

STUDY OF CREEP FUNCTION DETERMINATION OF TWO AMORPHOUS POLYMERS BY INDENTATION TECHNIQUE

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ABSTRACT

When considering polymeric materials for the components design, their behaviour under external actions (mechanical, temperature, time, etc.) must be known. Thus, the study of their mechanical properties is essential if these materials are going to use as structural elements. The traditional mechanical tests, as tensile test or dynamic mechanical analysis (DMA), are widely used to determining the mechanical properties of bulk polymers or films. However, when these materials are used as coatings or when the available component volume is limited, the traditional tests are not suitable to determining the mechanical behaviour. Depth sensing indentation test is a technique that allows obtaining the mechanical properties of a component, at surface level, even for very small samples.

In this work the possibility of using depth sensing indentation technique to characterize amorphous polymers was explore. The results were compared with those obtained by DMA.

KEYWORDS: Depth sensing indentation, mechanical properties, amorphous polymers.

1.- INTRODUCTION

In polymers, rather than other materials, the temperature and time significantly affect the mechanical properties. Therefore, their response is greatly influenced by the tests conditions: strain rate, temperature, magnitude of the imposed deformation, etc.

Instrumented indentation takes its origin in the indentation for hardness tests, and also here an indenter-tip of a known shape is pressed on to a material. Contrary to the hardness test, with instrumented indentation the load and the displacement are continuously recorded during a loading and unloading cycle, either under a constant loading rate or under a constant displacement rate [1]. One objective of using indentation methodology is to produce quantitative measurements of elastic modulus, E . When the material response is linear elastic during the unloading process, analytical expressions can be derived for the relation between the indentation load and displacement during the unloading process.

Since polymers exhibit an intermediate behaviour between elastic solids and viscous liquids they exhibit strong time dependence, varying with temperature and the experiments duration. This dependence can be expressed both in the time and the frequency domain. Consequently, the elastic response (stiffness and compliance) of

polymeric materials obtained from indentation tests will be dependent on time. This dependence is commonly dealt with the creep or relaxation functions.

During load-controlled indentation test, creep is frequently observed in three ways: (i) increasing displacement during a holding period at fixed peak load; (ii) forward-displacing creep during unloading, doing that the maximum displacement does not occur at peak load; (iii) different load-displacement responses resulting from loading at different rates.

Experimental creep introduces inaccuracies when traditional elastic-plastic (Oliver-Pharr) analysis of depth sensing indentation data is used ignoring time-dependence [1]. Various schemes trying to minimize these effects have been proposed, most applying a long holding time at peak load to extent the creep, in an attempt to obtain purely elastic (creep-unaffected) unloading, and then, using the Oliver-Pharr methodology [2]. However, another alternative addresses the problem by means of analytical models that take into account the effect of creep on the curves obtained from the indentation tests.

Linear viscoelastic indentation models have been developed for quasi static loading [3] and dynamic loading [4]. For quasi-static loading, the first linear viscoelastic indentation model was developed by Lee and Radok [5]. In their approach, the material constants in the elastic solutions of contact problems are replaced by the corresponding differential operators in the viscoelastic constitutive equation.

2.- MAIN OBJECTIVES

In this work the mechanical behaviour of two amorphous polymers, PMMA and PC, has been studied by spherical indentation . The main objective is to determine, the creep function of each material from the indentation tests and compare it with that obtained from the dynamic mechanical analysis (DMA) technique.

3.- THEORETICAL BACKGROUND

The elastic solution for a spherical indentation was proposed by Hertz [6]:

$$h^{3/2} = \frac{3}{8\sqrt{R}} \frac{(1-\nu)}{G} F \quad (1)$$

where h is the penetration depth, R is the spherical indenter radius, G is the shear modulus, ν is the Poisson ratio and F is the indentation load.

The stress-strain relations for linear isotropic viscoelasticity can be expressed as:

$$P\sigma_{ij} = Q\varepsilon_{ij} \quad (2)$$

$$P'\sigma_{ii} = Q'\varepsilon_{jj} \quad (3)$$

where P , Q and P' , Q' are the linear operators in the time variable corresponding to stress and strain deviators and hydrostatic components, respectively.

