

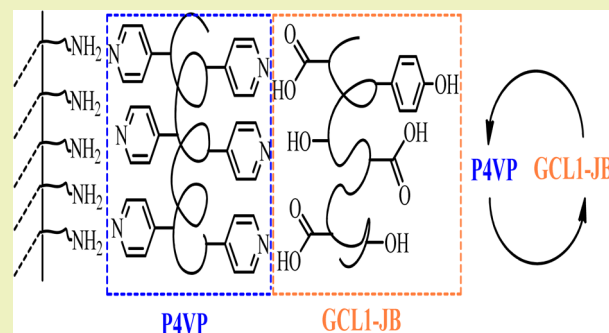
Layer-by-Layer Self-Assembled Films of a Lignin-based Polymer through Hydrogen Bonding

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ABSTRACT: A new type of layer-by-layer (LBL) self-assembled films of a lignin-based polymer (GCL1-JB) with Poly(4-vinylpyridine) (P4VP) has been obtained via hydrogen bonding interaction. Fourier-transform infrared spectroscopy results confirmed a strong hydrogen bonding between GCL1-JB and P4VP. And the hydrodynamic radius of the GCL1-JB/P4VP mixture was larger than individual polymer due to the hydrogen bonding. The adsorption characteristics of GCL1-JB self-assembled films based on hydrogen bonding or electrostatic interaction were investigated by UV-vis spectrophotometry and atomic force microscopy, respectively. Compared to the GCL1-JB self-assembled films based on electrostatic interaction, that based on hydrogen bonding has a larger adsorbed amount, a faster adsorption transfer rate from dipping solution to the substrate surface and a larger surface roughness. This study gives significant information to understand the adsorption characteristics of lignin-based polymers on the solid surface via different driving forces.

KEYWORDS: Lignin-based polymer, Self-assembly, Hydrogen bonding, Adsorption characteristics



INTRODUCTION

Lignin is the main component of a plant cell wall and the second most renewable resource in nature.^{1,2} It is also the main byproduct of the pulping and papermaking industry. Lignin can be modified and used as concrete water reducers.^{3–6} Lignin-based polymers can be adsorbed on the cement particles' surfaces to improve the stability of solid suspension in water. So, the dispersion performance of lignin-based polymers is closely related to their adsorption characteristics on the solid particles. Thus, studying the adsorption characteristics of lignin-based polymers can give significant information to understand the dispersion mechanism.

However, it is difficult to detect the adsorption characteristics of lignin-based polymers on cement particles directly due to the irregular shape of cement particles and the thin adsorption thickness of lignin-based polymers. To overcome these difficulties, flat substrates are chosen to replace the irregular cement particles and a layer-by-layer (LBL) self-assembly technique is used to prepare multilayer films with controllable thickness. It is one effective method to study the adsorption characteristics of lignin-based polymers.⁷

The LBL self-assembly technique can be traced back to 1966.⁸ Until 1991, Decher rediscovered to prepare electrostatic self-assembly multilayer films.⁹ Subsequently, Xi Zhang and Rubner reported the self-assembled adsorption of alternating hydrogen bonding acceptor and hydrogen bonding donor in 1997.^{10,11} In recently years, self-assembly multilayer films were prepared via different kinds of driving forces.^{9–14} Lignin-based polymers have various functional groups such as aromatic

backbone, carboxylic groups, hydroxyl groups and sulfonic groups. These groups can form different kinds of driving forces of self-assembly.

There have been a few reports about the LBL self-assembly of lignin under different driving forces. In 2001, Paterno et al.¹⁵ first proposed that the LBL multilayers of lignosulfonate and poly(ethoxy aniline) (POEA) were successfully prepared via electrostatic interaction. Norgren et al. suggested that the adsorption of lignin to oppositely charged polymeric substances is based on electrosorption.^{16,17} But Pillai et al. took another opinion that the self-assembled films of lignin on poly(diallyl dimethylammonium chloride) (PDAC) were based on cation- π interaction.¹⁸ And this opinion was supported by Liu and Fu.¹⁹ In further study, Ouyang considered that lignosulfonate could not adsorb on the PDAC layer without a hydrophobic interaction.²⁰ However, self-assembled films of lignin-based polymers based on hydrogen bonding are rarely reported and further investigation is necessary to understand the adsorption characteristics of lignin-based polymer on solid particles.

