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Nanoindentation of solvent-cast and compression-moulded poly(lactic-co-glycolic acid) to determine elastic modulus and hardness

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ABSTRACT

Nano- and micro-mechanical properties of solvent-cast and compression-moulded poly(lactic-co-glycolic acid) materials were investigated. Nanoindentation experiments were performed at different indentation depths and used to investigate the elastic modulus, hardness, contact stiffness, plasticity index and indentation pile-up behaviour of the material for a range of loading and unloading rates. The solvent-cast material was more elastically compliant and plastically softer than the compression-moulded material, and it also displayed lower work hardening characteristics. Loading rate dependence was found to be relatively insignificant. The measured elastic modulus and hardness were strongly depth dependent for both forms of the material, for indentations less than 3000 nm. The results allowed recommendations to be made on the choice of test protocol parameters for reliable nanoindentation testing of this material.

1. Introduction

Nanoindentation is a technique that has been widely used to characterise the mechanical properties of materials at micro- and nano-scales, and particularly to measure the elastic modulus and hardness. The application of nanoindentation has increased over recent years; however, applying this measurement technique to polymers, particularly soft polymers, remains challenging for a variety of reasons, including material rate dependence [1–3], adhesion [4–6] and size effects [2,7–17].

One facet of material rate dependence is viscoelasticity. In nanoindentation, viscoelasticity causes the penetration of the indenter into the indented material to continue during the initial part of unloading. This results in a forward-going *nose* in the unloading curve and, therefore, a negative contact stiffness which causes inaccurate mechanical property measurements [2,3,18]. A way to eliminate this nose is to use a holding time between loading and unloading at the maximum load. The holding time should be long enough such that the rate of increase in the indentation depth is less than 1% per minute [19]. Due to the time-dependent material properties, the unloading curve and, therefore, the contact stiffness depend on the unloading rate. A sufficiently fast unloading rate is desirable to limit the relaxation phenomenon for viscoelastic materials [20–22].

An important issue in nanoindentation of polymers is that the elastic modulus and hardness increase with decreasing the indentation depth. This phenomenon has been reported by many authors [1,2,4–17,23]. The factors which have been proposed to explain this phenomenon include: formation of a specific interfacial region between the indenter and the polymer surface during indentation [7], lower entanglement interactions at the surface due to the surface dynamics of polymers [1], surface roughness [17], changes in the material properties through thickness [2,10], tip imperfection [16], adhesion [4–6,24] and higher order displacement gradients [11–14].

For most polymeric and soft materials, adhesion between the indenter and the polymer surface occurs as the indenter approaches the surface (pull-on adhesion), causing a region of negative load in the load–displacement curve. This complicates the determination of the contact point (the point where the indenter first comes into contact with the sample surface) and, therefore,

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results in overestimation of the elastic modulus [25,26].

For most materials with low work hardening, the determination of the elastic modulus is affected by pile-up, where the sides of the residual impression are curved upward. When pile-up is large, the true contact area is larger than the projected contact area which is used in the calculations; consequently, the elastic modulus and hardness are overestimated [27,28]. The results of finite element analysis by Bolshakov and Pharr [28] have shown that pile-up is significant when the ratio of the residual depth to the maximum depth is larger than 0.7 and the degree of the work hardening is small.

Polymers such as poly(lactic-co-glycolic acid) (PLGA) are growing in industrial importance, in particular in biomedical applications for medical implants and devices [29,46]. Given this importance, and the complexities of performing nanoindentation on polymers generally, the present study is focused on the nanoindentation of PLGA. The first objective of this study is to characterise the material response under variation in applied load and loading rate. The second objective is to compare the effects of two different material processing methods on the material response. The final objective is to make practical recommendations on appropriate test parameters for successful nanoindentation testing of this material.

2. Experimental

2.1. Materials and sample preparation

DL-lactide-glycolide copolymer with a molar ratio of 50:50 (PURASORB PDLG 5010) was supplied by Purac Biomaterials, Gorinchem, Netherlands (M_n = 82,400 g mol^{-1}). Chloroform ($CHCl_3$) was purchased from Sigma Aldrich.

PLGA samples were prepared by two different methods: solvent casting and compression moulding. The compression-moulded sample was supplied by Proxy Biomedical Ltd. The thickness of the samples was 1.082 ± 0.006 mm. The sample was cut into 20 × 20 mm^2 test pieces. The density of the compression-moulded material was 1.2 ± 0.02 g cm^{-3}.