Following the methodology proposed by Lee and Radok [5], these operators are conveniently brought into equation 1, obtaining a relation between the indentation load and penetration depth depending on time (equation 4), where the Poisson ratio is considered constant:

$$h(t)^{3/2} = \frac{3}{8\sqrt{R}}(1-\nu)2\frac{P}{Q}F(t) \quad (4)$$

Using the Laplace transformed operators, the equation 4 can be expressed as follows:

$$\hat{h}(s)^{3/2} = \frac{3}{4\sqrt{R}}(1-\nu)\frac{\hat{P}}{\hat{Q}}\hat{F}(s) \quad (5)$$

If the integral operators are used, the convolution theorem provides the viscoelastic relation of equation 5 in terms of the creep function in shear, $J_d(t)$:

$$h(t)^{3/2} = \frac{3}{4\sqrt{R}}(1-\nu)\frac{1}{2}\int_0^t J_d(t-\tau)\frac{\partial F(\tau)}{\partial \tau}d\tau \quad (6)$$

$$h(t)^{3/2} = \frac{3(1-\nu)}{8\sqrt{R}}\int_0^t J_d(t-\tau)\frac{\partial F(\tau)}{\partial \tau}d\tau \quad (7)$$

being equation 7 only valid for nondecreasing $h(t)$.

3.- MATERIAL AND METHODS

Two commercial amorphous polymers have been chosen for this study: PMMA and PC (Table 1). Both materials were obtained in the form of extruded sheet of 3 mm thickness. No further thermal treatment was applied to the samples. Prior to the indentation tests, the sheet roughness was determined by a surface roughness tester (SurfTest SJ-310, Mitutoyo). A mean roughness, R_a , of about 20 nm was measured.

Indentation experiments were carried out using a nano-indenter XP (MTS Nano-Instruments, Oak Ridge, Tennessee). A spherical ruby indenter of 5 μ m radius was selected.

Since equation 7 is valid under linear viscoelastic conditions, the indentation tests carried out on both polymers have been made assuring that the relationship between the displacement and the radius of the indenter was below 0.16 [7]. This implied that the maximum penetration depth was less than 800 nm.

All indentation tests were controlled in force, imposing an indentation load function depending on time according to equation 8:

$$F(t) = v_0 t \quad (8)$$

where t was the time and v_0 was the velocity at which the indentation load was applied. A range of loading ramps between 0.01 mN/s and 1.8 mN/s was used to study the behaviour of PMMA and PC (0.01, 0.03, 0.05, 0.1, 0.2, 0.3, 0.6, 0.9, 1.8 mN/s). Four indentation tests were conducted for each ramp condition on both materials.

Table 1. Properties of Poly(methyl methacrylate) and Polycarbonate.

Amorphous polymers	Structural formula	T _g (°C)	M _w (g/mol)
Poly(methyl methacrylate) - PMMA	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{COOCH}_3 \end{array}$	117	2588744
Polycarbonate - PC	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4-\text{CO}- \\ \\ \text{CH}_3 \end{array}$	145	18000

Substituting equation 8 into equation 7 and differentiating the resulting equation leads to an expression for the creep compliance function in shear could be obtained:

$$J_d(t) = \frac{4\sqrt{R}}{(1-\nu)} h^{1/2}(t) \frac{dh}{dF} \quad (9)$$

This expression depends on the penetration depth evolution and similar equations were obtained by Lu et al. [7].

The creep function measured via instrumented indentation as contact creep compliance, $J(t)$, can be obtained from the creep compliance function in shear through the following expression [8]:

$$J(t) = (1-\nu)J_d(t) = 4\sqrt{R} \frac{dh}{dF} h^{1/2}(t) \quad (10)$$

The creep functions obtained by indentation were compared with those obtained by DMA analysis. Frequency sweep DMA tests were carried out through the single cantilever configuration by a Q800 TA instruments dynamic mechanical analyser.

4.- RESULTS AND DISCUSSION

Figure 1 shows typical force-displacement curves obtained from indentation tests at different loading ramps for PMMA (Figure 1a) and PC (Figure 1b).

Figure 1 reveals that both materials were sensitive to the loading ramp, v_0 . Consequently, a loading rate-dependent response was obtained for both materials. Wide deviations between indentation data could observe depending on the loading ramp. If $h^{3/2}$ data is divided by the corresponding loading ramp, all curves are grouped into a single curve (Figure 2). Therefore, the creep function via depth sensing indentation as contact creep compliance is unique for each material.

