Time - temperature superposition principle
- Application of WLF equation in polymer analysis and composites

Polymers are the most studied viscoelastic material. The shorter times (high frequencies) corresponding to lower temperatures and long times (low frequencies) to high temperatures. This represents the quantitatively applied time-temperature superposition (TTS). Use of the Williams-Landel-Ferry (WLF) equation and the time-temperature superposition principle enables prediction and modeling of the mechanical and rheological properties of polymeric systems outside the timescale of the experiment. Application and validity of the TTS principle and WLF equation in polymer blends, composites, biopolymers and polymer networks will be discussed in this review.

Keywords: TTS principle, WLF equation, application, polymers, composites, characterization.

1. INTRODUCTION

Perfectly elastic deformation and perfectly viscous flow are idealized cases that can exist only under limiting conditions. For real world systems, the rate of molecular reorganization in condensed matter depends on its relaxation time. In solids, molecular (structural) reorganization is a very slow response occurring in a mainly elastic manner while for liquids their relaxation times are fast with a response that is mostly viscous, except at very high frequencies. According to Reiner and his well-known dimensionless Deborah number (De) the distinction between solid- and liquid-like materials is based on their relaxation times vs. the time of the experiment (i.e. observation time) [1]. The Deborah number (Eqn. 1) [1] is defined as the ratio of relaxation time (response time) ($\lambda_c$) compared to the time of observation ($t_o$):

$$De = \frac{\lambda_c}{t_o}$$

Higher De values means longer response times and greater elastic behavior (solid-like) by the material, while lower De means shorter response times and more viscous (liquid-like) behavior.

The most studied viscoelastic materials are polymers where the properties of polymeric materials are often time-dependent in addition to having other temperature effects. The shorter times (high frequencies) correspond to lower temperatures and long times (low frequencies) to high temperatures.

This can be quantitatively applied and is known as the time-temperature superposition (TTS), one of the most important principles in the polymer physics. The TTS principle is based on the fact that the Deborah number determines quantitatively just how a viscoelastic material will behave mechanically. Changing either $t_o$ or $\lambda_c$ can change De. The nature of the applied deformation determines $t_o$, while $\lambda_c$ is a function of temperature. The higher the temperature, the more thermal energy the chain segments possess, and the more rapidly they are able to respond, lowering $\lambda_c$. The Williams-Landel-Ferry (WLF) equation is a model used to describe the time-temperature superposition more precisely. Thus, use of the WLF equation and TTS principle enables prediction of the mechanical properties of polymers outside of experimental timescale, and allows modeling predictions for rheological properties of polymeric systems [2, 3].

The aim of this review is to present relevant research where the WLF and TTS principles are applied in the analysis, modeling and prediction of rheological behavior of polymeric materials. Additionally, we will describe a different understanding of the validity of the WLF equation.

1.1. Origin of the wlf equation

The origin of the WLF equation stems from the work of Doolittle on the viscosity, $\eta$, of n-alkanes as non-associated and pure liquids. Based on the fact that a glass transition appears as a result of decreased molecular mobility, as well as the principle that molecular mobility at any temperature depends on remaining free volume, bulk and shear deformation can be expressed in a terms of specific free volume [4, 5]. The commonly used Eqn. 2 can be expressed in a term of the shift factor $\alpha_f$ (where is $f = n/\tilde{v}$, $\tilde{v}$ and $v_i$ are the occupied and the specific free volume, respectively) as:
\[
\log \alpha_f = \frac{B}{2.303} \left( \frac{1}{f} - \frac{1}{f_0} \right)
\]

where \( \alpha_f \) represents the horizontal shift in a master curve construction, \( f_0 \) is the fractional free volume at an arbitrary chosen temperature \( T_0 \) and \( B \) is constant. A small vertical shift factor is neglected when stating Eqn. 2. This vertical shift factor was first described in the work of Ferry based on the theory of ideal rubber elasticity [6]. Eqn. 2 is the basic form of the WLF equation (3, 5). With further modification Eqn. 2, the final equation identical to the WLF equation (Eqn. 3 and 4) is expressed as [7]:

\[
\log \alpha_f = -\frac{(B/2.303 f_0)(T-T_0)}{f_0/\alpha_f + T-T_0}
\]

or

\[
\log \alpha_f = -\frac{C_1(T-T_0)}{C_2+T-T_0}
\]

Identification of the constants are given as:

\[
C_1 = \frac{B}{2.303 f_0}, \quad C_2 = \frac{f_0}{\alpha_f}
\]

\[
f_0 = \frac{B}{2.303 C_1}, \quad \alpha_f = \frac{B}{2.303 C_1 C_2} = \frac{f_0}{C_2}
\]

The above equations, 3 and 5, apply to any arbitrary reference temperature \( T_0 \) [5]. Usually, the chosen reference temperature is \( T_g \) but only if the condition \( T_g < T < (T_g + 100 \, ^\circ C) \) is satisfied [4]. A list of \( C_1 \) and \( C_2 \) for several of the most common polymers can be found in reference [8, 9]. Furthermore, the relaxation time is temperature dependent. Using \( T_0 \) as reference temperature equation 4 can be modified to obtain the energy term as:

\[
\ln \alpha_f = C \left( \frac{T-T_g}{T} \right)
\]

where \( C \) in equation 5 is equal to \( \Delta H/RT_g \) [3, 4, 5].

