Thin Solid Films 527 (2013) 205–209

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Evaluation of elastic modulus of ultra-thin vermiculite membranes by contact mode atomic force microscopy imaging

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ARTICLE INFO

Article history:
Received 8 May 2012
Received in revised form 30 November 2012
Accepted 3 December 2012
Available online 22 December 2012

Keywords:
Vermiculite
Clay
Atomic force microscopy
Mechanical properties
Membrane
Finite element analysis

ABSTRACT

Mechanical properties of nanometer-thick multilayer vermiculite, a layered silicate, were investigated by atomic force microscopy (AFM) contact mode imaging. Membranes suspended over circular holes were with exfoliated vermiculite platelets. The elastic modulus and pre-stress of each membrane were obtained using AFM combined with finite element analysis. The exfoliated multilayer vermiculite membranes had an average in-plane elastic modulus and average pre-stress of 175 ± 16 GPa and 55 ± 13 MPa, respectively.

1. Introduction

Clay materials have been widely used in a variety of nanocomposites as functional fillers. Clay platelets, including at the single layer level, embedded in polymeric composites provide improved properties over the pristine polymers, such as mechanical reinforcement [1–3], thermal stability [2], fire retardancy [4–6], and reduced permeability to liquids or gases [7,8]. These intriguing property improvements in polymer/clay nanocomposites are a result of the high aspect ratio and good dispersion of such clay platelets throughout the polymer matrix. The layered clays have intralayer covalent bonding while interlayer bonding is relatively weak. The strong in-plane covalent bonds enable the use of these materials as reinforcing elements. Moreover, the high aspect ratio (the ratio of in-plane dimension to the thickness) of clay platelets maximizes the contact surface area between the clay and the matrix.

Most of the values for elastic moduli of layered silicates previously reported were obtained from bulk materials by ultrasonic pulse [9], inelastic neutron scattering [10], and Brillouin scattering [11] measurements, respectively. Single-layer clay platelets have a thickness of about one nanometer and can have lateral dimensions of about a micron. Due to such a high aspect ratio and a small lateral dimension, the flexible and fragile nature of these materials has made direct mechanical measurements on them challenging. Recently, Kunz et al., reported mechanical measurements, in particular to extract the C_{33} elastic modulus, on fluorohectorite by force–deformation curve mapping in a whole clay tactoid spanning a trench using atomic force microscopy (AFM) [12]. Lee et al., used nanoindentation techniques with an AFM tip to measure the mechanical properties of monolayer graphene exfoliated from graphite, another layered material [13]. We have previously described how the elastic modulus and pre-stress of monolayer graphene oxide, a chemically modified graphene, was mechanically characterized with contact mode AFM imaging and finite element analysis (FEA) mapping [14].

Here, contact mode AFM imaging was used to extract the mechanical properties of few-layer vermiculite membranes. The in-plane elastic modulus and pre-stress were obtained by using a mapping method based on FEA [14,15]. The measurement and analysis techniques enable us to obtain both the elastic modulus and pre-stress of ultra-thin membranes simultaneously [14,15].

2. Experimental details

Vermiculite membranes were made by depositing an aliquot of vermiculite (MicroLite® Vermiculite Dispersion 963++ made by W.R. Grace & Co. in the U.S.A.) dispersed in water over a carbon support film on a transmission electron microscopy (TEM) grid (QUANTIFOIL® holey carbon film; QUANTIFOIL Micro Tools GmbH in Germany) and dried in air. X-ray diffraction (XRD, Philips X'Pert PRO) was used to measure the interlayer spacing of vermiculite after dropping the vermiculite solution on a glass substrate and drying it in air. The thickness of the vermiculite platelets was measured by contact mode (model CP, Park Scientific Instrument) or non-contact mode AFM (XE-100, Park Scientific Instrument). Scanning electron microscopy (SEM, Quanta F600 ESEM, FEI) was used for observing the morphology of the membranes. Atomic

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0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2012.12.024

structures of the membranes were observed by selected area electron diffraction (SAED) patterns in TEM (JEOL 2010F) imaging.

The AFM imaging in contact mode was used to obtain the mechanical deformation of vermiculite membranes. Scanning an AFM tip (model MLCT cantilever E calibrated by resonance frequency measurement [16]; Veeco Instruments) over a suspended sample with a constant normal force generated mechanical deformation along a scanned line. Topology images were obtained at several different normal forces. The line profiles at the center of the membrane were extracted as a function of the applied loads from the obtained topography images. Then, the force–distance relationship was generated at the center of the membrane.

FEA was used to calculate center displacements at a given applied load with various values assumed for the Young's modulus and pre-stress. A three-dimensional (3D) map can be plotted with displacement difference ($\Delta d = d_{FEA} - d_{measured}$) between the FEA calculated (d_{FEA}) and experimentally measured displacement ($d_{measured}$), for a given elastic modulus and a pre-stress. When the measured displacement at a given load was equal to the calculated displacement, an infinite number of pairs of possible values of Young's modulus and pre-stress were obtained, which formed a line when they were plotted in a two-dimensional (2D) map with the Young's modulus (ordinate) and pre-stress (abscissa). By repeating this analysis for other given loads, other lines with different slopes were generated in the map. Therefore, the overlapping area provided the best estimate of the Young's modulus and pre-stress of the membrane. The detailed procedure has been described previously [14,15].

