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A Brief Review of Nanoindentation Technique and its Applications in Hybrid Nanocomposite Coatings

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ABSTRACT

Nanoindentation techniques are widely used for the study of nanomechanical properties of thin nanocomposite coatings. Theoretical concepts and practical use of nanoindentation method are summarized with reporting the applications of these tests in characterization of some particular thin nanocomposite hybrid coatings prepared by sol-gel process. The better mechanical properties can be obtained in the investigated hybrid coatings in compare with the pristine polymer coatings. It is demonstrated that the adding nano inorganic fillers can be influenced on physical-mechanical properties of coatings as well their microstructures. However, the adhesion of nanocomposite coatings is dependent on the chemical bond in the interface, microporous and defects in the network. Coating can be delaminated on exposure to extreme UV and humidity conditions. The mechanism of coating's failure as well microstructural changes can be studied by nanoindentation technique in statistic or dynamic modes.

Keyword: Nanoindentation; Coatings; Hybrid; Nanocomposite; Mechanical Properties.

1. INTRODUCTION

The mechanical properties of thin nanocomposite coatings can be evaluated by using the nanoindentation test [1-3]. This test is usually quick and easy to do. In the early twentieth century, this test is developed by Brinell using spherical balls and smooth ball bearings which were measured the plastic properties of the materials [1, 4 and 5].

During the past two decades, this testing method has been expanded at the nanometer range. In the newly developed system, very small loads at nano-Newton ranges and the small displacements of 0.1 nm can be exactly determined. Today, nanotechnology is considered as an important tool for studying the mechanical properties of the small parts of matter. In this test, an indenter tip with the known specific geometry is penetrated into the surface of coating or film with an applied specific load or penetration depth in static or dynamic mode.

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The various nanomechanical properties can be obtained based on the affected area such as elastic modulus, elastic and plastic deformation, hardness, wear and scratch resistance, etc [6-12].

In addition, nanoindentation can be used to estimate the fracture toughness of thin films which cannot be measured by other conventional penetration tests [13-16]. With tangential force sensors, nano-scratch and abrasion tests can also be measured at ramping loads. Atomic force microscopes (AFM) are ideal tools for monitoring of nano-sized influence and provide the usefulness of the information about the cracking and the deformation of material as a result of nano-indentation [17]. When the penetration force system is used in joint of an atomic force microscope, the in situ penetration image may be obtained simultaneously [18]. Diamond is often used as a tip of indenter because of its high hardness and elastic modulus which minimize its share of influence on the measured displacement [19, 20]. For measuring properties such as hardness and elastic modulus at the smallest possible scale, triangular pyramid Berkorvich tip is preferred over Vickers or Knoop indenter because three-sided pyramid tip is simply stable than the two others four-sided tips on one of the sharp point.

Continuous stiffness measurement (CSM) is a recently significant development in nano-indentation technique [1, 21-241. This technique is ideal for mechanical studies of thin films, poly-meric materials, multilayers which the micro-structure and mechanical properties change with indentation depth. In addition, this technique is less sensitive to thermal deviation [1, 24-26] as carrying out at frequencies greater than 40 Hz. In the CSM test, the indentation load is applied by a small sinusoidally varying motion of the indenter on the material's surface and analyzed the response of the material's surface by means of a frequency specific amplifier data. The CSM technique allows the measurement of mechanical properties at any point along the loading curve and not just at the point of unloading as in the conventional nanoindentation test. The CSM technique gives opportunity for measuring displacement and stress relaxation in creep test, utilizing a sinusoidal shape load at high frequencies allows doing fatigue tests at the nanoscale in thin films and microbeams by monitoring the change in contact stiffness because the contact stiffness is sensitive to damage formation. There are intensive studies and wide research articles on the use of nanoindentation techniques to characterize of the nanomechanical properties of hybrid nanocomposite coatings [1, 2, 8, 26 and 27]. The aim of this article is to demonstrate a brief review on the theoretical aspects and practical use of nanoindentation methods with illustration the applications of these techniques in characterization of some particular thin nanocomposite hybrid coatings prepared by sol-gel process. Figure 1 shows the standard indentation instrument which includes three essential elements: the first part of instrument is for applying force, the second part of instrument is an element through which the indent force is applied on the surface sample and finally, the third part is the sensors for measuring the indenter force and displacement.

