

NANOMECHANICAL PROPERTIES OF POLYANILINE AND AZO POLYELECTROLYTE MULTILAYER FILMS

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Abstract Nanomechanical properties of multilayer films constructed of polyaniline (PANI) and azobenzene-containing polyelectrolytes (PNACN and PPAPe) were studied by using nanoindentation method. The multilayer films were prepared by the electrostatic layer-by-layer self-assembly through alternately dipping in the polymer solutions. The multilayer films deposited onto the glass slides after proper dry were used for the nanomechanical property testing. The nanomechanical measurement indicated that the PANI/PNACN and PANI/PPAPe multilayers possessed the mean elastic modulus of 5.42 GPa and 4.35 GPa, and hardness of 0.26 GPa and 0.18 GPa, respectively. The nanoscratch properties of the PANI/PNACN and PANI/PPAPe multilayer films were also measured. The critical loads of PANI/PNACN and PANI/PPAPe films were 103.52 mN and 100.59 mN. The degree of electrostatic cross-linking in the multilayers could be altered by exposing the films to aqueous solutions with different pH values. As a result, the modulus and hardness of the multilayer films were changed through the solvent treatment. Both modulus and hardness of the PANI/PNACN films obviously increased after dipping the multilayer films in solutions with pH in a range from 9 to 11.

Keywords: PANI; Electrostatic self-assembly; Nanomechanical.

INTRODUCTION

The electrostatic layer-by-layer (LBL) self-assembly technique, introduced by Decher *et al.* in 1991, has been widely used for constructing multilayer thin films from two oppositely charged polyelectrolyte pairs^[1–4]. The multilayer films were prepared by alternatively dipping a proper substrate in solutions of polycation and polyanion. Typically, after each deposition step, the substrate needs to be rinsed with water and dried properly. The single layer thickness can be controlled by adjusting the factors such as the concentration, pH and ion strength of the dipping solutions^[5–10]. The total thickness of multilayer films depends on the single layer thickness and number of deposition cycles. The conducting polymers (CPs) show many interesting optical and electrical properties and have attracted great research enthusiasm for several decades. Water-soluble/dispersible CPs or precursors have been used for the multilayer build-up since the early development stage of the electrostatic LBL self-assembly technique^[5–7]. Polyaniline (PANI), as one of the most widely investigated CPs, has been used for the electrostatic LBL applications. A method to use partly doped polyaniline (PANI) aqueous solution as the polycation has been developed for the purpose^[7]. The electrostatic multilayers were prepared by using PANI and sulfonated polystyrene (PSS) through LBL deposition^[11]. More recently, multilayers containing PANI and negatively ionized nanoparticles of iron-hexacyanoferrate (Prussian Blue) have been developed, which can exhibit multiple electrochromic conversions^[12]. Utilizing template assistant self-assembly strategy, PANI-containing core-shell structures have been prepared by using polystyrene (PS) colloidal particles^[13].

Azobenzene and many of its derivatives are well known for their *trans-cis* isomerization induced by the

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irradiation of UV and visible light^[14]. Azobenzene-containing polymers (azo polymers for short) can show a variety of photoresponsive properties upon light irradiation^[15]. By introducing azobenzene groups into polyelectrolytes, the photoresponsive thin films can be prepared through the electrostatic LBL self-assembly^[16–22]. Multilayers of azo polyelectrolytes have been prepared by the sequential electrostatic adsorption, which can show optical second-harmonic generation (SHG) without electric-field poling^[16–18]. Electrostatic multilayer films composed of azo polyelectrolytes can also show other photoresponsive properties such as photo-switching^[19], film optical thickness change^[20] and surface hydrophilicity variation^[20, 21]. In authors' earlier work, multilayer films of PANI and azo polyelectrolytes were prepared by electrostatic LBL deposition. The multilayer films can show some interesting optical and electrical properties, such as photoinduced dichroism, photoinduced surface-relief-gratings (SRGs) and electrochromic properties^[22]. Although the electrochemical and photonic properties have been explored for possible applications, the mechanical properties of this type of multilayers are still unclear until very recently.

