

TTS

the solution

16.07.2020

Methodology

1. *Rephrase the problem indicating very clearly what you have been asked to do.*
2. *List all the data provided.*
3. *Make a list of the assumptions. justifying each of them.*
4. *Write down an algorithm for the solution you are proposing (no calculations are needed at this stage)*
5. *Answer the question*
6. *if needed check in the web for technical papers to support your answer.*
7. *List the references used in the solution of the problem.*

Rephrase the problem indicating very clearly what you have been asked to do.

1. Question/Problem to be solved:

Get the master curve at 210°C and get the complex viscosity at $T = 180^\circ\text{C}$

2. List all the data provided:

I have the elastic ($G'(\omega)$) and the loss ($G''(\omega)$) moduli for a HDPE at five temperatures: 170, 190, 210, 230, 250°C.

3. Make a list of the assumptions, justifying each of them.

a) *All the specimens were run at the same % strain and using the same geometry and gap between the plates.*

b) *The polymer was protected with antioxidants, so decomposition is not present.*

c) *Assume that the lowest temperature is greater than $T_g + 100$ so I can use the Arrhenius equation for the calculation of the shift factors*

4. Write down an algorithm for the solution you are proposing (no calculations are needed at this stage)

***1**

1. Decide the reference temperature
2. According to the abstract of the Mavridis paper^{*1}
 - a) Get the $\tan \delta$ vs. frequency using the data at each T to get a_T
 - b) Get the $\tan \delta$ vs. G^* to get b_T
3. Do the calculations of $\tan \delta$ and G^* where:
 - a) $\tan \delta = G''(\omega)/G'(\omega)$
 - b) $G^*(\omega) = [(G''(\omega))^2 + (G'(\omega))^2]^{0.5}$
4. Plot $\tan \delta$ vs. ω for all temperatures in the same graph.
 - a) Multiply all the frequencies of a given temperature by a factor a_T until it coincides with the reference plotted data.
 - b) Do that for each temperature
5. Plot $\tan \delta$ vs. $G^*(\omega)$
 1. If needed multiply G^* by a b_T like in point 4

