Mechanical properties under nanoindents in gold-reinforced poly(vinyl alcohol) nanocomposite of free standing films

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ABSTRACT

Free-standing films of gold nanoparticles reinforced poly(vinyl alcohol) (PVA) nanocomposites, with Au-contents varied from 0.1 to 2.0 wt%, are synthesized by using a novel in-situ chemical method. Microstructure in these films reveal the presence of spheroid or cuboid shaped Au-nanoparticles (NPs) in 0.1 wt% Au-content sample to thin platelets of triangular, square, rectangular, or hexagonal shaped NPs in sample with 2.0 wt% Au-content. The structural anisotropic NPs are formed as a result of the preferential adsorption of PVA on selective Au-crystals facets. In correlation to the microstructures the measurement of reduced elastic modulus (E_r) and hardness (H) under nanoindentation technique show the influence of Au-reinforcement in the virgin PVA film. The H-value changes from an initial value 0.29 GPa in the virgin PVA to a value 0.23 GPa in a 0.5 wt%, or 0.31 GPa in a 2.0 wt% Au-content. Similarly, the E_r-value decreases from 8.19 GPa in the PVA film to that of 6.48 GPa in the 0.5 wt% Au-PVA films and then results in an increase of the final value up to 7.3 GPa in the 2.0 wt% Au-PVA films.

Keywords: Gold nanomaterials, Polyvinyl alcohol, Nanocomposites, Mechanical properties, Nanoindentation.

INTRODUCTION

In recent years, the physical and chemical properties of metal-polymer nanocomposites have attracted much attention for their promising applications in catalysis, electronics, and photonics technologies [1-3]. Such nanocomposites not only recombine the advantageous properties of the metals and polymers but also offer many new characters that are often missing in a single phase material. The intrinsic properties of a metal nanoparticle are mainly determined by its size, shape, composition, crystalinity, and structure. Under certain conditions of morphological anisotropy, gold nanoparticles exhibit anisotropic optical absorption properties associated with the collective oscillation of conduction electrons known as the surface plasmon resonance. The uniqueness of Au-NPs and the unique inorganic-organic interactions of them with certain polymer molecules have motivated us to synthesize Au-NPs of different sizes and shapes in polymer nanofluids and Au-polymer nanocomposite films of selective compositions. In part of our extensive studies of the optical, electrical, and mechanical properties in the Au-PVA free-standing nanocomposite films here in this investigation, we report the preliminary results of the mechanical properties such as hardness (H) and reduced elastic modulus (E_r) under nanoindentation technique.

One of the key areas of interest in the study of nanocomposites is the characterization of their mechanical properties at the macro-, micro- or nano-levels. The mechanical property measurement is very much essential for proper design and device fabrication using the Au-PVA optical films. Traditional mechanical test methods are currently not desirable options since they require a larger size specimen (i.e., more material of the nanocomposite) than is normally available due to their limited or one of a kind fabrication method. Hence, a desirable method such as nanoindentation is one which would require a small size specimen or a limited quantity of material for characterizing mechanical behavior from a small quantity of available material [4,5]. Nanoindentation offers a unique method by which the in situ properties of a nanocomposite may be probed. Using this technique, mechanical properties such as elastic modulus, hardness, and fracture toughness can be determined from the simple indentation load–displacement relationship at the micro or nanoscale without imaging the indentation.

Small metal particles as filler support a large interfacial area in the composite system. The surface-interface controls the degree of interaction between two components and thus controls the final properties of the nanocomposite. Geometry of the sample as films, with a molecularly oriented structure of polymer, governs the microstructure and other properties of interest. In this work of Au-PVA nanocomposite films, the changes in the E_r and H-values with Au-content indicate the role of the Au-reinforcement in modifying such properties in virgin PVA. The results useful for fabricating stable optical films for possible applications are analyzed in correlation to the microstructure.