To prepare the samples by solvent casting, the polymer was first dissolved in chloroform. A 0.1 g ml^{-1} solution of PLGA in chloroform was prepared. A 2 ml of the solution was then cast onto a glass Petri dish (diameter 40 mm) using a pipette. To prevent the formation of air bubbles, the Petri dishes were covered by glass lids. The samples were put into desiccators for 48 h at room temperature and then dried in vacuum for a week. The thickness of the solvent-cast films was 0.120 ± 0.002 mm. The density of the solvent-cast material was 1.06 ± 0.06 g cm^{-3}.

2.2. Nanoindentation

Indentation tests were carried out at room temperature with a nanoindenter (CSM instruments SA, Switzerland) using a Berkovich indenter tip. A linear force-controlled mode was used for loading and unloading. The contact load was first increased to a maximum preset force at a constant rate, kept at this force for 60 s, and finally decreased to zero at the same rate as for the loading [29]. A typical load–displacement curve obtained for the PLGA in this study is shown in Fig. 1, illustrating success in the nanoindentation procedure for this material.

Different loading and unloading rates and maximum indentation forces were used for the compression-moulded and solvent-cast PLGA materials (Table 1). A matrix of 4 × 5 indents was used to perform a single batch of identical indentations with spacing of 300 μm between indents (to avoid overlapping the elastic field of each indent).

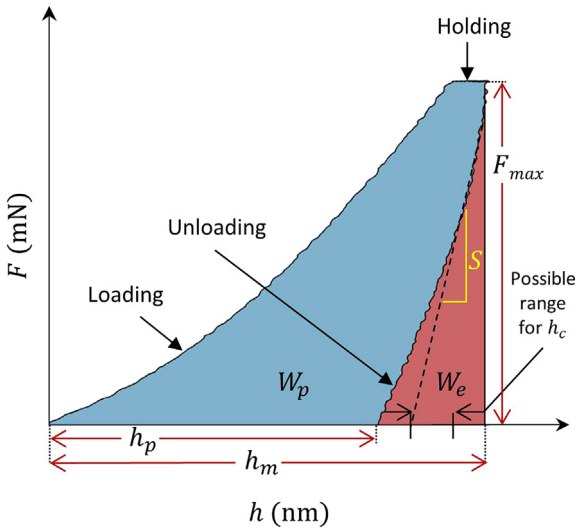

Fig. 1. Representative load–displacement (F–h) curve for the PLGA material indicating the parameters used in the analysis based on the Oliver and Pharr [30] method.

The elastic modulus and the hardness were obtained from the load–displacement curves based on the Oliver and Pharr method [30]. In this method, the projected contact area $A(h_c)$ is determined from the following tip function:

$$A(h_c) = C_1 h_c^2 + C_2 h_c + C_3 h_c^{0.5} + \ldots \quad (1)$$

where h_c is the contact depth of the indenter when the specimen is at the maximum force (see Fig. 1); the constant C_1 is typically 24.5 for a perfect Berkovich indenter. The remaining constants (C_2, C_3, …) account for the tip rounding and other departures from the ideal shape [27]. The tip shape function was calibrated from nanoindentation of fused silica.

The unloading curve is described by the power law expression as follows [30]:

$$F = \alpha(h - h_p)^m \quad (2)$$

where F is the applied force, α is a geometric constant depending on the indenter tip, h is the displacement, h_p is the permanent indentation depth (see Fig. 1), and m is the power law exponent. The constants m and h_p are determined by a least squares fitting procedure.

The initial contact stiffness S is evaluated by fitting Eq. (2) to the unloading data and then finding the derivative at the maximum force, F_{max}, as follows:

$$S = \left(\frac{dF}{dh}\right)_{max} = mF_{max}(h_m - h_p)^{-1} \quad (3)$$

where h_m is the maximum indentation depth (see Fig. 1).

The reduced elastic modulus E_r is determined from the contact stiffness and the projected contact area as follows:

$$E_r = \frac{\sqrt{\pi}S}{2\beta\sqrt{A(h_c)}} \quad (4)$$

where β is a correction factor which equals 1 for an asymmetric tip when the half-included angle of the indenter is 90°, and varies slightly for other indenter geometries. A wide range of values has been reported for β in different studies and there is no consensus on what value should be taken; however, Oliver and Pharr [27]