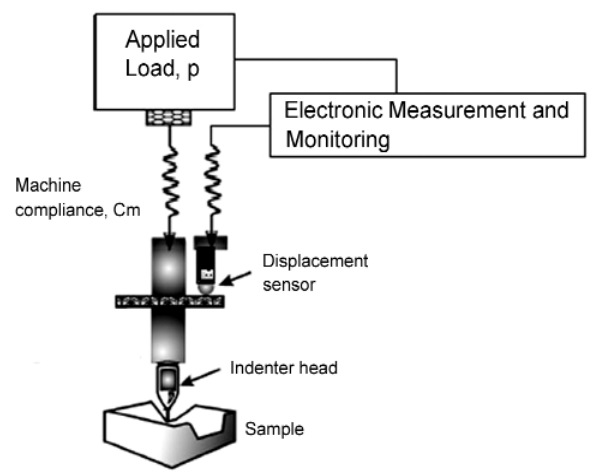

Figure 1: *Different parts of a typical indentation instrument [2].*

The various shapes of indenter head used in nanoin-dentation technique such as pyramidal, spherical, cube corner or conical geometry according to selected data. However, the most common shape of indenter is a Berkovich pyramidal tip.

2. A typical nanoindentation curve

Figure 2 indicates a typical nanoindentation curve including loading and unloading force as a function of displacement of indenter head as well as a schematic loading cycle force on the indenter in the CSM technique. The displacement response of the indenter at the excitation frequency and the phase angle between the two are measured continuously as a function of depth.

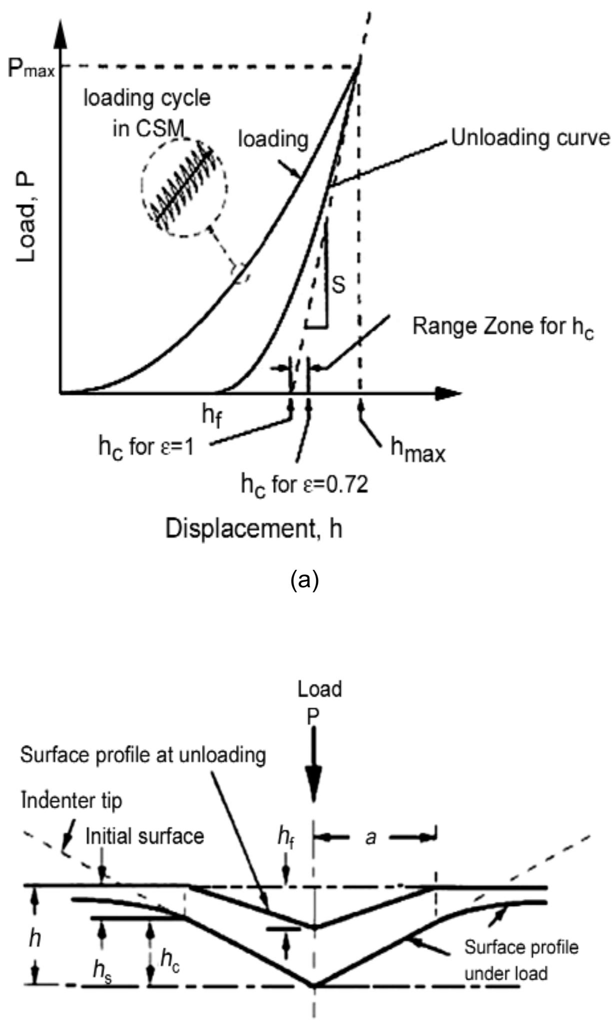

__Figure 2:__ (a) A typical nanoindentation : load and unloading -displacement curve and schematic loading cycle in CSM technique (b) schematic deformation pattern of substrate surface with an elastic-plastic behavior after indentation test [1, 14].

Any inconsistency observed in the curve indicates cracking, delamination or another failure in the coating. In the coated substrate, it needs to pay attention to the coating thickness in nano-indentation assay. The penetration depth should not exceed of the 10% of the coating thickness [8, 28]. Otherwise, the nanomechanical data is normally influenced by the underlying substrates. The coating is considered quantitatively with good toughness if after the indentation test, no cracking occurs, in it. However, this description needs the measurement of crack length, which is extremely difficult in thin films even under SEM observation [6, 29].

