Polymer 139 (2018) 177–187

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Large strain/time dependent mechanical behaviour of PMMAs of different chain architectures. Application of time-temperature superposition principle

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ARTICLE INFO

Article history:
Received 14 September 2017
Received in revised form
4 January 2018
Accepted 12 February 2018
Available online 16 February 2018

Keywords:
PMMA
Time/temperature superposition
Mechanical behaviour

ABSTRACT

The relevance of equivalent strain rate at reference temperature derived from time/temperature superposition principle is validated as a constitutive parameter at large strain for PMMAs of different chain architecture. Shift factors were obtained from DMTA at infinitesimal strain, then identified according to Williams-Landel-Ferry or Arrhenius equations and finally extended to large deformations. Mechanical behaviour was characterized under cyclic tensile loading. So-called 3D digital image correlation was used to measure local strain. It is demonstrated that for different experimental conditions having same equivalent strain rate, the macroscopic behaviour will be the same. This was validated for elastoplastic, viscoelastic and rubbery behaviours. Such experimental observations indicate that time/temperature superposition at low strain can be extended for large deformation for PMMA. Additionally, the study opens a new way of addressing the temperature and strain rate dependencies in constitutive model by using the equivalent strain rate at reference temperature as a unique parameter.

1. Introduction

Understanding the mechanical behaviour of amorphous polymers and/or amorphous phase in semicrystalline polymers close and/or above their glass transition temperature, *Tg*, appear to be key issue in the field of polymers mechanics. Indeed, polymers can be intensively used above *Tg* either for their use when semicrystalline or for being processed in their rubbery state through thermoforming, stretch blow molding, hot embossing and other techniques when amorphous.

It is well known that polymers exhibit a drastic change in their mechanical behaviour when temperature increases from glassy to rubbery region. Rigorously speaking, temperature is not the only driving force as strain rate has also coupled effects that have to be accounted for. Let's just remind that mechanical behaviour is highly sensitive to temperature, T, and strain rate, $\dot{\varepsilon}$, especially in the viscoelastic region around their alpha transition temperature, T_α, where a change of temperature or strain rate affect greatly the molecular mobility [1–6]. This makes mechanical properties of polymers challenging to be predicted.

Many studies were devoted to describe the complex mechanical behaviour of amorphous polymers under large deformations (see in example [7–18]). Despite some promising results, the material models available in the literature still display difficulties to capture the material response over a wide range of temperature and strain rates and require a large number of parameters, which makes numerical modelling and parameters identification difficult. Within that frame, we are looking for more efficient parameters that would enable to simplify the characterization and modelling.

To overcome these issues, it was suggested in previous studies [19,20] that constitutive model could take advantage of time/temperature superposition principle through the use of so-called “equivalent strain rate at reference temperature” as constitutive parameter. This allows coupling the dependencies of other parameters on strain rate and on temperature. To define equivalent strain-rate, classical Williams-Landel-Ferry (WLF) approach [21] was found to be appropriated in the case of one polyamide 66 [20] and one poly(methyl methacrylate) (PMMA) [19]. This strategy could be used whatever the model is but have to be first experimentally validated at large strain. Therefore, the aim of the present

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https://doi.org/10.1016/j.polymer.2018.02.021
0032-3861/

paper is to systematically explore the ability of equivalent strain rate at reference temperature to be a convenient parameter to account for temperature and strain rate effects at large deformations, which may minimize the number of parameters. To achieve that point, we focus on amorphous material PMMA by exploring the effect of chain architecture.

The time/temperature superposition is widely used in the linear viscoelastic region (or infinitesimal strain) when characterizing mechanical relaxation in polymers science. Given any experimental set up close to *Tg* in terms of strain rate, $\dot{\varepsilon}_1$, and temperature, T_0, such principle results in the fact that storage and loss moduli should be equal to storage and loss moduli for all other conditions close to *Tg*, ($\dot{\varepsilon}_2$, T_2), using a shift factor, a_t [5,6,21] that depends only on T_0 and T_2 such as:

$$\dot{\varepsilon}_2 = a_{T_2/T_0}\dot{\varepsilon}_1 \tag{1}$$

According to classical WLF equation in the range [Tg, Tg+100 °C]:

$$a_{T_2/T_0} = 10^{\left(\frac{-c_1(T_2-T_0)}{c_2+T_2-T_0}\right)} \tag{2}$$

where 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 building up of master curves using dynamic mechanical and thermal analysis technics such as DMTA that allows the measurement of complex modulus as a function of temperature and frequency at very low strain level (i.e. 10^{-3}).

Roughly speaking, mechanical properties in the linear viscoelastic region and non-linear domain exhibit similarly trends with respect to the explicitly use of this time/temperature superposition principle for tensile tests. This has been seen in the case of amorphous as well as semi-crystalline polymers either in monotonic conditions [22–25] or in cyclic conditions [19,20]. To the author knowledge, no data exist concerning the validation of the time/temperature superposition principle at large deformation for material exhibiting different chain architecture such as molecular weight and cross-link degree. Therefore, this study aiming at validating the relevance of time/temperature superposition principle in the case of cyclic tensile tests performed at large deformation and temperatures ranging from T_α–50 °C to T_α + 70 °C as a function of chain architecture appears to be useful. In our case, five grades of an amorphous polymer PMMA with different molecular weights were investigated in this study.