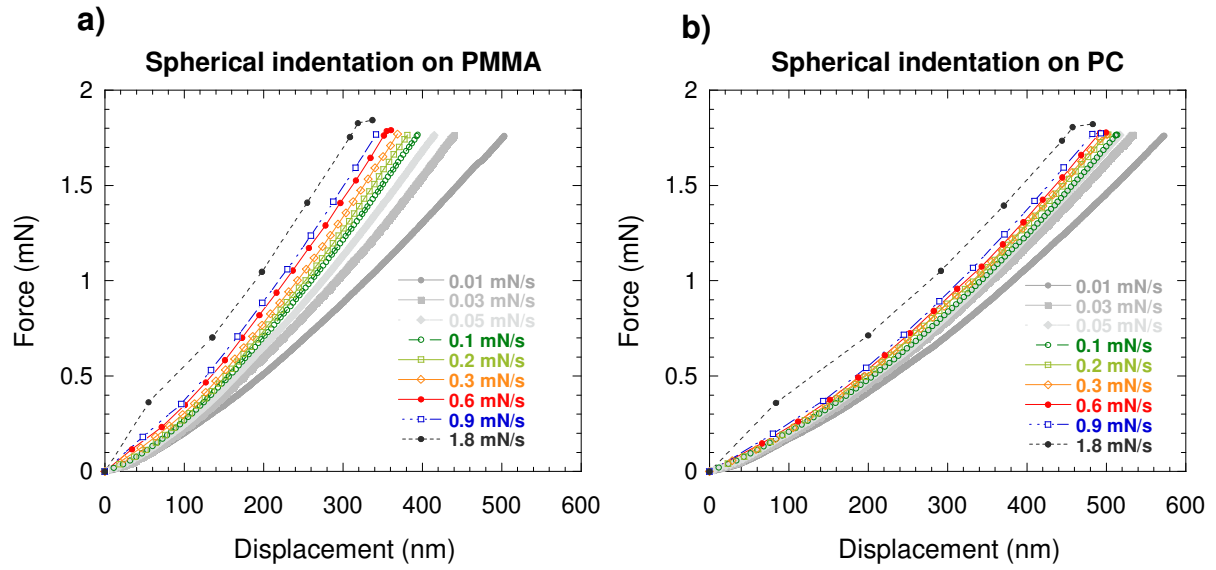


Figure 1. Representative force-displacement indentation curves at different loading ramps; a) PMMA, b) PC.

Using equation 10 the indentation creep functions for each indentation loading ramp could be obtained. Figure 3 represents the average evolution of the $J(t)$ for each loading ramp. Additionally, a global fitting of the $J(t)$ for all loading ramps was also included.