The ANSYS Parametric Design Language was used to model the contact between the AFM tip and the membrane with varying elastic moduli and pre-stresses. Numerical calculations were done with 2-node shell elements for axisymmetric analysis of the membrane. The AFM tip was modeled as a hemisphere with a radius of 23.9 nm and the material properties of silicon nitride. The Poisson's ratio was assumed to be 0.28 [17]. Displacements at the center of the membrane were calculated at 50 GPa and 20 MPa increments for elastic moduli and pre-stresses, respectively. Each calculated displacement was compared with one measured displacement at a given force. Based on the calculations and comparisons with the measured displacements at four different forces, 3D and 2D maps were constructed.

3. Results and discussion

Vermiculite was chosen as a model material among other clay minerals due to its use for mechanical reinforcement of nanocomposites [18,19] and its use in generating thin 'paper-like' materials [20]. Vermiculite is a layered silicate, particularly a '2:1 clay' having two tetrahedral sheets for every one octahedral sheet. The silicate layers of vermiculite are separated by an interlamellar region composed of water molecules associated with metallic cations such as Mg^{2+}. The vermiculite used here is Li-exchanged vermiculite. Therefore, its level of hydration is a function of the relative humidity in ambient environment. In our lab the humidity was essentially constant and all measurements were done at a relative humidity of 40–45%.

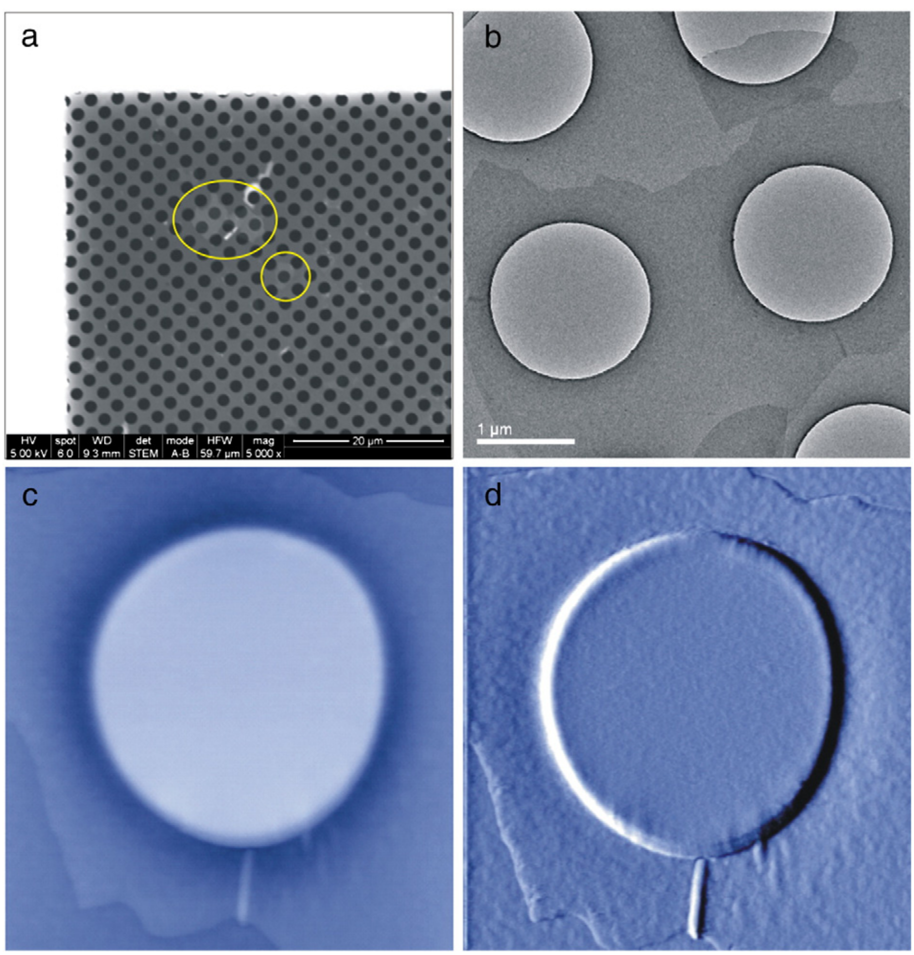

Fig. 1. Vermiculite platelets covering open holes; SEM (a) and TEM (b) images show that individual vermiculite platelets cover one or two holes. The yellow circles in the SEM image indicate the membranes. AFM images of topology (c) and error signal (d) clearly show one vermiculite membrane. The scanned area is $2.8 \times 2.8\ \mu m^2$.