186 On the Usefulness of Time Temperature Superposition Principle for Characterising Non-Linear Mechanical Behaviour of Polymers and Composites

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Abstract. The so-called time-temperature equivalence principle in polymers can be extended to large deformations. This enable to build up experimental protocol et modelling strategy that meke experimental characterisation much simpler (by combining effects of temperature and strain-rate in one variable) and modelling more robust.

Introduction

The change in polymers when temperature varies from glassy to rubbery region combined with the strain-rate effects [1] drastically constrains the characterisation of their mechanical behaviour close to their glass transition temperature, Tg. The use of classical approach, consisting in accounting for temperature and strain-rate in a separate manner, results in complex experimental designs and numerous parameters to be identified for modelling. This is particularly true when mechanical behaviour additionally depends on some parameters such as moisture (Fig.1), which enlarges number of needed parameters.
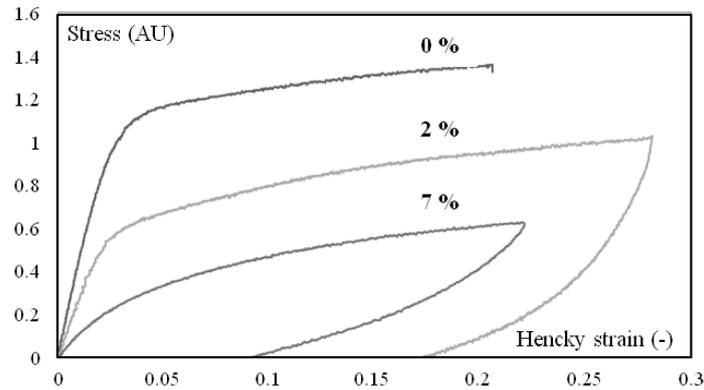

Figure1 Loading-unloading stress vs. strain cycles in tension at 23 °C for 3 different water contents (in weight) for PA 6-6. Strain-rate is 4 10^{-3} s^{-1}

In parallel, the time/temperature superposition principle, widely used in the linear viscoelastic region (or infinitesimal strain) to characterize the mechanical relaxations in polymers, allows to combine effects of temperature and strain-rate (or time or frequency). Given any experimental set up (close to Tg) in terms of strain-rate (frequency), $\dot{\varepsilon}_1$, and temperature, T_0. such principle expresses that storage and loss moduli should equal to storage and loss moduli for all other conditions, $(\dot{\varepsilon}_2, T_2)$, provided that one shift factor, a_t that depends only on T_0 and T_2 exists and is such as :

$$\dot{\varepsilon}_2 = a_{T_2/T_0}\dot{\varepsilon}_1 = 10^{\left(\frac{-C_1(T_2-T_0)}{C_2+T_2-T_0}\right)}\dot{\varepsilon}_1 \tag{1}$$

This classical WLF equation is valid in the range [Tg, Tg+100].
C_1 and C_2 are parameters related to T_0, named reference temperature in that context. Very often those parameters are deduced from the built up of master curves in the DMA technics, e.g. measurement of complex modulus as a function of temperature and frequency, at very low strain (i.e. 10^{-3}).
It was suggested and validated, in previous studies [2, 3], that constitutive models could be defined as depending on the so-called "equivalent strain-rate at reference temperature" ($\dot{\varepsilon}_2$, in Eq. (1)) taking advantage of this time-temperature superposition principle. This allows not accounting for separated, but coupled, dependencies on strain-rate and on

temperature. Classical WLF approach was used and idea was rapidly validated on PA66, PA66GF composites, PET, PS and PMMA samples. One typical result is given in Fig. 2.
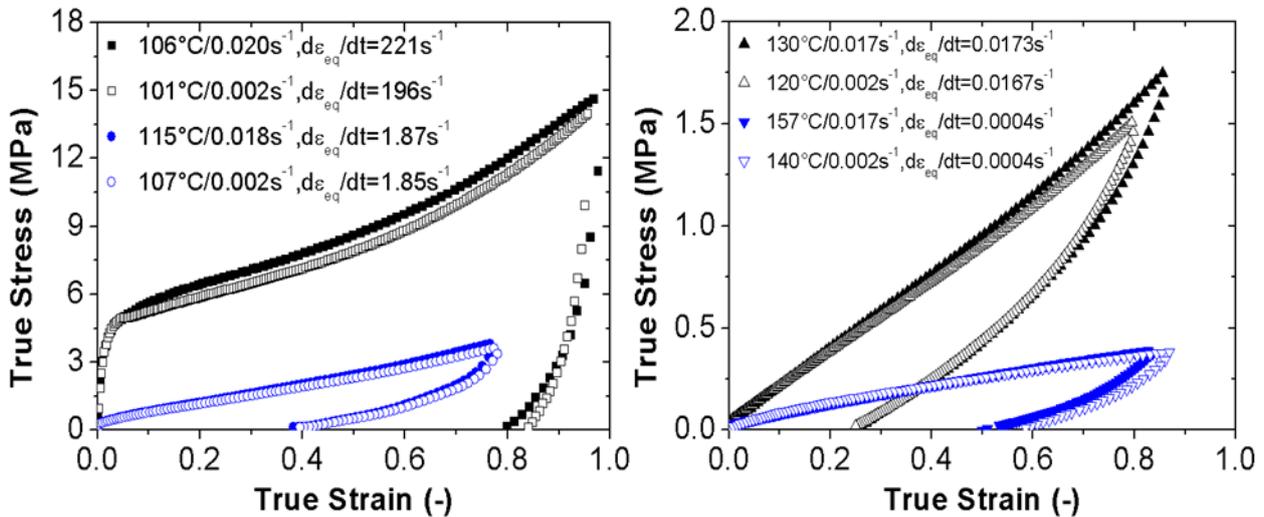

Figure 2 True stress-true strain curves obtained at the same equivalent strain rates (see legend) at a reference temperature of 130°C for PMMA [4].

In parallel, when external parameters (such as moisture) induces change in Tg it is possible to extend this approach combining temperature, strain-rate and external parameter to define equivalent loading conditions (Fig. 3).
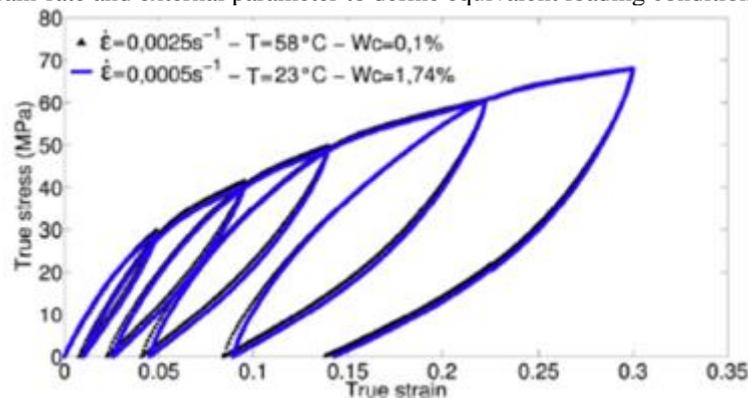

Figure 3 Time-temperature-water content equivalence on upload-unload tensile behaviour of PA66 [4]

Present conference will make a summary of these observations and demonstrate how they can opportunely be used to define experimental designs.

References

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