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EXPERIMENTAL DETAILS

PVA (average molecular weight 72000, and fractional hydrolysis 98%) solution was prepared by heating and stirring a 3 g/dl PVA in distilled water at 50-60°C. An aqueous $HAuCl_4 \cdot 3H_2O$ (0.05 M) was added to the PVA solution drop by drop at the same temperature as used in preparing a polymer precursor solution of reactive PVA molecules with refreshed surfaces. The Au-contents were varied from 0.1 to 2.0 wt%, in the Au-PVA composition series in an attempt to exploring mechanically reliable, stable, and practically useful optical films in a semiconductor of hybrid polymer nanocomposite structure. Changing of an achromatic color in the virgin PVA solution in the beginning to a light blue, a bluish violet, a purplish red or to the equilibrium faint yellowish according to the final Au/PVA ratio ensured a caloric $Au^{3+} \rightarrow Au$ reaction. The sample was kept for 20-30 h of aging and then excess water was evaporated at bit high temperatures 60-70°C to cast films in specific moulds of a silicate glass. The films could be pilled off easily without any surface roughness and used for the microstructure and mechanical properties measurements.

A scanning electron microscope (SEM) (Oxford model Leo 1550 of accelerating voltage 10 kV) was used to study size and shape in nanocrystals in the films. The emission spectra of Au-PVA films were studied using a Perkin Elmer Model-LS 55 luminescence spectrometer, with a pulsed xenon lamp of excitation source (20 kW power). The mechanical properties of these free standing films were measured using a nanoindenter (Nanoindenter XP with Berkovich triangular diamond indenter). The force required to press the sharp a sharp diamond indenter into tested material was recorded as a function of indentation depth. During an indentation, corresponding values of load and displacement of the diamond tip (indentation depth) were recorded, and from the resulting curve the H and the E_r-values were calculated.

RESULTS AND DISCUSSION

A mechanochemical stretching in stirring under heating conditions dispersed PVA molecules get as thin as molecular layer [6,7]. PVA molecules of such enlarged surfaces (involve refreshed OH groups free from the H-bonding) serve as a reducer to induce a surface enhanced $Au^{3+} \rightarrow$ Au reaction [8-10]. It occurs in templates of such PVA molecules. As the Au atoms mainly confine to the vicinity of the template surface, once the concentration of them reaches a critical value, they nucleate and grow as nanocrystals (NCs) in a core-shell structure with the surface oxidized PVA molecules.

Fig. 1 shows the SEM images in (a) 1.0 and (b) 2.0 wt% Au-PVA free standing films. In 1.0 wt% Au-PVA film, Au NCs of near cuboids or spheroids (80-100 nm diameters d) are observed. A magnified region of the film for visual clarity is given in the inset. Whereas thin platelets (20-30 nm thickness δ) of platelets triangular, pentagonal and hexagonal shapes, with average width β = 300-700 nm are observed in 2.0 wt% Au-PVA sample as shown in Fig. 1b. Also there are few cuboids with some typical rods, bowels, or tea-cup shaped particles. Multi-shaped particulates as observed here are useful for designing reinforced composites of superior optical and other useful properties.

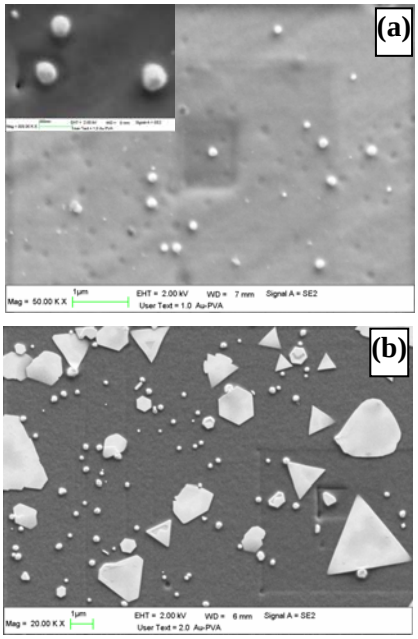

Fig. 1. SEM images in (a) 1.0 and (b) 2.0 wt% Au-PVA films. A magnified image of a selected area in Fig. 1a is given in the inset.

