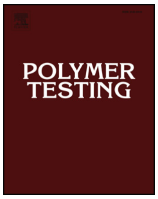
Polymer Testing 70 (2018) 297–309

Contents lists available at ScienceDirect

Polymer Testing

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



Test Method

Defining the limits to long-term nano-indentation creep measurement of viscoelastic materials

X.D. Hou[a,b,*], N.M. Jennett[a]

[a] *Coventry University, Priory Street, Coventry, West Midlands, CV1 5FB, UK*
[b] *National Physical Laboratory, Teddington, Middlesex, TW110LW, UK*

ARTICLE INFO

Keywords:
Indentation
Long-term creep
Viscoelastic
Modulus

ABSTRACT

An ultra-stable instrumented nano-indentation tester (UNHT, Anton Paar) was used to study extremely long (30,000 s) indentation creep of polymers. Total drift rate, measured on fused silica and sapphire samples, was less than 0.2 pm/s for up to 10 h, enabling collection of valid, low-uncertainty, long-term creep data - orders of magnitude longer than previously possible. Fits of the popular *N*-element Kelvin model to indentation creep data gave values of instant elastic modulus E_0^* and infinite modulus E_∞^* strongly dependent on the time-span of data fitted. Comparison with the long-term experimental data showed that the model was unable to use short term data to predict creep at the much longer times required by industry. A new analysis method is proposed to obtain a better estimate of the true value of infinite modulus, E_∞^*, which is the simplest indicator of maximum dimensional change of polymeric material components subject to long-term stress.

1. Introduction

Polymeric material components are increasingly used in many industries, such as automotive and aerospace, as lightweight replacements for metal parts, to improve overall energy efficiency and reduce carbon emissions [1–3]. Accurate dimensional control and stability is crucial for the success of a polymeric product, especially when a component is subject to a constant load over an extended period of time. Compared to metal or ceramic components, polymers exhibit more pronounced time dependent properties and deform continuously (creep) under an externally applied load. Creep is often the life limiting property of polymer components. Their creep behaviour is, therefore, of great interest to allow accurate prediction of component life time. The simplest test setup to measure uniaxial creep uses dead weights to provide a constant applied force (stress) and measures the creep (displacement) using an extension-measuring device; this kind of setup can be used to test long-term creep (months to years) with very little effort. Controlled force uniaxial mechanical testing instruments are also frequently used for polymer creep measurements, which allow more control of the running experiments (i.e. easy change of applied load during the creep). These creep measurement methods are well established and even standardized [4].

In recent years, the increasing demand for miniature, pocket-sized and compact devices is requiring material components (including polymeric components) to be made smaller. The reduced dimensions are a challenge for traditional mechanical testing techniques, as the specimen isn't big enough to meet standard measurement requirements, and can't be made large and stay representative of the original component. To address this issue, instrumented Indentation testing (IIT) is becoming popular as a useful tool, capable of testing small volumes of materials [5,6]. IIT-based creep testing can provide high-resolution mechanical property mapping as the contact size can be reduced down to the sub-micrometre range, commonly called nano-indentation. This technique is particularly useful for probing the mechanical properties of individual phases in composite materials, such as fibre reinforced polymeric matrix composites used in the aeronautical industry, where nano-indentation is the only technique that can be used to get the properties of the matrix (i.e. resin pockets) of the final composite.

As in macro-scale rheology, indentation creep measurements measure longer time constant effects (properties) than oscillation methods such as Dynamic Mechanical Analysis (DMA), which produces distinctly different (frequency dependent) results. Rapid AC oscillation dynamic indentation methods also exist but typically require additional hardware, whereas, indentation creep measurements can be made by any instrumented indentation system capable of force control (without any additional equipment). All that is required is a ramp in force followed by holding the indenter at the selected test force for a period of time to monitor the creep compliance, i.e. the indentation displacement vs.

---

[*] Corresponding author. Coventry University, Priory Street, West Midlands, CV1 5FB, UK.
E-mail address: xiaodong.hou@coventry.ac.uk (X.D. Hou).

https://doi.org/10.1016/j.polymertesting.2018.07.022
Received 8 June 2018; Accepted 25 July 2018

time as the indenter creeps into the sample [7,8]. The measurement stability of the instrument and the thermal (or other drift) sensitivity of the instrument to its unique environment determine the uncertainty of the creep and creep rates measured. This sets the minimum creep rate that can be measured acceptably/validly. Thermal expansion induced displacement is a particular problem. The measured indentation displacement includes all components of displacement (including thermal drift) within the "measurement loop". Thermal expansion can be considerable and, as most IIT systems are "bottom referenced" (the entire frame of the machine is included in the displacement measurement loop), a considerable amount of thermally induced displacement drift can be included in the test results. Tests in the EC INDICOAT project showed that systems with a thermal expansion of 1000 nm/K are not unusual [9]. In quasi-static IIT tests on non-viscous materials, the thermal drift can be measured and subtracted by measuring the indentation displacement of a stable contact at constant force over a period of time; typically a constant average drift rate is assumed and a linear correction is applied to the displacement data [10]. Since stable contacts are not possible for any material that creeps, indentation creep data cannot be corrected using this method.