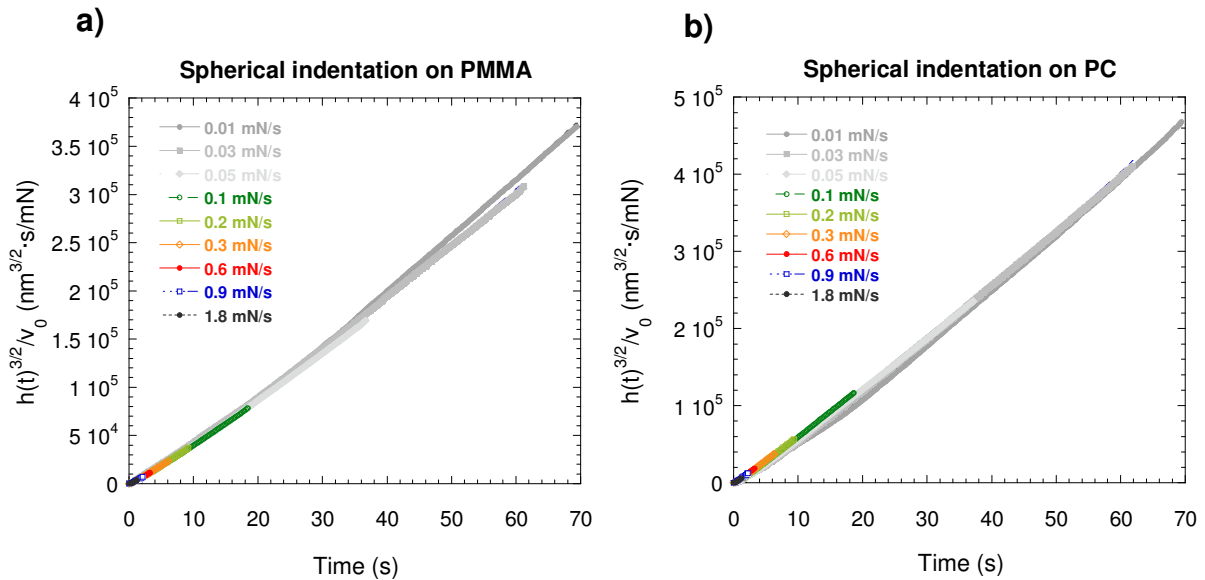


Figure 2. 3/2 power law of the displacement versus indentation time for each loading ramp.

In order to compare the indentation creep function with the DMA results, a transformation from the time dependence to the frequency dependence had to be done. To do that, it is assumed that both materials can be idealized through a standard solid model. For the standard linear solid model, the creep compliance function is given by:

$$J(t) = J_{\infty} + (J_0 - J_{\infty})e^{-t/\tau_c} \quad (11)$$

where J_{∞} is the creep for asymptotic time ($t \rightarrow \infty$); J_0 is the creep for $t=0$ (instantaneous response) and τ_c is the characteristic creep time of the material.

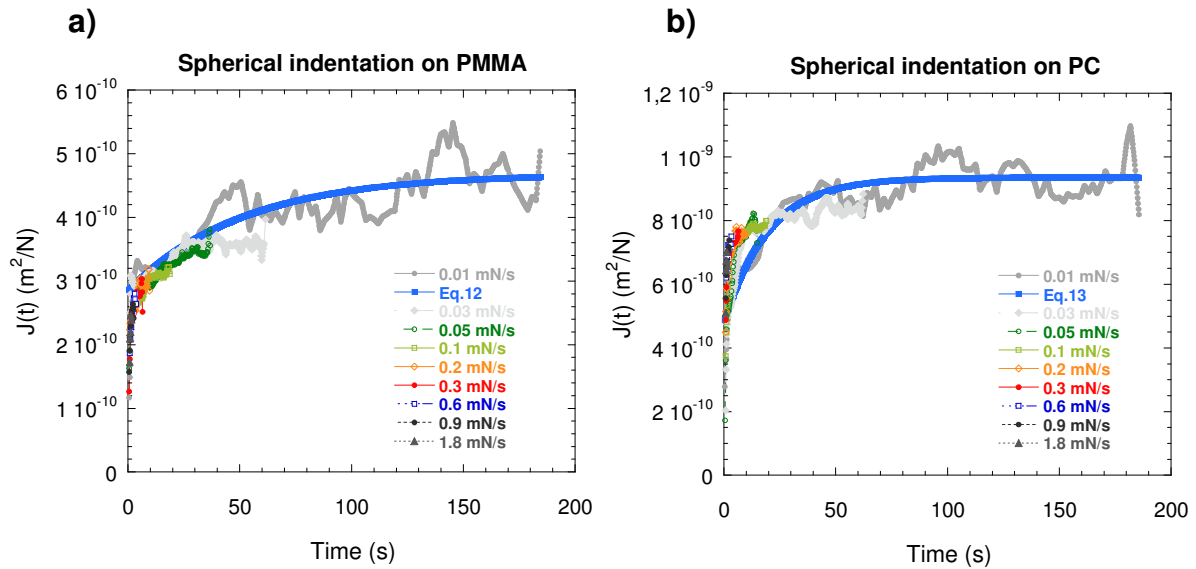


Figure 3. Average indentation creep functions $J(t)$ of a) PMMA, b) PC.