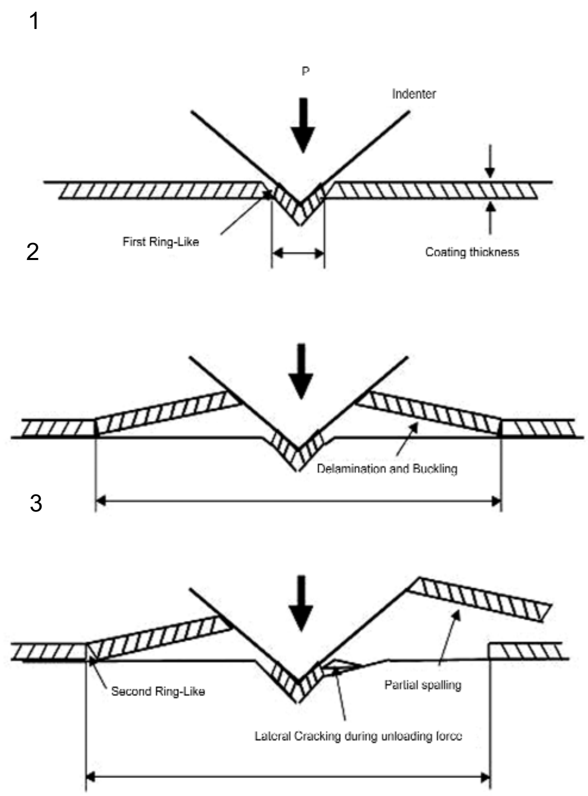

__Figure 3:__ Schematic presentation of cracking, delamination and spallation in failure of coating from substrate in nanoindentation test [6, 30].

In addition, it depends on the type of the used indenter head. Fracture can occur in three steps as schematically represented in Figure 3. In the first step, a ring form of crack surrounded around the indenter contact area, in the second step, high lateral pressure induce delamination and buckling of coating from substrate around the indented area and in third step, the crack is seen as a second ring and high bending stresses induce the spallation of coating at the edges of the buckled area.

3. Hardness and Young's modulus of coating

Hardness (H) and Young's Modulus (E) of Coating materials can be calculated from the load and displacement curve as following equations:

$$H = \frac{P_{\max}}{A} \tag{1}$$

$$A = C_0 h_c^2 \tag{2}$$

$$H_c = h_{\max} - \varepsilon \frac{P_{\max}}{S} \tag{3}$$

Which Pmax is the maximum load and A is the indented area, hc is the contact depth at maximum load Pmax and C_0 is a parameter depends on the indenter tip. C_0 is 24.56 for the Berkovich diamond tip [1, 31]. S is stiffness that can be measured from the slope of the unloading curve at Pmax and is the passion ratio which is 0.75 for the Berkovich diamond tip. Hardness analysis depends on the calibration of indenter tip. Fused quartz silica with known mechanical properties is usually used for this purpose. The stiffness Smax can be measured from the force-displacement indentation curve by considering the fused silica has a constant elastic modulus. The indented contact area A can be calculated from following equation:

$$A = \left(\frac{\pi}{4}\right)\left[\frac{S_{\max}}{E_r}\right]^2 \tag{4}$$

Where E_r is the reduced elastic modulus depends on the elastic modulus fused quartz silica (E_s) and it's of indenter tip (E_i), Er can be obtained as following equation:

$$\frac{1}{E_r} = \frac{1-\nu_S^2}{E_S} + \frac{1-\nu_i^2}{E_i} \tag{5}$$

Where ν and E are the Poisson's ratio and elastic modulus and index i and s are indicated for the sample and the indenter, respectively. For diamond, E_i = 1141 GPa and ν_i = 0.07 [1, 14].

The area function A(hc) calibration is needed to obtain in practical nanoindentation testing. A can be obtained by plotting of A versus hc and curve fitting according to the following polynomial equation (6):

$$A = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/6} + C_5 h_c^{1/8} \tag{6}$$

In this equation, C_1 through C_5 are constants. The elastic modulus E_s of the material can be determined using Equations (5) and (7).