An alternative method when performing dynamic IIT tests on non-viscous materials, is to use the reference modulus method to estimate the drift rate by calculating the area of contact (and thence actual contact depth) from the values of contact stiffness continuously measured during the indentation cycle [11]. This method assumes the elastic modulus of the sample remains constant with both indent size and indent depth, and also with time. The method requires the IIT system to have the necessary oscillation hardware and presumes that there is no change in properties of the contact as a function of shear rate or hysteretic adiabatic heating of the material as a function of frequency. In an investigation where the aim is to measure the (potentially variable) elastic modulus of a material using instruments not equipped for dynamic indentation, assuming these things is not appropriate, so thermal drift cannot be calculated using this method either. Indentation instrument drift is an increasingly significant contribution to the total creep data as the contact size decreases. This is particularly the case for long-term indentation creep measurements, where the creep rate is reducing over time, but the thermal drift is constant and accumulates over time. As a result, indentation creep tests, especially nano-indentation creep tests, are normally of short duration (e.g. tens of seconds) to minimise this problem. It is clear that much longer nano-indentation creep measurements on viscoelastic materials are desirable if long term creep is the lifetime determining property of a material or component. This is a challenge that requires a stable IIT measurement system with extremely low thermal drift to overcome.

Standard rheological material mechanical ('kinematic') models can be used to model and simulate indentation creep in order to assign fixed property parameter values to describe the viscous behaviour of polymeric materials [8,12]. The models adopted here used linear-elastic "Hookean springs" and "Newtonian dashpots" to represent the combination of the instant response (the purely elastic component) and a time-dependant material response (the viscous component) [13–15]. Normalising to the area of contact converts these spring constants and damping coefficients to values of modulus and viscosity that can be used as representative parameters to describe the material viscoelastic properties. It is commonly assumed that any plastic deformation is negligible for shallow indentations [16]. In principle, the mathematical response functions of these models can be fitted to indentation data and the indentation-derived parameter values for modulus, viscosity and time constant for the material, and this function used to calculate the longer term creep of the material. (Expectations derived from uniaxial rheology might be up to two decades time longer than the experimental duration). This would be very useful to accelerate the prediction of creep behaviour of polymeric components expected to serve a long-life time. However, the reality is that there is little evidence for the validation of such models, due to the lack of high quality long-term nano-indentation creep data.

In this study, an IIT platform with extremely low thermal drift (< 0.2 pm/s) was used to obtain extremely long indentation creep data (30,000 s) from a piece of commercial polymer (PS-3). The long duration indentation creep data was then used to investigate the appropriate number of elements required for creep simulation using a generalised n-time-constant ($N = 2n+1$ elements) Kelvin viscoelastic model. A new method is also proposed to obtain a more robust estimate of the indentation time-independent modulus (E_∞^*).

2. Viscoelastic model for creep data analysis

The linear elastic contact with a conical-pyramidal indenter is normally given by Refs. [17,18]:

$$\boldsymbol{P} = \frac{A}{2}\boldsymbol{E}^* \cot\varphi \tag{1}$$

where P is the contact force, A is the contact area, E^* is the indentation elastic modulus and $\boldsymbol{\varphi}$ is the cone semi-angle.

The expression in Equation (1) can be rewritten to include linear viscoelasticity by replacing the elastic constant P/E^* with integrals involving the creep response functions $J(t)$ [19]:

$$\boldsymbol{A}(\boldsymbol{t}) = 2\int_0^{\boldsymbol{t}} \boldsymbol{J}(\boldsymbol{t}-\boldsymbol{u})\frac{\boldsymbol{dP}(\boldsymbol{u})}{\boldsymbol{du}}\mathrm{du} \tag{2}$$

where $A(t)$ is the contact area with time and u is a dummy variable for integration that takes into account the incrementing of the applied force over a finite time.

In this study, the maximum indentation displacement was about 2 μm, which is below the 6 μm limit specified in ISO 14,577 for the use of a perfect indenter geometry (with less than a 1% error in contact area due to tip rounding effects) [10]. The actual area function of the Berkovich nano-indenter used in this study was, therefore, obtained directly by a metrological atomic force microscope (AFM). Indentation displacement, h, can be relatively large when investigating soft materials, and in other studies, where close to mm penetration depths were reported, an assumption of perfect (ideal shape) indenter geometry was used [20,21]. This simplification enables the contact area in Equation (2) to be easily expressed as a function of the indentation displacement. For bigger indenters and indentation depths, optical methods can be a more convenient way for three-dimensional shape measurement, even for high slope angles [22].

The generalised n-time-constant ($N = 2n + 1$ elements) Kelvin model was used to simulate the viscoelastic behaviour, as shown in Fig. 1. The creep function corresponding to the N-element Kelvin model is:

$$\boldsymbol{J}(\boldsymbol{t}) = \frac{1}{\boldsymbol{E}_0^*} + \sum_{\boldsymbol{i}=1}^{\boldsymbol{n}}\left\{\frac{1}{\boldsymbol{E}_{\boldsymbol{i}}^*}\left[1 - \boldsymbol{exp}\left(\frac{-\boldsymbol{t}}{\tau_{\boldsymbol{i}}}\right)\right]\right\} \tag{3}$$

where the creep compliance $J(t)$ is the sum of the instantaneous elastic response ($1/E_0^*$) and a response from a series of n pairs of parallel springs and dashpots. Creep compliance is zero at $t = 0$ and increases to $\sum\frac{1}{E_i^*}$ after an infinite time, E_0^* is the instantaneous storage indentation modulus, τ_i are the time constants and E_i^* is the corresponding modulus

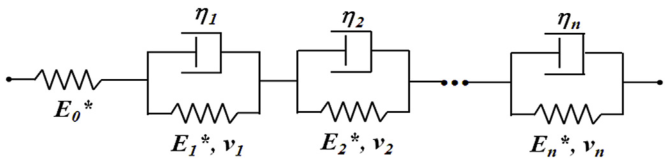


Fig. 1. The generalised N (= $2n + 1$)-element Kelvin model to simulate the viscoelastic behaviour; when $N = 2n+1 = 3$, it is known as the standard linear solid (SLS) model.