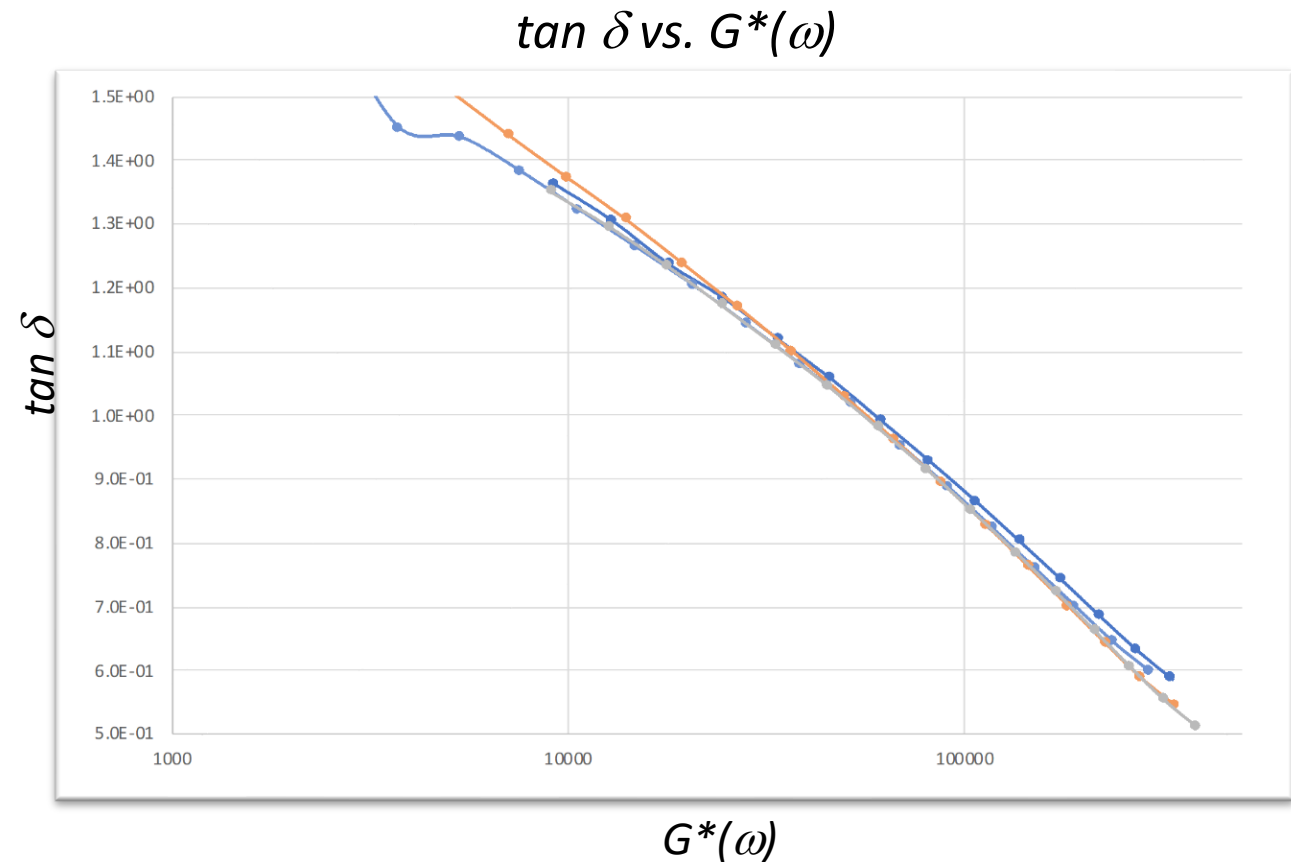
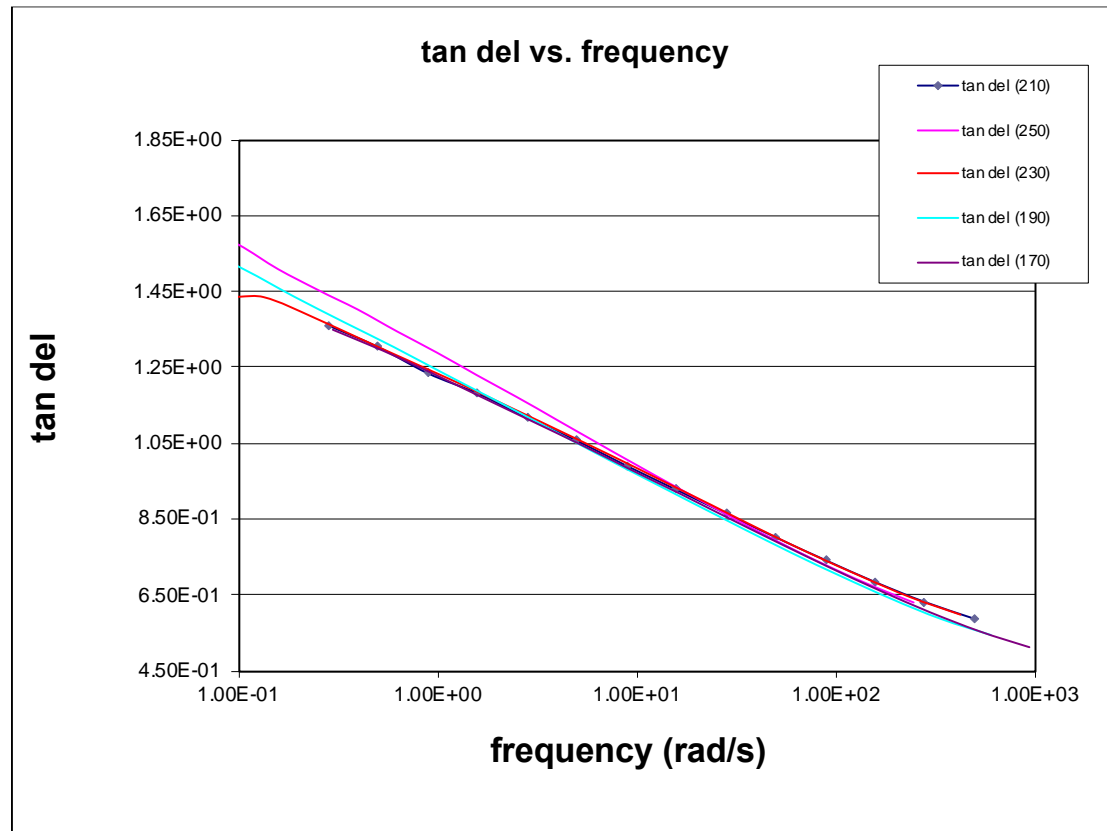
The rheology of polymer melts depends strongly on temperature. Quantifying this temperature dependence is very important for fundamental, as well as practical, reasons. The purpose of this paper is to present a unified framework for handling the temperature dependence of rheological data. We considered the case (by far the most common in polymer melts) where all relaxation times (in the context of linear viscoelasticity) have the same temperature dependence (characterized by a "horizontal shift activation energy") and all relaxation moduli have the same temperature dependence (characterized by a "vertical shift activation energy"). The horizontal and vertical activation energies were extracted from loss tangent vs. frequency and loss tangent vs. complex modulus data, respectively. This is the recommended method of calculation, as it allows independent estimation of the two activation energies (statistically uncorrelated). It was shown theoretically, and demonstrated experimentally, that neglect of the vertical shift leads to a stress (or modulus) dependent activation energy and necessitates different activation energies for the superposition of loss and storage modulus data. The long standing problem of a stress-dependent activation energy in long chain branched LDPE was identified as originating from the neglect of the vertical shift. The theory was applied successfully to many polyolefin melts, including HDPE, LLDPE, PP, EVOH, LDPE, and EVA. Linear polymers (HDPE, LLDPE, PP) and EVOH do not require a vertical shift, but long chain branched polymers do (LDPE, EVA). Steady-shear viscosity data can be superimposed using activation energies extracted from dynamic data.