The emission in 2.0 wt% Au-PVA film occurs over shorter wavelengths 400-600 nm to the absorption region, with three to four distinct bands as given in the Fig. 2. It compares 440 nm emission observed in Au-nanocolloids (~ 5 nm size) in water [11]. We measured the sample by irradiating under identical conditions at excitation wavelength λ_{ex} = 372 nm by a xenon lamp. The λ_{ex} -value 372 nm is chosen according to the maximal excitation of the emission as demonstrated with a typical excitation spectrum in the inset of Fig. 2, which corresponds to an average 475 nm emission value in a 2.0 wt% Au-sample. A multiplet band structure of excitation spectrum (of four bands 266, 342, 372, or 400 nm) is very similar to the emission bands.

The four bands, which for example have 412, 437, 468 and 500 nm values in 2.0 wt% Au-PVA sample, include part of the surface-enhanced vibronic PVA transitions in a complex composite system. The first two bands ascribe the $5d^{10}6s^1 \longrightarrow 5d^9 6s^1 p^1$ interband transition (IBT), viz., IBT-I (core) and IBT-II (shell) bands, while the other two ones refer to a vibronic band 2905 or 2885 cm^{-1},

i.e., the C-H stretching vibration ν (CH) of 2917 cm^{-1} in the IR spectrum [6]. It confirms that the PVA molecules extend a short of chemical bonding to the Au-metal surface of a metal-polymer complex (shell). A vibronic band thus occurs in the electron-phonon coupling in a core-shell structure. Thin platelets, which share large interfaces in such specific structure, favor an intense emission in such multiplet bands.

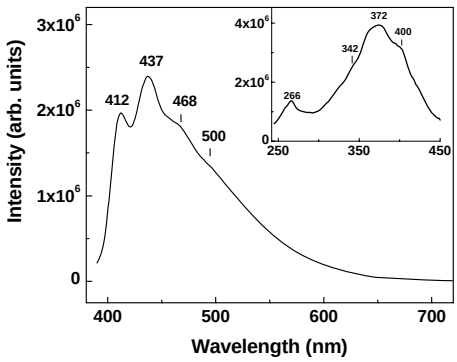

Fig. 2. An emission spectrum in 2.0 wt% Au-PVA film with λ_{exc} = 372. The inset represents a typical excitation spectrum for average emission band 475 nm in the sample.

To observe the mechanical reliability of these optical Au-PVA films, the load-displacement curves were studied under nanoindenter. The load-displacement curves for 0.1 to 2.0 wt% Au-PVA samples along with virgin PVA film are shown in Fig. 3. Quantitative analyses of the each load-displacement indent cycle of mechanical property variation determine the H and E_r of the Au-PVA films. Indentations were performed in load-control mode to a load as high as 1000 μN. Evidently, no fracture is observed during loading.

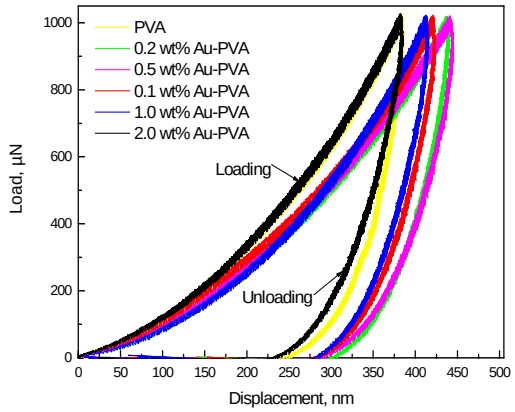

Fig. 3. Load–displacement curves for PVA and Au-PVA films. The film compositions are given in the plot as inset.

Several models have been proposed to provide the mechanical properties of materials using the data from nanoindentation tests by Doerner and Nix [12], Cheng and Cheng [13], Oliver and Phar [5] etc. Liu et al. in 2006 proposed a model based on the Burgers viscoelastic concept to describe the nanoindentation behaviors of polymeric materials [14]. In our case also the viscoelasticity behaviors of the Au-PVA nanocomposite films can be confirmed from Fig. 3. A nose like shape is observed during the unloading in all the samples indicates the decrease in the viscosity parameter as proposed by Liu et al.

