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Time-Temperature superposition in linear and non-linear domain

Alen Oseli^a, Alexandra Aulova^a, Marina Gergesova^a, Igor Emri^{a,*}^aUniversity of Ljubljana, Faculty of Mechanical Engineering, Center for Experimental Mechanics, Aškerčeva 6, 1000, Ljubljana, Slovenia.

Abstract

Long-term behavior of polymers and their composites is related mainly to their time-dependent mechanical properties, i.e. material functions or master curves, usually obtained by time-temperature superposition (tTS) principle. The “weakest” point utilizing tTS lies in “manual or hand” shifting procedure, which can lead to over- or under-estimated life span of polymeric materials. This problem was solved by using closed form mathematical solution called Closed-Form-Shifting (CFS) algorithm which completely removes issues of “manual or hand” shifting procedure. However, it is important to acknowledge that tTS is well established only within the realm of linear viscoelastic theory. Results have shown that utilizing tTS in non-linear domain, where time-dependent properties become dependent on magnitude of external load, may lead to construction of misleading master curves, i.e. overestimated long-term behavior of polymers that could consequently cause premature failure of polymeric products.

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1. Introduction

To predict long-term behavior of products made of polymers and their composites one needs time-dependent material functions either in creep or in relaxation. To obtain material functions we commonly use the so-called time-temperature superposition (tTS) principle, which allows us to generate master curves at selected reference

* Corresponding author. Tel.: +386 1 6207 100; fax: +386 1 6207 110.

E-mail address: cem@fs.uni-lj.si

temperature, T_{ref} , and thereby extend the time scale beyond the range that could normally be covered in a single experiment [1]. This is schematically shown in Figure 1.

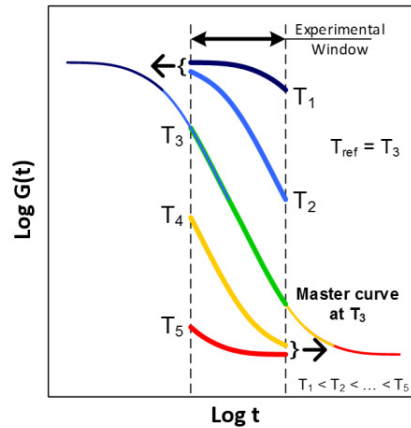


Fig. 1. Schematics of shear relaxation modulus segments and corresponding master curve at $T_{ref} = T_3$

The time-temperature superposition (tTS) principle used in characterization of time-dependent materials in molten as well as in solid state requires shifting of measured data along the logarithmic time scale. The shifting procedure “weakest point” is in its “person dependency”. Starting from the same set of experimental data two different researchers will construct most likely two different master curves, as shown in Figure 2.

Figure 2 represents “manual or hand” shifting performance of 5 different authors. Segments of synthetically prepared “true” shear relaxation modulus, $G(t)$ simulating real polymeric material, i.e. polyamide 6 (PA6). Experimental data were simulated by adding 5 % “experimental” error to the segments corresponding to different temperatures, Figure 2a. Different authors then constructed by “hand-shifting” master curves at reference temperature of 50°C; one of such is shown in Figure 2b. Figure 2c shows errors in modulus brought by “manual or hand” shifting procedure by different authors in respect to the underlying synthetically generated master curve representing shear relaxation modulus, $G(t)$, of PA6. The error ranges from 6,3 % to 12,7 %. After subtracting the 5% experimental error we obtain the error caused solely by the hand-shifting procedure, which is between 1,3% and 7,7%.

