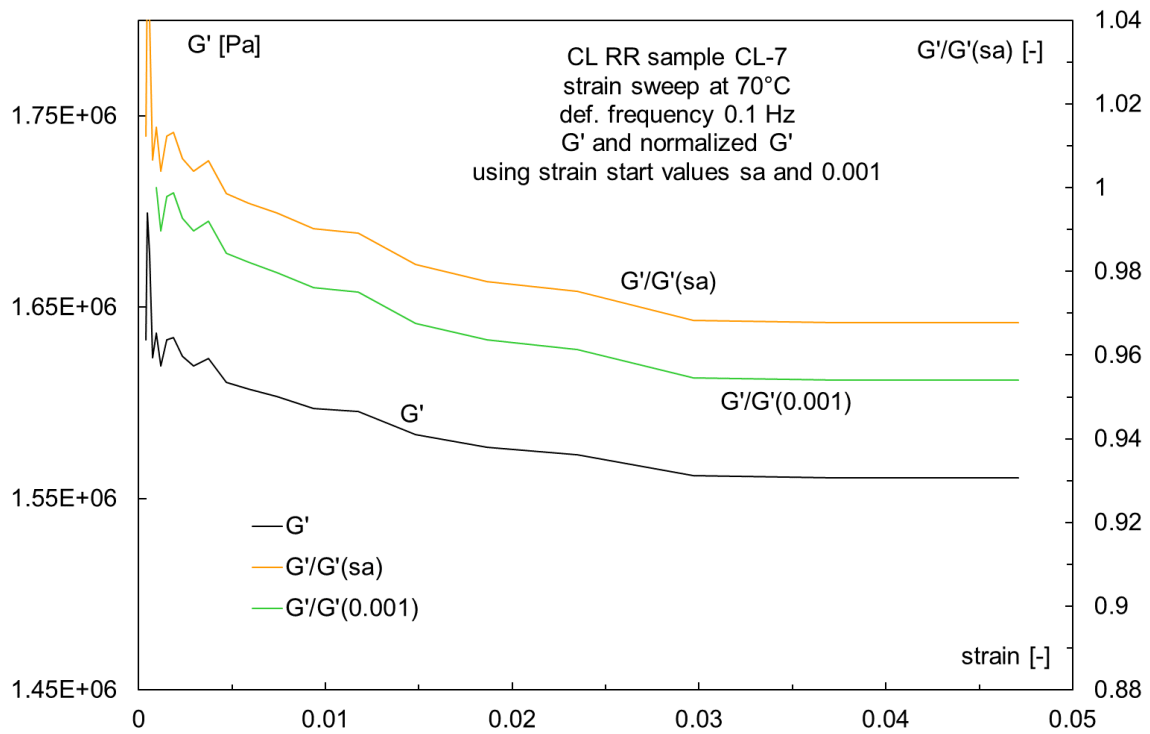


Figure 9: Strain sweep at 70°C and 0.1 Hz deformation frequency, but with normalized G' to show in enlarged way the drifts.

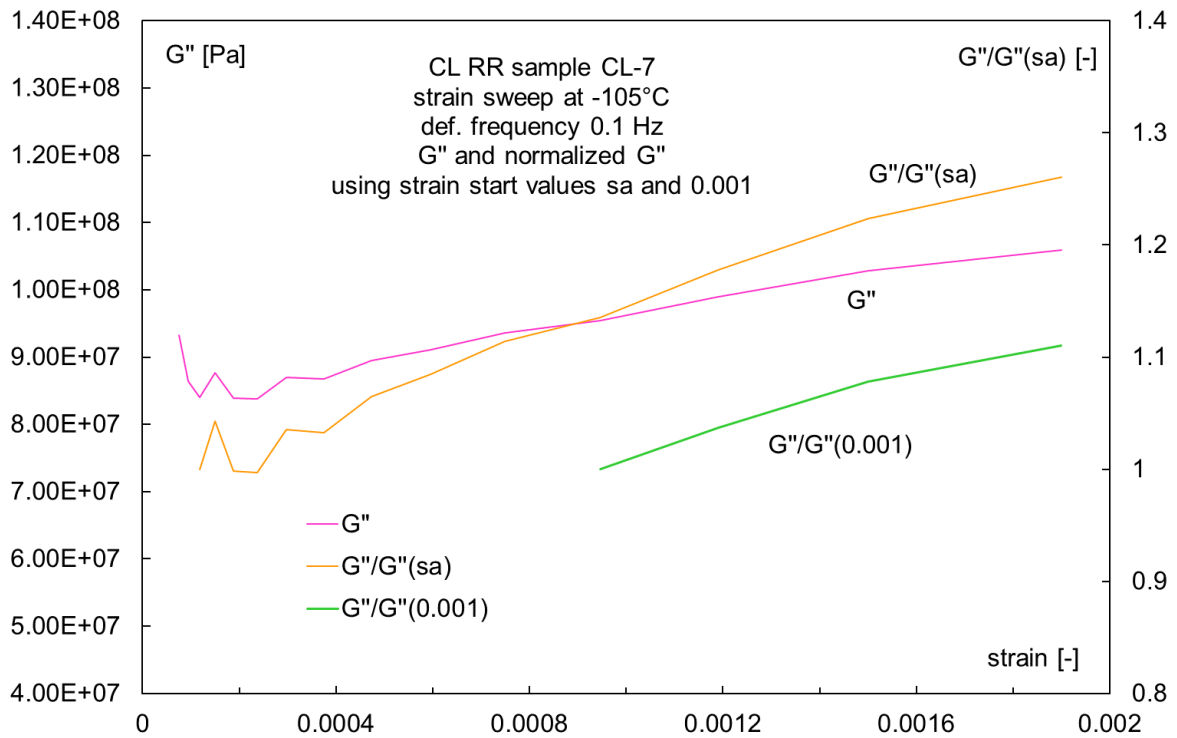


Figure 10: Strain sweep at -105°C and 0.1 Hz deformation frequency, with G'' and normalized G' to show in enlarged way the drifts.

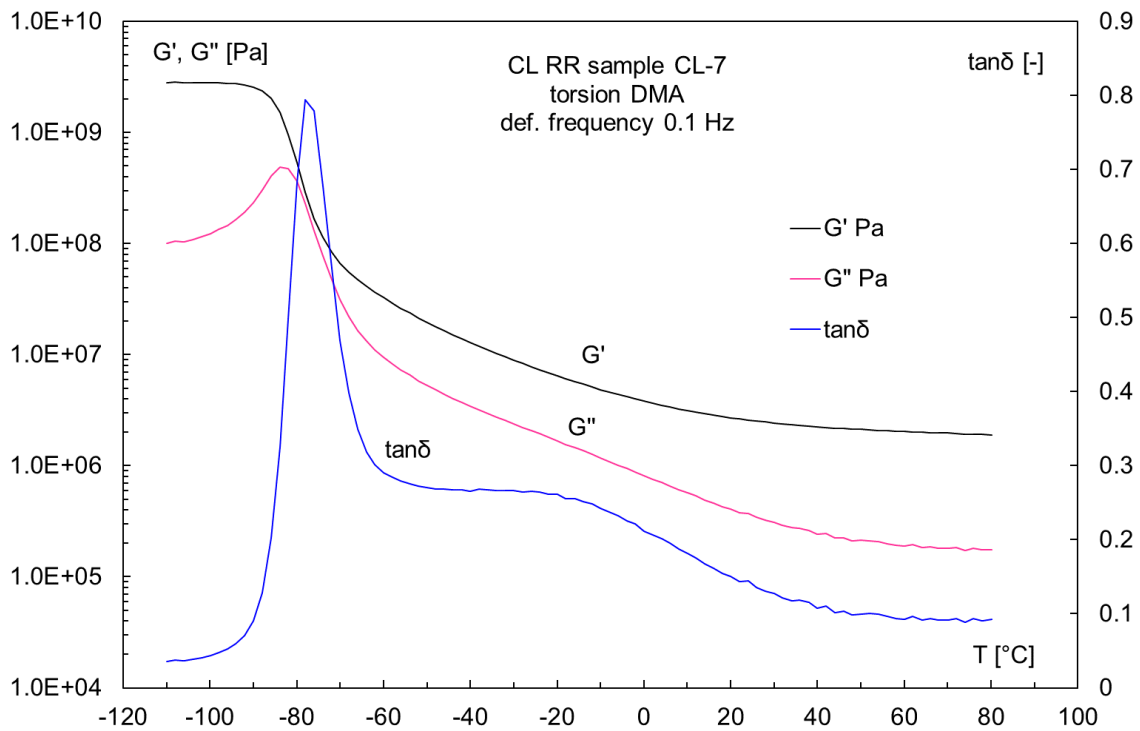


Figure 11: Presentation of the three important measurement results G' , G'' and loss factor $\tan\delta$.