The mechanical properties of ultra-thin films are usually investigated with atomic force microscopy (AFM). The finite sample thickness effects on elasticity measurements have been studied by Walker and co-worker^[23]. Young's modulus of polycarbonate (PC) and polystyrene (PS) thin films have been monitored with AFM using the analysis of the AFM indentation force curves with the method by Oliver and Pharr^[24]. The dynamic interactions and frictions of adsorbed polyelectrolytes multilayers have also been measured by using AFM^[25–27]. The elastic properties of polyelectrolytes capsules, developed by Caruso^[28], have been studied for their deformations^[29–31]. Barrett *et al.* have investigated the relative Young's modulus of the electrostatic self-assembly films. They found that the films assembled with the high charge-density polyelectrolytes possessed a larger elastic modulus than those assembled with the low charge density polyelectrolytes^[32]. These interactions between the polycation and polyanion layers are considered as the "ionic cross-links". This kind of cross-linked multilayers exhibits better mechanical properties reflected by the Young's modulus^[33]. The reversible mechanical property change has been demonstrated for ultrathin polyelectrolyte complexes by exposing the films to a NaCl solution^[34]. The nanoindentation analysis of the thin films was first introduced by Oliver and Pharr in 1992, which can measure the mechanical properties of thin films directly^[35]. The mechanical properties of multilayer films constructed of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) have been studied by using the quasi-static nanoindentation method^[36].

In this study, the multilayers of PANI and azo polyelectrolytes were prepared through electrostatic LBL self-assembly. The nanomechanical properties of PANI-containing multilayer films were studied by the nanoindentation method. The Young's modulus and hardness of these films were studied in some detail. The mechanical property variation after exposed to the different pH HCl solutions was also studied.

EXPERIMENTAL

Materials

Milli-Q water (resistivity > 18 M Ω cm), obtained from a Millipore water purification system, was used in the multilayer preparation process. Polyaniline (PANI) was synthesized through a traditional way as described in the Macdiarmid's paper^[37]. The PANI was then undoped in the ammonia for about 24 h to obtain the emeraldine form PANI. The azo polyelectrolytes (PNACN and PPAPE) were synthesized in authors' laboratory. The synthesis and characterization have been reported in the previous papers^[22, 38, 39]. The degree of functionalization of PNACN and PPAPE was 27.7% and 14.9%, respectively, which characterized the percentages of azobenzene-containing units among the total structure units. The number-averaged molecular weights (M_n) of PNACN and PPAPE were 15000 and 48000, respectively.

Multilayer Preparation

The PANI dipping solutions were prepared by using the procedure reported by Rubner *et al.*^[7]. The emeraldine-base PANI was dissolved in *N,N*-dimethylacetamide (DMAc) (10 mg/mL) by first stirring the solution overnight and then sonicating it for another 8–10 h. The PANI aqueous solution was prepared by slowly mixing one part

(by volume) of the DMAc solution with nine parts of water, whose pH was adjusted to about 2.5–3.0 with HCl. The dipping solutions were filtered through 0.45 μm membranes before use. The azo polyelectrolytes were dissolved in deionized water by first adjusting the media to alkalinity with NaOH and then neutralizing the solutions with HCl. The concentrations of the dipping solutions were adjusted to 0.25 mg/mL. The quartz, glass and silica slides were pretreated in hot 98% H_2SO_4 /30% H_2O_2 (Piranha solution) for 2 h and then in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ ($V:V = 3:1$) for 3 h, which were thoroughly rinsed with deionized water after each treating step. The multilayer films were prepared by alternately dipping the substrates in the PANI and azo polyelectrolyte dipping solutions. In the processes, the substrates were immersed in each solution for 10 min and subsequently rinsed with excess water. After each dipping and rinsing step, the films were blown to dry by clean air stream. The multilayer films were carefully dried and kept in desiccator for further measurements.