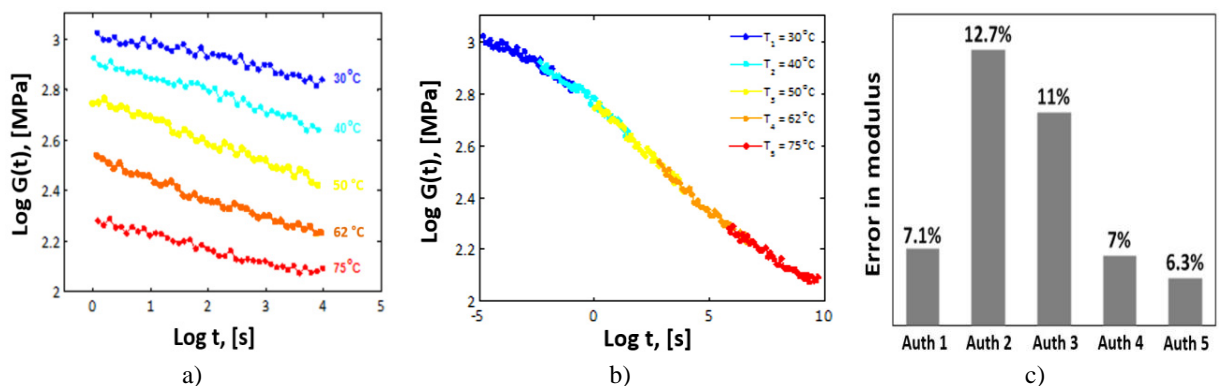


Fig. 2. a) Segments of shear relaxation modulus at different temperatures, b) master curve of shear relaxation modulus at reference temperature of T_3 and c) error in modulus brought by 5 different authors utilizing tTS

Recently we have resolved this problem by proposing the closed form mathematical methodology, called

Closed-Form-Shifting (CFS) algorithm [2], which completely removes issues related to “manual or hand” shifting procedure. CFS is proposed as a new ISO standard (ISO 108-Part 6) for performing tTS [3].

Prediction of long term behavior of polymers using tTS is well established within linear theory of viscoelasticity where time-dependent material functions are independent of the magnitude of external loading either in creep or relaxation. This was shown by many contributions examining various polymers in the past, see [4] and references therein. Moreover, many investigations utilizing tTS were conducted also in non-linear domain, where time-dependent material function become dependent on the magnitude of external loading. Authors used tTS for examination of non-linear time-dependent behavior for creep process at different stress levels [5,6] and for relaxation process at different strain levels [7]. Investigation were performed bellow and above glass transition temperature, mainly on amorphous polymers, such as polymethyl methacrylate (PMMA) and polycarbonate (PC). Authors claim that for PMMA and PC tTS can be applied also when material exhibit non-linear time-dependent behavior, however authors did not provide sufficient verification and proof if this is true for all thermoplastic polymers.

The scope of this contribution is to review the CFS algorithm, and check the validity of tTS in linear and non-linear domain for amorphous thermoplastic polyethersulphone (PESU).

2. Closed Form Shifting (CFS) Algorithm

The proposed mathematical formulation of the shifting procedure takes into account that material functions measured at two different temperatures represent behavior of the material at two different thermodynamic states, which differ in the corresponding Gibbs free energy [8] by

$$\Delta W = \int_{T_k}^{T_{k+1}} S dT, \quad (1)$$

where W denotes Gibbs free energy, V is the volume of the specimen, S is the internal entropy of the material, while T_k and T_{k+1} represent the two selected equilibrium thermodynamic states at which the corresponding segments of the material function have been measured. The rate at which mechanical energy is absorbed per unit volume of a viscoelastic material at a given temperature T_{k+1} is equal to the *stress power*, i.e. the rate at which work is performed. The stress power at time t is defined as

$$dW(t, T_{k+1})dt = \sigma(t, T_{k+1}) \frac{d\varepsilon(t)}{dt}. \quad (2)$$

The absorbed mechanical energy causes material inherent structural (molecular) rearrangements during the relaxation or creep process. Thus, any two segments of the material function, measured at first state T_k , and any other selected state T_{k+1} , that need to be superimposed (shifted) into a master curve (in our case shear relaxation modulus) should have the same energy release rate at all points of the superimposing interval. This criterion may be expressed as

$$\left. \frac{dW(G, t, T_k)}{d \log t} \right|_{t=t_k, L_k} = \left. \frac{dW(G, t, T_{k+1})}{d \log t} \right|_{t=t_{k+1}, U_{k+1}}. \quad (3)$$

The condition (3) is fulfilled when the overlapping area S between the two segments is equal to zero, as shown in Figure 3.

