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Review of “Thermal and energy analysis of DMTA tests”

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Review of version 1

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Reviewer 1 (Anonymous)

Reviewer This is an interesting paper which considers temperature rises in viscoelastic polymers undergoing cyclic deformation. More specifically, the authors consider polymers undergoing the common DMTA test to evaluate the complex modulus of the material. The paper provides theoretical calculations of the temperature rise and compares these to data obtained using a thermal camera. It seems very complete, and I have no particular comments on the science, which I think is good.

Authors Thank you for these encouraging comments.

Reviewer I have a few presentational comments:

I don't really like the title, as I don't think 'mechanical spectrometry tests' is a widely used term. The heading used on subsequent pages (Calorimetric analysis of DMTA tests) would be a better title!

Authors This remark is funny because we don't particularly appreciate this term either. It was while preparing a conference in France two years ago, to be given in front of a polymerist audience, that this expression was suggested to us... It is therefore without any problem that we propose as new title: Thermal and energy analysis of DMTA tests. If possible, we will keep the same running title.

Reviewer To what extent was Yadav involved in the work? I was surprised to see no acknowledgements to anyone, and also that graphs from Yadav's thesis were incorporated without acknowledgement.

Authors In this article, we have taken up some experimental data obtained collectively during this thesis, and we have systematically mentioned these sources but the reviewer is right; we have added acknowledgements at the end of the new version of the paper and added the link to the manuscript of Yadav's thesis online in the bibliography.

Reviewer The paper is not particularly easy to read, this is partly because of the subject matter, and the authors try to help by giving partial conclusions as we go along, but perhaps the key points from each section could be highlighted in a couple of sentences. 3.3.1. (c), for example, contains further analysis, which I don't think is appropriate for concluding remarks.

Authors The reviewer has clearly understood our desire to move forward step by step. In this second version, we have tried to emphasize even more the partial results obtained without heralding their possible consequences that will be resumed and analyzed later in the rest of the paper. We understand that these "anticipations" (i.e., indicating some prospects in partial concluding comments) may have made the reading more difficult. You will see in the "partial concluding comments" sections, the prospect sentences that have been crossed out and the concluding

comments have been completely rewritten (p. 17).

Reviewer The paper would benefit from a further proof-read and some tightening up of the language. It can all be read and understood, but because it is quite a dense subject it would make things easier if the writing was a bit more concise.

Authors We asked for our article to be proofread by a native English expert translator, but he did not agree to proofread it because of the Latex formatting and the fact that we only had a pdf to send him, and not a format with correction tracking (like Word). We hope the English of the article is correct and we have tried to make things more understandable.

Reviewer I couldn't find any reference to online software or data.

Authors All fully corrected DMTA measurements (storage and loss moduli as a function of the loading frequency and temperature set point of the environmental chamber) for two polymers (Polystyrene and Polyamide 6.6) have been deposited on Zenodo open repository website [zenodo.7257481](https://zenodo.org/record/7257481), in csv format, together with the average temperature variation of the sample measured by quantitative infrared camera along each test (one text file per testing conditions and polymer). The data also contains Matlab® program that allows for the simulation of the thermomechanical response of a Zener-type rheological model (section 3.3.5 and the new Appendix A2).

Reviewer 2 (Anonymous)

Reviewer This paper presents an investigation of the viscoelastic characterization of polymers throughout Dynamic Mechanical Analysis (DMA) and quantitative infrared thermometry to evaluate the dissipated and thermoelastic energies. Classic determination of E' , E'' and $\tan \delta$ are challenged with a thorough analysis of the contribution of thermoelastic couplings and dissipated energy. The study considers a limited range of frequency (from 0.1 to 10Hz), three temperatures below T_g for two neat thermoplastics (PS and PA66). The careful measurements and analysis performed illustrate that: (i) classic hypothesis of isothermal conditions for DMTA tests are valid; (ii) the additional input of the influence of thermoelastic couplings brings in only limited corrections to the usual analysis of E' , E'' , $\tan \delta$ for the conditions considered; (iii) for very low frequencies, the contribution of thermoelastic couplings to the apparent dissipation (i.e. the hysteresis loop) could be significant; (iv) even for very low amplitudes, classic analysis relying on linear visco-elasticity may be disputable, especially for the evolution of viscosity with increasing frequency. The topic is of interest and fits well the scope and spirit of the journal. Furthermore, the paper details very well the experiments and the analysis performed, with a persistent idea to explain as well as possible a quite tricky aspect of thermodynamics balance.