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S_{\max}}{\sqrt{A}} \tag{7}$$

Where, S_{max} is the slope of unloading curve at the Pmax which can be determined directly from the unloading curve (i.e. at start of unloading in Figure 2) and A is the contact area between tip and the material at that point.

4. Dynamic mechanical behavior

The viscoelastic properties can be measured by nanoindentation technique [2, 12, 23 and 32]. The storage (E') and loss modulus (E″) of coating materials can be calculated under sinusoidal loading in linear viscoelastic domain by Equation (8) and (9):

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos\varphi \tag{8}$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin\varphi \tag{9}$$

$$E = E' + iE'' \tag{10}$$

Where σ_o is the stress, ε_o is the strain amplitude, ϕ is the difference in phase of stress and strain. The term of loss factor or tan ϕ, is also the ratio E'/E″ represent the damping characteristic of a linear viscoelastic material. In order to study the dynamic nanoindentation of the material's surface, the indenter head vibrates at a certain frequency, and the resulting response is measured and subtracted the contribution of instrument to determine the unique response from the material.

5. Scratch test, wear resistance and coefficient of friction

The scratch resistance of coating can be precisely determined in the nanoscale as well as the mechanism of deformation and delamination by nanoindentation technique. In a typical scratch test, a sharp indenter head is applied on the surface of material at a constant or ramp-up load in the normal direction as it moves simultaneously on the sample surface in a lateral direction. By recording the lateral force and normal displacement as a function of time, Critical information such as the coefficient of friction, cross profile topography, residual deformation and pile- up of material during the scratch can be measured as a function of scratch distance. Scratch and wear resistance are considered where scratch depth at a given load or the load at which material fails catastrophically. Scratch resistance is measured by in situ tangential (friction) force and observed by light optical microscopy (LOM) imaging of the scratches after tests [1, 33-35]. By using a diamond head to scratch a magnetic tape, nanoscratch data on magnetic tapes and their individual layers can be investigated.

In practical scratch experiment, an indenter head with a tip radius of 1 mm conical diamond and an included angle of 60° is drawn over the coating surface. The load is ramped up until substantial damage occurs. The coefficient of friction is monitored during scratching. It needs to be minimized for most sliding applications. In order to minimize test duration, accelerated friction test are commonly used by a ball-on-flat tribometer, for example, a sapphire ball with a 3 mm diameter under reciprocating motion. Normal and frictional forces are measured with semiconductor strain gages mounted on a crossed-I beam structure and the data are digitized and collected on a personal computer. Wear tracks of a tape can be monitored by LOM imaging.

6. Nanoindentation test on thin nanocomposite hybrid coatings

The nanocomposite hybrid coatings have been widely used for good adherence to the substrate. The varieties of organic resins and inorganic fillers have been usually used in such coating composition to obtain desiring formulation with good mechanical properties. However, such coating formulations are susceptible to consist of defect sites such as pinholes and cavities that can be influenced the coating properties and enable failure of it. Davies et al. studied the epoxy adhesive joints of different thicknesses between aluminum substrates by nanoindentation test. Their results indicate that the modulus value of the aluminum substrate is about 70 GPa while it drops to 2 GPa corresponding to the adhesive layer [36]. Shi et al. studied the effect of inorganic filler in a commercial epoxy resin. Their results indicated 1 wt% of SiO_2 nanoparticles can be induced significant enhancement in Young's modulus up to 10 times than that of neat epoxy coating. However, the adding other modified nanoparticle such as Zn, Fe_2O_3 and halloysite clay in coatings did not show such enhancement in the mechanical properties [37]. Woo et al. studied the mechanical properties of nano clay modified epoxy based nanocomposites after they were exposed to artificial weathering test. They found the organoclay had little effects on the variation of elastic modulus with UV exposure time. However, an increasing in the modulus of surface material was observed by nanoindentation test after UV exposure, with less extent in the nanocomposite in compare with the neat epoxy. It may be attributed to embrittlement of top layer after