Both E_r and H can be readily extracted directly from the nanoindentation curve [5,12-14]. E_r is determined based on the knowledge of the tip shape function (A) and the load-displacement curve (load P and displacement h) [5,14]. The E_r value accounts for the fact that the measured displacement includes contributions from both the specimen and the indenter.

$$E_r = \frac{\sqrt{\pi}}{2} \cdot \frac{dP}{dh} \cdot \frac{1}{\sqrt{A}} \qquad (1)$$

Here, dP/dh is the slope of the unloading curve (Fig. 3). The H-value was calculated using the relation between indention load and projected contact area as follows.

$$H = \frac{P_{max}}{A_{prjected}} \qquad (2)$$

The variation of H and E_r -value as a function of selective Au-contents was plotted in Fig. 4.

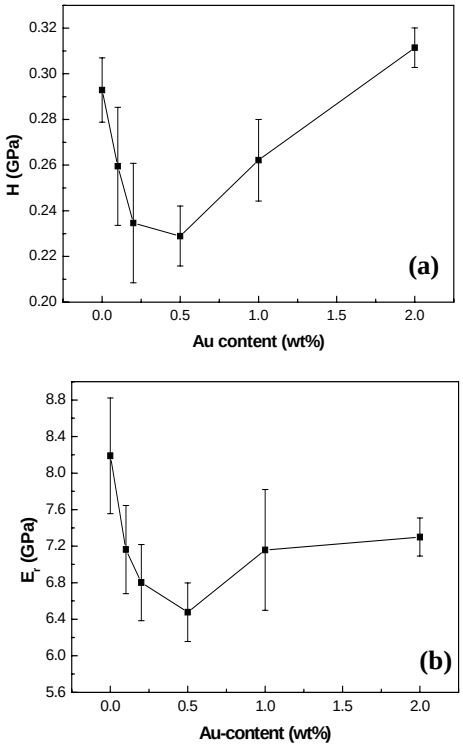

Fig. 4. Variation of (a) hardness H and (b) reduced modulus E_r as a function of selective Au-contents.

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The Au-reinforcement is found to influence very sensitively both the Er and H values. A nonlinear variation is observed in the H-value while increasing Au-content in the film. The H-value changes from an initial value 0.29 GPa in the virgin PVA to a value 0.23 GPa in a 0.5 wt%, or 0.31 GPa in a 2 wt% Au-content (Fig. 4a). The H attains a value as low as 0.23 GPa in a 0.5 wt% Au-PVA. The morphology of the Au in PVA for this particular Au-content leads to the minimum value of the H-value in the film. After 0.5 wt% of Au in Au-PVA, the H-value instantaneously increases and attains a maximum in 2.0 wt% Au-content. Similarly, the E_r -value decreases from 8.19 GPa in the PVA film to that of 6.48 GPa in the 0.5 wt% Au-PVA films and then results in an increase of the final value up to 7.3 GPa in the 2 wt% Au-PVA films (Fig. 4b). These results can be correlated to the microstructures obtained in the composite films.

Interestingly, both the H and E_r -values decrease up to 0.5 wt% Au-content with the formation of nearly spherical shaped Au-NCs, but above that there is an increase in the hardness with the formation of polygonal Au-platelets in the nanocomposite structure. Also beyond 0.5 wt% Au-content the E_r -value of the film increases but it is lesser than that of the virgin PVA film. These changes in the E_r and H-values indicate the role of the Au-reinforcement in. modifying such properties in PVA and similar linear polymers. The Au-polymer surface interfaces in these examples seem to be one of the sensitive chemical parameters, which are responsible for the variation in the physical properties as a function of the Au-content.

CONCLUSIONS

Au-nanoparticles doped poly(vinyl alcohol) (PVA) composite films are synthesized with selective Au-contents from 0.1 to 2.0 wt% and their mechanical properties are studied under nanoindentation technique. The changes in the E_r and H-values indicate the role of the Au-reinforcement in modifying such properties in PVA and similar linear polymers. These results are useful for fabricating stable optical films for possible applications.

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