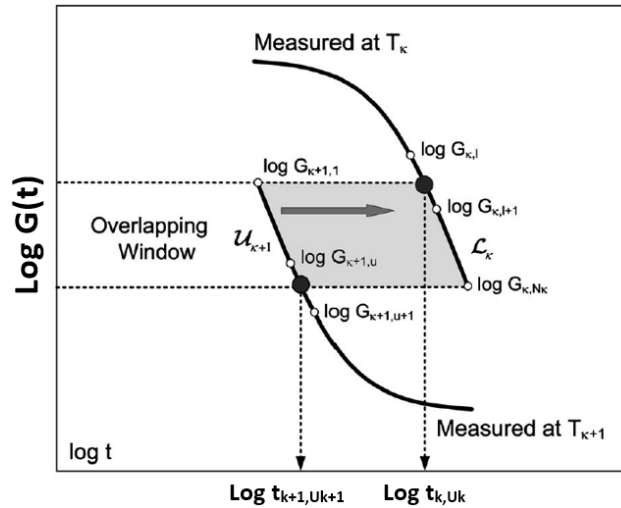


Fig. 3. Schematics of the CFC procedure for an example of shear relaxation modulus [2]

This yields the closed form equation for the shift factor, where its derivation can be found elsewhere [2]. The shift factor can be expressed as

$$\log a_{k+1} = \frac{A_k - \sum_{n=1}^{U_{k+1}-1} \left[\frac{\log t_{k+1,n+1} + \log t_{k+1,n}}{2} (\log G_{k+1,n+1} - \log G_{k+1,n}) \right]}{\sum_{n=1}^{U_{k+1}-1} (\log G_{k+1,n+1} - \log G_{k+1,n})}, \quad (4)$$

where A_k is

$$A_k = \sum_{n=1}^{N_{k+1}-1} \left[\frac{\log t_{k,n+1} + \log t_{k,n}}{2} (\log G_{k,n+1} - \log G_{k,n}) \right] \quad (5)$$

Figure 4 demonstrates the performance of the Closed Form Shifting (CFS) algorithm. Master curve (referring to Figure 2) was constructed at reference temperature 50 °C utilizing segments of shear relaxation modulus, $G(t)$ with 5% noise. Error brought by researchers ranges from 1,3 % to 7,7 %, whereas an error brought by CFS algorithm is only 0,4 % applying that CFS gives an ultimate shifting solution.

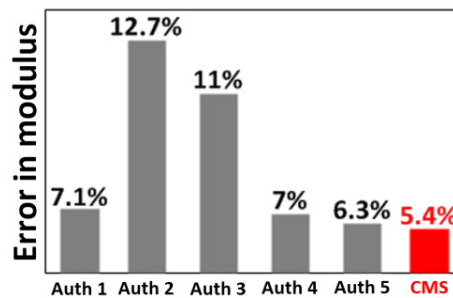


Fig. 4. Performance of Closed-Form Shifting (CFS) algorithm

3. Time-Temperature Superposition in Linear and Non-linear Domain

Prediction of time-dependent behavior of polymers using time-temperature superposition (tTS) is currently well established within linear theory of viscoelasticity, where two conditions should hold. The first condition states that the response of a material (stress in relaxation or strain in creep) is proportional to the magnitude of the external load (strain in relaxation or stress in creep). The second condition states that material responses through the history of external loads are additive (Boltzmann-superposition principle). If one of the conditions become invalid, material exhibits non-linear behavior [9].

These conditions directly suggest that when material is exposed to small external loads its time-dependent mechanical properties are independent of external load magnitude, hence material exhibits linear behavior. However, when a material “leaves” the realm of the linear theory of viscoelasticity its time-dependent mechanical properties become load dependent, which means that material behave non-linearly [9]. It was shown by several authors [5,6,7] that tTS can be applied either in creep or relaxation for selected amorphous thermoplastic materials. However, their investigations did not provide sufficient verification if this is true for all thermoplastic materials.

We have conducted similar investigation on amorphous thermoplastic polyethersulphone (PESU) by measuring shear creep compliance, $J(t)$ at different shear stress levels, i.e. 5 MPa (linear domain), 10 MPa (non-linear domain) and 15 MPa (non-linear domain). Measurements of shear creep compliance, $J(t)$ at specified shear stress levels were done in temperature range from 90 °C up to 190 °C, with the step of 10 °C.

For the clarity reason we show in Figure 5a isothermal segments measured at temperatures 90°C and 100°C for shear stress levels 5 MPa, shown as dashed lines, and 15 MPa, shown as solid lines, only. From Figure 5a one may observe, that (i) at the applied load of 15MPa creep compliance, $J(t)$, is larger than that measured at 5MPa, indicating that material has entered the non-linear viscoelastic domain; and (ii) segment measured at the temperature 100°C and 5MPa requires horizontal shift of 0,6 decades to superimpose with the segment measured at 90°C, whereas the corresponding shift for the two isothermal segments measured at 15MPa is 1,8 decades! This clearly indicate that the creep compliance measured at 15MPa will result in a “longer” master curve, as shown in Figure 5b.