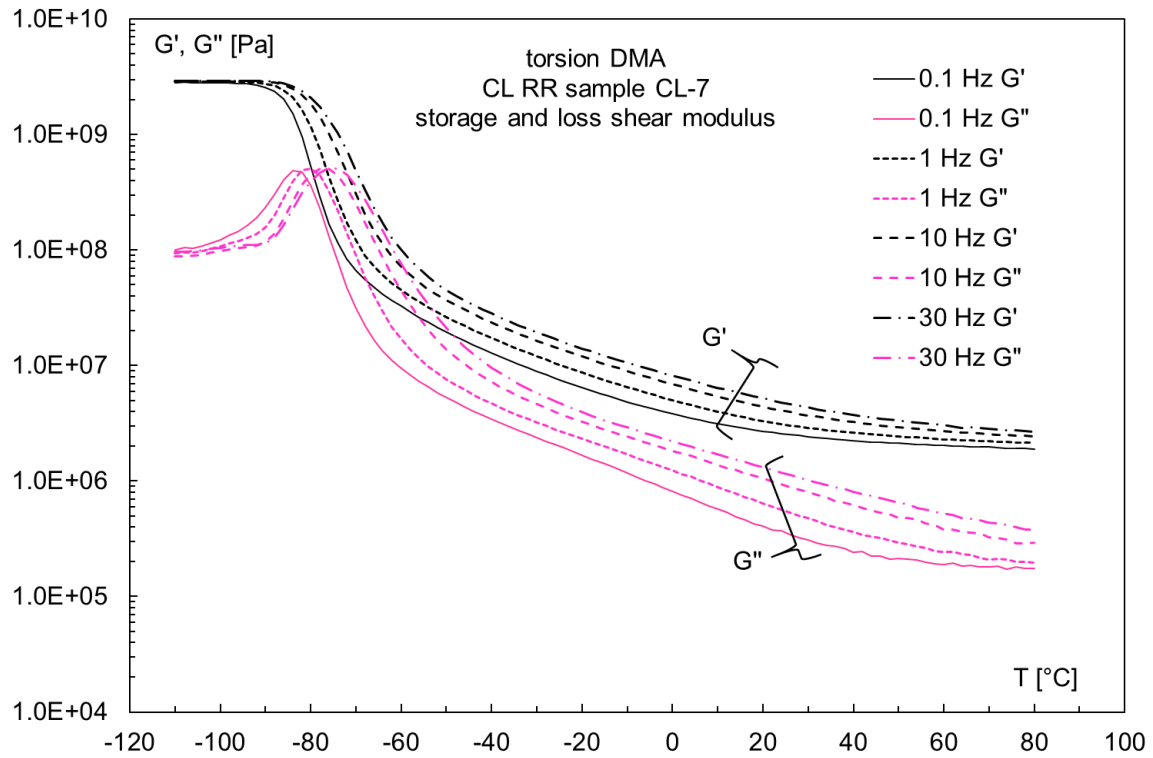


Figure 12: Storage and shear modulus as function of measurement temperature at four deformation frequencies.

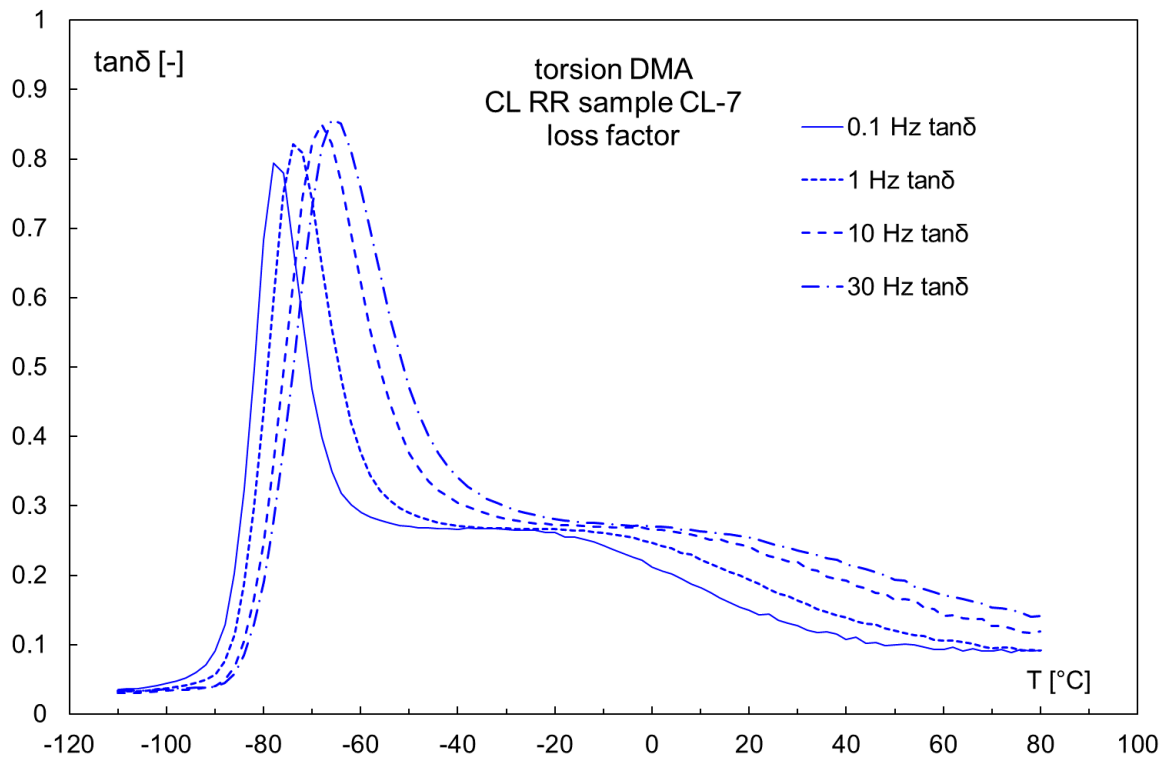


Figure 13: Loss factor $\tan\delta = G''/G'$ as function of measurement temperature at four deformation frequencies.

