



Approach of Electrostatic Interaction Based Layer-by-Layer Assembly of Cationic Guar Gum and Poly (Carboxylic acid)

Mahmoud H. M. A. Shibraen^{a*}, M. R. El-Aassar^{d,e}, Rabie A. M. Asad^a, Hajo Yagoub^b, Shuguang Yang^{b,c}

^aDepartment of Textile Engineering, Faculty of Industries Engineering and Technology, University of Gezira, Wad Madni P.O.Box 20, Sudan

^bState Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, China.

^cCenter for Advanced Low-Dimension Materials, Donghua University, 2999 North Renmin Road, Shanghai 201620, China.

^dPolymer Materials Research Department, Advanced Technology and New Material Institute, City of Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City 21934, Alexandria, Egypt.

^eDepartment of Chemistry, College of Science, Jouf University- Sakaka- 2014, Saudi Arabia.



CrossMark

THE present study evaluated the possibility to form thin film of cationic guar gum (CGG) associated with poly (carboxylic acid) such as carboxymethyl cellulose (CMC) and poly (acrylic acid) (PAA) through layer-by-layer (LbL) assembly. The thin film thickness and morphology show dependence on pH value, ionic strength and temperature. For pH 3 to pH 4 CGG and poly (carboxylic acids) assemble and form thin film through LbL. For neutral pH region and high pH values CGG and poly (carboxylic acids) do not interacted. In contrast to synthetic polyelectrolyte complex thin film, such as polystyrene sulfonate (PSS)/ poly (diallyldimethylammoniumchloride) (PDDA) and PSS/ poly (allylamine hydrochloride) (PAH), the LbL assembly of CGG/CMC and CGG/PAA take place only at low salt concentrations. Deposition at high temperature (up to 60°C) results thicker CGG/ poly (carboxylic acids) films.

Keywords: Cationic guar gum, poly (carboxylic acid), polymer complex, layer-by-layer assembly.

Introduction

Guar gum, a high-molecular weight water-soluble nonionic natural polysaccharide, is extracted from the refined endosperm of cluster bean seeds [1,2]. Chemically classified as galactomannan, it made of a straight chain of D mannose units linked by β (1-4) glycosides and bears a single D-galactose unit on approximately every alternate mannose, joined to it by an α (1-6) glycoside linkage [3-5]. Guar is grown in India and Australia, with small

corps in USA, China, Pakistan and Africa. India produces 1-1.25 million tons of guar per year, and nearly 80% of world guar production [6]. Due to their unique rheology properties, low cost, easy availability, non-toxicity and biodegradability, guar gum and its derivatives have been widely used in industrial applications [7] such as food [8], textile [9], cosmetics [10], paper [11], oil well drilling [12], water treatment [13] and pharmaceutical industry [14, 15].

*Corresponding author e-mail : shibraen@yahoo.com

Received 22/08/2019; Accepted 15/01/2020

DOI: 10.21608/EJCHEM.2019.15950.1982

© 2020 National Information and Documentation Center (NIDOC)

In the early 1990's, Decher et al. developed a simple but effective way to prepare ultrathin polyelectrolyte multilayer film via layer-by-layer (LbL) assembly [16,17]. Polyelectrolyte multilayers (PEMs) have received extensive attention in the past decade due to their promising applications in very diverse fields[18] such as chemical sensors [19] optical devices [20], biosensors [21] light-emitting diodes[21], biomedical coatings [22-24], Antioxidative and Antibacterial Self-Healing [25]. The driving force for the LbL assembly of oppositely charged polyelectrolyte chains is mainly attributed to the electrostatic interactions [17]. However LbL can also be fabricated based on other molecular interactions, e.g. hydrogen bonds [26-28], covalent chemical bonds [29], coordinate bonding [30], charge transfer interactions [31], and hydrophobic interactions [32], which have greatly widened the scope of LbL assembly.

Although guar gum is easily soluble in water, it is not suitable as such to fabricate thin film via LbL assembly based on electrostatic interaction or hydrogen bonding. Guar gum is considered as non-ionic polysaccharide which precludes electrostatic interaction. Due to strong hydration of the guar gum and its ability to form hydrogen bonding with water [8], fabrication of thin films based on hydrogen bonding is not possible. Nonetheless Guar gum can be modified so as to be suitable for the LbL assembly technique.

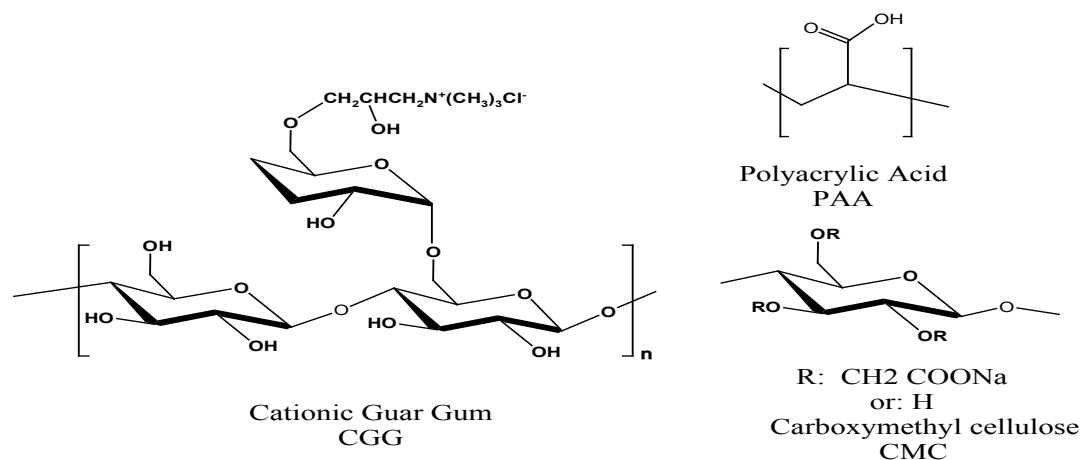
Many researchers attempted modification of guar gum [33] like carboxymethylation [5, 34, 35], methylation [36], cationic guar gum [4] etc. In cationic guar gum (CGG) the hydroxyl groups are replaced with trimethyl ammonium groups.

It is excellent non-gelling thickener, viscosity, foam enhancer and volume. With its ammonium groups, it carries a net positive charge and can be easily assembled with other anions polymers [37, 38].

Kuar et al. prepared domperidone bioadhesive films of CGG and xanthan gum (XG) via interpolymer complex [37]. Moin et al. organized polyelectrolyte complex micro particles of CGG and xanthan gum and investigated the controlled drug release from the CGG/XG complex [38]. Wu et al. reviewed the research work on LbL assembly involving cationic guar gum. They studied the effect of ionic strength on the assembly behavior of cationic guar with sulfated chitosan (SC) and poly (sodium 4-styrenesulfonate) [18] and the subsequent the protein adsorption onto those polyelectrolyte multilayer [39].

In practice CGG is used in food industry and pharmaceutical applications such as drug delivery and protein adsorption. An alternative application which would be to build thin films of CGG and poly (carboxylic acids) (CMC & PAA) for anti-fogging and anti-frosting properties.

In this context the present contribution explores how solution parameters such as (pH value, ionic strength and temperature) influences the LbL assembly behavior of cationic guar gum and poly (carboxylic acids) such as carboxymethyl cellulose (CMC) and poly (acrylic acids) (PAA). It indicates that the thickness growth of the CGG/ poly (carboxylic acids) film exhibits a different dependence on ionic strength and pH value compared with films of synthetic polyelectrolyte pairs.



