Polymer Testing 52 (2016) 157–166

Contents lists available at ScienceDirect

Polymer Testing

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

Test method

The effects of pile-up, viscoelasticity and hydrostatic stress on polymer matrix nanoindentation

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ARTICLE INFO

Article history:
Received 29 February 2016
Accepted 8 April 2016
Available online 11 April 2016

Keywords:
Nanoindentation
Pile-up
Viscoelasticity
Hydrostatic stress

ABSTRACT

It is well known that a clear disparity exists between the elastic modulus determined using macroscopic tensile testing of polymers and those determined using nanoindentation, with indentation moduli generally overestimating the elastic modulus significantly. The effects of pile-up, viscoelasticity and hydrostatic stress on the indentation modulus of an epoxy matrix material are investigated. An analysis of residual impressions using scanning probe microscopy indicates that material pile-up is insignificant. Viscous effects are negated by increasing the time on the sample during the loading/hold segment phases of the indentation test, and by calculating the contact stiffness at a drift-insensitive point of the unloading curve. Removing the effects of viscous deformation reduces the modulus by 10–13%, while also significantly improving the non-liner curve fitting procedure of the Oliver and Pharr method. The effect of hydrostatic stress on the indentation modulus is characterised using relations from literature, reducing the measured property by 16%. Once viscous and hydrostatic stress effects are accounted for, the indentation modulus of the material compares very well with the bulk tensile modulus, and modifications to standard indentation protocols for polymers are proposed.

1. Introduction

Nanoindentation has proven itself to be an extremely useful technique for testing polymer matrix composite (PMC) material constituents at the microscale. The technique has been successfully used to compare the properties of in-situ matrix constituents with the same materials in their bulk form [1–3], and for characterising the interphase region which lies adjacent to the fibre-matrix interface [4–9]. While this comparative analysis is interesting, a number of authors have reported a disparity between the values of the elastic modulus property determined using conventional macroscale mechanical testing, and those determined using indentation testing at the microscale, with moduli from indentation studies generally overestimating the elastic modulus of the material [10,11]. This overestimation has often been attributed to material pile-up and the viscoelastic behaviour of polymer materials [11–14], while other authors have postulated that the subsurface hydrostatic stress may also play a role [15–17]. The overestimation of the specimen elastic modulus using nanoindentation remains a predominant issue preventing the accurate quantitative characterisation of the in-situ matrix properties of polymer matrix composites (PMCs) at the microscale.

The elastic theory on which the nanoindentation analysis technique is based assumes that "sink-in" behaviour has occurred in the region around the indentation, as this behaviour is characteristic of elastic conical indentations. However, depending on the substrate material, the behaviour can vary at the maximum indentation depth, as illustrated in Fig. 1. During pile-up, the contact depth (h_c) is greater than the maximum indentation depth (h_{max}). Fig. 1b shows the shapes of the projected contact areas at maximum depth in each case, for indentations carried out using a Berkovich indenter. For the case of pile-up, the flat sides of the indentation impression curve outwards as the material piles up, mostly on the flat regions between the sharp edges of the indenter tip. During sink-in, the flat sides of the impression bow inward as the material sinks-in, mostly in the same regions. While the assumption of sink-in behaviour is valid for most materials, there have been numerous reported cases where the theory has failed to correctly predict the true contact area for the elastic-plastic indentation, depending on the modulus to yield stress ratio of the material [18]. This leads to overestimated indentation moduli

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http://dx.doi.org/10.1016/j.polymertesting.2016.04.003

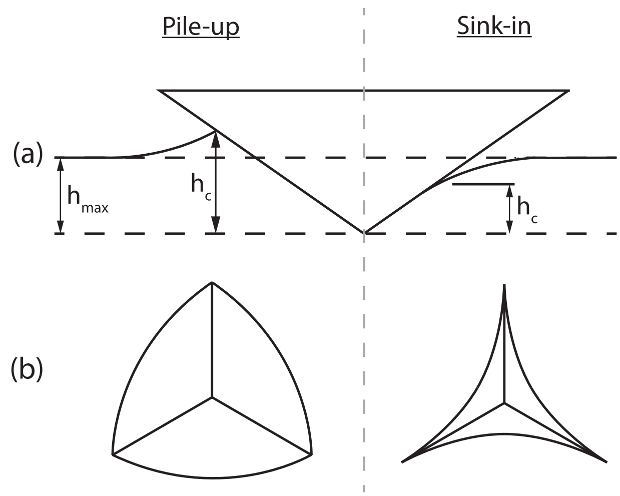

Fig. 1. Pile-up and sink-in material behaviour at maximum indentation depth (a) side profile of indentation, (b) geometry of projected contact areas for each case.

values [19–26].