4.3 Comparison of RR samples from Bourges and China Lake

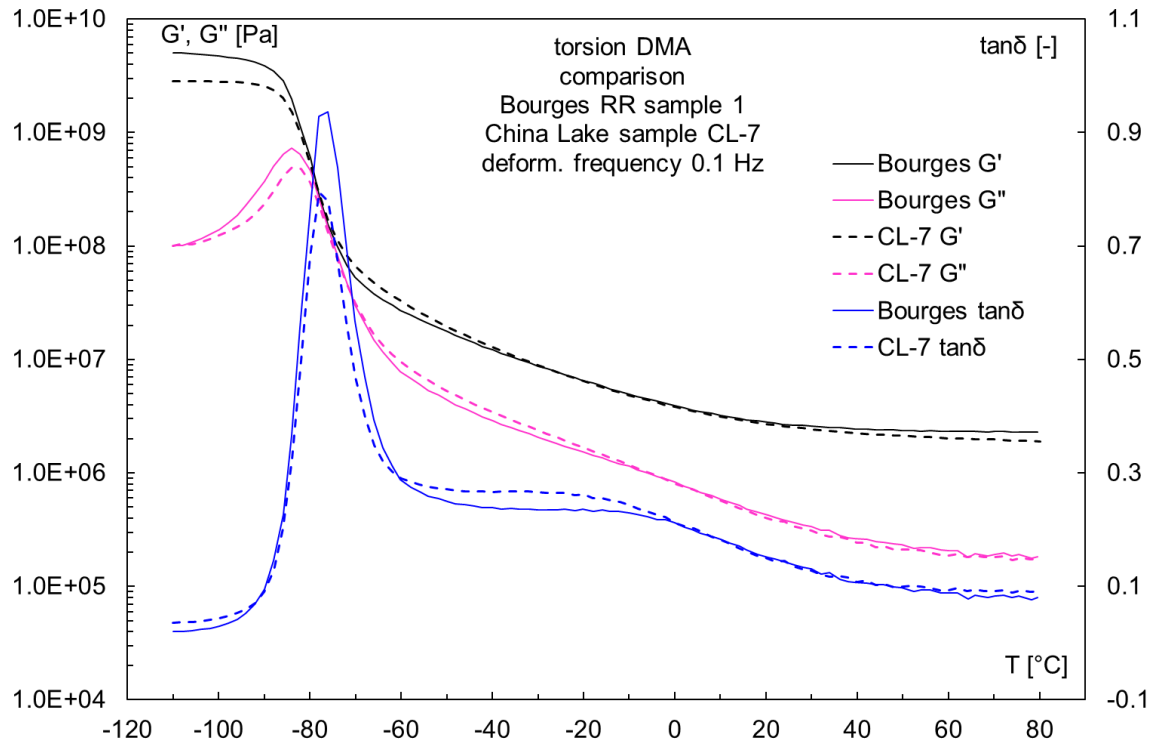


Figure 14: Comparison between Bourges and CL sample with all three quantities at 0.1 Hz deformation frequency. The loss factor is in the main maximum higher with the Bourges sample, G' is also higher at low temperatures.

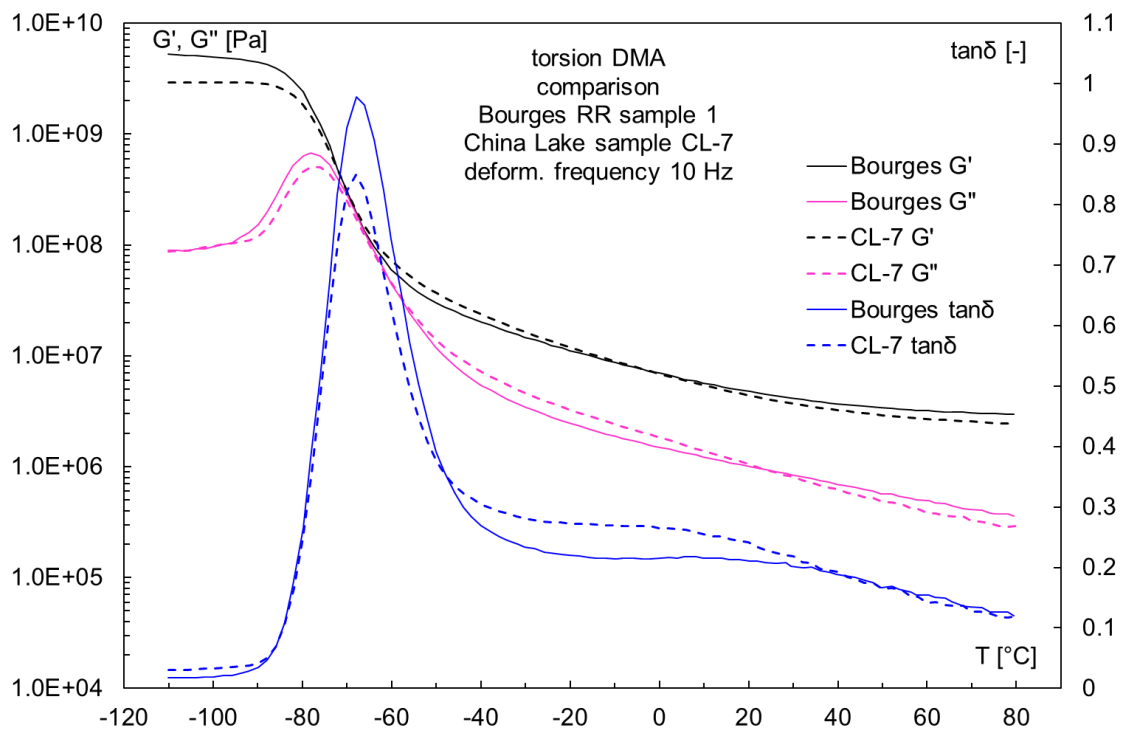


Figure 15: Comparison between Bourges and CL sample with all three quantities at 10 Hz deformation frequency. The loss factor is in the main maximum higher with the Bourges sample, G' is also higher at low temperatures.

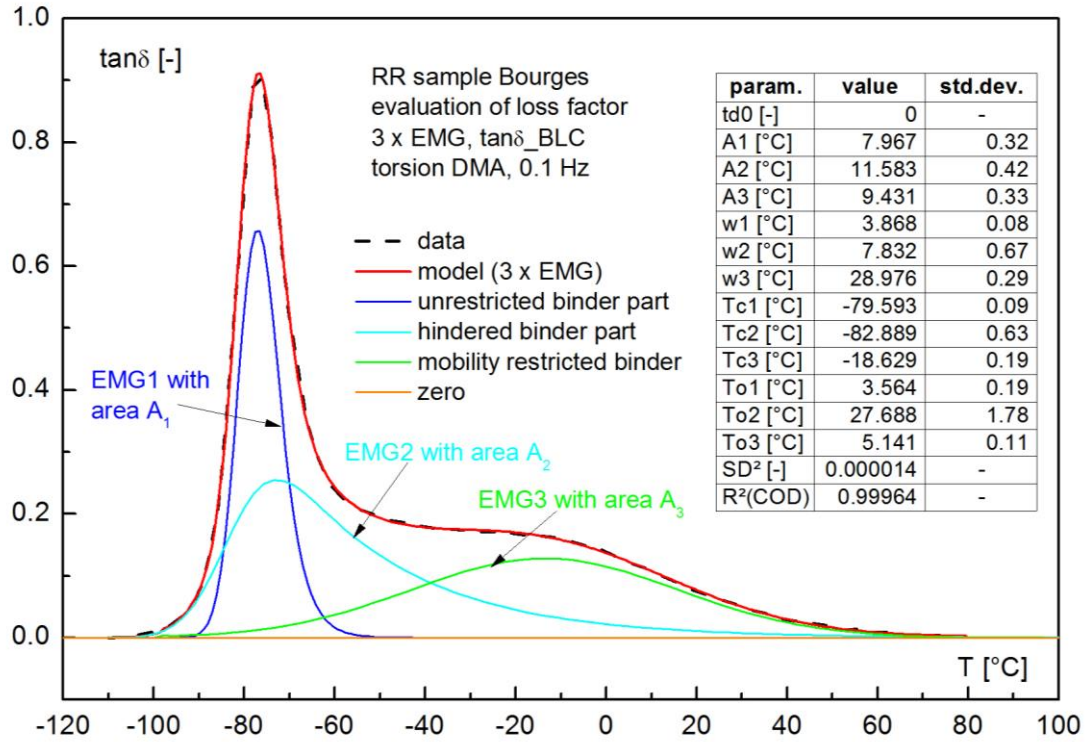


Figure 16: EMG modelling of Bourges RR sample 1, 3 EMG to describe the whole loss factor curve and separation in different mobility regions.