Authors Thanks for this faithful synthesis, thanks also for the interest in this work and for constructive suggestions.

Reviewer Nevertheless, it seems that several points could be improved before publication in JTCAM. Scientific comments:

The team, and in particular Prof. Chrysochoos have been publishing works on the topic for a long time and have written several reference articles. This study provides indeed a good way to illustrate the application of the analysis and of the thermo-visco-elastic model (Fig. 10). Nevertheless, the original aspects of this work, and how it fit in the previous studies would need to be emphasized, in the introduction and the discussion sections.

Authors The reviewer is right, our willingness to better understand the energy signature of viscoelastic mechanisms is not new. Already in Moreau et al. (C.R. Mécanique, 2005), tests on PMMA and PC polymers led us to add thermoelasticity in the classic Zener and Kelvin-Voigt models. An analysis of the mechanical and calorimetric effects then showed that, for small deformations ($\epsilon < 2 \times 10^{-2}$) and low strain rates ($\dot{\epsilon} < 5 \times 10^{-4} s^{-1}$), i.e., low stress levels ($\sigma < 50 MPa$), the intensity of the viscous dissipation remained negligible (i.e., experimentally unreachable at that time) compared to the thermoelastic source amplitude. We also showed that in this viscous-thermoelastic framework, the Zener-type and Kelvin-Voigt-type models were no longer equivalent. We added a comment on this subject at the end of the introduction (p. 2).

- Reviewer** On the materials aspects, one main point raised with the PA6.6 matrix, as this material is very sensitive to water uptake, leading to important variation of the Tg and thus the visco-elastic response. The aspects related to conditioning, humidity ratio, storage and water content evolution should therefore be addressed.
- Authors** The reviewer is right, the Tg reported in Table 1 (in the new version of the manuscript) has been measured by DSC on similar samples as the ones used during the DMTA test. The samples were stored in the air-conditioned room (i.e., regulated in temperature and humidity) of the DMTA. We measured, by weighing and drying in an oven, a water content of about 1%, which quite well agrees with the measured glass transition temperature of 336 K (Reimschuessel, 1978) but not with the ones measured in Fabre et al. [2018] and Launay et al. [2013]. However, it's known that the way the Tg is measured, and the frequency of the measurement, has an effect on its value [Achorn et al., 1994; Rieger, 2001]. Moreover, in all our DMTA measurements we expect to be always below Tg as can be seen on the (new) tan δ plot in Figure 5 (and Figure 4 for PS). Some comments have been added in the manuscript on that point close to Table 1 in the experimental setup part (p. 2).
- Reviewer** On the experimental aspects, the infrared protocols are well detailed and carefully performed. It would however be important, taking into account the very limited temperature variations observed, to present the typical NETD maps obtained for the experiments. This would illustrate both the thermal resolution and the validity of the NUC performed, which is an important aspect, in particular with a window and a dummy sample to correct the ambient variations. Narcissus effect is not evoked in the section: how was it ruled out?
- Authors** In subsection 2.1. (before and after Eq. (2) p. 3) it is stated that we use a pixel-to-pixel calibration method that leads us to bypass the NUC and BPR operations. The calibration is performed over almost the entire dynamic range of the sensor (not limited to the linear part) using a polynomial fit. The resolution is estimated at 10 mK. (Honorat et al., 2005). Regarding the Narcissus effect, it has been ruled out by slightly misaligning the camera from the IR lens axis, a comment has been added on that point at the top of p. 3. The calibration using a black body was done with the same geometrical configuration as the DMTA test, as already explained in the manuscript, just after the one on the Narcissus effect.
- Reviewer** On the analysis aspects, several points deserve a in depth discussion.
- First, as suggested in the formal remarks, a single section should discuss the modelling fold.
- Authors** To meet the reviewer's expectations, an appendix dedicated to the models mentioned in the main text has been added. We preferred the appendix to an additional section in order not to unbalance the article which is more centered on the interpretation of DMTA tests rather than on the performances from a thermomechanical standpoint of visco-thermo-elastic models.
- Reviewer** - Second, the analysis suggested are 1D only (even if written in a thermodynamic framework). This is consistent with the usual DMTA analysis but it would be very valuable to discuss 1D vs 3D analysis, especially when it comes to analysis of thermo-elasticity and volume variations.
- Authors** The transition to 3-D models should not pose any problem for isotropic thermoelasticity. However, for the viscous deformation mechanisms, things become more complicated: if we consider the simple Kelvin-Voigt model, we need a viscosity tensor; for the Zener or Generalized Maxwell model it becomes even more complicated. It is certain that the identification of these viscosity parameters would require many additional tests, and probably not straightforward. We have mentioned this important challenge in the appendix.
- Reviewer** Third, the range of temperature for the two materials studied covers the end of the glassy plateau, going down to the Tg. This is a peculiar case for which tan δ is increasing. How specific are the analysis provided? On the same line, the frequency is modified over this range of temperature by several decades and so is the Tg. It would be convenient to analyze the results from a (T-Tg) point of view.
- Authors** In the case of the PA66 samples, it is well known that their mechanical behavior depends on the