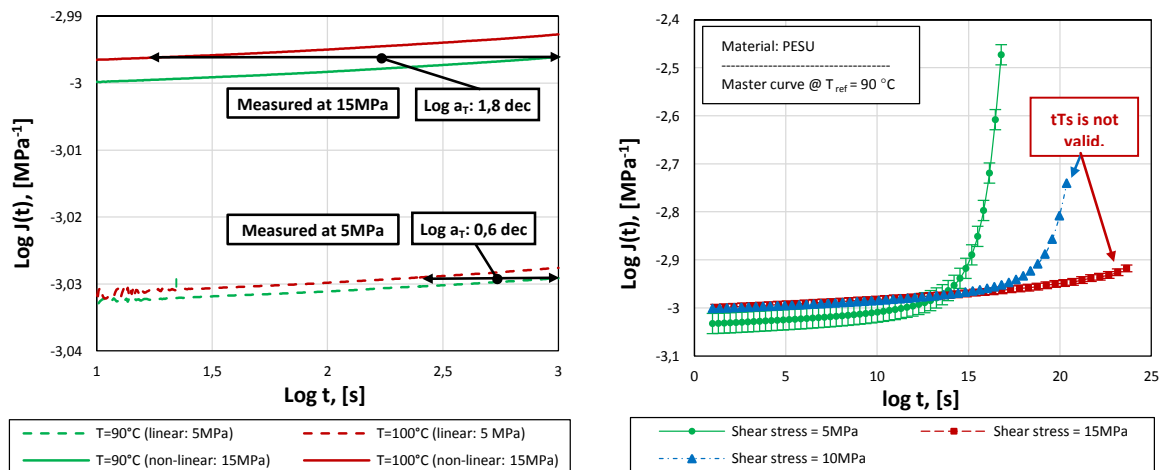


Fig. 5. a) Measured isothermal segments at 90 °C and 100 °C of shear creep compliance, $J(t)$ at shear stress levels 5MPa and 10MPa, and b) master curves of shear creep compliance, $J(t)$ determined at $T_{ref} = 90^\circ\text{C}$ for three shear stress levels 5MPa, 10 MPa and 15MPa

Figure 6 shows shift factors corresponding to the three shear stress levels as function of temperature difference ($T - T_{ref}$) indicating that using time –temperature superposition in non-linear domain results in overestimation of the material long-term behavior. Hence, for the amorphous thermoplastic polyethersulphone (PESU) time-temperature superposition in non-linear domain is not valid.

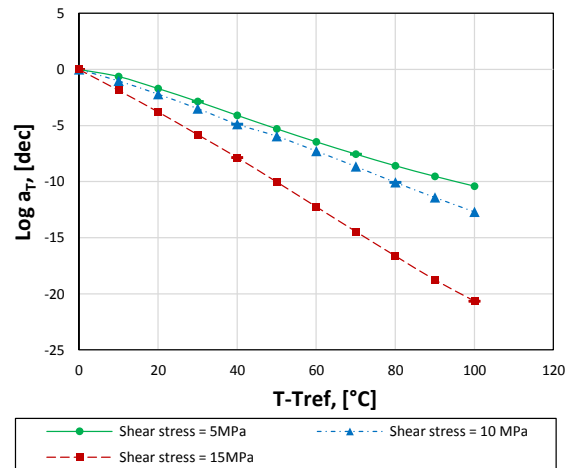


Fig. 6. Shift factors as a function of temperature difference determined through tTs for shear stress levels 5MPa, 10MPa and 15MPa

4. Concluding remarks

Time-Temperature Superposition (tTS) is the most important method for predicting long-term behavior of polymer based structures and products. Its validity is well established for materials in linear viscoelastic domain. Recently developed mathematical methodology, called Closed Form Shifting „CFS“ algorithm completely removes issues related to the „manual or hand“ shifting procedure and is in the process of standardization for the new ISO standard (ISO 108-Part6). However, when materials enter non-linear viscoelastic regime using tTs may lead to erroneous results. Within the non-linear domain material time-dependent properties become load magnitude dependent, causing larger horizontal shifts along the logarithmic time-scale. This results in overestimation of long-term behavior of examined polymers, as demonstrated for the case of PESU, for which the tTs in non-linear domain is not valid.

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