In our previous work, a lignin-based polymer (GCL1-JB) was obtained by grafted sulfonation of alkali lignin from bamboo pulp black liquor²¹ and it was found to be excellent concrete water reducer. GCL1-JB has carboxylic and hydroxyl groups, which can be used as a hydrogen bonding donor. Therefore, it

Received: March 5, 2015

Revised: April 14, 2015

Published: April 22, 2015

may form hydrogen bonding to stabilize the cements particles in the concrete. In the current work, GCL1-JB can be used to prepare LBL multilayers with P4VP, a good hydrogen bonding acceptor, based on hydrogen bonding. Fourier-transform infrared (FTIR) spectroscopy measurement was used to confirm the hydrogen bonding between GCL1-JB and P4VP. The comparisons of adsorption characteristics will also be made between the GCL1-JB/P4VP self-assembled films based on hydrogen bonding and the GCL1-JB/PDAC self-assembled films based on electrostatic interaction by using UV-vis spectrophotometry and the atomic force microscopy (AFM).

EXPERIMENTAL SECTION

Materials. A lignin-based polymer (GCL1-JB, as shown in Figure 1) was prepared by graft sulfonation of alkali lignin from bamboo pulp

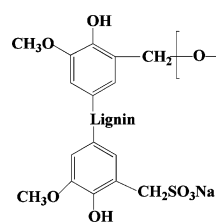


Figure 1. Possible structure of GCL1-JB.

black liquor. It was purified by filtration and ultrafiltration through an ultrafiltration apparatus (Wuxi Membrane Science and Technology Co., China) with a 2500 Da cutoff membrane. The molecular weight and the polydispersity index of GCL1-JB, which determined by gel permeation chromatography (GPC), were about 24 000 and 2.33, respectively. Poly(4-vinylpyridine) (P4VP) with pyridine groups (Molecular weight of 16 000, Sigma-Aldrich) was dissolved in methanol with a concentration of 1.0 g/L and was used as a hydrogen bonding acceptor. Poly(diallyl dimethylammonium chloride) (PDAC) with molecular weight from 200 000 to 350 000 (20% solution, Aldrich) was diluted to a concentration of 0.1 mmol/L (repeated unit) and was used as a polycation. The ultrapure water with the resistivity larger than 18 MΩ·cm was obtained from a Millipore water purification system. Other reagents used in this work were analytical grade products and were purchased commercially.

Layer-by-Layer (LBL) Self-Assembled Films. The GCL1-JB/P4VP LBL self-assembled films were fabricated by dipping the quartz slide (4 × 1 cm) alternately into the GCL1-JB and P4VP solutions. The quartz slides were immersed in a 98% H₂SO₄/30% H₂O₂ (7:3) solution for 1 h, and immersed in a 25% NH₄OH/30% H₂O₂/H₂O (1:1:5) solution for 1 h, then was rinsed with ultrapure water and dried with air stream. The GCL1-JB was dissolved in water to obtain a 0.1 wt % solution as a hydrogen bonding donor. The pH of GCL1-JB solution was adjusted to 3.0. The P4VP was dissolved in methanol with a concentration of 1.0 g/L and was used as hydrogen bonding acceptor. The construction of the LBL self-assembled films was described as follows. The quartz slide was first immersed in the P4VP solution for 10 min. After being rinsed with the corresponding solvent and dried with the air steam, the substrate was added with a P4VP layer as a hydrogen bonding acceptor. Then the slide was transferred into the GCL1-JB solution for 10 min, then rinsed with the water and dried with the air stream. In this way, the substrate was covered with a GCL1-JB layer as a hydrogen bonding donor. The LBL self-assembled films were prepared by alternately depositing of GCL1-JB and P4VP by repeating the above steps for 10 cycles.

The GCL1-JB/PDAC LBL self-assembled films based on electrostatic interaction were fabricated in the same step with the process of GCL1-JB/P4VP LBL self-assembled films, except using 0.1 mmol/L PDAC water solution to replace the P4VP solution.

Characterization. A UV-vis spectrophotometer (UV-2550, Shimadzu Corp., Japan) was used to monitor the process of LBL

self-assembled films. Air was scanned at the wavelengths of 700–190 nm as a baseline. The atomic force microscopy (AFM) was used to observe the surface morphological images of LBL self-assembled films with the noncontact mode. FTIR spectroscopy was performed with a Nexus spectrometer (Nicolet 380, Thermo, USA) from 4000 to 400 cm⁻¹. Tested sample was prepared by mixing 2 mg of dried GCL1-JB with 100 mg of KBr (for background) and pressing at 12 MPa for 3 min. Dynamic light scattering (DLS) (IB-90 Plus, Brookhaven, USA) was applied to determined the hydrodynamic radius at a detector angle of 90° under 298 K.

