Analytical solutions for elastic response of coated mesoporous materials to pore pressure

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A B S T R A C T

Pore fluid adsorption-induced deformation of mesoporous materials is an important physical phenomenon. Experimental results show that the adsorption-induced elastic deformation can be quantified in terms of pore-load modulus (i.e., the radio between pore pressure and overall strain). In practical applications, most mesoporous materials are functionalized by post-fabrication processes such as surface coating. In this paper, we develop a theoretical model to predict the adsorption-induced deformation of ordered mesoporous materials with uniform and functionally graded coatings. Closed-form solutions of the pore-load modulus are obtained as a function of porosity, elastic properties of bulk materials and coating phases, thickness of coating, and geometrical arrangement of pores. Deformation of a coated triangular lattice of cylindrical pores representing the mesoporous materials with inner fluid pressure is also simulated by the finite element method, showing excellent agreement with the established theoretical solutions. The proposed model provides a general description of the elastic response of heterogeneous mesoporous materials subjected to the inner pressure loading.

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1. Introduction

Mesoporous materials with ordered porous networks have attracted increasing attention in recent years, due to their broad range of applications including optoelectronics, sensors, and separation technologies (Amato, Delerue, & Von-Bardeleben, 1998; Canham, 2014; Davis, 2002; Sailor, 2012). Understanding of the relationship between their mechanical properties and pore structures is necessary to fulfill their functional applications (Canham, 2014; Sailor, 2012). Most previous works focus on the effective properties of the porous samples, such as the bulk and Young's moduli (e.g., Bellet, Lamagnere, Vincent, & Brechet, 1996; David & Zimmerman, 2011; Dourdain, Britton, Reichert, & Gibaud, 2008; Niu & Yan, 2015), to characterize the elastic response to external mechanical loads. For the applications of gas or fluid adsorption in mesoporous materials, the porous solids may contract or expand due to the physical and/or chemical interactions between the guest molecules and the solid pore walls (Gor & Neimark, 2010, 2011; Rasaiah, Garde, & Hummer, 2008). This phenomenon is called as the adsorption-induced deformation and is common in various porous media with ordered channel-like pores (Dolino, Bellet, & Faivre, 1996; Herman, Day, & Beamish, 2006; Kucheyev, Bradby, Williams, Jagadish, & Swain, 2002). Recently, the issue of adsorption-induced deformation has received renewed attention due to their potential applications of sensors and actuators in engineering applications (Biener et al., 2009; Melde, Johnson, & Charles, 2008).

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Owing to the recent advances in reliable experimental techniques, such as in situ small-angle X-ray and neutron diffractometry (Muroyama et al., 2008), one can easily measure the adsorption deformation for highly ordered mesoporous materials (Findenegg, Jähnert, Müter, Prass, & Paris, 2010; Grosman, Puibasset, & Rolley, 2015; Prass, Müter, Fratzl, & Paris, 2009). The measured adsorption-induced strain is a function of capillary pressure which acts as a radial stress on the pore walls and can be basically described by the Kelvin–Laplace equation (Horikawa, Do, & Nicholson, 2011). The ratio between the pore pressure and the overall deformation of the porous sample is defined as an effective elastic constant called as the pore-load modulus (Prass et al., 2009). Experimental results show that pore-load modulus can be expressed as a function of porosity and is also related to the elastic constants of the matrices. In order to quantitatively describe the aforementioned relationship, there are several theoretical models proposed in recent years (Dolino et al., 1996; Findenegg et al., 2010; Gor et al., 2015; Grosman et al., 2015; Günther, Prass, Paris, & Schoen, 2008; Liu, Wu, Gan, & Chen, 2016; Prass et al., 2009). One of the representative analytical model is given by Gor et al. (2015), where a single cylinder pore is taken as the unit cell. By adopting the elastic solution of a pressurized thick-walled cylinder, the engineering strain of the single unit cell is calculated and assumed to be equal to the overall elastic strain. On this basis, Liu et al. (2016) proposed a size-dependent theoretical model for the pore-load modulus to take into account the influence of surface energy. It has been shown that the size effect is significant when the pore size reduces to nano-scale. However, the surface effect is negligible when the pore size is larger than several tens of nanometers.