Schema 1. Chemical structure of CGG, CMC and PAA.

Experimental Section

Materials

Cationic guar gum (CGG) (the viscosity of a 1.0 wt% water solution is ~ 3000 mPa·s, DS=1.2) (by Yan Cheng Xin Yuen Chemical Co. Ltd), carboxymethyl cellulose (CMC, the viscosity of 2.0 wt. % water solution is ~ 550 mPa·s at pH = 6.15) (Sino Pharm Chemical Reagent) [40] and Poly acrylic acid (PAA, Mw = 450000) (Sigma-Aldrich) were utilized without further purification. Further reactants and solvents were hydrogen peroxide (H_2O_2) (Sino Pharm Chemical Reagent), sulfuric acid (98 wt. %), sodium hydroxide (NaOH) (Shanghai Ling Feng Chemical Reagent) and hydrochloric acid (HCl, 36.5 wt. %) (Ping Hu chemical). Deionized water (DI) was used in all aqueous solutions and rinsing procedures.

Thin Film Preparation.

Assembly solutions (CGG, CMC and PAA) were prepared at the 1mg/ml concentration. The pH values of the assembly and rinsing solutions were monitored with pH meter (SevenMulti, Mettler Toledo) and adjusted with HCl and NaOH. The thin films were deposited on the substrates of quartz slides or silicon wafers. Before film deposition the substrates were cut into the desired dimension (1.2 cm \times 4.5 cm), and were cleaned by immersing into piranha solution (H_2SO_4/H_2O_2 , v/v, 7:3) for 30 minutes, rinsed with DI water and dried with nitrogen. The LbL assembly was conducted with an automatic dipping machine (Kejing Auto Instrument, Shenyang) with dipping times in the CGG solution and the poly (carboxylic acids) (CMC, PAA) of 4 min alternatively, followed by three-times-rinsing (1 min each) in separate bins to remove the excess polymer, using deionized water at the polymer solution pH. The ionic strength of the assembly solution was adjusted by adding NaCl. The temperature was controlled by a water bath [40].

Characterization

Ultraviolet-visible spectroscopy.

The UV-visible spectra of the films deposited

on quartz substrates were obtained using a Shimadzu UV-2550 spectrophotometer.

Fourier transform infrared spectroscopy (FT-IR)

The films were deposited on silicon slides and characterized with a Nicolet 8700 FT-IR spectrometer. Blank silicon wafer was used as background.

Quartz crystal microbalance (QCM)

QCM chips were modified using 5 mM 3-mercaptopropionic acid solution in ethanol. A dry chip was mounted in flow-through modules to establish a reference zero baseline. The resonance frequencies were monitored at the third overtone number. The QCM technique consists of measuring the change of the resonance frequency of a quartz crystal (Δf) [45], which is induced by polyelectrolyte adsorption onto the crystal. The reference frequency is given by the resonance frequency of the crystal in contact to water. For the PEM buildup the polyelectrolyte solution is rinsed over the crystal for 15 min, followed by washing for 10 min. All solutions employed in one multilayer formation process are adjusted to the same pH value, even the washing solution. During the switching of the assembling solution, the solvent (60 μ L/min) was followed for several minutes to rinse the chamber and the all experiments were conducted at $25 \pm 0.02^\circ C$ [40].

Optical reflectometry (OR).

The optical instrument NanoCalc-XR (Ocean Optics, Germany) was used to measure the near-normal reflection spectroscopy of the thin film deposited on silicon wafer, and calculate the film thickness based on the reflection spectrum. The thickness of the thin film was determined by optical reflectometry (λ range 200-1100 nm) [41] with a blank silicon slide as reference.

Results and Discussion

Influence of pH value

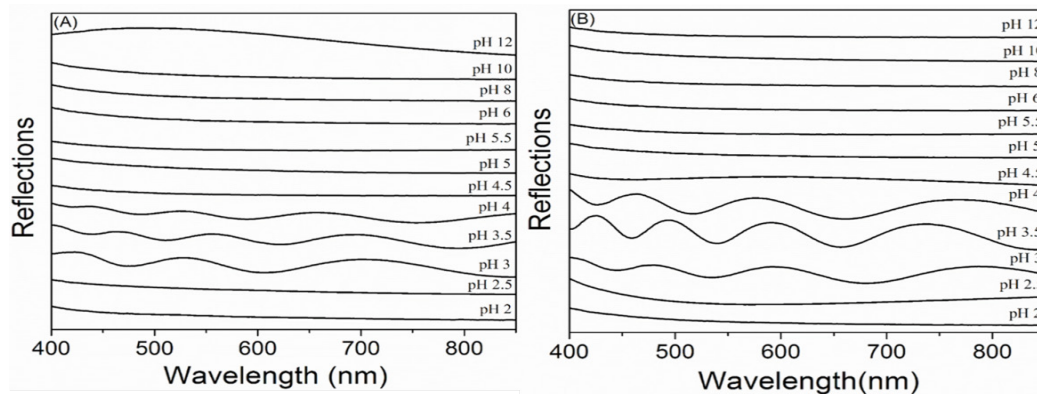


Fig. 1. Reflection spectra of the CGG/ poly (carboxylic acids) thin films prepared at different pH values. (A) (CGG/CMC)₃₀ (B) (CGG/PAA)₃₀ (for clarity the spectra are intentionally offset).

CGG and poly (carboxylic acids) (CMC; PAA) were alternately deposited on the silicon substrate with 30 assembly cycles at different pH values. Their reflection spectra are shown in figure 1. Only in limited range of pH (3-4) oscillation in the spectra indicates that oscillation in the spectrum occur. These oscillations are Fabry-Perôt fringes originate from interferences between light beams transmitted and partially reflected at the film - air and film – silicon interfaces. The thickness of the film can determine through the equation [42]:

$$2d = \frac{m\lambda_k\lambda_{k+m}}{n(\lambda_k + \lambda_{k+m})} \quad (1)$$

where d is the film thickness; n is the effective refractive index of the film; λ_k and λ_{k+m} are the peak positions of the kth and (k + m) th interference in the spectrum; and m is the difference of the level between these two peaks. The peaks of Fabry-Perôt fringes are determined by the optical thickness of the thin film (production of the physical thickness and refractive index of the thin film) and the thicknesses of the thin films prepared at different pH value are calculated based on Equation (1), and further confirmed by data fitting using the software of NanoCalc-10n. The thickness of the thin films prepared at different pH values were shown in Figure 2.

Absence of Fabry-Perôt fringes for pH > 4 does not necessary means that there is no

thin film deposit. S. Yang et al. shown that the optical interference phenomenon will be present if the three conditions are fulfilled; firstly there should be an obvious refractive index contrast between thin film and substrate, secondly, the film thickness should reach the level of the wavelength of the light source, thirdly the film should be very smooth [42].

The thin film is made from CGG/ poly (carboxylic acids) and the refractive index of the thin film is about 1.50. The substrate is silicon and the refractive index of silicon is about 3.87. There exists an obvious refractive index contrast between the thin film and the substrate. If the film does not have optical interference, the reason could be that the film does not meet thickness requirement or the thin film is too rough. If the thin film is thinner than 200 nm, it will be difficult to observe the apparent oscillation in the visible spectrum. If the thin meets the thickness requirement but the thin film is very rough, the light scattering will suppress the optical interference. FT-IR spectra able to detect thinner thin film. The FT-IR spectra of the CGG/CMC and CGG/PAA prepared at different pHs are shown in Figure 3. At pH 2.5 or less for both systems and at pH ≥ 4.5 [(CGG/CMC)₃₀] and at pH ≥ 5 [(CGG/PAA)₃₀], IR signal of the CGG/CMC and CGG/PAA cannot be detected. The combined reflection and infrared data thus confirm that CGG/ poly (carboxylic acids) (CMC, PAA) deposit on silicon substrate as thin film.