RESULTS AND DISCUSSION

Process of GCL1-JB/P4VP LBL Self-Assembled Films.

The GCL1-JB solution was used as a hydrogen bonding donor to fabricate LBL self-assembled films with the P4VP, which was recognized as a hydrogen bonding acceptor. The self-assembled process of GCL1-JB/P4VP self-assembled films was monitored by UV-vis spectroscopy. The UV-vis spectra of the GCL1-JB/P4VP self-assembled films with different bilayer numbers is shown in Figure 2. Dependent on the Lambert-Beer law, the

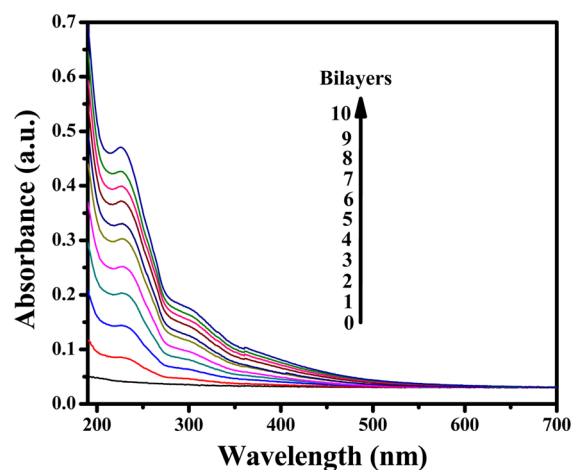


Figure 2. UV-vis spectra of GCL1-JB/P4VP self-assembled films with different numbers of bilayers. The dipping solutions were 1.0 g/L GCL1-JB in water and 1.0 g/L P4VP in methanol.

absorbance is related to the concentration of sample. The absorbance of GCL1-JB/P4VP self-assembled films enhanced with increasing number of bilayers, indicating the adsorption amount of GCL1-JB/P4VP self-assembled films increased. Thus, the GCL1-JB/P4VP LBL self-assembled films successfully formed via hydrogen bonding. The fabrication schematic of GCL1-JB/P4VP layer-by-layer self-assembled films based on hydrogen bonding is shown in Figure 3.

280 and 256 nm are the characteristic adsorption wavelengths of GCL1-JB and P4VP, respectively. The adsorption condition of GCL1-JB and P4VP were determined by UV-vis

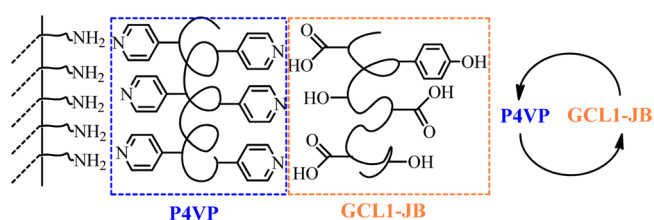


Figure 3. Fabrication schematic of GCL1-JB/P4VP layer-by-layer self-assembled films based on hydrogen bonding.

spectroscopy at $\lambda_{280\text{ nm}}$ and $\lambda_{256\text{ nm}}$ varying with the number of bilayers, as shown in Figure 4. A linear increase of the

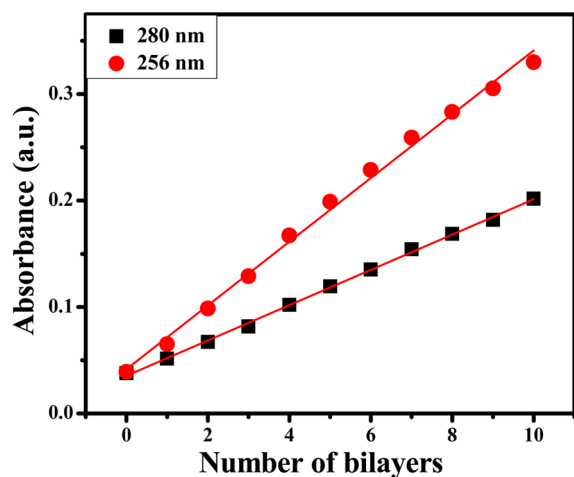


Figure 4. Absorbance at $\lambda_{280\text{ nm}}$ and $\lambda_{256\text{ nm}}$ of GCL1-JB/P4VP self-assembled films versus number of bilayers.