2. APPLICATION OF THE TTS PRINCIPLE AND THE WLF EQUATION

The first application of the TTS principle was reported in the work of Leaderman [10] followed by Tobolsky [11, 12], Williams, Landel and Ferry [6]. In all of the reported studies, horizontal shifting at different temperatures was used for the single creep curve construction called “master curve”, against time. Since then, the TTS principle has been applied in many studies of homo and linear polymers. Using recent research TTS was applied in the construction of a single master curve from data obtained in testing different polymer properties such as creep and stress compliance vs. time, dynamic modulus vs. frequency, etc. The application of TTS and WLF was also reported for materials used in the food science industry [13]. The most limiting factor in the application of TTS and WLF is whether the polymeric material behaves as a thermorheologically simple or complex material. Thermorheologically simple polymers are those in which relaxation (retardation) mechanisms and stress magnitudes at all frequencies have the same temperature dependence. In other words, if construction of the master curve requires applying only a horizontal shift vs. time (Fig. 1) material is than thermorheologically simple. For the rheological complex materials the vertical shift is necessary to construct the master curve along with horizontal shift [2, 5, 14]. Usually, vertical shift factors need to be applied to compensate the changes in material density, thermal expansion contraction, etc. [15].

![Figure 1 – Example of (a) creep curves obtain at different temperatures and (b) shift process of this curves in the idealized creep test of the polymer sample [15].](image)
In the work of Zlatanovic and Petrovic [16] the viscoelastic properties of polyurethanes, based on model triglycerides of vegetable oils, were studied in order to examine the structure-properties relation in this model polyurethane networks. This is an example where both shifting factors were required. The viscoelastic behavior of two model highly regular polyurethane networks (prepared from the triglycerides of oleic acid, linoleic acid and MDI) were analyzed and compared. The TTS principle was applied on the storage modulus ($E'$) vs. frequency isotherms obtained from DMA under the assumption the change of temperature will affect the relaxation processes by the same degree. This assumption made the construction of the master curves (Fig. 2), possible over the range of 39 frequency decades. The characteristic WLF parameters ($\alpha$, $\beta$, and $C_2$) at $T_g$ (DSC), as a reference temperature were successfully determined and the data were fitted to the WLF equation. The shift factors (horizontal and vertical) and $E'$ vs. frequency curves showed the same temperature dependence which means that vegetable oil based polyurethane networks have the same temperature dependent rheological behavior. However, a small vertical shift was necessary to obtain a smooth master curve meaning the polyurethane networks behave as rheologically complex systems. This complex behavior is attributed to the existence of the dangling chains in the network due to imperfect network formation and heterogeneous composition of polyurethane networks based on vegetable oils [17].

The application of TTS and WLF on the cross-linked polymers and polymers obtained via a polycondensation reaction presented above prove the versatility of TTS and WLF. In addition, the TTS principle has been widely applied in the analysis of homopolymers. Another example of such use is reported by Capodaglio and Lakes [18]. An amorphous poly(methylmethacrylate) (PMMA) polymer and crystalline low-density polyethylene (LDPE) polymer were used in viscoelastic measurements to evaluate and compare the validity of TTS and WLF when applied to amorphous and crystalline polymers. The broadband viscoelastic spectroscopy (BVS) measurements were performed over a wide range of frequencies at various temperatures. From the BVS measurements, the data for shear creep compliance, complex shear modulus, and loss tangent were obtained for both polymers. Data for the shear modulus was shifted horizontally and a master curve generated for both polymers but, master curves for loss tangent were not possible to construct. The reason for this behavior in crystalline polymers is due to the overlapping of multiple internal friction mechanisms in the same temperature region (multiple transitions occur). This leads to thermorheological complexity in crystalline polymers. For PMMA the Arrhenius approach works better than WLF in the glassy region, and existence of strong $\beta$ transition when $T_g$ is chosen as reference temperature. Similar to the work of Zlatanov and Petrovic, [16] the vertical shift factor for LDPE and PMMA was also applied. LDPE is an unambiguously thermorheological complex material not only due to the structure of the polymer chains but also because of the presence of different phases.