Mechanical Property Measurements

The nanomechanical properties were investigated with an MTS Nano-Indenter XP by using continuous stiffness measurement (CSM) technique. The Berkovich diamond indenter tip was employed in all the experiments. The displacement used for the measurement depended on the thickness of the multilayer films. The maximum displacement used in this study was 150 nm. The frequency of 45 Hz was used in the measurement to decrease the sensitivity to thermal drift.

RESULTS AND DISCUSSION

The chemical structures of components used for the multilayer preparation are given in Fig. 1. The polycation solution was obtained by properly dissolving the emeraldine-base PANI in DMAc/ H_2O mixture (1 to 9, V/V). The polyanion solutions were aqueous solutions of PNACN or PPAPE, which were two azobenzene-containing poly(acrylic acid)-based polyelectrolytes. The multilayer films were prepared through a typical electrostatic LBL self-assembly procedure as described in Experimental Part. The characterization details and properties of the multilayers can be seen in our previous paper^[22].

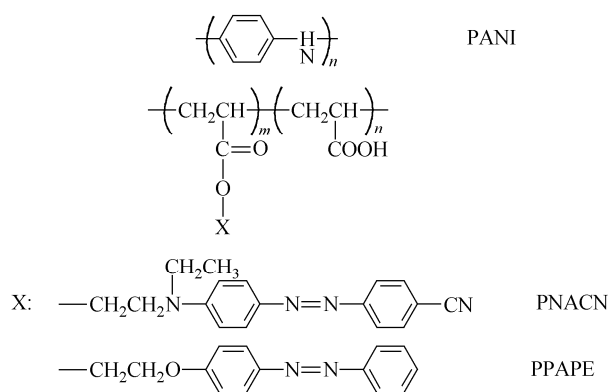


Fig. 1 Chemical structures of polyaniline (PANI) and the azo polyelectrolytes PNACN and PPAPE

Nanomechanical testing was carried out by using the 60-bilayer electrostatic self-assembled multilayer films deposited on the glass slides. The typical loading pattern was trapezoidal, which included three steps, *i.e.* the load step at a special loading rate, the hold step with the maximum force, and the unloading step. Figure 2 shows the typical loading-penetration depth curves for the PANI/PNACN and PANI/PPAPE multilayer films. The deformation during the load step is considered to be both elastic and plastic. Hold segment is used to minimize the effects of the films creep, and during the unloading step only elastic displacements are recovered. The maximum displacements are determined by the thickness of the multilayer films. The load-displacement curves during the unloading segment are utilized for the calculation of the nanomechanical properties, based on the method by Oliver and Pharr^[35]. The slope of the unloading curve at maximum displacement gives the contact

stiffness S . The effective elastic modulus E_r is defined as follows,

$$E_r = \frac{\sqrt{\pi}}{2} S \frac{1}{\sqrt{A}} \quad (1)$$

where A is the projected area of the contact area. A is a function of the contact depth h_c , and both of them are relied on the geometry of the indenter tip. E_r is a combination of the characterizations of the indenter and tested films, which is given by

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (2)$$

E and ν are Young's modulus and Poisson's ratio of the multilayer films. Generally, the Poisson's ratio for most polymers lies in 0.25–0.45 range. In this study, the Poisson's ratio of the multilayer films is 0.25 approximately. E_i and ν_i are the elastic parameters of the diamond indenter, which are 1170 GPa and 0.07 respectively. The sample hardness H is defined by the following equation:

$$H = \frac{P_{\max}}{A} \quad (3)$$

where $P_{\max}$ is the maximum load in the load-displacement curve.