temperature, the loading frequency and the water content (Benaarbia et al., 2016; Fabre et al., 2018; Launay et al., 2013). Our intend here was to stay below T_g and to have the same amount of water in all the tested sample, whatever the testing temperature. This is why we use one (new) sample per testing temperature with a quite short frequency sweep (less than 1h) to reduce the change in water content during each testing temperature, or aging (see new comments on p. 5). Moreover, we can see in Figures 4 and 5, especially with the new $\tan \delta$ plots, that we have never crossed the T_g . Our analyze here is specific from the glassy plateau and we know that other mechanisms appear above T_g , like entropic elasticity or fusion/crystallization. These coupling effects are far more intensive than thermoelastic coupling (Benaarbia et al., 2016). Concerning the analysis in T - $T_g(H,f)$, our intend was not to study time-temperature-water content equivalence and we do not have the data to make this correction.

Reviewer Forth, the analysis is for strain-driven tests. What would be the differences for stress-driven tests?

Authors We are not sure we clearly understood this remark. Naturally, a strain-driven test is not a stress-driven test. From an experimental viewpoint, it may be more delicate (even dangerous) to perform stress/force-driven tests than strain/displacement-driven tests. However, for tests where strain ranges remain small, if no localization phenomenon appears and if the imposed stresses remain at a reasonable level, stress-driven tests should give viscoelastic responses of the same form as those obtained during strain-driven tests. From a thermal viewpoint, for tests at the same frequency, the thermal responses (cyclic response due to thermoelasticity and self-heating due to dissipation) should also be similar. From a numerical simulation viewpoint, for a given visco-thermo-elastic model, whatever the loading variable, the same behavioral constitutive equations are used... In any case, in this paper, we have only focused on displacement-driven tests.

Reviewer Finally, the conclusions on the frequency ranges leading to either a significant or a negligible contribution of thermoelastic coupling are likely dependent on the ratio between the test frequency and the characteristic thermal time. For example, a change in the sample geometry could modify the ranges determined. A more detailed discussion should be done on this point.

Authors Yes, we completely agree with the reviewer, and we thank him/her for this remark and the opportunity he/she gives us to complete this discussion in the new version of the paper! The preponderance of thermoelastic effects on dissipation is not an intrinsic characteristic of the material, but of the material, the geometry of the specimen and the conditions of heat exchange between the specimen and the environment. For the 1D heat diffusion equation proposed in Eq. (11) (Chrysochoos and Louche, 2000), the time constant τ_{th} is written as:

$$\tau_{th} = \frac{\rho C e l}{2h(e + l)} \quad (1)$$

where ρ is the masse density, C the specific heat, h the heat exchange coefficient between the sample and the surroundings, e and l being respectively the thickness and width of the sample cross-section. This means that the “coupling viscosity” is consequently not a “pure” material characteristic. A comment on this non-intrinsic “coupling viscosity” parameter has been added in the new version of the paper (p. 11 between Eqs. (10) and (11)).

Reviewer Figure 6b page 7. The stationary phase seems disputable and should be correlated in a clearer way to the thermal characteristic time illustrated in Figure 7. How well could this evaluation be performed for test achieved at 10 Hz, with an acquisition frequency of 31 Hz (3 points per cycle could lead to a limited evaluation of the envelope over a limited time window)?

Authors It seems that there are in this remark at least three distinct parts.

(i) In figure 6b, it is certain that a “stationary” state (from a thermal standpoint) is not completely reached, (“stationary” in the sense of the mean temperature per cycle). But this is not crucial here because our objective was to use the thermo-signal to estimate, on the one hand, a temperature range associated with the thermoelastic periodic response and on the other, an order of magnitude of the viscosity-induced self-heating over a long enough period during which the values of E' and E'' make sense (stabilized hysteresis loop). It is however true that the observed

(sometimes not...) values of self-heating have been compared in tables 7 and 8 with the theoretical asymptotic values of self heating calculated using the measured E'' values (Eq. (21))... In section 3.3.2c and in the general conclusion, we mentioned the unexpected nature of these experimental results which led us to discuss the thermodynamic suitability of linear viscoelasticity.