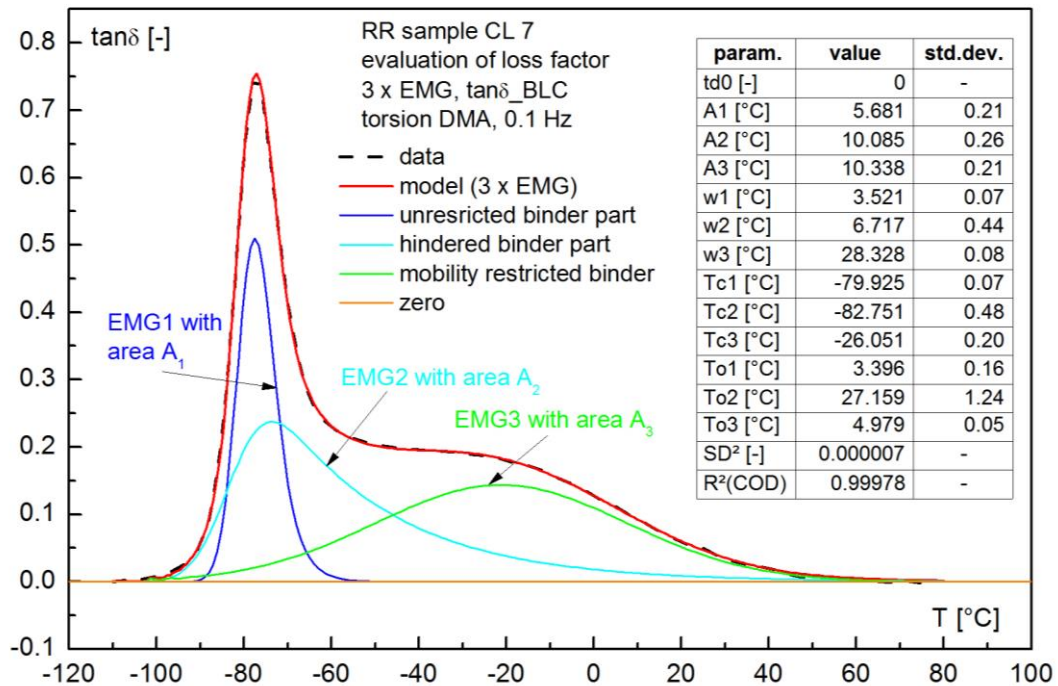
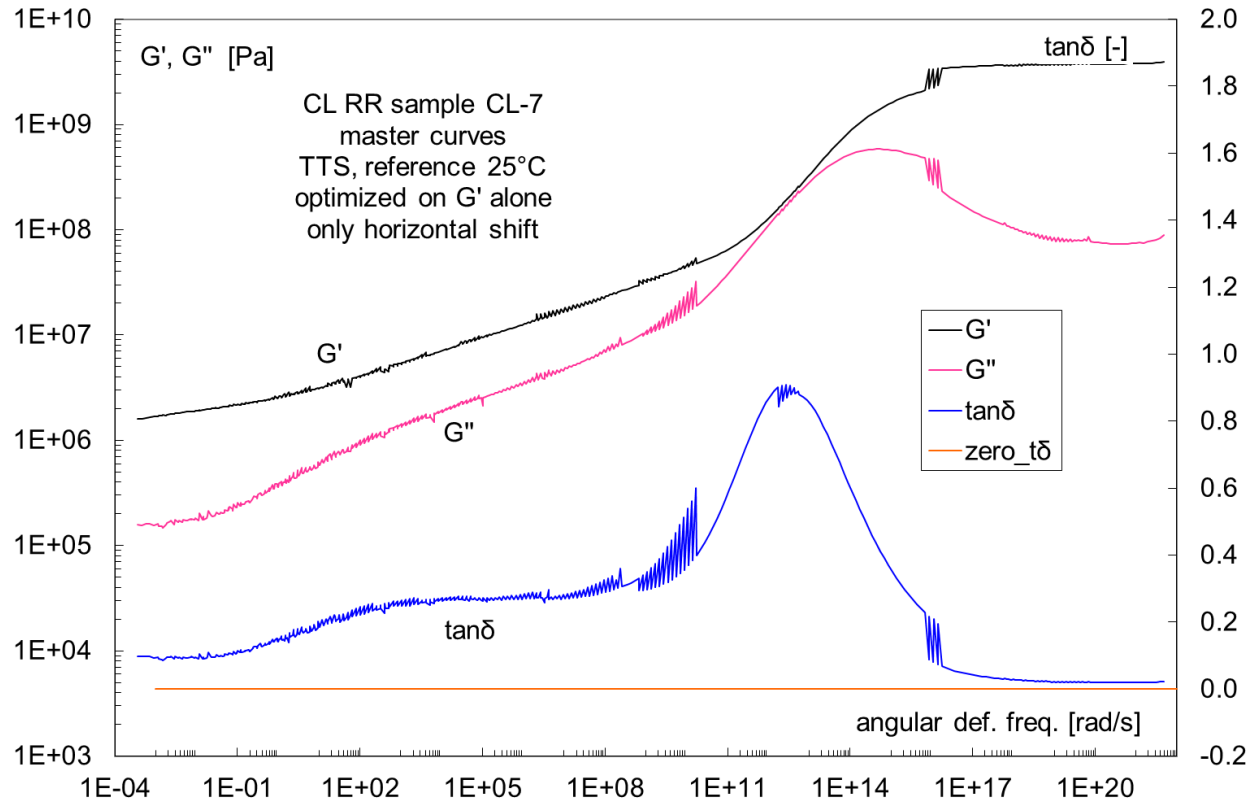


Figure 17: EMG modelling of China Lake RR sample CL -7, 3 EMG to describe the whole loss factor curve and separation in different mobility regions.

Table 2: Data of the fit parameters of the EMG (exponentially modified Gauss) modelling for both RR sample materials.

RR sample CL-7, 0.1 Hz			RR sample B-1, 0.1 Hz		
parameter	value	std.dev.	parameter	value	std.dev.
td_0 [-]	0	-	td_0 [-]	0	-
A_1 [°C]	5.681	0.21	A_1 [°C]	7.967	0.32
A_2 [°C]	10.085	0.26	A_2 [°C]	11.583	0.42
A_3 [°C]	10.338	0.21	A_3 [°C]	9.431	0.33
sum A_i [°C]	26.104	-	sum A_i [°C]	28.981	-
w_1 [°C]	3.521	0.07	w_1 [°C]	3.868	0.08
w_2 [°C]	6.717	0.44	w_2 [°C]	7.832	0.67
w_3 [°C]	28.328	0.08	w_3 [°C]	28.976	0.29
T_{c1} [°C]	-79.925	0.07	T_{c1} [°C]	-79.593	0.09
T_{c2} [°C]	-82.751	0.48	T_{c2} [°C]	-82.889	0.63
T_{c3} [°C]	-26.051	0.2	T_{c3} [°C]	-18.629	0.19
T_{o1} [°C]	3.396	0.16	T_{o1} [°C]	3.564	0.19
T_{o2} [°C]	27.159	1.24	T_{o2} [°C]	27.688	1.78
T_{o3} [°C]	4.979	0.05	T_{o3} [°C]	5.141	0.11
SD^2 [-]	0.000007	-	SD^2 [-]	0.00001	-
$R^2(COD)$	0.99978	-	$R^2(COD)$	0.99964	-

4.4 Master curves of the RR samples

**Figure 18:** Master curves for CL RR sample CL-7. Application of Time-Temperature Shift (TTS) Theorem, shift only horizontal (along x axis) and optimized for storage modulus G' .