Figure 2 – Storage modulus vs. frequency master curve of the triolein-based polyurethane (reference temperature: $T_g=30$ °C) [16].

Another straightforward example of successful TTS and WLF application is a creep test at constant load and specific temperatures. This is a case of TTS application in the analysis of Kevlar 49 yarns reported in the work of Alwis and Burgoyne [15]. In a conventional creep test of the aramid fibers, at low stresses, a very long time is required to obtain stress at break data. However, the failure of the fiber can be obtain more rapidly (a few hours) by changing the temperature over the course of the creep test to cause acceleration of the creep rate. The creep curves at different temperatures were than obtained, shifted along the time axis to generate a single master curve. The shift factors follow the Arrhenius Law, which proves that creep is a thermally dependent process (Eqn. 5). This data can provide stress at break data for time periods exceeding that of the experiment. An interesting point in the reported work is their discussion about the validity of the TTS application in creep test for the Kevlar 49 yarns. They postulated that if the results obey the TTS and WLF equation, the master curve should reflect the real long time behavior at the reference temperature. Therefore, curves at different temperatures must follow the same temperature dependence in order to obtain smooth master curve. Furthermore, Alwis and Burgoyne suggested an additional validation of TTS. The TTS master curve must be independent of the test regime applied and the same curve should be generated from tests performed at different times and temperatures.
Polymers, specifically plastics, such as ultrahigh molecular weight polyethylene (UHMWPE) are used in biomedical applications for the load bearing purposes of artificial hips and knees. Due to the high strength and durability that this materials require, the viscoelastic model for UHMWPE for a biomedical application was developed and proposed by Guedes [23]. Dynamic viscoelastic properties were evaluated both with experimental and theoretical analysis (model based on TTS and WLF). Application of the TTS principle on this material was confirmed and master curves were constructed by applying the vertical and horizontal shift factors to superimpose the dynamic modulus vs. frequency curves. A new method for the shift factors calculation was also proposed. Both vertical and horizontal shifts were well fitted to the WLF and UHMWPE can be consider as a thermorheologically simple material in the range of frequencies applied. Similarly, Zhao et al [24] obtained data from the application of TTS and WLF modeling for the dynamic response of polyurea. The samples were subjected to high strain rates at different temperatures over a time domain. Application of TTS and WLF was confirmed, master-relaxation curves were constructed and mechanical behavior for quasi-static deformations over 16 decades of time was evaluated. Thus, modeling along with direct application of TTS and WLF can be used in dynamic property response and lifetime as well, as in modeling the desired properties.

For some of the most important and studied bulk plastics [25–29], rubbers [30, 31] and other elastomer materials [15, 16, 32] there are results reported for functional polymers. The TTS principle is successfully applied in conductive polymer viscoelastic property analysis by Hillman et al [33]. The TTS and WLF along with activation and Rouse-Zimm models, mainly developed for bulk polymers, were applied to evaluate the relation between polyaniline thin film macroscopic responses and molecular level mechanisms. The shift factors were used for the relaxation single master curve construction followed by calculation of the activation energy for the relaxation process at \( T_p \). Thus, a relation between changes in the redox state (variation of the film charge) of a polyaniline film and the viscoelastic properties are described in this research with good analogy to that of TTS and WLF (mainly applied for bulk polymers). Furthermore, they applied TTS and WLF in polymer solutions and polymer melts. Cheng and Yang [34] suggested a new methods in the study of the temperature-dependent physical properties through transition kinetics in the coil-globule transitions of PNIPAM. The two-step coil-globule theoretical transition predictions were confirmed in this study using TTS and WLF. The rheological properties of microphase separation of the polyurethane melts [35] were reported as a new field for the application of TTS and WLF. A microstructure of the polyurethane used in this research is based on hard and soft domains that undergo phase separation at low temperatures. Velankar and Cooper found that non-crystalline PU below its melt temperature exhibited thermorheological complexity (TTS and WLF cannot be applied) while above its melt temperature, smooth master curves were constructed using a horizontal shift factor. This demonstrates that PU melts behave as thermorheological simple materials. The reason is that for temperatures above the melt temperature, microphases are mixed completely and morphology of the melted polymer becomes homogeneous.