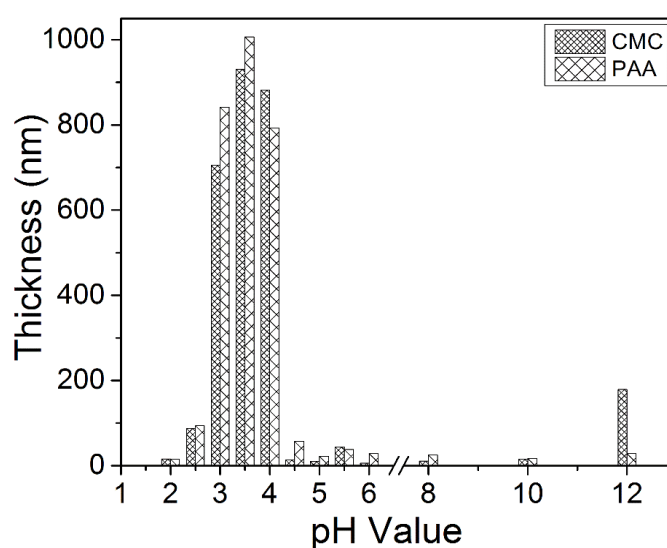


Fig. 2. The thickness of (CGG/ poly (carboxylic acids))₃₀ thin films prepared at different pH values.

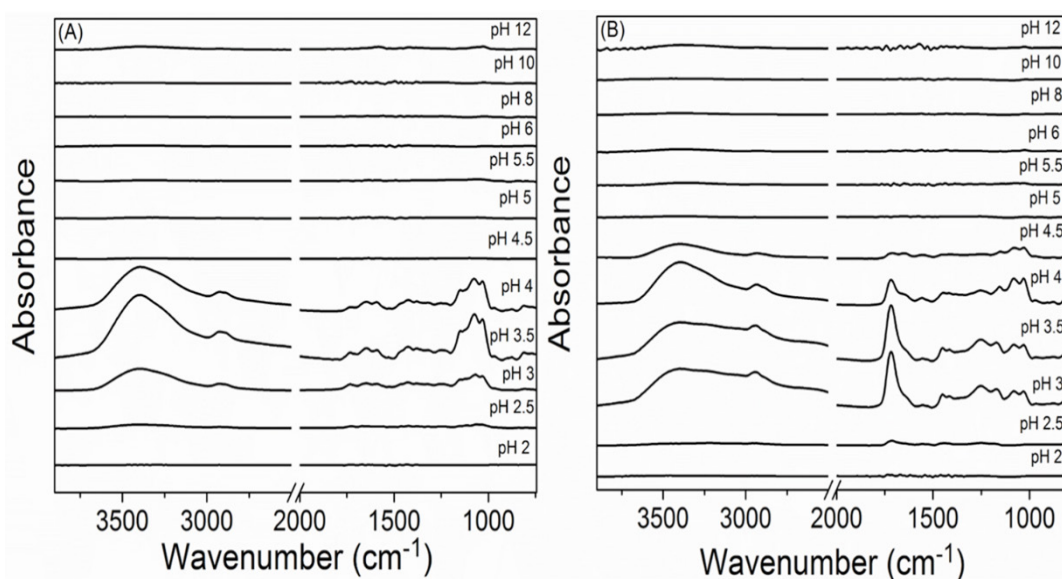


Fig. 3. The FT-IR spectra of CGG/ poly (carboxylic acids) thin films prepared at different pH values. (A) (CGG/CMC)₃₀; (B) (CGG/PAA)₃₀ (for clarity the spectra are intentionally offset).

pH is an important processing parameter for controlling thickness of LbL assembly film. It has been used to tune the assembly process of weak polyelectrolytes because pH affects their charge density and chain conformation via their degree of ionization. Since CGG is a strong polyelectrolyte, the influence of pH upon charge density is limited. In contrast CMC and PAA are weak polyelectrolytes. As the pH value of the solution increases, the degree of ionization of CMC and PAA and their charge density correspondingly increases. The charge density and chain conformation of CMC and PAA affects their interaction with CGG. It has been reported that FT-IR can be used to characterize the ionization degree of CMC [40] and PAA[43, 44] by using the following equation:

$$\delta = \frac{A_{COO^-}}{A_{COOH} + A_{COO^-}} \times 100\% \quad (2)$$

where δ is the degree of ionization of CMC and PAA, A_{COO^-} and A_{COOH} are the absorbances of COO⁻ and COOH, respectively. In acidic conditions, at pH 2.0 CMC shows 14 % ionization degree whereas the PAA exist in the nonionized form. When the pH higher than 8.0, the CMC is 100 % ionized, and at pH 9.5, the PAA is almost fully ionized. PAA is a vinyl polymer and its main chain is hydrophobic, whereas the main chain of CMC is hydrophilic. Being composed of glucose

rings, it has a higher hydration level than PAA. Conversely, the pH is an effective way to control the chain conformation of PAA.

As the ionization degree of poly (carboxylic acids) increases, their electrostatic interaction with CGG also increase, favors their complexation and thus their LbL assembly. Increasing further the pH, the hydration of CMC and CGG both change as well as chain conformation of PAA. At pH 2 or less than pH 2, the ionization degree of poly (carboxylic acids) are relatively low and CGG and poly (carboxylic acids) do not have enough electrostatic interaction to form the thin film. When the pH value of the solution increases, the electrostatic interaction strengthens and can overcome the hydration effect, so CGG and poly (carboxylic acids) can be LbL assembled. In the neutral pH value region and above, the hydration becomes dominated and poly (carboxylic acids) and CGG are hard to prepare the thin film.

It is known that the chain conformation has a significant influence on the multilayer growth because the extent of surface charge overcompensation is governed by the chain conformation on the surface. pH is an essential and effective way to control the chain conformation of polyelectrolyte but mainly for flexible polyelectrolytes such as PAA and PAH. CGG and CMC are semiflexible polyelectrolytes whereas PAA is flexible one. The chain conformations of CGG and CMC do not change much when the pH

value of the solution changes. In sharp contrast with the behavior of PAA. At lower pHs, only a few or none of the carboxyl groups of PAA are ionized, and they hydrogen bond between them: the chain has compact conformation. As pH increases, more carboxyl groups are ionized, the impact of intermolecular H bonding is reduced and the polymer chain expands. In short, when the pH shifts from low to high values, the PAA chains conformation shifts from compact to expand. Overall, this expansion explain the formation of a slightly thicker thin film prepared form CGG/PAA in compared to CGG/CMC at same pH value.

