Colloids and Surfaces A: Physicochem. Eng. Aspects 471 (2015) 11–18

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Solvent effect on hydrogen-bonded thin film of poly(vinylpyrrolidone) and poly(acrylic acid) prepared by layer-by-layer assembly

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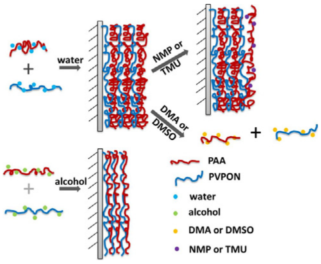
HIGHLIGHTS

- The hydrogen-bonded PVPON/PAA film can be prepared in the acidic water and alcoholic solvents rather than in DMA, NMP, TMU and DMSO.
- The thickness and roughness of the film dependent on the polymer–solvent interaction and polymer chain conformation in the assembling solution.
- The hydrogen-bonded thin film will disintegrate in strong polar aprotic solvents with high dielectric constant.

GRAPHICAL ABSTRACT

Film growth and film disintegration in different solvents.



ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form 25 January 2015
Accepted 28 January 2015
Available online 4 February 2015

Keywords:
Solvent effect
Hydrogen bond
Layer-by-layer assembly
Polymer complex

ABSTRACT

The hydrogen-bonded thin film of poly(vinylpyrrolidone) (PVPON)/poly(acrylic acid) (PAA) was prepared via layer-by-layer (LbL) assembly. A serial of solvents has been selected to study the formation and disintegration of the thin film. The film could be produced in acidic water and alcohols but could not be fabricated in some polar aprotic solvents, such as dimethylacetamide (DMA), dimethylsulfoxide (DMSO), tetramethylurea (TMU) and N-methyl pyrrolidone (NMP). In acidic water, the film growth was much quicker than that in alcohols. The solvent effect on the film growth was analyzed from the aspects of the polymer–solvent interaction and polymer chain conformation in the assembling solution. In addition, the thin films prepared in aqueous solution were immersed into the polar aprotic solvents to observe the disintegration process. At the room temperature, DMSO dissolved the thin film quickly, DMA dissolved the thin film in 1–2 days, but in NMP or TMU the thin film could keep intact for several weeks. As the temperature elevated, the disintegration would accelerate. The thin film prepared by the higher molecular weight PVPON and PAA showed stronger resistance to the polar aprotic solvents.

1. Introduction

In early 1990s, Decher et al. developed a method, alternately depositing the polymers with opposite charges on solid substrate to prepare thin films, which was named as layer-by-layer (LbL) assembly [1–5]. A few years later, Rubner [6] and Zhang [7] applied LbL assembly to operate neutral polymers to prepare thin film basing on hydrogen-bonding. Through two decades' development, LbL assembly has been proved to be a simple but effective way to realize polymer complexation in a controllable way at interface to prepare thin films, coatings, or microcapsules with various applications, such as separation, sensor, optical filter, controlled drug release, anti-fogging and anti-fouling [8–15].

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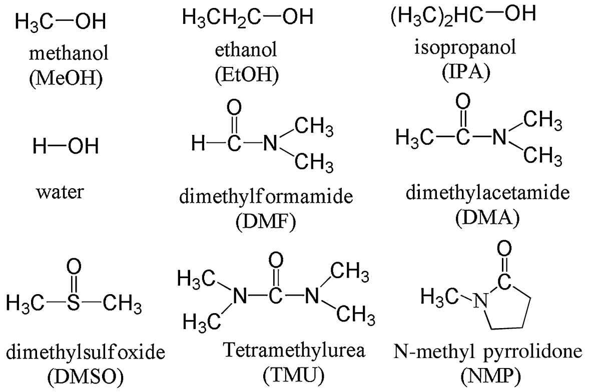
http://dx.doi.org/10.1016/j.colsurfa.2015.01.057
0927-7757/

To deeply explore LbL assembly technique, the factors that can finely tune the film properties are intensively investigated. Ionic strength, temperature, pH values, concentration and assembling time are parameters that can adjust the film thickness and morphology [16–18]. For the strong polyelectrolyte pair, the thin film growth shows strong dependence on ionic strength. Increasing the ionic strength of the solution shields charge repulsion among the repeat units of the polyelectrolyte and the chains take relatively compact conformation, resulting in the thicker and rougher films [19,20]. But to the weak polyelectrolyte pair, such as poly(allylamine hydrochloride) (PAH) or poly(acrylic acid) (PAA), pH value of the solution affects the film thickness greatly, because their charge density depends on the pH value of the solution [21,22].

Solvent is the essential component of solution. The LbL assembly of polyelectrolyte mainly conducts in aqueous solution. However, compared with other factors, solvent effect on LbL assembly of polyelectrolyte has seldom been studied, due to the hardness of polyelectrolytes to dissolve in organic solvent. Schlenoff and Dubas [16] conducted complexation of poly(diallydimethylammonium) (PDADMAC) and polystyrenesulfonate (PSS) with water/ethanol mixture as a medium and investigated how ethanol fraction affected the film growth. Adding ethanol into water, the solvent will become poorer, which is favorable for transferring PSS and PDADMAC to the interface and producing the thicker film. Caruso et al. [23] studied the effect of solvent composition on the assembly of PAH and PSS with water/ethanol mixture as solvent and also found that increasing acohol fraction results in the thicker film.