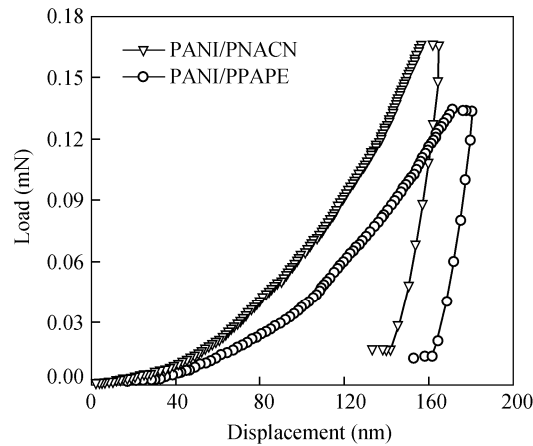


Fig. 2 Typical load-penetration displacement curves for the 60-bilayer PANI/PNACN and PANI/PPAPE films

Table 1 lists the elastic modulus and hardness of nine testing points on the PANI/PNACN and PANI/PPAPE multilayer films. The elastic modulus and hardness are calculated by using the Eqs. (1)–(3), according to the load-displacement curves. The mean elastic modulus and hardness of PANI/PNACN films are 5.42 GPa and 0.26 GPa. In the same way, the nanomechanical properties of PANI/PPAPE multilayer films have been also obtained from the load-displacement curves. For PANI/PPAPE multilayer, the mean elastic modulus and hardness are 4.35 GPa and 0.18 GPa, respectively.

Figure 3 gives a typical diagram of the nanoscratch distance versus penetration depth for the PANI/PNACN multilayer films. The first profile curve shows the surface relief of the self-assembled films without any load on the diamond tip. During the scratch segment, the tip was first moved 100 nm far without changing the contact force, and then moved at a special rate for 500 nm so that a nanoscratch was made on the film. In the final segment, the tip detected the relief of the scratch. The critical load is defined as the nanoscratch states to fluctuate at around point B in Fig. 3. Since the special mechanical properties of multilayers, the intense fluctuation can be observed in the finale profile. In fact, after loading, some segments of the nanoscratch are even higher than the original surface. According to the scratch of the PANI/PNACN and PANI/PPAPE films, the

critical load, scratch width and the residual scratch depth at the critical load were also measured (Table 2). The critical load of the PANI/PNACN films is 103.52 mN, and that of PANI/PPAPE films is 100.59 mN.

Table 1. Elastic modulus and hardness of the PANI/PNACN and PANI/PPAPE multilayer films, obtained from the nanomechanical tests

	E (GPa)	Standard deviation	H (GPa)	Standard deviation
PANI/PNACN	5.42	1.94	0.26	0.10
PANI/PPAPE	4.35	1.06	0.18	0.03

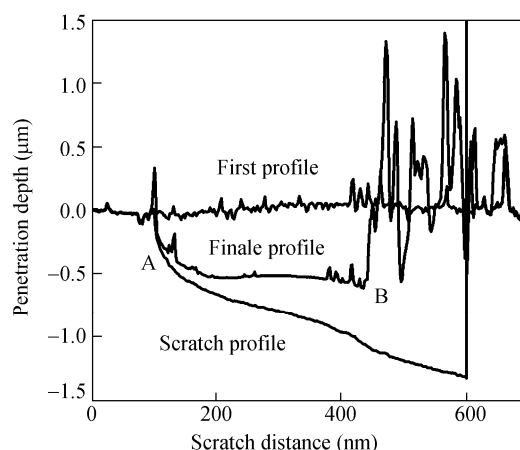


Fig. 3 A typical diagram from the nanoscratch tests

In the first segment, the diamond tip detected the films surface profile for 700 nm long without any load; In the scratch segment, the tip scratched from the 100 nm position to 600 nm position at a constant rate of the force; The surface profile was detected without any load in the final segment.