A QCM was used to monitor the CGG/ poly (carboxylic acids) films growth in Situ. QCM is a powerful techniques to follow the film formation process that further provides insights into their molecular composition. When a rigid layer is evenly deposited on one or both sides of the electrodes on the quartz crystal, its resonant frequency will decreases proportionally to the mass of the absorbed layer according to the Sauerbrey equation [45]:

$$\Delta m = -\frac{\rho_q l_q}{f_0} \frac{\Delta f}{n} = -C \frac{\Delta f}{n} \quad (3)$$

Where Δm is the mass increment, f_0 is the fundamental frequency, ρ_q and l_q are the specific density and thickness of the quartz crystal, respectively, C is the constant of the

resonant chip and n is the overtone number. Fig. 4 illustrates the variation during the assembly cycle. The frequency exhibit a large decrease, when CGG/CMC and CGG/PAA were deposited at pH 3.5, but a very small one at pH 7.0. Consistent with the Sauerbrey equation, at pH 3.5 the CGG/ poly (carboxylic acids) film growth is very fast, whereas at pH 7.0 growth is extremely slow, which is consistent with the results in Fig. 1 and Fig. 2. Applying the Sauerbrey equation ($C=17.7 \text{ ng/ Hz}^1\text{cm}^2$ and $n=3$) to these data indicates thatthe stable mass growth for CGG/PAA and CGG/CMC at pH 3.5 are 11.976 and 9.441 $\mu\text{g/ cm}^2$ per assembly cycle respectively. However, at pH 7.0, the mass growth for CGG/PAA and CGG/CMC are only 0.268 and 0.237 $\mu\text{g/ cm}^2$ per assembly cycle respectively.

Influence of Ionic Strength

Ionic strength is one of an important parameters governing the formation of polyelectrolyte multilayer films. The influence of ionic strength on film growth has been studied systematically, mostly for PEMs based on synthetic polyelectrolytes such as PSS/PDDAand PSS/PAH [46-48], and the film thickness was found increase with ionic strength [49, 50].

The thickness growth of polysaccharides thin film dependence on ionic strength differs from that of synthetic polyelectrolyte complex thin films. Lundin et al. have shown that the film thickness of chitosan (CHI)/heparin (HEP) increases with ionic strength [51]. Recent studies

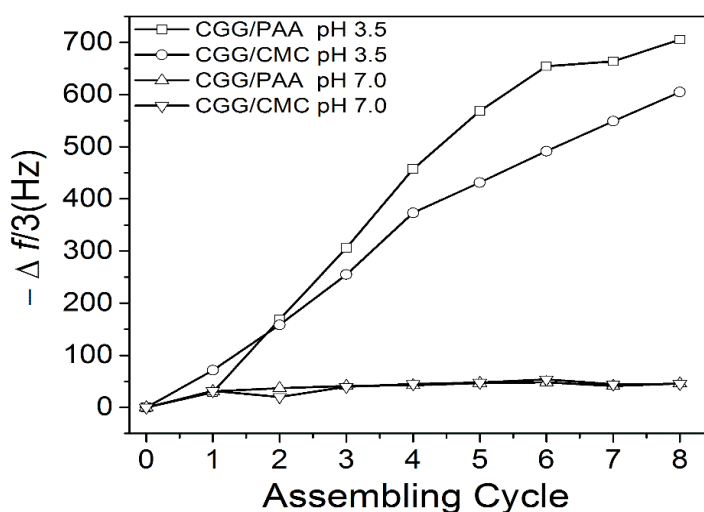


Fig. 4. The frequency shift of the CGG / poly (carboxylic acids) films as a function of assembly cycle.

have shown that, the thickness of poly (L-lysine) (PLL)/hyaluronan (HA) and Cationic starch/anionic starch film are increases initially with but decreases with higher ionic strength concentration [18, 52]. We also showed that the ionic strength dependence of the QC/CMC film thickness differs from that of synthetic polyelectrolyte complex thin films: With increasing the ionic strength, the growth becomes slow when adding 0.5 M NaCl, the thin film growth is almost hindered [40].

Generally speaking the growth of PEMs with ionic strength is governed by the weakening of electrostatic interaction between (a) identically charged groups in the same chain (b) between the adjacent layers. For synthetic polyelectrolyte complex films, as the ionic strength concentration increases the chains adopt a more coiled conformation because of the reduction of electrostatic between the similar charge groups along the same chain. But at high salt concentration more loops and tails are present at polymer/ solution interface, which enhances the extent chain interpenetration and a higher surface charge overcompensation, causing the multilayer to grow exponentially [49]. The effect of ionic strength on thickness grows in natural polyelectrolyte is dominated by weakening the electrostatic interaction between the neighboring layers at high salt concentration.

In the present study, CGG and poly (carboxylic acids) are deposited on silicon substrate at pH 3.5 with sodium chloride concentration ranging from 0.001 to 1 M. The FT-IR spectra of the films prepared at different sodium chloride concentration are display in Figure 5. The behavior of CGG/CMC and CGG/PAA are significantly when Concentration of NaCl from 0.001 M and 0.1 M. At higher NaCl concentration CGG/CMC shows no absorbance as shown in figure 5A, whereas a small signal remains for CGG/PAA from NaCl concentration ≥ 0.4 M as shown in figure 5B. These results indicate that the film formation follows two distinct regimes: significant film growth at low ionic strength, and virtually no CGG/CMC or very limited CGG/PAA as soon as NaCl concentration > 0.1 M.

The reflection spectra of the (CGG/ poly (carboxylic acids))₃₀ thin films were also recorded and are displayed in Figure 6. Only the thin film prepared at 0.001M or 0.01M, show strong oscillations in the reflection spectrum. However, the oscillations of CGG/PAA films significantly clearer than those off CGG/CMC once. Whereas the infra-red results would suggest that the CGG/PAA and CGG/CMC are comparable, the reflection spectra indicate that CGG/PAA films have much more regular organization thin film surface.

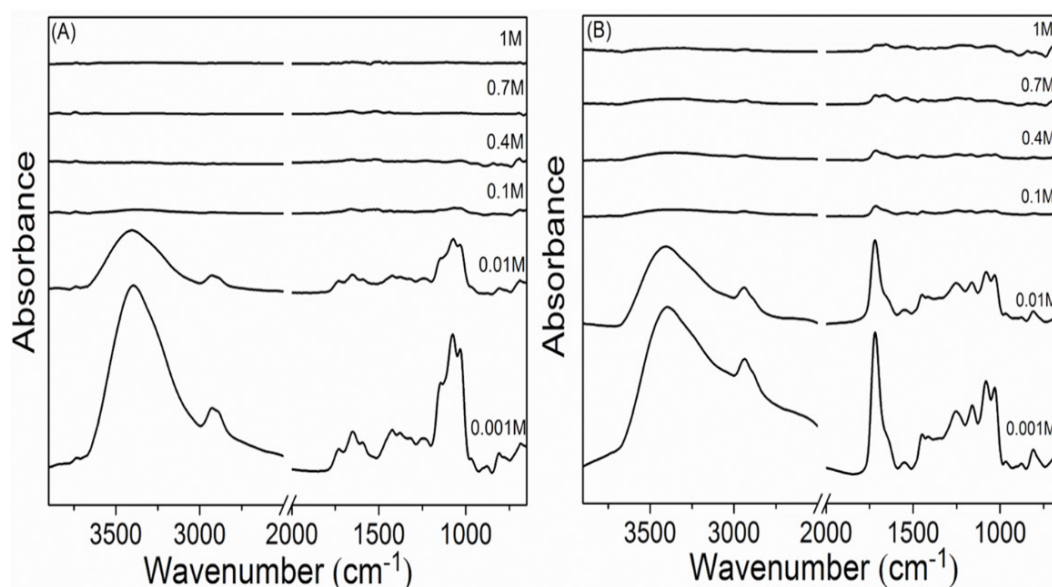


Fig. 5. (A) (CGG/CMC)₃₀ (B) (CGG/PAA)₃₀ (for clarity the spectra are intentionally offset).