The main advantages of fabricating mesoporous materials include the flexibility of the synthesis routes and the possibility of using different types of post-fabrication processes (Innocenzi & Malfatti, 2013). Thus, one can design and produce a desired material with a particular functionality and microstructure. In practical applications, in order to improve surface stability for catalytic reactions and control the pore size and topography of the pore wall, most of the mesoporous materials are functionalized by surface treatment after the synthesis processes (El Kadib, Finiels, & Brunel, 2013; Feng et al., 1997; McInnes et al., 2015; Van Rhijn, De Vos, Sels, & Bossaert, 1998). Mesoporous materials have also been integrated in different ways in functional coatings for self-cleaning, hydrophobic, and antireflective applications (Fateh, Ismail, Dillert, & Bahnemann, 2011; Faustini et al., 2010). It should be noted that the coating layer of the mesoporous materials affect their overall physical properties, particularly the mechanical properties (Chen et al., 2015; Duan, Wang, Karihaloo, & Huang, 2006; Wang & Pindera, 2016). However, there are less theoretical models to describe the influence of surface coating on the adsorption-induced deformation of mesoporous materials.

In this paper, the contribution of surface coating is taken into account for the elastic response of ordered mesoporous materials subjected to inner pressure. By extending the micromechanical model of homogeneous ordered porous materials to the coated mesoporous materials, a theoretical framework with coating effect on the pore-load modulus of ordered mesoporous materials is developed. Note that the pore size of the considered mesoporous materials are assumed to larger than tens of nanometers. Under such a condition, the surface effect is negligible (Liu et al., 2016). Two typical coating structures are considered, i.e., uniform coating and functionally graded coating. Both can be generated by corresponding surface coating technologies (Birman, 2014; Bonfoh, Coulibaly, & Sabar, 2014; Cherkaoui, Sabar, & Berveiller, 1995; Mohammadi, Saha, & Akbarzadeh, 2016; Sburlati, 2012). In order to validate the proposed analytical models, the pore-load modulus of cylindrical pores distributed on a triangular lattice is calculated numerically using the finite element method (FEM) for both the uniform and gradient coating. The analytical predictions are in good agreement with the FEM results.

2. Theoretical analysis of the pore-load modulus

Consider a typical ordered mesoporous material shown in Fig. 1(a). The cylindrical pores are arranged on a well ordered as two-dimensional (2D) triangular lattice. Gor et al. (2015) pointed out that the overall dilatational strain in the plate with many pores can be approximated by the engineering strain of the unit cell of a homogeneous pressurized cylinder with free outer surface. Liu et al. (2016) further showed that each unit cell is affected by its neighboring cylinders, implying that the outer boundary conditions of the cylinder are related to the geometrical arrangement of the pores. Considering the thickness of the plate is much larger than the pore diameter, the porous plate can be regards as under plane strain condition. Ignoring the surface effect, the pore-load modulus can be obtained as (Liu et al., 2016)

$$M_{pl} = \frac{E(1-\xi)}{(1+\nu)[(1-2\nu)(1-\alpha)+(1-\alpha\xi)]\xi},$$ (1)

where E and ν are the Young's modulus and Poisson ratio of the homogeneous solid matrix, respectively, α is a geometrical factor depend on the arrangement of pores and $\alpha=1/3$ for mesoporous materials with a triangular lattice, and $\xi = a^2/c^2$ is a dimensionless porosity factor related to the porosity φ of the porous material by $\xi = \pi/2\sqrt{3} \cdot \varphi$ for a triangular lattice. Note that the porosity discussed in the following is defined after the coating procedure. It can be found that the pore-load modulus depends on the material properties (E and ν), porosity φ, and the geometrical arrangement factor α.

It is noted that most mesoporous materials are functionalized by surface coating. The existing of coating phases affects the overall mechanical properties of the inhomogeneous composite structures. To explore the influence of the pore surface coating on the adsorption-induced deformation of mesoporous materials, the unit cell of coated structure can be treated as bilayer hollow cylinder, in which the inner layer is either uniform or functionally graded coating phase subjected inner pressure p_i, and the outer layer is a homogeneous matrix subjected the outer pressure p_o (see Fig. 1(b) and (c)). The matrix and uniform coating are linear elastic and isotropic, with Young's modulus being E_2 and E_1, respectively. The grated coating