Table 2. Critical loading, penetration depth, scratch width and residual scratch depth of the PANI/PNACN and PANI/PPAPE multilayer films, obtained from the nanoscratch tests

Sample		Critical load (mN)	Penetration depth at critical load (nm)	Scratch width (μm)	Residual scratch depth (nm)
PANI/PNACN	Mean	103.52	1199.91	26.50	336.52
	Standard deviation	18.65	91.80	16.45	93.33
PANI/PPAPE	Mean	100.59	1092.58	39.67	412.75
	Standard deviation	15.11	120.74	20.92	37.43

The above results show that the PANI/PNACN and PANI/PPAPE multilayer films possess the mechanical properties comparable with those of typical polyelectrolyte multilayers. The mean elastic modulus and hardness of PANI/PNACN films (5.42 GPa and 0.26 GPa) are obviously larger than those of the PANI/PPAPE multilayer films (4.35 GPa and 0.18 GPa). The result shows that the mechanical properties of the multilayer are closely related with the azo polyelectrolyte used. Although the molecular weight of PPAPe is significantly larger than that of PNACN, the elastic modulus and hardness of the latter are larger. This result could be attributed to the stronger dipolar moment of the azo chromophores in PNACN and higher chromophore loading density (higher DF). For the critical loading obtained by nanoscratch test, the results of the two type multilayers do not show difference. The reason is that the first layer of the films is polyaniline and adhesion of multilayer to the substrate is very similar.

In the electrostatic layer-by-layer self-assembled films, the electrostatic ion-pair interactions between polyanions and polycations can yield partially cross-linking structures with reversible physical junctions. It has

been reported that by exposure the strong polyelectrolytes multilayer films to the NaCl solutions of different concentrations, the degree of the internal cross-linking can be adjusted reversibly and the nanomechanical properties are also changed^[34]. To investigate the effect of the physical electrostatic cross-linking interactions, the PANI/PNACN multilayer films were dipped into different pH solutions for 3 h. After the dipping process, the films were rinsed with the same pH aqueous solutions, blown dry with cold air stream and further dried under vacuum for 24 h. Figure 4 shows the elastic modulus and hardness of the PANI/PNACN films. Both modulus and hardness of the composite films significantly increase when the pH increases in the range from 9 to 11. The carboxyl group in PNACN is a weak acidic group, whose ionization degree can be influenced by pH value of the solution. Moreover, the doping degree of PANI is varied in solutions with different proton concentrations. In this process, a significantly amount of carboxyl groups are ionized, which could cause the enhancement of the electrostatic ion-pair interaction.

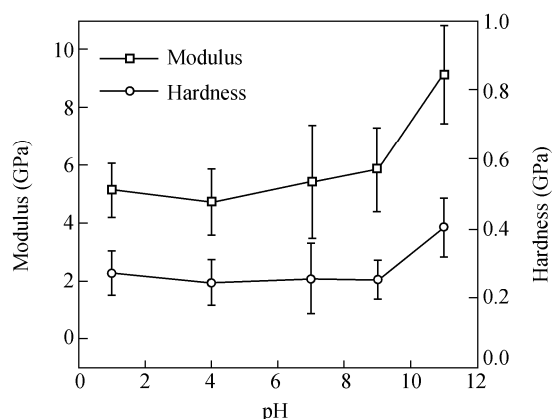


Fig. 4 The mean elastic modulus and hardness of the 60-bilayer PANI/PNACN films
The films were dipped in the aqueous solutions with different pH for 24 h and then dried.

CONCLUSIONS

This study investigated the nanomechanical properties of the electrostatic self-assembly multilayer films composed of the conducting polymer PANI and azo polyelectrolytes (PNACN and PPAPE). The measurements indicate that the multilayer films possess the elastic modulus and hardness of 5.42 GPa and 0.26 GPa for PANI/PNACN multilayer and 4.35 GPa and 0.18 GPa for PANI/PPAPE multilayer. The critical loads of PANI/PNACN and PANI/PPAPE films, which obtained from the nanoscratch tests, were 103.52 mN and 100.59 mN, respectively. The PANI/PNACN multilayer films doped in different pH solutions show that both modulus and hardness of the films obviously increase in a pH range from 9 to 11.

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