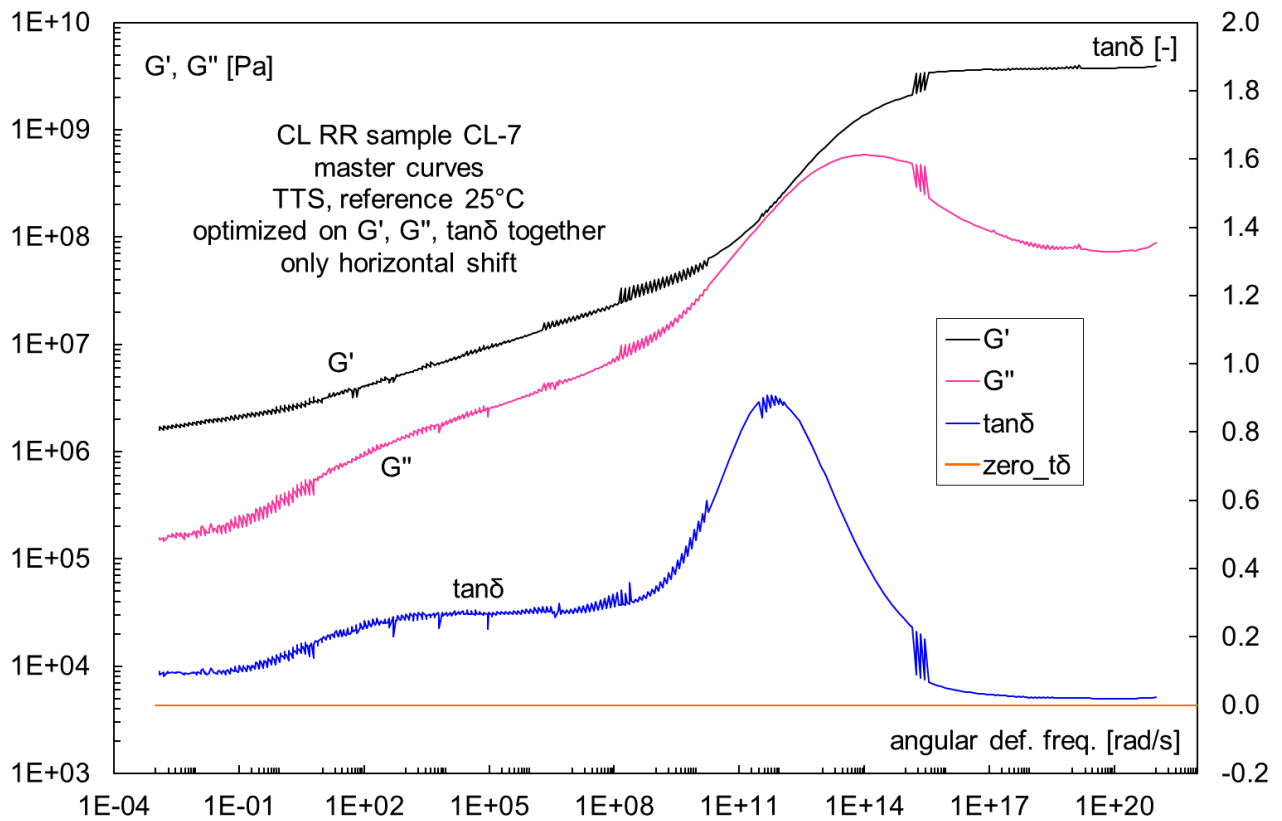


Figure 19: Master curves for CL RR sample CL-7. Application of Time-Temperature Shift (TTS) Theorem, shift only horizontal (along x axis) and optimized together for storage modulus G' , loss modulus G'' and loss factor $\tan\delta$.

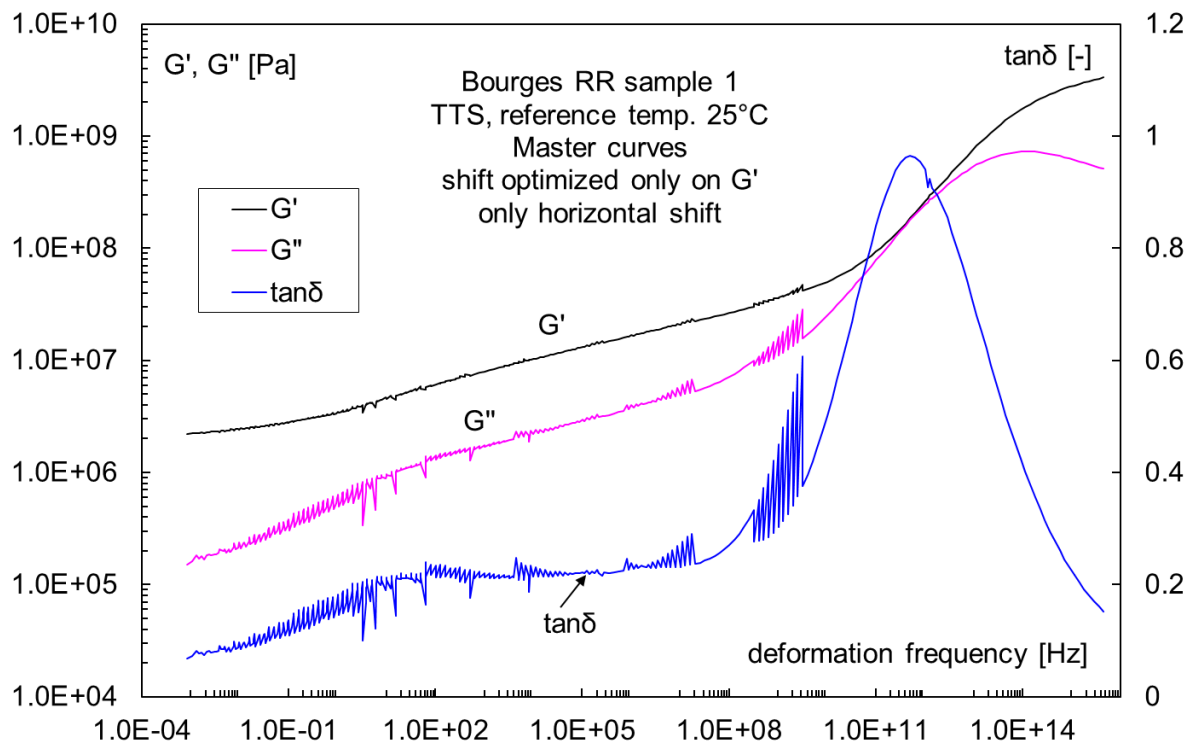


Figure 20: Master curves for Bourges RR sample 1. Application of Time-Temperature Shift (TTS) Theorem, shift only horizontal (along x axis) and optimized for storage modulus G' .