The paper proceeds first by a description of the materials and experimental protocols used in this study to provide a clear picture of the measurements. Next, we illustrate the mechanical relaxations on the PMMAs and their dependence on strain rate through the resulting master curves in tensile loading. Then, so-called equivalent strain rate at reference temperature are validated for uploading-unloading tensile tests at large strain. Then, the effect of the molecular weight and cross-linking degree on the polymer mechanical properties using the equivalent strain rate at reference temperature is discussed.

2. Material and experimental

Five semi-industrial ALTUGLAS® PMMAs provided by Arkema Company were used. .Table 1 summarizes the molar masses (weight, *Mw*, and number *Mn*), the density at room temperature (ρ) and the alpha transition temperature at 1 Hz of each of them. Additionally, the crosslinked PMMA is not highly crosslinked (<1%) and contain a small amount of acrylate commoner. Those different molar masses cannot be processed in similar conditions due to difference in viscosity. Consequently, the PMMA exhibiting the higher molar masses could not be injection moulded. It is the reason why Table 1 also addresses the processing protocol. Materials did not show any relevant molecular orientation.

For clarity in the following, the PMMAs are referred to using their molar mass. For instance, the PMMAs with $M_w = 80$ kg/mol, $M_w = 93$ kg/mol were named “PMMA 80” and “PMMA 93”, respectively. Finally the cross-linked PMMA was named “PMMA CL”. Materials were tested as received, i.e. without any annealing protocol.

Samples were carefully tooled to avoid any heating to dimensions appropriated for experimental technics. Time/temperature superposition principle was addressed through DMTA (Dynamic Mechanical and Thermal Analysis). For the loading, oscillatory tensile tests were chosen. Specimen of dimensions 30 mm × 4 mm × 1 mm were analyzed using a DMTA Tritec 2000 machine. Isothermal frequency sweep tests were performed at a strain of 0.1%. It was checked in a preliminary step that such conditions are in the linear viscoelastic regime. Tests were performed for frequencies ranging from 0.1 Hz up to 100 Hz and for temperatures ranging from 25 °C up to 150 °C every 10 °C for PMMA 80, 93 and 120 and ranging from 25 °C up to 200 °C for PMMA 3500 and PMMA CL (obtained by casting molding). Shift factor were graphical determined using storage modulus, *E'*. Despite this, it was checked that same shift factors were relevant for both storage and loss moduli. No vertical shifts were applied.

Behaviour at higher strain level was addressed using uploading-unloading tensile tests performed on an Instron 596 electro mechanical load frame with a thermal chamber. Samples were home designed dog bone samples of dimensions which allow promoting a transversally uniform truly uniaxial loading in the central zone (see Fig. 1(a)) whereas deformation was analyzed during the test using digital image correlation (DIC) [26,27] on random speckle patterns (Fig. 1(b)). Two cameras in stereo-correlation were used to account for out of plane displacement during testing. Digital image correlation was carried out using VIC-3D version 7. An “area of interest” (AOI) was defined on the specimen face and then meshed (Fig. 1(b)). An example of the true longitudinal strain field is presented in Fig. 1(c) for a tensile test performed at 130 °C - 1.5 s^{-1} on PMMA 93. Careful attention was paid to calibration and analyses. To get a good compromise between accuracy and computational time, a mesh sensibility study was performed. A subset size of 21 by 21 pixels, a step size of 2 pixels and a filter size of 15 were used for the correlation [28–31].

Longitudinal, ε_{yy} and transversal, ε_{xx}, Hencky's strains were estimated in the AOI (Fig. 1(c)). It was checked that transverse deformation was reasonably isotropic, which means that $\varepsilon_{xx} = \varepsilon_{zz}$. The true stress could then be expressed as:

$$\sigma_T = \frac{F}{A_{(t)}} = \frac{F}{A_0 exp(2\varepsilon_{xx})}. \tag{3}$$

where $A_{(t)}$ and A_0 are the local cross section and the initial local cross section of the sample in the measuring area.

For addressing the mechanical behaviour evolution as a function of temperature (or strain-rate), tests were performed from the viscoelastic region, to higher temperatures corresponding to the rubbery plateau and until reaching the onset of the flowing. Specimens pre-heating duration was calibrated using one thermocouple glued on the sample surfaces and one embedded in the bulk. Ten minutes was found to be enough to get a homogeneous temperature in the material prior performing tensile test. A local constant true strain rate, $\dot{\varepsilon}_T$, was obtained during stretching by thanks to an exponential cross-head velocity, *v*. The local constant true strain rates ranged from 10^{-3} s^{-1} to 10^{-2} s^{-1}. All the tests were