(ii) The second aspect of the remark seems to be related to the signal processing itself. It is certain that at 10 Hz, the thermo-signal is under-sampled. But as mentioned in section 2.2, at the bottom of p. 5, we used the monochromatic character of the thermoelastic response (in the case of a monochromatic loading), to estimate the range of this periodic thermal component via a synchronous demodulation. As for the dissipation effects, the self-heating was assessed via the mean temperature per cycle $\tilde{\theta}(t)$ (cf. Eq. (3)).

(iii) Finally, the link between the thermal response in Figure 6b and that of Figure 7 is difficult to establish. In the first case, sources of different natures coexist, in the second, there should be, (we hope so very much!), no more heat source. In Figure 7, the temperature variations of the sample are induced by the temperature variations of the environmental chamber (heat exchanges).

Reviewer Section 3.1. The hypotheses of the DMTA analysis are recalled in the introduction. Are they met for the conditions tested?

Authors The set of equations (1) only makes sense once the mechanical hysteresis loop is stabilized. In our case, we observed stabilized loops from the very first loading cycles. We therefore used all the mechanical data recorded since the beginning of the test to identify the dynamic moduli. Regarding the monochromatic spectrum of the loading and the response of the material, the question has been discussed in the text (see Fig. 3). Finally, concerning the "isothermal" character of the test, the temperature T_0 of the environmental chamber remains, from a strictly thermal standpoint, representative of the loading conditions.

Reviewer The use of Figure 7 is unclear for the reviewer. Why isn't the characteristic time identified from the cooling phase only?

Authors The time constant τ_{th} of heat losses is sometimes called time constant of thermal return. The reviewer's remark is therefore quite justified. But it is also possible to identify τ_{th} during more complex thermal loadings. This is what we have done here. Indeed, if we consider Eq. (11) for example, by eliminating the heat source term from the second member of the equation, we obtain: $\frac{d\theta}{dt} + \frac{\theta}{\tau_{th}} = 0$ where $\theta = T - T_0$. If T_0 is now a time function $T_0(t)$ (it is possible to control the temperature of the environmental chamber), the simplified heat equation becomes: $\frac{dT}{dt} + \frac{T-T_0}{\tau_{th}} = \frac{dT_0}{dt}$. If T_0 is constant, we find as a solution, the traditional exponential return branch to equilibrium. In the general case, we find the constant τ_{th} by solving numerically a least squares minimization problem.

Reviewer Presentation comments:

The organization of the paper could be modified to be clearer and more standard when it comes to the discussion of the modeling aspects. First, an analysis based on DMA approach is performed, then, another analysis is provided based on a Zener-like visco-thermo-elastic model, and finally, another non-linear modelling option is discussed in the conclusion. This does not help drawing a clear picture of the limits, hypothesis and possible improvements. A dedicated section would be an asset to the paper, in which 1D vs 3D aspects could be also discussed.

Authors We understand the reviewer's suggestion. However, we would like to stress that the aim of this paper is to focus on the thermal and energy analysis of observations made during tests and to interpret them in the light of DMTA rheological equations. It has then been necessary to consider these equations by relying on a thermomechanical framework and referring to several viscoelastic models. To facilitate the reading of the main text, we have presented the main energy balance characteristics associated with these modes in a new Appendix. Indeed, the very structure of these equations (a single kinematic state variable) naturally leads to an elasticity and a viscosity developing in parallel, hence a first allusion to the Kelvin-Voigt model (section 3.3). Other richer parallel models exist in the literature such as the visco-thermo-elastic Zener-like model or the Generalized Maxwell model. We have simply alluded to these models,

not to identify and used them, but simply to put forward a particular property: (i) the relative importance of coupling and dissipative effects (with the Zener-type model, section 3.3.5), the relevance of a linear viscoelasticity, where the viscosity is a material parameter constant with respect to the strain rate (i.e. loading frequency) and where the associated energy rate is entirely dissipated (cf Eqs. (29) and (30) in the general conclusion). Finally, it is true that at no time did we move away from the 1D structure of the rheological equations of the DMTA. A comment on the implementation of a 3D viscosity-thermo-elastic model, energetically consistent (i.e., in the sense of the 1st principle of thermodynamics), is a major perspective. To try to respond to the reviewer’s suggestion, we propose to add an appendix in which the different behavioral models are briefly discussed, essentially from an energy standpoint. The new text now refers the reader interested in these modeling aspects to this appendix with some relevant references.