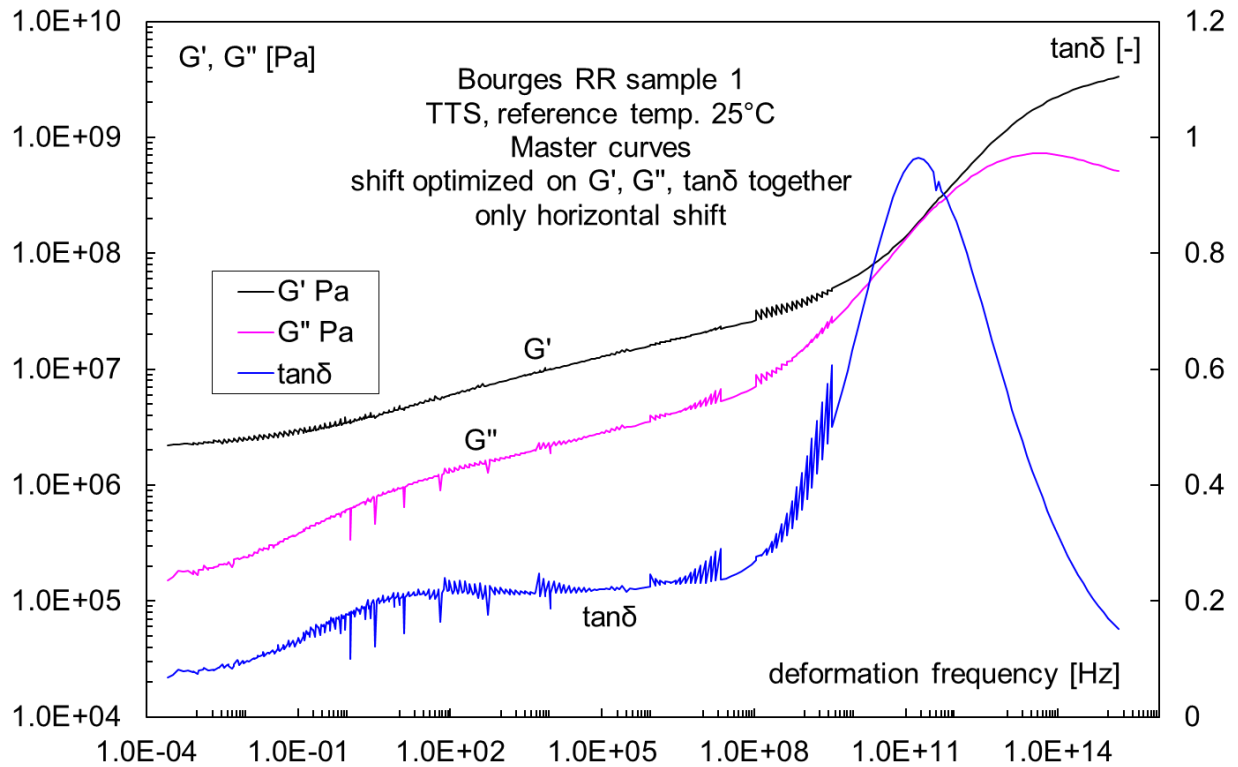


Figure 21: Master curves for Bourges RR sample 1. Application of Time-Temperature Shift (TTS) Theorem, shift only horizontal (along x axis) and optimized together for storage modulus G' , loss modulus G'' and loss factor $\tan\delta$.

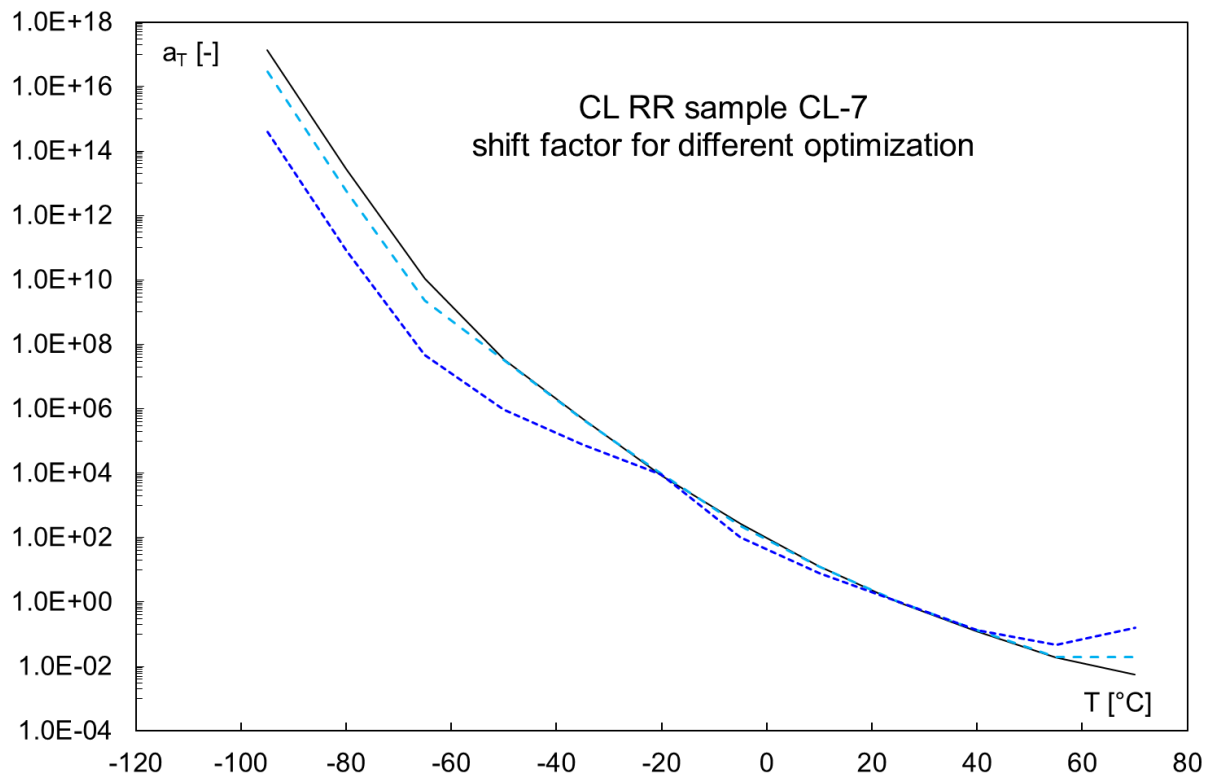


Figure 22: Comparison of the shift factors obtained according to different optimization to data.

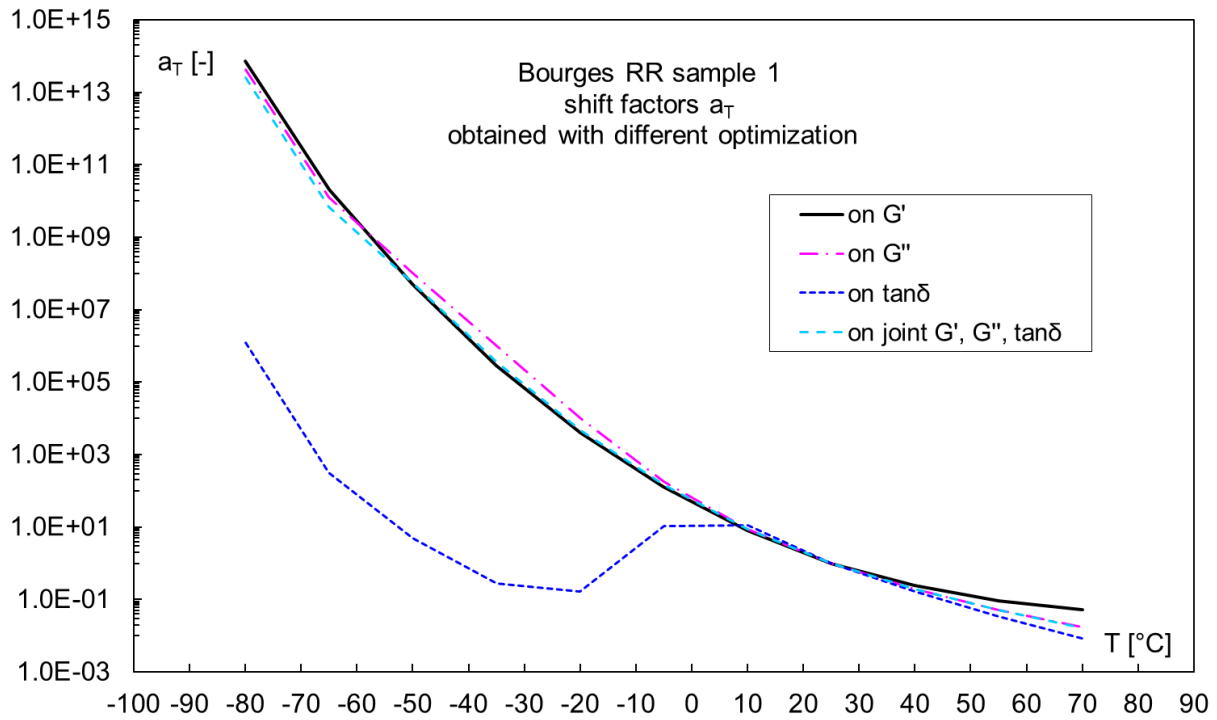


Figure 23: Comparison of the shift factors obtained according to different optimization to data.

5. Discussion

The EMG (exponentially modified Gauss distribution) modelling quantifies the differences in the two samples. First to say both samples are quite similar in DMA behaviour. But some differences can be seen in storage modulus and loss factor. The first peak is higher for the Bourges sample. This means the Bourges sample has more unrestricted binder part than the CL sample. The cause can be different plasticizer content and / or different amount of solid fillers. The second EMG peak (a hidden peak) has also more intensity in the Bourges sample. The third EMG peak characterizes the mobility restricted binder part, which is less in Bourges sample than in CL peak. Together with full data on the compositions (which are not available), these differences can be traced back to the molecular origins.