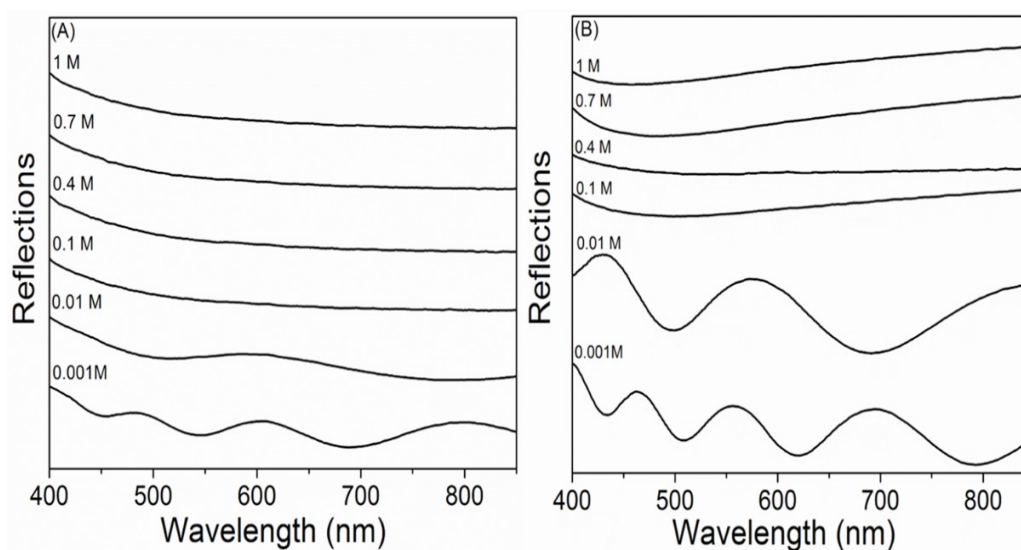


Fig. 6. Reflection spectra of the CGG/ poly (carboxylic acids) thin films prepared at pH 3.5 with adding different content of sodium chloride. (A) (CGG/CMC)₃₀ (B) (CGG/PAA)₃₀ (for clarity the spectra are intentionally offset).

Generally speaking, the polyelectrolyte conformation is determined by the total chain persistence length (L_p), which is a measure of effective chain rigidity of the polyelectrolyte. L_p expressed as [18, 53]:

$$L_p = L_0 + L_e \quad (4)$$

Where L_0 is the bare persistence length, corresponding to the rigidity of an uncharged chain L_0 is independent of the salt concentration [54], and the electrostatic persistence length L_e is given by the following equation [53]:

$$l_e = \frac{l_B \tau^2}{4k^2} \quad (5)$$

Where l_B is the Bjerrum length, τ is the linear charge density and k^{-1} is the Debye length [18, 54]. L_e is result from the electrostatic repulsion between identically charged groups from the same chain, since k^{-1} is inversely proportional to the square root of ionic strength, L_e depend on salt concentration [55]. At all ionic strength decrease, L_p results, contributions of L_0 and L_e . In other word as L_0 is constant L_p varies as L_e . At low salt concentration, L_e increase, which lead to increase L_p . Subsequently, the polyelectrolyte chains would adopt a more coiled conformation at polymer / solution interface with because the electrostatic repulsion between identically

charged groups becomes weaker, which favors the multilayer growth due to higher chain interpenetration surface charge overcompensation. In addition, the strength of electrostatic attraction between oppositely charged chains from the neighboring layers decreases with the increasing salt concentration, which unfavorable for the multilayer growth [18].

In the present case, the ionic strength impact on the interfacial complexation of CGG and poly (carboxylic acids) is similarly by (a) the delicate balance between the weakening of electrostatic repulsion between the identically charged groups and (b) the decrease of electrostatic attraction between neighboring layers. For CGG/CMC, at low salt concentration the growth of multilayer is dominated by the weakening of electrostatic repulsion between identically charged groups. When the salt concentration is ≥ 0.1 M, the L_e values of CMC and CGG decrease, and thus the contribution of L_e to L_p can be neglected. L_p would keep almost constant with salt concentration, therefore the chain conformation and the extent of surface charge overcompensation slightly change with ionic strength even though the electrostatic repulsion is gradually screened by the added salts. In contrast, with the increase of ionic strength, the electrostatic attraction between the neighboring layers is also screened, which is unfavorable for multilayer growth due to decreased of chain interpenetration. At high salt concentration the

effect weakening of electrostatic attraction on the multilayer dominates over that of the weakening of electrostatic repulsion.

The behavior of CGG/PAA at $C_{NaCl} \leq 0.4$ M is similar to that of CGG/CMC $C_{NaCl} \leq 0.1$ M. When the ionic strength is above 0.4 M the electrostatic persistence length L_e of CGG and PAA decrease, therefore the extent of surface charge overcompensation induced by the adsorption of CGG chains slightly changes with salt concentration. However the PAA chains adopt a more coiled conformation. A stronger surface charge overcompensation thus results with increasing ionic strength. It is also worth noting that the electrostatic attraction between neighboring layers always decreases with increasing ionic strength. Consequently, the growth of CGG/PAA at salt concentration above 0.4 M is prohibited.

For further evidence of the effects of salt on the complexation behavior of CGG and poly (carboxylic acids) (CMC and PAA), the CGG solution and the poly (carboxylic acids) solution were mixed at a 1:1 molar ratio with different ionic strength concentration. The solution turbidity, which can be used to evaluate the complexation behavior of polyelectrolyte. The mixed was measured with UV-visible

spectrometer. As shown in Figure 7. At low salt concentration, the solution is cloudy, which indicate the possibility to fabricate a thin film. When the salt concentration is higher than 0.1 M, the mixed solution becomes clear, which indicate solid-like polymer complexes are hard to form, and interfacial complexation is prohibited [56].

Influence of Temperature

Temperature, which changes the chain conformation of the polyelectrolyte in the solution. It modifies and thus can be used to control and adjust the thickness of LbL films produce with synthetic polyelectrolyte complexes or the hydrogen-bonded material. The thicknesses of the thin films in the present work are calculated based on Equation (1) and further confirmed by data fitting using the software of NanoCalc-10n. As shown in Figure 8, the thicker films are produced at higher temperatures investigated.

To further demonstrate the effect of temperature on the complexation behavior of CGG and poly (carboxylic acids), The FT-IR spectroscopy was applied to characterize the fabricated thin films at different temperatures. As shown in the Figure 9 FT-IR spectra indicate that at a temperature from 10 °C to 60°C, CGG and poly (carboxylic acids) are successfully transferred to the silicon substrate.

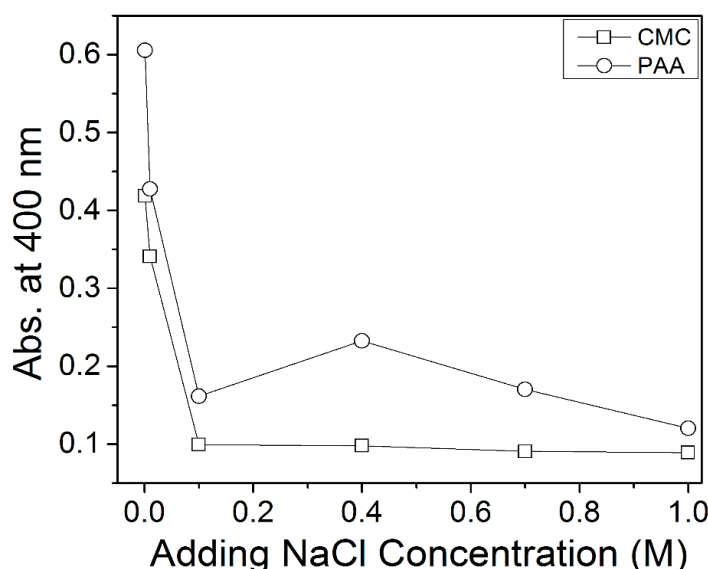


Fig. 7. Reflection spectra of the CGG/ poly (carboxylic acids) thin films prepared at pH 3.5 with adding different content of sodium chloride. (A) $(CGG/CMC)_{30}$ (B) $(CGG/PAA)_{30}$ (for clarity the spectra are intentionally offset).