UV light exposure [38]. Li et al. investigated the mechanical properties of epoxy resin containing various percentages of coiled carbon nanotubes (CCNTs) and single-walled carbon nanotubes (SWNTs) by the nanoindentation and tensile tests. They found that the hardness and modulus of nanocompsites depends on nanotube concentration and dispersion [39]. In a separate study, the physical and mechanical properties of a suspension of nano-alumina in an epoxy acrylate resin were investigated by nanoindentation and nanoscratch tests. They found that the hardness of nano composite films containing nano-alumina to be less than that of the samples without any nano-particles [40]. Lionti et al. synthesized hybrid silica coatings based on 3-glycidoxypropyltriethoxysilane (GPTES), tetraethylorthosilicate (TEOS) and colloidal silica on polycarbonate (PC) by the sol-gel method, in order to enhance scratch resistance of substrate properties. Their results indicated that scratch resistance can be improved by irrespective of the alkoxysilanes/colloidal silica ratio or the sol aging time [41]. Sun et al. studied the adhesion of thin film interfaces by Cross-Sectional Nano-indentation (CSN) technique. Figure 4 shows the orientation of the three-sided Berkovich diamond tip as well as its positioning with respect to the interface in the CSN test which are critical parameters for controlled delamination.

The optimum orientation of the indenter is schematically shown in the figure, where one of the sides of the triangular indentation mark is parallel to the interface and the optimum distance tip to the interface (d) is 1 to 5 [42]. A sudden Jump in Load-displacement curve can be interpreted as delamination (see Figure 4c) [42]. Tiwari et al. have recently reported the basic fundamental principles as well as the experimental analyzing in modern nano-indentation techniques with a brief survey of silicone based nanocomposite coatings [9]. Barth et al. investigated thin Al_2O_3-nanoparticles coatings on solid stainless-steel substrates. The influence of particle size and width of the particle size distribution on the mechanical properties was studied by nanoindentation technique. Their results indicated the maximum indentation force decreases with decreasing particle size to a minimum, and then it increases in very small sizes of the nanoparticles. In addition, the micromechanical properties and coating structure can be varied by a change in the width of the particle size distribution [43].

The mechanical behavior of nanocomposite coatings containing silane modifed and unmodified nanosilica fillers into a UV cured urethane acrylate resin was recently investigated using nanoindentation, nano scratch and micro-hardness and dynamic mechanical thermal analysis [44]. The results indicated the surface modification of nanoparticles can be induced stronger interfacial interaction with the polymeric matrix and improved storage modulus. In addition, based on nanoindentation and microindentation measurements it proposed a homogenous reinforced structure was formed in the bulk and surface of hybrid coatings by the modified nanosilica [44].

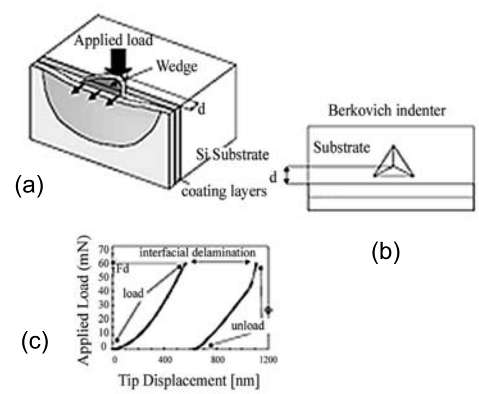

Figure 4: (a) A schematic presentation of cross-sectional nanoindentation (CSN) technique in multi-layer thin films, (b) Berkovich indenter with respect to thin film interface, (c) a sudden jump in Load-displacement curve corresponding to thin film delamination [42].

7. CONCLUSIONS

Nanoindentation and viscoelastic tests are very effective techniques to investigate mechanical properties of thin nanocomposite coatings. However, there are many experimental nanoindentation methods which provide quantitative mechanical data such as elastic modulus, hardness, scratch and wear resistance as well as viscoelastic properties. The practical use of nanoindentation technique was investigated in various organic-inorganic hybrid nanocomposite coatings by sol-gel process. It is demonstrated that the physical-mechanical properties of these thin nanocomposite coatings depend on the nature, particle size and distribution as well as the surface modification of the inorganic nano fillers. They can be also influenced on the microstructural properties of thin coatings. In addition, the organic polymerization, cross linking density of organic matrix can be affected the materials stiffness. The adhesion of such nanocomposite coatings is dependent on the chemical bonding by reactive functionality between coating and substrate. However, the delamination of coating layer can be produced on exposure to UV or humidity conditions and artificial accelerating weathering test. These microstructural changes can be detected by various nanomechanical techniques such as nanoindentation in statistic or dynamic states.

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