absorbance at $\lambda_{280\text{ nm}}$ and $\lambda_{256\text{ nm}}$ was observed with increasing number of bilayers. The absorbance slope at $\lambda_{280\text{ nm}}$ versus that at $\lambda_{256\text{ nm}}$ was 0.55:1. Because the absorbance at $\lambda_{280\text{ nm}}$ and $\lambda_{256\text{ nm}}$ of the GCL1-JB/P4VP self-assembled films represented the adsorption amount of GCL1-JB and P4VP, the GCL1-JB and P4VP alternately deposited on the substrate according to the adsorption amount ratio of 0.55:1. It indicated that GCL1-JB and P4VP could build up a self-assembled film with the characteristic of homogeneous thickness.

Evidence of Hydrogen Bond between GCL1-JB and P4VP. FTIR spectroscopy is the most convenient method to detect the specific intermolecular interactions between polymers. The evidence for hydrogen bonding between GCL1-JB and P4VP was obtained from FTIR spectroscopy in the range from 4000 to 400 cm^{-1} , as shown in Figure 5. For the molecular structure of P4VP, the absorption peaks at 1598, 1556, 1451 and 1415 cm^{-1} were corresponding to the pyridine ring vibration such as C=N and C=C. The absorption peak at 3023 cm^{-1} was corresponding to the stretching vibration of -CH of pyridine ring,^{10,22} as shown in curve of P4VP. For the

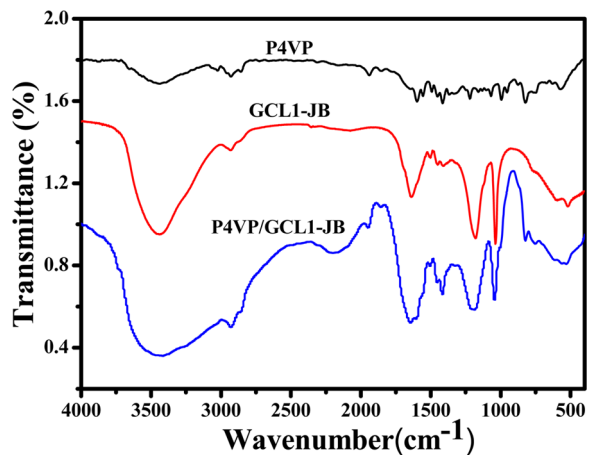


Figure 5. FTIR spectra of P4VP, GCL1-JB and GCL1-JB/P4VP (50/50) complex.

molecular structure of GCL1-JB, the band at 3443 cm^{-1} was the characteristic absorption peak of -OH phenolic groups. The band at 1507 cm^{-1} was signed to the aromatic ring vibration. The bands at 1646 and 1185 cm^{-1} were characteristic of the stretching vibration of carbonyl groups (C=O) and sulfonic groups (S-O), respectively.²³ After the GCL1-JB and the P4VP mixed uniformly with the mass ratio of 1:1, the curve of GCL1-JB/P4VP complex appeared a new band at 2169 cm^{-1} contrasting to the separate polymers, which is assignable to vibration of -OH groups.²⁴ In addition, the absorption peak of -OH phenolic groups became broader and shifted to 3425 cm^{-1} . These evidence indicated that hydrogen bond formed between GCL1-JB and P4VP. Furthermore, the driving force of GCL1-JB and P4VP was not the electrostatic interaction or cation- π interaction but the hydrogen bonding, since the absorption peaks of aromatic ring and sulfonic groups had no obviously change. The FTIR result demonstrated that the self-assembled films of GCL1-JB with P4VP were formed via hydrogen bonding interaction.