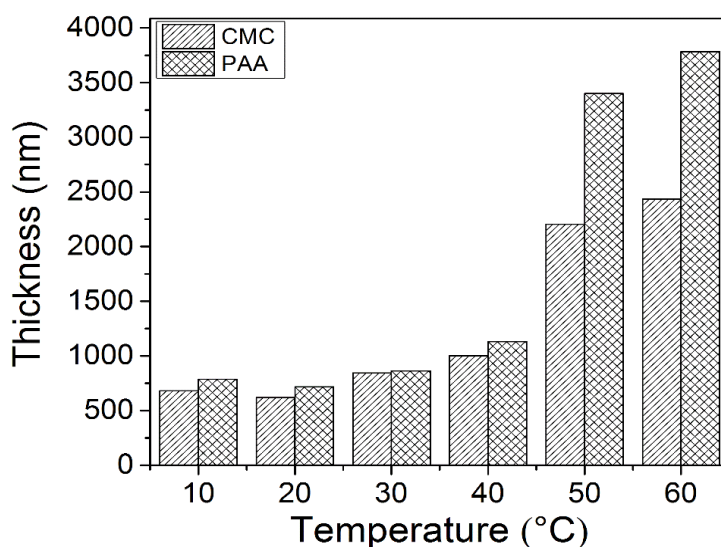


Fig. 8. Thickness of the (CGG/ poly (carboxylic acids))₃₀ thin films prepared at different temperature) and at pH 3.5.

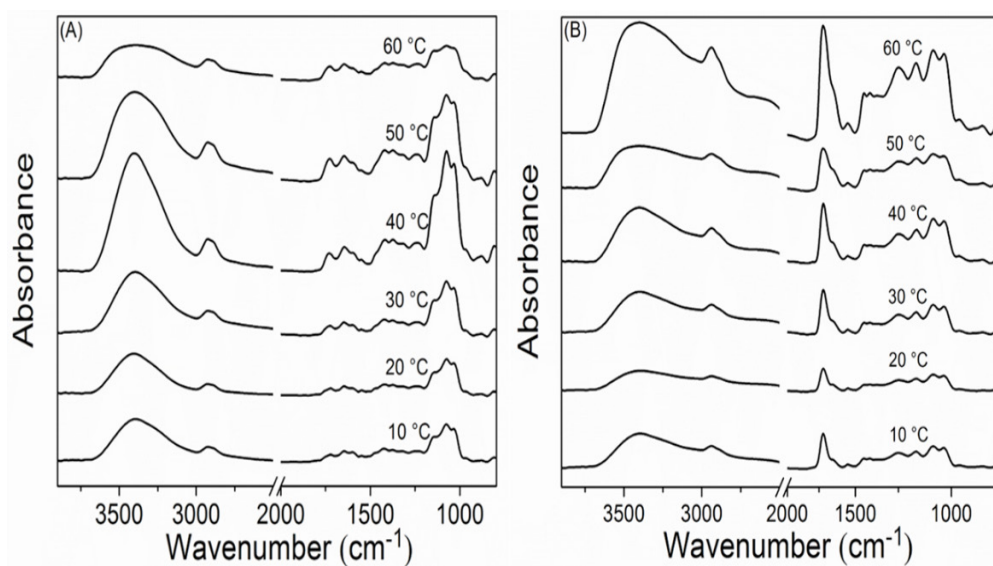


Fig. 9. The FT-IR spectra of the CGG/ poly (carboxylic acids) thin films prepared at pH 3.5 and at different temperatures. (A) (CGG/CMC)₃₀ (B) (CGG/PAA)₃₀ (for clarity the spectra are intentionally offset).

Tan et al. explored the temperature dependence of PSS/PDDA multilayers buildup in terms of film swelling and melting [57]. They suggested, that an increased temperatures result in an increased in tendency to send loops and tails into the solution, thus the film and providing the kinetic energy necessary to surmount the barriers to conformational changes. Salomaki et al. studied the effect of temperature on the buildup of

PEM systems made of PSS/PDDA and PSS/PAH pairs [58]. They observe that initial growth in the multilayer is independent of temperature and that high temperature the buildup regime changes from totally linear to partially exponential. Ma et al. investigated the effect of temperature of hydrogen-bonded films of poly (vinylpyrrolidone) PVPON/PAA. They confirmed that the PVPON/PAA thickness growth and cloudiness increases

significantly with temperature [59]. In our previous study on natural polyelectrolyte complex thin film. We also confirm that higher temperatures accelerate the thickness growth of the film [40].

Oppositely charged polyelectrolytes interact electrostatically and form complexes in a process that is promoted by an increase in entropy which is due to a release of counterions. It means that the entropy is positive and it can compensate the unfavorable enthalpy. Increasing temperature amplifies the entropy contribution and induces more negative free energy. From the thermodynamic view point, increasing temperature helps to form thin films. Very frequently, LbL assembly does not generate a "clean" laminated structure since interpenetration of layers occurs to some degree. For weak polyelectrolyte or hydrogen-bonded films, the level of interpenetration is significant as indicated by the strong polymer diffusion inside the film. Picart et al. put forward in- and out-diffusion mode to establish the mechanism of the exponential growth mode of the PLL/HA film [60]. There are two kinds of diffusion: diffusion from the solution to the interface, and polymer diffusion inside the film. From the faster kinetic, we observe that increasing temperature speeds up the diffusion.

Conclusion

The LbL assembly of CGG and poly (carboxylic acids) as exemplified in this study (CMC and PAA) are affected by hydration and electrostatic attraction. Their thin film growth can be controlled by the pH, ionic strength and temperature. As the temperature increases, the film growth is faster. We establish that the growth of thin films with ionic strength is determined by delicate balance between the weakening of electrostatic repulsion between the identically charged groups and the decrease of electrostatic interaction between the neighboring layers. Therefore, at low salt concentration CGG and poly (carboxylic acids) can be LbL-assembled, as the ionic strength increases, the film growth is gradually restricted. In neutral pH, high pH value and pH value less than 2.5, CGG and poly (carboxylic acids) do not assemble.

Acknowledgments

S. Y. gratefully acknowledges the support from National Natural Science Foundation of China (NSFC, Grant Nos. 51103022, 51373032), Science and Technology Commission of Shanghai Municipality (STCSM, Pujiang Talent Plan,

Grant No. 12PJ1400100), Innovation Program of Shanghai Municipal Education Commission, Fundamental Research Funds for the Central University and DHU Distinguished Young Professor Program.