Fitting the average indentation creep functions (Figure 3) to equation 11, the parameters for the standard linear solid model could be obtained for each material:

$$\text{PMMA: } J(t) = 4.6822 \cdot 10^{-10} + \left(2.8420 \cdot 10^{-10} - 4.6822 \cdot 10^{-10} \right) e^{-t/51} \quad (R=0.996) \quad (12)$$

$$\text{PC: } J(t) = 9.3504 \cdot 10^{-10} + \left(4.7640 \cdot 10^{-10} - 9.3504 \cdot 10^{-10} \right) e^{-t/20} \quad (R=0.997) \quad (13)$$

To obtain the relaxation modulus, $E(t)$ from the creep function $J(t)$, the relation between them had to be used for a standard linear solid model [9]:

$$E(t) = \frac{1}{J_{\infty}} - \frac{J_0 - J_{\infty}}{J_0 J_{\infty}} e^{-t/\tau_R} \quad (14)$$

where τ_R is the retardation time:

$$\tau_R = \tau_c \frac{J_0}{J_{\infty}} \quad (15)$$

Substituting the values from equations 12 and 13 into equations 14 and 15, the relaxation function, $E(t)$, for PMMA and PC could be calculated (Figure 4a). These

relaxation functions are depending on time; consequently, they should be changed to frequency dependence in order to compare them with those obtained from DMA analysis [9].

$$E'(\omega) = \frac{1}{J_{\infty}} - \frac{J_0 - J_{\infty}}{J_0 J_{\infty}} \frac{\omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2} \quad (16)$$

Figure 4b shows the comparative of the relaxation function obtained by the two methodologies, indentation and DMA. This result showed that the indentation is revealed as a promising technique to characterize PMMA and PC.

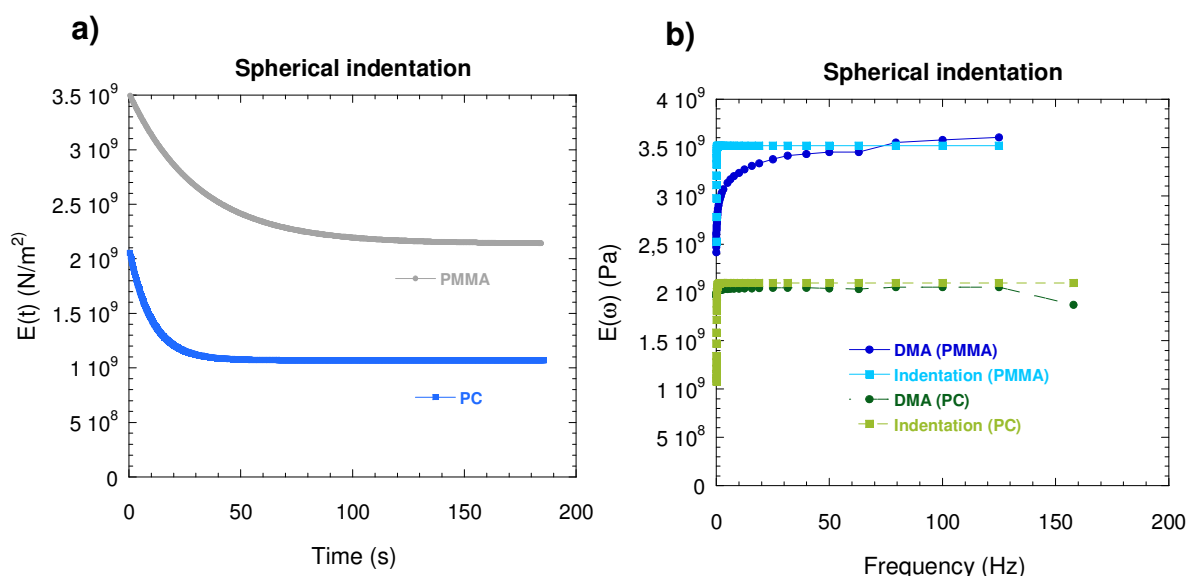


Figure 4. a) Time dependent relaxation functions of PMMA and PC obtained from indentation tests; b) frequency dependent relaxation functions of PMMA and PC obtained from indentation and DMA tests.

5.- CONCLUSIONS

In this work, the suitability of indentation technique to characterize two amorphous polymers, PMMA and PC has been studied. Specifically, the possibility to obtain the creep or relaxation function of both materials has been analyzed. These functions have been compared with those obtained by the DMA technique. Both techniques provide similar relaxation functions. However, the methodology based on indentation technique presented some difficulties. A behavioral model for both materials had to be supposed, which is a weakness of the method. Moreover, the equations used required the computation of derivative of indentation depth with respect to the indentation load. Therefore, the experimental data showed high scatter. Consequently, more studies concerning the indentation as a technique for obtaining such time-dependent functions should be done.

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