Compared with the polyelectrolyte complex thin films, there are more solvent choices to fabricate the hydrogen-bonded polymer complex thin films with LbL assembly. Rubner [6] demonstrated hydrogen bonding LbL assembly with water as solvent, while Zhang [7] used methanol as solvent. Chen and Cao [24] also applied methanol as a solvent for LbL assembly of diazo-resin (DR) and phenol-formaldehyde resin (PR). Sukhishivili conducted interfacial hydrogen bonding complexation of poly(carboxylic acids) with several neutral polymers, such as poly(ethylene oxide), poly(vinylpyrrolidone) (PVPON), poly(vinyl methyl ether) (PVME), poly(vinylcaprolactam) (PVCL), etc., in aqueous environment [25–27]. The LbL assembly of poly(4-vinylpyrridine) and poly(4-vinylphenol) was reported to conduct in ethanol/DMF mixture solvent [28]. Khutoryanskiy et al. [29] investigated solvent effects on the formation of nanoparticles and coatings based on LbL assembly of PAA and homo- and co-poly(vinylpyrrolidone) (PVPON) with alcohols and dioxane as solvents. The hydrogen-bonded polymer complex thin films have been reported to be prepared in water, alcoholic solvents, dioxane, DMF, or mixed solvent [30–43]. But there are rare works to conduct hydrogen bonding LbL assembly using many different solvents for one system and discuss how solvent–polymer interaction affects the assembly process.

To investigate the solvent effect, it is necessary to find a series of solvents which can dissolve both hydrogen-bonding donor and acceptor polymers. PVPON and PAA are widely used water soluble polymers. In previous work, we investigated pH effect and temperature effect on the hydrogen-bonded PVPON/PAA film [44,45]. Besides water, PAA and PVPON can both dissolve in the alcoholic and some aprotic solvent. In this work, we selected a series of co-solvents for PVPON and PAA, and study the solvent effect on the thin film growth and morphology. In addition, we also investigated the film's resistance to some strong aprotic solvents.



Scheme 1. Chemical formula of methanol (MeOH), ethanol (EtOH), isopropanol (IPA), water, dimethylformamide (DMF), dimethylacetamide (DMA), dimethylsulfoxide (DMSO), tetramethylurea (TMU) and N-methyl pyrrolidone (NMP).

2. Experimental

2.1. Materials

Poly(vinylpyrrolidone) (PVPON) (K90, $M_w = 360{,}000$; K30, $M_w = 40{,}000$), poly(acrylic acid) (PAA, $M_w = 450{,}000$), PAA sodium salt solution (35 wt%, $M_w = 15{,}000$) were purchased from Sigma–Aldrich. Polyethyleneimine (PEI, branched, $M_w = 70{,}000$, 50 wt% aqueous solution) were from Aladdin. Tetramethylurea (TMU) was brought from Alfa. Methanol (MeOH), ethanol (EtOH), isopropanol (IPA), dimethylformamide (DMF), dimethylacetamide (DMA), dimethylsulfoxide (DMSO), N-methyl pyrrolidone (NMP) and other chemicals used in this study are of analytical grade. All chemicals were used as received (Scheme 1 and Table 1).

2.2. Thin film preparation

PVPON and PAA dissolved in different solvents at a concentration of 1.0 mg/mL. Before the LbL assembling, the PAA solution and the PVPON solution were mixed to check whether the polymer complex could be formed in different solvents.

The hydrogen-bonded complex thin films were deposited on the silicon or quartz substrates. The substrates were cleaned before use with the procedures: first immerse into the piranha solution (H_2SO_4/H_2O_2, 7/3, v/v) for 30 min (caution: this solution is extremely corrosive), then rinse with deionized water several times, and finally dry with pure nitrogen flow.

An automatic machine (Kejing Auto-Instrument Co., Ltd., Shenyang, China) was utilized to perform LbL assembly. This machine alternately dipped the substrates into the PAA and the PVPON solutions, with the interval of three rinses in the corresponding solvents. The assembling time and the rinsing time were set to 4 and 1 min, respectively. After assembling, the wet film was dried in the ambient and then preserved in the desiccator. The prepared film expressed as $(\mathrm{PVPON/PAA})_n$ means the film fabricated from PVPON and PAA through n assembling cycle(s).

Table 1
The dipole moment (μ) and dielectric permittivity (ε) of the solvents [45].

Solvents	Water	MeOH	EtOH	IPA	DMF	TMU	NMP	DMA	DMSO
$\mu(p/D)$	1.83	1.66	1.66	1.66	3.80	3.40	4.09	3.80	3.96
ε	78.3	32.7	24.6	20.3	36.7	23.1	32.2	37.8	46.7