The powerful phenomenon to examine that hydrogen bonding formed between polymers is a larger complex obtained after they mixed.²⁴ Liu²⁴ considered that the mixture of monocarboxy terminated polystyrene (MCPS), another hydrogen bonding donor, and P4VP could be formed a larger complex due to the hydrogen bonding. Thus, if GCL1-JB exhibits hydrogen bonding with P4VP in the solution, the hydrodynamic radius (R_h) of the mixture of GCL1-JB and P4VP will be larger than that of GCL1-JB or P4VP. The distributions of R_h for GCL1-JB, P4VP and their mixture were monitored by DLS, as shown in Figure 6. The R_h of GCL1-JB

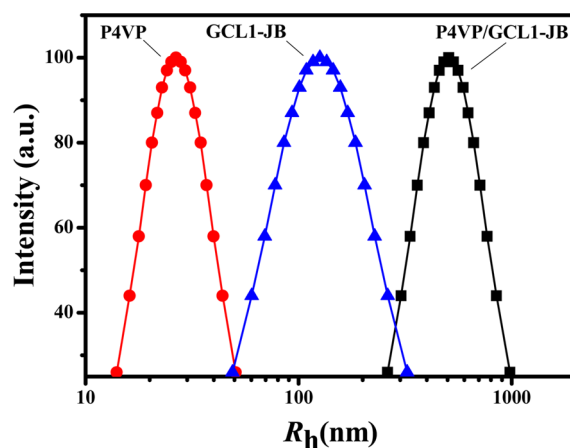


Figure 6. Distribution of R_h for GCL1-JB, P4VP and GCL1-JB/P4VP (50/50) complex (both the GCL1-JB and P4VP were dissolved in the water of pH = 3.0).

was 125.8 nm and the R_h of P4VP was 26.6 nm. However, the R_h of their mixture was up to 213.7 nm, which is obviously larger than that of GCL1-JB or P4VP. The R_h of the GCL1-JB/P4VP mixture should be from 26.6 to 125.8 nm if there is no specific intermolecular interaction between GCL1-JB and P4VP. Therefore, it was reasonable to consider that hydrogen bonding had formed between GCL1-JB and P4VP.

Comparison of the GCL1-JB Self-Assembled Films Based on Hydrogen Bond and Electrostatic Interaction. Different driving forces will drive to perform different adsorption characteristics of GCL1-JB self-assembled films. GCL1-JB is one kind of polyelectrolyte with a large amount of

anion groups. GCL1-JB can form a self-assembled film with PDAC via electrostatic interaction.²³ However, the self-assembled films of GCL1-JB with P4VP based on hydrogen bonding are quite different from that of GCL1-JB/PDAC self-assembled films. To understand the different adsorption characteristics of GCL1-JB driven by hydrogen bonding and electrostatic interaction, the adsorption amount, adsorption kinetics and adsorption morphologies were investigated.

Self-assembled films of GCL1-JB with PDAC were prepared by alternately dipping in the GCL1-JB solution with the concentration of 1.0 g/L and the PDAC solution with the concentration of 0.1 mmol/L (repeated unit). The pH value of the GCL1-JB solution was 3.0. The UV-vis spectra of GCL1-JB/PDAC self-assembled films as a function of bilayer numbers is shown in Figure 7. Though the absorbance of GCL1-JB/

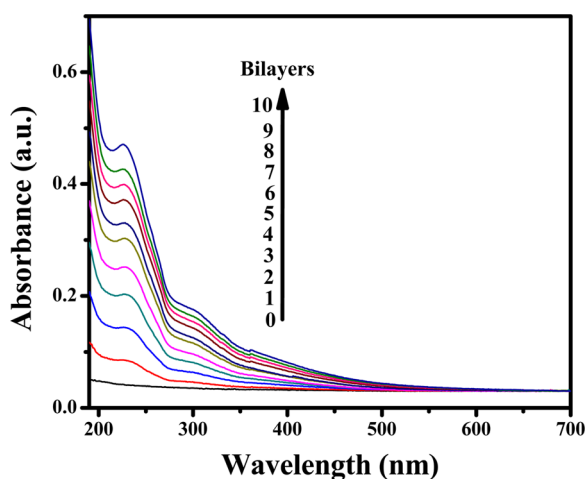


Figure 7. UV-vis spectra of GCL1-JB/PDAC self-assembled films with different number of bilayers (the dipping solutions were 1.0 g/L GCL1-JB in water and 0.1 mmol/L PDAC in water).

PDAC self-assembled films increased with increasing number of bilayers, the shape of the absorption curve was quite different from that of GCL1-JB/P4VP self-assembled films (as shown in Figure 2), indicating the GCL1-JB adsorption based on hydrogen bonding is clearly different from that based on electrostatic interaction. At the same time, the absorbance of GCL1-JB/P4VP self-assembled films was greater than that of GCL1-JB/PDAC self-assembled films, indicating that the adsorbed amount of GCL1-JB/P4VP self-assembled films was larger. The fabrication schematic of GCL1-JB/PDAC layer-by-layer self-assembled films based on electrostatic interaction is shown in Figure 8.