At temperatures below the melt temperature, the polyurethane exhibits microphase separation, due to specific microstructures (soft-hard domains) and acts as pseudo-blend where the viscoelastic properties were examined by TTS and WLF at low and high temperatures. This means that TTS and WLF can be applied in polymer blends and polymer composites. However, validity of TTS and WLF in this system is the most questionable. Generally speaking, it is expected that a blend of two completely miscible polymers obeys the TTS principle. Hagen and Weiss [36], in the study of TTS applied on blends of two miscible polymers, N-methylated nylon-2,10 (mPa) and lightly sulfonated polystyrene ionomers (SIPS), reported such results. Three key points, to validate the application of TTS and WLF were described. The first is that polymers were completely miscible (in the studied composition range of 30-70% of ionomer). Second, the two polymers strongly interacted through intermolecular forces, and last point was that the linear viscoelastic behavior of the blend was confirmed by dynamic mechanical analysis. However, the applicability of TTS and WLF mainly depends on miscibility. This was proven by preparing three polymer blends: mPa with Li-SPS (containing Li cation), Na-SPS and Zn-SPS, respectively. The first blend was completely miscible whereas the last blend was only partially miscible. Both blends (miscible and partially miscible) obeyed TTS and WLF. Application of TTS and WLF failed for the blends prepared from Na-SPS and mPa. Colby [37] in the study of TTS in two miscible polymers, poly(ethylene oxide), PEO, and poly(methyl methacrylate), PMMA, has reported a failure to use TTS for a composition of 20% PEO in the blend. A possible reason is that the two polymers are partially miscible (depends on chosen miscibility criterion) and thermorheologically complex. The similar breakdown of the TTS in multicomponent/multiphase
polymer systems was reported in the reference [38] which confirms the limited application and validity of the TTS principle in this systems.

The successful application of TTS and WLF in the polymer composites was reported by Vaidyanathan et al. [39] and Yao et al. [34]. The results are different than those reported for polymer blends. In the former study TTS and WLF were applied for the extended creep behavior of dental composites and in the later TTS and WLF were used for the study of linear viscoelastic behavior of thermosetting epoxy asphalt concrete. In both cases, the validity of TTS applied in these systems was confirmed. However, the validity of TTS for the composites based on biodegradable polymer such as poly(ε-caprolactone) and nanoclays was not confirmed due to a strong influence of the filler on crystallinity of polymer matrix [40]. Results reported for biopolymers and their blends (chitosan-starch and chitosan-pullulan films, mung bean starch blended with sodium chloride and sucrose), in the food science research field, confirm validity of the TTS (chitosan blends). While other cases do not (mung bean starch blend) [41, 42]. For the chitosan-based blend, the reason for the TTS success is probably due to chemical similarity of polysaccharides and consequently their compatibility. In the case of mung bean, starch reasons for the TTS failure are likely due to a thermal instability of polymers at the chosen analysis temperature, heterogeneity of the polymer system (presence of NaCl) and a gelation process during the reaction. However, they did construct a master curve with some violations in the shifting.

3. CONCLUSION

The time-temperature superposition (TTS) is one of the most important principles in polymer physics. Applications of TTS along with the WLF equation are well established for bulk linear and homopolymers finding them to be thermomechanically simple materials. Application of these principles to more complex polymeric materials (individual, blend or composite) with different structures and morphologies is a challenge. The application and validity of TTS principle and WLF equation in the polymeric materials (different from linear polymers and homopolymers), polymer blends and composites, and biopolymers was discussed in this paper. TTS and WLF were successfully applied in crosslinked polymers (polyurethanes and epoxy), Kevlar 49, polyolefin for biomedical application, polymer blends, polymer composites and biopolymers. Among them, dynamic mechanical and viscoelastic properties were examined and modeling of the properties was done by applying TTS and WLF. Furthermore, application of TTS and WLF was used for spreading in civil and engineering food science. The versatility of the TTS and WLF equations is unambiguous. Overall, the TTS principle and WLF equation are very useful tools in the study of a broad range of materials, their properties and predictions of lifetime (service life) for final products.

REFERENCES

IZVOD

PRINCIP SUPERPOZIRANJA VREMENA I TEMPERATURE
- PRIMENA WLF JEDNAČINE ZA ISPITIVANJE POLIMERA I KOMPOZITA

Polimeri su najproučavaniji viskeoelastični materijali. Kraće vreme (odnosno visoke frekvencije) odgovaraju nižim temperaturama, a duže vreme (odnosno niske frekvencije) odgovaraju visokim temperaturama. Ovaj odnos vremena (frekvencije) i temperature predstavlja kvantitativnu primenu principa superponiranja vremena i temperature (TTS). Upotreba Viliams-Lendl-Ferry (Williams-Landel-Ferry, WLF) jednačine i principa superponiranja vremena i temperature omogućava predviđanje i modelovanje mehaničkih i reoloških svojstava polimernih sistema izvan vremenske skale eksperimenta. Upotreba i validnost TTS i WLF jednačine na polimerne blende, kompozite, biopolimere i polimerne mreže biće predstavljeni i razmatrani u ovom radu.

Keywords: TTS princip, WLF jednačina, primena, polimeri, kompoziti, karakterisanje

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