References

- Huang Y., Yu H., Xiao C., pH-sensitive cationic guar gum/poly (acrylic acid) polyelectrolyte hydrogels: Swelling and in vitro drug release. *Carbohydrate Polymers*, **69**(4),774-783 (2007).
- Panchal B. P., Bhatt M. B., Patel N. N., Patel G., Bhimani B., Patel D.U., Emerging Natural Polymer Used in Floating Drug Delivery System *International Journal of Pharmaceutical Research and Bio-Science*, **3**(1), 237-251 (2014).
- Behari K., Kumar R., Tripathi M., Pandey P. K., Graft Copolymerization of Methacrylamide onto Guar Gum Using a Potassium Chromate/Malonic Acid Redox Pair. *Macromolecular Chemistry and Physics*,**202**(9),1873-1877 (2001).
- Wan X., Li Y., Wang X., Chen S., Gu X., Synthesis of cationic guar gum-graft-polyacrylamide at low temperature and its flocculating properties. *European Polymer Journal*, **43**(8), 3655-3661(2007).
- Dodi G., Hritcu D., Popa M. I., Carboxymethylation of Guar Gum: Synthesis and Characterization. *Cellulose Chemistry and Technology*, **45**(3-4), 171-176(2011).
- Tripathy S., Das M.K., Guar Gum: Present Status and Applications. *Journal of Pharmaceutical and Scientific innovation*, **2**(4), 24-28(2013).
- Gittings M. R., Cipelletti L., Trappe V., Weitz D. A., In M., Marques C., Structure of Guar in Solutions of H₂O and D₂O: An Ultra-Small-Angle Light-Scattering Study. *The Journal of Physical Chemistry B*, **104** (18) 4381-4386(2000).
- Mudgil D., Barak S., Khatkar B., Guar gum: processing, properties and food applications—A Review. *Journal of Food Science and Technology*, **51** (3), 409-418(2014).
- Sharma R., Guar Gum Grafting and Its Application in Textile. *Asian Journal of Experimental Sciences*,**19** (2), 77-81(2005).
- Chudzikowski R. J., Guar gum and its applications. *Journal of The Society of Cosmetic Chemistry*, **22** (1), 43-60(1971).

11. Nemade I. D., Green Biopolymer Guar Gum and its Derivatives. *International Journal of Pharma and Bio Sciences*, **4** (3), 423-435(2013).
12. Olatunde A. O., Usman M. A., Olafadehan O. A., Adeosun T. A., Ufot O. E., Improvement of Rheological Properties of Drilling Fluid Using Locally Based Materilas. *Petroleum & Coal*, **54** (1), 65-75 (2012).
13. Priyadarsini M., Biswwal T., Recent Progress on the Design and Applications of Guar Gum based Nano hydrogel "Guar Gum-g-P(HEMA-co-AM)/Chicken Egg shell" as Superabsorbent. *Egyptian Journal of Chemistry*, DOI: 10.21608/EJCHEM.2019.11081.1711
14. Kadajji V. G., Betageri G. V., Water Soluble Polymers for Pharmaceutical Applications. *Polymers*, **3** (4), 1972-2009(2011).
15. PankagW., Sushikumari P., Amol M., Guar Gum: A Potential Hydrocolloid, *An International Journal of Advances in Pharmaceutical Sciences*, **1**(2), 157-166(2010).
16. Decher G., Hong J.D., Schmitt J., Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces. *Thin Solid Films*, **210-211**(0), 831-835(1992).
17. Decher G., Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. *Science*, **277**(5330), 1232-1237(1997).
18. Wu B., Li C., Yang H., Liu G., Zhang G., Formation of Polyelectrolyte Multilayers by Flexible and Semiflexible Chains. *The Journal of Physical Chemistry B*, **116**(10), 3106-3114(2012).
19. Hoshi T., Saiki H., Kuwazawa S., Tsuchiya C., Chen Q., Anzai J., Selective Permeation of Hydrogen Peroxide through Polyelectrolyte Multilayer Films and Its Use for Amperometric Biosensors. *Analytical Chemistry*, **73**(21), 5310-5315(2001).
20. Nolte A. J., Rubner M. F., Cohen R. E., Creating Effective Refractive Index Gradients within Polyelectrolyte Multilayer Films: Molecularly Assembled Rugate Filters. *Langmuir*, **20** (8), 3304-3310(2004).
21. Bertrand P., Jonas A., Laschewsky A., Legras R., Ultrathin polymer coatings by complexation of polyelectrolytes at interfaces: suitable materials, structure and properties. *Macromolecular Rapid Communications*, **21** (7), 319-348(2000). *Egypt.J.Chem.* **63** , No.8 (2020)
22. Boulmedais F., Frisch B., Etienne O., Lavallo P., Picart C., Ogier J., Voegel J. C., Schaaf P., Egles C., Polyelectrolyte multilayer films with pegylated polypeptides as a new type of anti-microbial protection for biomaterials. *Biomaterials*, **25** (11), 2003-2011(2004)
23. Boudou T., Crouzier T., Ren K., Blin G., Picart C., Multiple Functionalities of Polyelectrolyte Multilayer Films: New Biomedical Applications. *Advanced Materials*, **22** (4), 441-467 (2010).
24. Liu W. C., Wang H. Y., Wang A. N., Tseng C. H., Liu H. L., Chung R. J., Preparation of Chitosan/Poly(γ -Glutamic Acid Polyelectrolyte Multilayers on Biomedical Metals for Local Antibiotic Delivery. *metals*, **7**(10), 418-429(2017).
25. Liu X., Han W., Zhu Y., Xuan H., Ren J., Zhang J., Ge L., Anti-Oxidative and Antibacterial Self-Healing Edible Polyelectrolyte Multilayer Film in Fresh-Cut Fruits. *Journal of Nanoscience and Nanotechnology*, **18**(4), 2592-2600(2018).
26. Stockton W. B., Rubner M. F., Molecular Level Processing of Conjugated Polymers 4 Layer- by-Layer Manipulation of Polyaniline via Hydrogen-Bonding Interactions. *Macromolecules*, **30** (9), 2717-2725(1997).
27. Sukhishvili S. A., Granick S., Layered, Erasable Polymer Multilayers Formed by Hydrogen-Bonded Sequential Self-Assembly. *Macromolecules*, **35** (1), 301-310 (2001).
28. Takemoto Y., Ajiro H., Akashi M., Hydrogen-Bonded Multilayer Films Based on Poly(N-vinylamide) Derivatives and Tannic Acid. *Langmuir*, **31**(24), 6863-6869(2015).
29. Liu X., Wen N., Wang X., Zheng Y., Layer-by-Layer Self-Assembled Graphene Multilayer Films via Covalent Bonds for Supercapacitor Electrodes. *Nanomaterials and Nanotechnolog*, **5**(14), 141-147(2015).
30. Mwaura J. K., Thomsen D. L., Phely-Bobin T., Taher M., Theodoropoulos S., Papadimitrakopoulos F., Luminescent Rare-Earth Multilayer Chelates from Segmented Poly(urethane ureas). *Journal of the American Chemical Society*, **122**(11), 2647-2648(2000).
31. Zhang Y., Cao W., Stable Self-Assembled Multilayer Films of Diazo Resin and Poly(maleic anhydride-co-styrene) Based on Charge-Transfer Interaction. *Langmuir*, **17**(16), 5021-5024(2001).
32. Serizawa T., Hashiguchi S., Akashi M., Stepwise