To understand the two different adsorption processes of GCL1-JB based on hydrogen bonding and electrostatic

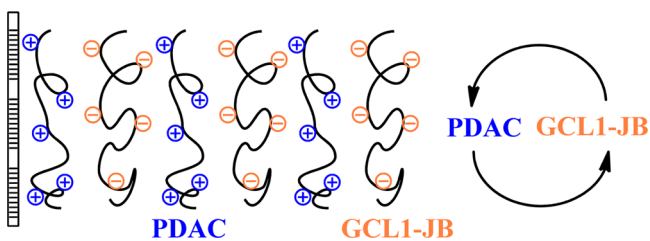


Figure 8. Fabrication schematic of GCL1-JB/PDAC layer-by-layer self-assembled films based on electrostatic interaction.

interaction, the adsorption kinetics of GCL1-JB self-assembled films via different driving forces were characterized by UV-vis spectroscopy. The GCL1-JB/P4VP 10-bilayers self-assembled films and the GCL1-JB/PDAC 10-bilayers self-assembled films were used as substrates to eliminate the substrate effect. Figure 9 shows the absorbance at $\lambda_{280\text{ nm}}$ of GCL1-JB deposited on the

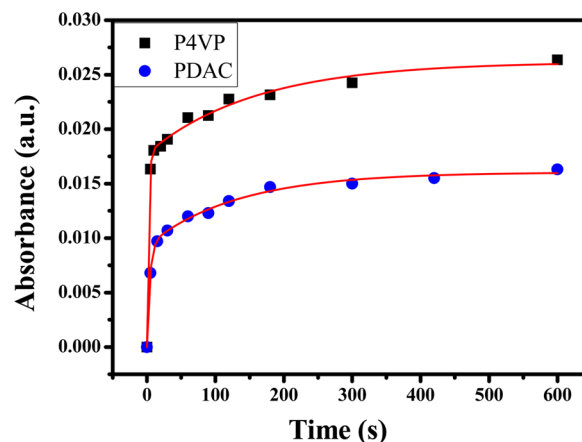


Figure 9. Absorbance at $\lambda_{280\text{ nm}}$ of GCL1-JB deposited on P4VP layer and PDAC layer versus immersion time.

two substrates versus the immersion time. The two adsorption rates of GCL1-JB became slow as the immersion time increased. And the adsorption reached a balance within 10 min. Thus, the immersion time of self-assembled processes was chosen 10 min to be balanced. However, the adsorbed amount of GCL1-JB layer based on hydrogen bonding was larger than that based on electrostatic interaction.

The adsorption kinetics curves can be fitted by a second-order exponential decay equation, shown as eq 1.^{7,25} And the corresponding parameters are shown in Table 1.

$$A = A_0 + k_1 \exp[-(t + t_0)/\tau_1] + k_2 \exp[-(t + t_0)/\tau_2] \quad (1)$$

where A is the real absorbance, A_0 is the saturation absorbance, k_1 and k_2 are the constants, t is the immersion time, t_0 is the delay time and τ_1 and τ_2 are the characteristic times. Here, the reciprocal of characteristic time is the adsorption rate of GCL1-JB at the self-assembled process. As shown in Table 1, for the GCL1-JB deposited on the P4VP substrate, τ_1 and τ_2 were 2.14 and 159.7 s, respectively. For the GCL1-JB deposited on the PDAC substrate, τ_1 and τ_2 were 4.16 and 132.3 s, respectively. Obviously, there were two step processes of the GCL1-JB adsorption, no matter what kind of driving force. The first-step process was fast and the adsorbed amount increased suddenly, but the second-step process was slow and the adsorbed amount rose a little.

However, there were some differences of GCL1-JB deposited on the two substrates. The first-step process corresponded to the polymer molecules moving from the solution to the substrate and the second-step process was related to the adjustment of polymer molecules on the substrate.⁷ That is to say, for the GCL1-JB deposited on the P4VP substrates, the GCL1-JB molecules move faster from the solution to the substrate but adjust slower on the substrate by contrasting to the GCL1-JB deposited on the PDAC substrates.