Procedure

1. *Decide the reference temperature*
2. *According to the abstract of the Mavridis paper*1*
 - a) *Get the $\tan \delta$ vs. frequency using the data at each T to get a_T*
 - b) *Get the $\tan \delta$ vs. G^* to get b_T*
3. *Do the calculations of $\tan \delta$ and G^* where:*
 - a) $\tan \delta = G''(\omega)/G'(\omega)$
 - b) $G^*(\omega) = [(G''(\omega))^2 + (G'(\omega))^2]^{0.5}$
4. *Plot $\tan \delta$ vs. ω for all temperatures in the same graph.*
 - a) *Multiply all the frequencies of a given temperature by a factor a_T until it coincides with the reference plotted data.*
 - b) *Do that for each temperature*
 - c) *Once you have all the plots together you have the MASTER CURVE*
5. *Plot $\tan \delta$ vs. $G^*(\omega)$*
 1. *If needed multiply G^* by a b_T like in point 4*
6. *Plot each $\ln a_T$ vs. $(1/T - 1/T_{ref})$*
7. *Get the slope from that plot and is equal to E_a/R*
8. *Plug that slope into the Arrhenius equation and then you have now an equation from where you can calculate the shift factor for any other temperature (T):*

$$a_T = \exp[(E_a/R)((1/T) - (1/T_{ref}))]$$
9. *Then you multiply the frequency axes (ω) by that new a_T to move the master curve to the desired temperature.*
10. *You can use the shift factors to get the master curve for the G' and G'' curve*

5. Answer the question:



[3B TTS homework solved.xls](#)

6. *If needed check in the web for technical papers to support your answer.*

TS and Trios Software

<https://www.youtube.com/watch?v=Tty4MsoV7sc>

Time Temperature Superposition

<https://www.youtube.com/watch?v=1toVAagbfXg>

Time Temperature Superposition: predicting the future in space

<https://www.youtube.com/watch?v=YaTPocMOh-s>

7. *List the references used in the solution of the problem.*

**Temperature Dependence of Polyolefin Melt
Rheology**

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H. MAVRIDIS and R. N. SHROFF