Table 3: Comparison of area data obtained from the EMG modelling of the two materials

	CL-7	B-1
A_1 [°C]	5.681	7.967
A_2 [°C]	10.085	11.583
A_3 [°C]	10.338	9.431
sum A_i [°C]	26.104	28.981

The horizontal shift factors a_T obtained from the construction of the master curves according to TTS (Time-Temperature Shift (TTS) Theorem) can be described by several formulas. Two are here given. The standard is the Williams-Landel-Ferry (WLF) equation, Eq.(1). In Eq.(2) a so-called WLF invariant is given, the temperature T_∞ . It is interpreted as the temperature where every molecular movement is frozen. The Arrhenius parameterization is shown in Eq.(3). Often it works not so well as WLF. The modified Arrhenius parameterization works very well, Eq.(4). Here a limit value T_0 is introduced. In normal Arrhenius parameterization this limit value is $T_0 = 0$ K, means all is related to 0 K. But because the molecular movements of polymer segments stops at higher than zero Kelvin, normal Arrhenius parameterization is not adequate. The results of the description of the shift factor a_T are shown in Fig. 24 to Fig. 27 and the data of the

fits are compiled in Table 4. The two equations, WLF and modified Arrhenius (mod Arr), are totally equivalent in description quality and meaning. With mod Arr one gets an activation energy and the limit value T_0 is connected to C_2 via T_∞ . There are differences to recognize between the samples. The freeze-in temperature T_∞ is much lower with CL-7 and the activation energy for CL-7 is much higher than the one of the Bourges sample, based on the present measurements of master curve data of the Bourges sample.

$$\lg(a_T(T, Tr) [-]) = -\frac{C_1 \cdot (T - Tr)}{C_2 + (T - Tr)} \quad \text{Eq.(1)}$$

$$T_\infty = Tr - C_2 \quad \text{Eq.(2)}$$

$$\lg(a_T(T, Tr) [-]) = \frac{Ea}{R} \cdot \left(\frac{1}{T} - \frac{1}{Tr} \right) \cdot \lg(e) \quad \text{Eq.(3)}$$

$$\lg(a_T(T, Tr) [-]) = \frac{Ea}{R} \cdot \left(\frac{1}{T - T_0} - \frac{1}{Tr - T_0} \right) \cdot \lg(e) \quad \text{Eq.(4)}$$

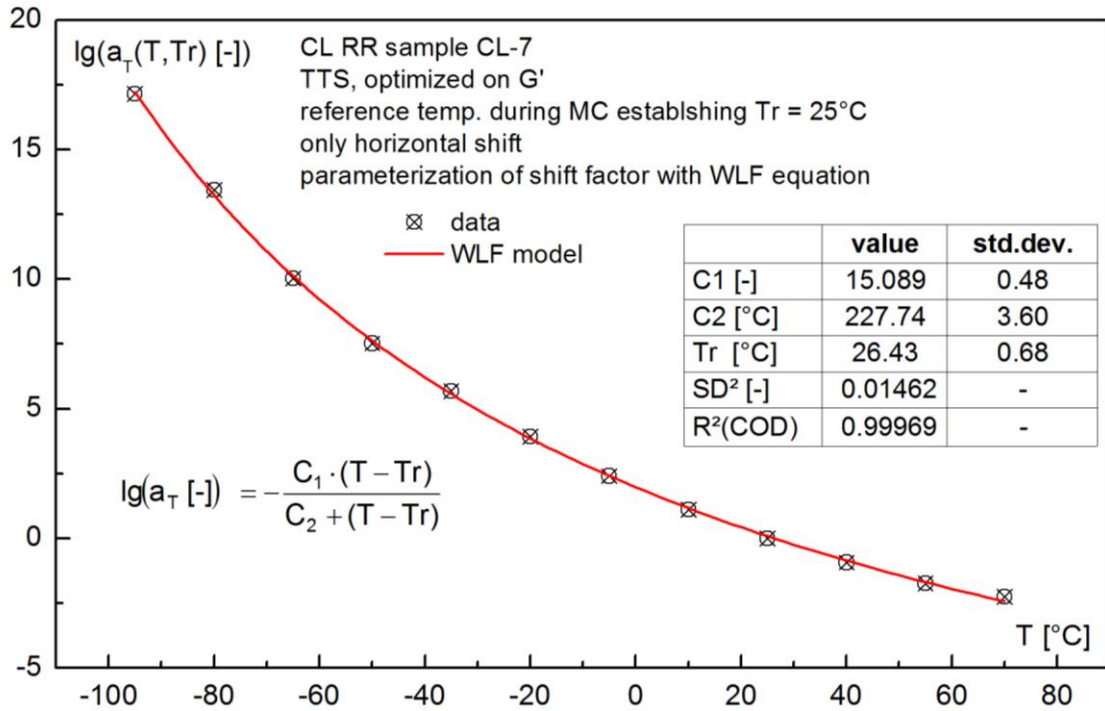


Figure 24: TTS obtained shift factor a_T for CL RR sample CL-7, optimized for storage factor G' , according to WLF (Williams-Landel-Ferry) description.

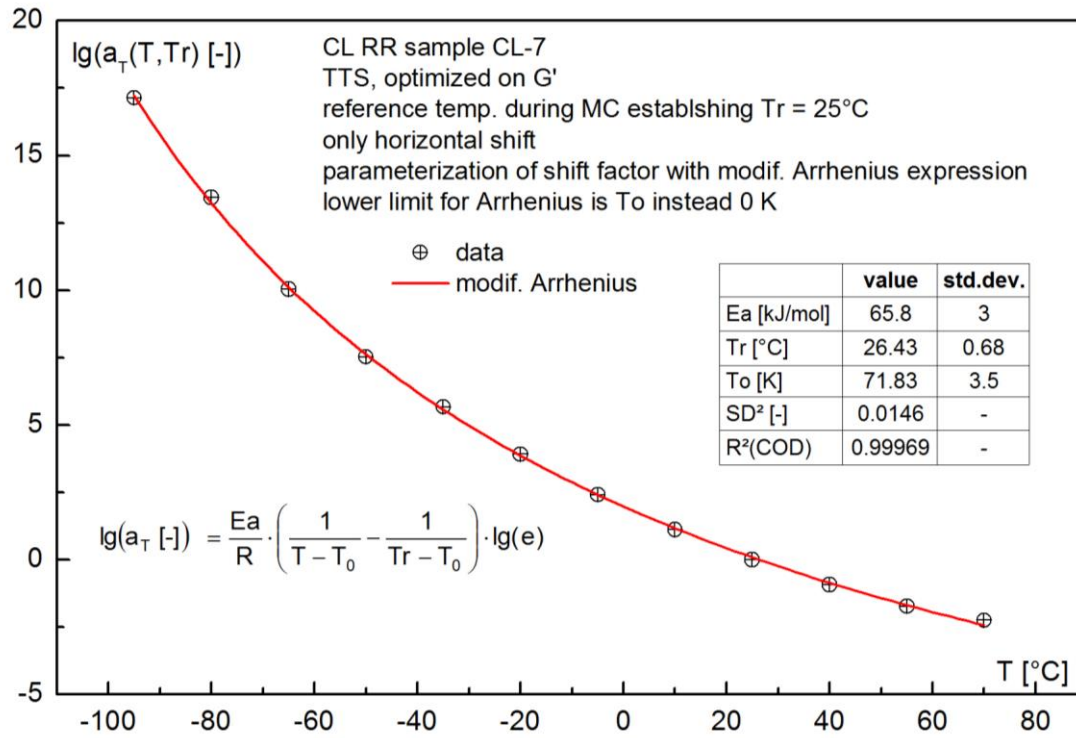


Figure 25: TTS obtained shift factor a_T for CL RR sample CL-7, optimized for storage factor G' , according to modified Arrhenius description.