AFM is the important method to observe the surface morphology. Figure 10 shows the AFM images of GCL1-JB/

Table 1. Parameters of Kinetic Equation to Fit the Experimental Data of Figure 9

name	A_0	t_0 (s)	k_1	τ_1	k_2	τ_2 (s)	R^2
GCL1-JB(P4VP)	0.026	3.391	-0.087	2.14	-0.0086	159.7	0.9937
GCL1-JB(PDAC)	0.016	2.721	-0.018	4.16	-0.0069	132.3	0.9944

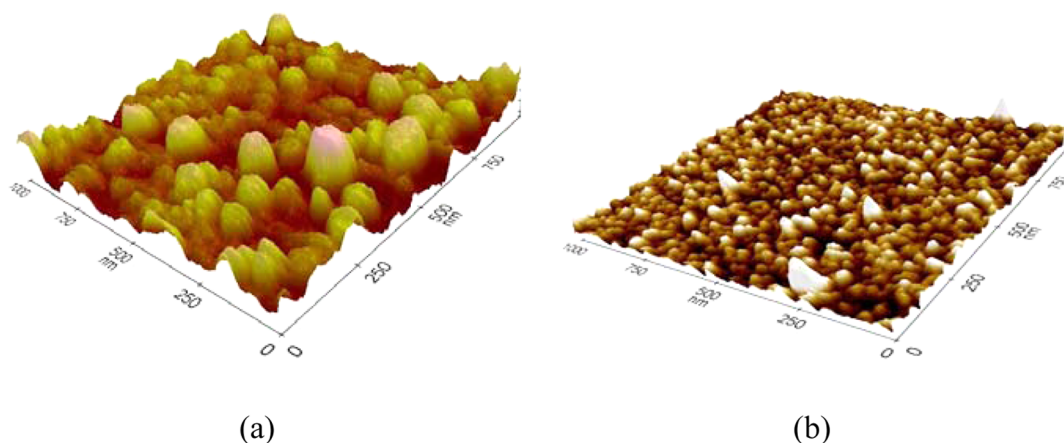


Figure 10. AFM images of GCL1-JB/P4VP self-assembled films and GCL1-JB/PDAC self-assembled films with GCL1-JB as the outermost layer, scan size was $1 \times 1 \mu\text{m}$; (a) GCL1-JB/P4VP films; (b) GCL1-JB/PDAC films.

P4VP self-assembled films and GCL1-JB/PDAC self-assembled films, the outermost layers were GCL1-JB. The surface roughness of GCL1-JB/P4VP self-assembled films was 4.03 nm, while that of GCL1-JB/PDAC self-assembled films was 1.57 nm. Besides, the particles of GCL1-JB/P4VP self-assembled films were greater than those of GCL1-JB/PDAC self-assembled films. The AFM results indicated that the surface of GCL1-JB/P4VP self-assembled films was rough and loose but that of GCL1-JB/PDAC self-assembled films was smooth and compact.

Comparing with the GCL1-JB/PDAC films fabricated via the electrostatic self-assembly process, the GCL1-JB/P4VP self-assembled films made with the hydrogen bonding process were quite different, reflecting in the larger adsorption amount, the faster rate of adsorption transferred from the solution to the substrate and the larger surface roughness. This is in accord with Stockton and Rubner's result: self-assembly with the hydrogen-bonding polymers produces thicker bilayers and rougher surface, because there is no electrostatic repulsion between hydrogen-bonding polymers and they tend to be a coiled conformation.¹¹

CONCLUSIONS

A layer-by-layer self-assembled film of GCL1-JB can be obtained with P4VP based on special molecular interaction. The FTIR result demonstrated that hydrogen bonding was formed between the GCL1-JB and the P4VP during the self-assembly process, which was confirmed by evidence that the hydrodynamic radius of the GCL1-JB/P4VP mixture was larger than the individual polymer. Compared with the GCL1-JB self-assembled films via electrostatic interactions, the GCL1-JB self-assembled films based on hydrogen bonding had a larger adsorption amount, a faster adsorption transfer rate from the dipping solution to the substrate surface and a rougher surface. This study is helpful to understand the adsorption characteristics of GCL1-JB under different driving forces, and gives a significant foundation of application of lignin-based polymers in concrete water reducers.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the State Key Program of National Natural Science of China (21436004), and the National Natural Science Foundation of China (21374032).

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