Studies have also indicated that the time-dependent behaviour of polymers affects the predictions of elastic moduli using the nanoindentation technique [10]. In particular, it has been shown that the initial phase of the unloading curve is abnormal compared to the rest of the unloading curve, due to the notable effects of viscoelastic deformation [27]. These effects lead to an increase in the contact stiffness, poor non-linear curve fits of the unloading data, and theoretically invalid fitting exponents [10,15,27]. In severe cases, indentation creep can actually lead to a negative slope at the initiation of indenter unloading, which makes analysis of the unloading curve impossible [28]. However, even in the absence of this phenomenon, the unloading data can still be adversely affected by viscoelastic deformation, leading to overestimation of the sample modulus.

During indentation testing, the stressed material underneath the indentation tip becomes constrained by the surrounding unstressed material, leading to a build-up of large compressive hydrostatic stress [29]. It has been postulated by a number of authors that, for polymers, the overestimation of the indentation modulus could be influenced by the existence of this hydrostatic stress state [13,15–17], as the tensile modulus of polymers has been shown to increase with increasing hydrostatic pressure when tensile tests were performed in a thick-walled cylindrical pressure chamber [30,31]. However, the effect of the surrounding hydrostatic stress state on polymeric indentations has yet to be quantified.

The objectives of this paper are to investigate the effects of material pile-up, viscoelasticity and hydrostatic stress on the indentation modulus of bulk 6376 epoxy material. This material is the epoxy matrix in the carbon-fibre reinforced polymer (CFRP) material HTA/6376, commonly used in the aerospace industry. Optical and Scanning Probe Microscopy (SPM) techniques have been used to investigate the residual impressions of indentations for evidence of pile-up, with area corrections applied to the nanoindentation results based on direct area measurement techniques. The effect of viscoelastic deformation has also been investigated by carrying out a large number of indentations using a wide range of experimental settings in order to determine the optimum configuration and analysis techniques to produce results free from the influence of time-dependent deformation effects. The effect of varying these experimental and analytical parameters on the curve-fitting procedure has been detailed. Finally, relations from literature are used to quantify the value of the constraining hydrostatic stress, and characterise its influence on the calculated indentation modulus of the 6376 material.

2. Theory

2.1. Nanoindentation theory

The Oliver and Pharr [32] method is currently the most extensively used method of determining modulus and hardness. Hardness (H) is defined as the load on the indenter tip (P) divided by the projected contact area (A):

$$H = \frac{P}{A} \tag{1}$$

According to the methods derived by Sneddon [33] and Oliver and Pharr [32], the unloading curves from nanoindentation tests should accurately fit the power law relation in Equation (2):

$$P(h) = B\left(h - h_p\right)^m \tag{2}$$

where B, h_p and m are best fit constants. The constant h_p represents the depth of the residual plastic impression left after the indenter has been withdrawn from the specimen, while the exponent m is equal to 1 for elastic indentations with a flat punch indenter, and equal to 2 for elastic indentations with a conical indenter. Experimentally, the value of the exponent m generally lies between these two values due to the effects of plasticity [34]. The contact stiffness is obtained by evaluating the slope of curve fit at the onset of unloading. The contact stiffness is related to the reduced elastic modulus using Equation (3):

$$S = \frac{dP}{dh} = \frac{2E_r\sqrt{A}}{\sqrt{\pi}} \tag{3}$$

where S is the slope of the unloading curve or 'contact stiffness' and E_r is the reduced modulus of the contact. In practice, the contact area (A) is deduced using the Oliver and Pharr method by using the area function for the indenter tip geometry used. This function expresses the projected contact area as a function of the contact depth (h_c).

$$\begin{aligned} A &= F(h_c) \\ &= 24.56h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + C_3h_c^{1/4} + C_4h_c^{1/8} \ldots + C_nh_c^{1/2n} \end{aligned} \tag{4}$$

where the constants C_n are used to account for any deviation of the tip geometry from that of the ideal geometry. Using this technique, the contact depth is estimated based on Sneddon's expression for the shape of the surface outside of the area of contact for an elastic indentation by a paraboloid of revolution [35]. It is assumed that the depth of material in contact with the indenter tip is less than the maximum indentation depth according to Equation (5):

$$h_c = h_{max} - \varepsilon\frac{P_{max}}{\frac{dP}{dh}} \tag{5}$$

where h_{max} and P_{max} are the maximum displacement and load, respectively, and ε is equal to 0.75 for a paraboloid of revolution [36]. The specimen modulus (E) can be related to the reduced modulus (E_r) using Equation (6), provided the indenter modulus (E_i) is known and the Poissons ratios of the specimen and indenter, υ_s and υ_i respectively, are known or can be estimated.