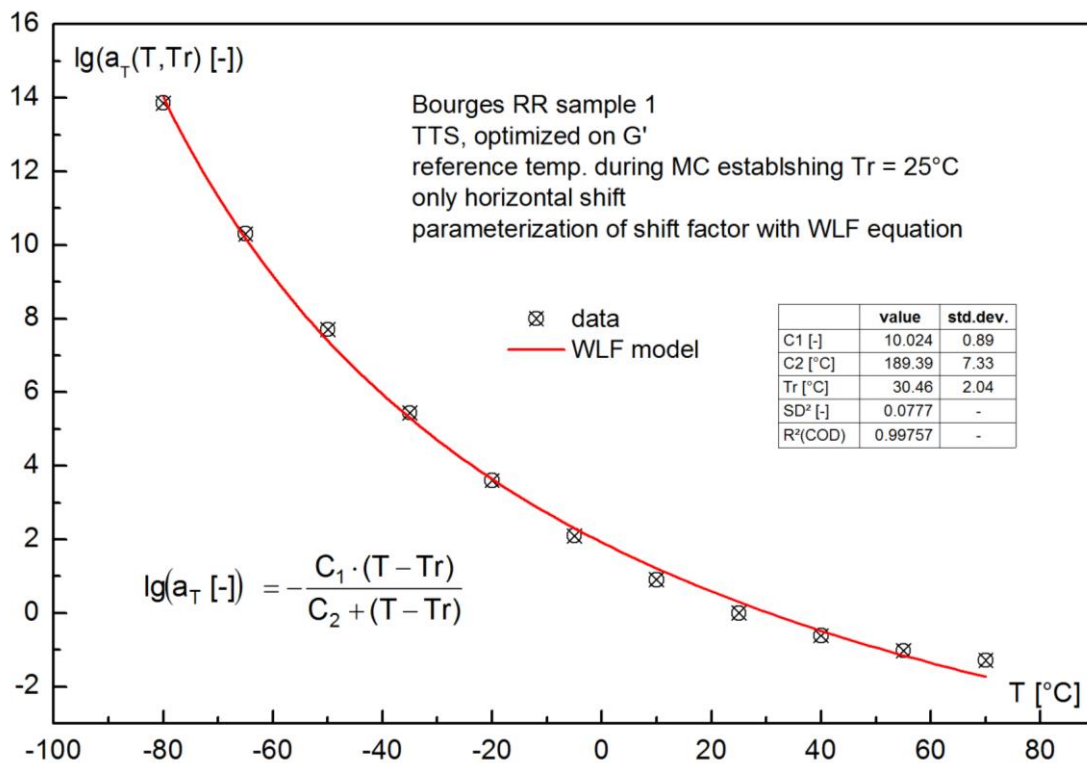


Figure 26: TTS obtained shift factor a_T for Bourges RR sample 1, optimized for storage factor G' , according to WLF (Williams-Landel-Ferry) description.

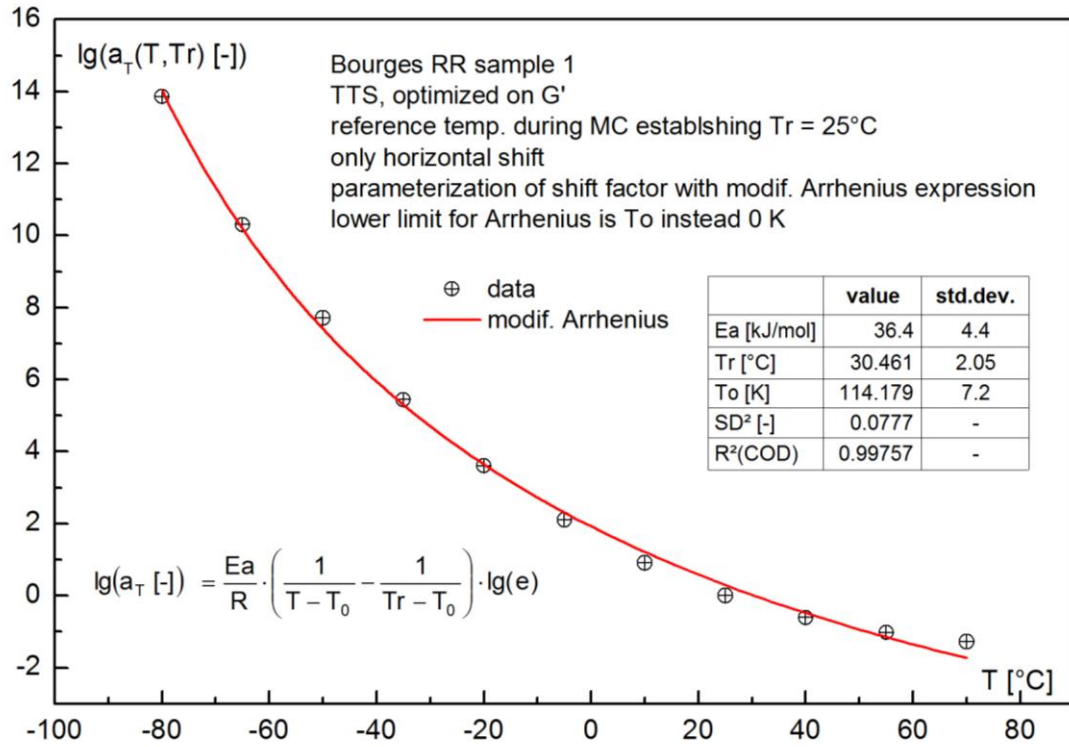


Figure 27: TTS obtained shift factor a_T for Bourges RR sample 1, optimized for storage factor G' , according to modified Arrhenius description.

Table 4: Compilation of the data of fit parameters according to the two descriptions, WLF and modified Arrhenius of the horizontal shift factor a_T

WLF	CL-7	Bourges
C ₁ [-]	15.084	10.024
C ₂ [°C]	227.74	189.39
Tr [°C]	26.43	30.46
T _∞ = Tr - C ₂ [°C]	-201.31	-158.93
T _∞ [K]	71.84	114.22
Tr [°C], MC	24.993	25.00
SD² [-]	0.0146	0.0777
R² (COD)	0.99969	0.99757
Modified Arrhenius	CL-7	Bourges
Ea [kJ/mol]	65.8	36.4
Tr [°C]	26.43	30.46
To [K]	71.83	114.18
T _∞ = -273.15+To [°C]	-201.32	-158.97
Tr [°C], MC	24.993	25.00
SD² [-]	0.0146	0.0777
R² (COD)	0.99969	0.99757

6. Summary and conclusions

Two inert elastomer samples have been measured in torsion DMA and compared. Both are based on polyurethane elastomer HTPB-IPDI as binder. One sample (Bourges) is filled with bimodal aluminium oxide and represents a composite rocket propellant formulation, the other is filled with trimodal glass beads and stands for a plastic bonded high explosive. Their behaviour in DMA is very similar. The description of loss factor with EMG (exponentially modified Gauss) distributions reveal the differences quantitatively. Master curves for the quantities storage shear modulus G' , loss shear modulus G'' and loss factor $\tan\delta$ have been constructed with only horizontal shifting of curve parts. The resulting shift factors could be described well by WLF (Williams-Landel-Ferry) equation and by a new modified Arrhenius equation. The description qualities of both equations are totally equivalent. With the Arrhenius description, one gets the activation energy for the shift process. The modification of the Arrhenius equation introduces a lower reference limit differently from zero Kelvin as it is with standard Arrhenius.

Acknowledgement

My colleagues from the NATO 'Working group on Mechanical Analysis of explosive materials' of NATO A/C 326 SG1 EMT are very much thanked for many interesting and friendly discussions during our meetings.

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- (3) Pierre Besont and Manuel Ducros from DGA Techniques terrestres, Bourges, France, who provided the second RR sample;
- (4) Daniel Lewis, AWE, Aldermaston, UK;
- (5) Wim de Klerk, TNO Defense, Safety and Security, Rijswijk, The Netherlands, the working leader;
- (6) Dr. Jeremy Rice, USARMY RDECOM AMRDEC, Huntsville, Alabama, USA;
- (7) Marc.Brassard, Defence Research and Development Canada; Valcartier Research Centre, Québec (Québec) G3J 1X5 Canada, former member of the working group with whom intensive data exchange and discussions have been made;
- (8) To all other participants former and present, not named here explicitly, from whom I got valuable information.

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