Reviewer The bibliography is quite focused on the previous works from the team. Some other research teams with valuable works have studied these aspects even if in a less thorough way (Rittel, ...).

Authors We agree and we added new references on:

- the glass transition temperature of PA6.6 (Reimschuessel 1978; Batzer et al. 1981) and the effect of water (Benaarbia et al., 2016; Fabre et al., 2018; Launay et al., 2013),
- the effect of the way the glass transition temperature is measured on its value (Achorn et al., 1994; Rieger, 2001),
- energy balance during cyclic test (Rittel, 2000),
- the Thermodynamics of Irreversible Processes (Sidoroff’s website; Germain, 1973).

Reviewer Introduction “(i.e. in tension-compression)”. Many other kinds of solicitations are possible for DMTA tests. Please modify.

Authors Sorry but we did not use in the first version the Latin acronym i.e. (id est) but e.g (exempli gratia) which is equivalent to “for example”.

Reviewer Introduction. If not mistaken, T_0 is not defined.

Authors T_0 appears at line 4 of the Introduction (p. 1) and, again, 6 lines before the last paragraph of this section (on the top of p. 2).

Reviewer Introduction. Define what would be considered as “significant” for temperature variations. Consequently, are the temperature variations of the sample undergoing DMTA testing significant or not?

Authors The answer to the question “what is a significant temperature variation” probably depends on where one stands:

- For the operator controlling the temperature of the environmental chamber, a satisfactory response will be in the range of 500 mK.
- If this person uses an infrared camera to make fine measurements, the camera manufacturer will guarantee a NETD of about 20 mK.
- If now these temperature measurements are used to perform energy balances and verify that the behavioral models are thermo-mechanically consistent, we have shown in Fig. 9 that the temperature variations induced by thermoelastic effects (of the order of 40 mK), were associated with energy rates several ten times greater than the deformation energy rates.

As for the 2nd question: «are the temperature variations of the sample undergoing DMTA testing significant or not? », we answer yes insofar as these very low temperature variations have led us to question the preponderance of thermoelastic effects at low frequency, (which leads to a reinterpretation of the loss modulus induced by thermal instead intrinsic dissipation). The thermal and energy analysis also led us to question the thermodynamic suitability of the assumption of a linear viscosity, exclusively dissipative.

Reviewer Thermal expansion and specific heat values should be given in a “Material” section (beginning of section 2, for example).

Authors Why not! This is fixed.

- Reviewer** Page 5. “The recordings ... a stabilized cyclic regime ...” Please precise “stabilized” according to mechanical or thermal points of view.
- Authors** It is indeed important to specify that this is a stabilization in the mechanical sense to identify the dynamic moduli from the hysteresis loops. Given the small temperature variations induced by dissipation disturbed by the thermal noise, the oscillatory nature of thermoelastic effects, there is never thermal stabilization, strictly speaking. We have clarified this in the new version of the paper (3rd item of the partial concluding comments p. 17).
- Reviewer** Figure 4. Providing the evolution of tan delta would help the readers used to this presentation of DMTA tests.
- Authors** Ok! We have added in figures 4 and 5, the evolution of tan(d) as a function of the loading frequency.
- Reviewer** Conclusion. “... (pure) branch is active AND its viscosity ...”
- Authors** Ok thanks, that’s fixed!

Review of version 2

Permalink: hal-03697346v2

- Reviewer** The authors have comprehensively addressed the comments of both referees and modified the paper accordingly. I think the paper is now suitable for publication.
- Reviewer** The authors took the recommendations into account and provided detailed and convincing answers. Ok for publication in the present version.

Editor’s assessment (Laurence BRASSART)

This paper investigates the relative significance of (usually neglected) coupled thermo-elastic effects induced by strain-induced temperature variations during DMTA tests on the rheological response of polymers. To this end, an infrared thermal measurement setup capable to reach very small temperature variations is presented. Experimental measurements are analysed using a thermodynamically consistent rheological model accounting for thermoelastic couplings. Both reviewers considered that the submitted manuscript was of high scientific quality and well worthy of publication in JTCAM. The reviewers mainly requested further details and clarifications, as well as some improvement to the presentation. The authors comprehensively addressed all the reviewers’ comments, and both reviewers recommended the revised manuscript for publication as is.

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