- Assembly of Ultrathin Poly(vinyl alcohol) Films on a Gold Substrate by Repetitive Adsorption/Drying Processes. *Langmuir*, **15**(16), 5363-5366 (1999) .
33. Iqbal D. N., Hussain E. A., Naz N., Synthesis and Characterization of Guar Gum Derivatives with Antioxidant Moieties. *International Journal of Pharma and Bio Sciences*.**4**(4), 305-316 (2013).
34. Pal S., Carboxymethyl guar: Its synthesis and macromolecular characterization. *Journal of Applied Polymer Science*, **111**(5), 2630-2636(2009).
35. Jana P., Sarkar K., Mitra T., Chatterjee A., Gnanamani A., Chakraborti G., Kundu P. P., Synthesis of a carboxymethylated guar gum grafted polyethyleneimine copolymer as an efficient gene delivery vehicle. *RSC Advances*, **6**(17), 13730-13741(2016).
36. Risica D., Dentini M., Crescenzi V., Guar gum methyl ethers. Part I. Synthesis and macromolecular characterization. *Polymer*,**46**(26), 12247-12255(2005).
37. Singh M., Tiwary A. K., Kaur G., Investigations on interpolymer complexes of cationic guar gum and xanthan gum for formulation of bioadhesive films. *Research in pharmaceutical sciences*,**5** (2),79-87(2010).
38. Sandeep C., Deb T. K., Moin A., Shivakumar H., Cationic guar gum polyelectrolyte complex micro particles. *Journal of Young Pharmacists*,**6**(4), 11-19(2014).
39. Wu B, Liu G, Zhang G., Craig V J, Stiff chains inhibit and flexible chains promote protein adsorption to polyelectrolyte multilayers. *Soft Matter*, 2014, 10: 3806-3816.
40. Shibraen M., Wang C., Yagoub H., Yuan Q., Yang S., Xu J., Interfacial complexation behavior of anionic and cationic cellulose derivatives. *RSC Advances*, **4**(98), 55459-55465(2014).
41. Yang S., Zhang Y., Wang L., Hong S., Xu J., Yongming C., Chengming L., Composite Thin Film by Hydrogen-Bonding Assembly of Polymer Brush and Poly(vinylpyrrolidone). *Langmuir*, **22** (1), 338-343(2006).
42. Yang S., Tan S., Zhang Y., Xu J., Zhang X., Fabry-Pérot fringes of hydrogen-bonded assembly films. *Thin Solid Films*,**516** (12), 4018-4024(2008).
43. Yang S., Zhang Y., Zhang X., Xu J., The influence of pH on a hydrogen-bonded assembly film. *Soft Matter*,**3**(4), 463-469(2007).
44. Choi J., Rubner M.F., Influence of the Degree of Ionization on Weak Polyelectrolyte Multilayer Assembly. *Macromolecules*, **38**(1), 116-124(2005).
45. Sauerbrey G Z. Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. *Zeitschrift für Physik*, **155**(2), 206-222(1959).
46. Dubas S. T., Schlenoff J. B., Factors Controlling the Growth of Polyelectrolyte Multilayers. *Macromolecules*,**32**(24), 8153-8160(1999).
47. Steitz R., Leiner V., Siebrecht R., Klitzing R., Influence of the ionic strength on the structure of polyelectrolyte films at the solid/liquid interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **163**(1), 63-70(2000).
48. McAloney R. A., Sinyor M., Dudnik V., Goh M. C., Atomic Force Microscopy Studies of Salt Effects on Polyelectrolyte Multilayer Film Morphology. *Langmuir*,**17**(21), 6655-6663(2001).
49. Liu G., Zou S., Fu L., Zhang G., Roles of Chain Conformation and Interpenetration in the Growth of a Polyelectrolyte Multilayer. *The Journal of Physical Chemistry B*,**112**(14), 4167-4171(2008).
50. Guzman E., Ritacco H., Rubio J., Rubio R. G., Ortega F., Salt-induced changes in the growth of polyelectrolyte layers of poly(diallyldimethylammonium chloride) and poly(4-styrene sulfonate of sodium). *Soft Matter*,**5**(10) 2130-2142(2009).
51. Lundin M., Solaqa F., Thormann E., Macakova L., Blomberg E., Layer-by-Layer Assemblies of Chitosan and Heparin: Effect of Solution Ionic Strength and pH. *Langmuir*,**27**(12) 7537-7548(2011).
52. Mjahed H., Cado G., Boulmedais F., Senger B., Schaaf P., Ball V., Voegel J.C., Restructuring of exponentially growing polyelectrolyte multilayer films induced by salt concentration variations after film deposition. *Journal of Materials Chemistry*,**21**(23) 8416-8421(2011).
53. Dobrynin A., Electrostatic Persistence Length of Semiflexible and Flexible Polyelectrolytes. *Macromolecules*,**38**(22), 9304-9314(2005).
54. Schönhoff M., Layered polyelectrolyte complexes: physics of formation and molecular properties. *Journal of Physics: Condensed Matter*,**15**(49), R1781-R1808(2003).
55. Solomon T., The Definition and Unit of Ionic

- Strength. *Journal of Chemical Education*, 2001, **78**(12), 1691-1692(2001).
56. Sukhishvili S. A., Kharlampieva E., Izumrudov V., Where Polyelectrolyte Multilayers and Polyelectrolyte Complexes Meet. *Macromolecules*, **39**(26), 8873-8881(2006).
57. Tan H. L., McMurdo M. J., Pan G., Van Patten P. G., Temperature Dependence of Polyelectrolyte Multilayer Assembly. *Langmuir*, **19**, 9311-9314 (2003).
58. Salomäki M., Vinokurov I. A., Kankare J., Effect of Temperature on the Buildup of Polyelectrolyte Multilayers. *Langmuir*, **21**(24), 11232-11240 (2005).
59. Ma J., Yang S., Li Y., Xu X., Xu J., Effect of temperature on the build-up and post hydrothermal processing of hydrogen-bonded PVPON/PAA film. *Soft Matter*, **7**(19), 9435-9443 (2011).
60. Picart C., Mutterer J., Richert L., Luo Y., Prestwich G. D., Schaaf P., Voegel J. C., Lavalle P., Molecular basis for the explanation of the exponential growth of polyelectrolyte multilayers. *Proceedings of the National Academy of Sciences*, **99**(20), 2531-12535 (2002).

قيمت الدراسة الحالية إمكانية تشكيل طبقة رقيقة من صمغ الغوار الكاتيوني (CGG) المرتبط بالبولي (حمض الكربوكسيل) مثل كربوكسي ميثيل السليلوز (CMC) وبولي (حمض الأكريليك) (PAA) بواسطة تجميع طبقة تلو طبقة (LbL). يُظهر سمك ومورفولوجيا الطبقة الرقيقة بأنها تعتمد على متغيرات محلول البوليمر مثل الرقم الهيدروجيني وتركيز القوة الأيونية ودرجة الحرارة. نجد أنه عند قيمة أس الهيدروجيني تتراوح من 3 إلى 4 تم تجميع وتشكيل طبقة رقيقة من صمغ الغوار الكاتيوني. أما بالنسبة لمنطقة الأس الهيدروجيني المحايدة وقيم الأس الهيدروجيني العالية نجد أنه لا يوجد تفاعل بين (CGG) المرتبط بالبولي (حمض الكربوكسيل). على النقيض من الأغشية الرقيقة المعقدة متعددة الإلكتروليت الاصطناعية، مثل سلفات البوليسترين/ (PSS) بولي (كلوريد الديال إيثيل الأمونيوم) (PDDA) (وأبضا بولي (هيدروكلوريد الأليامين) (PSS) PAH) /، نجد أن تجمع LbL المتكون من (CGG) المرتبط بالبولي (حمض الكربوكسيل) يتكون عند استخدامه تركيزات منخفضة من الملح. من ناحية أخرى يؤدي الترسيب عند درجة حرارة عالية (حتى 60 درجة مئوية) إلى إنتاج أفلام بين (CGG) المرتبط بالبولي (حمض الكربوكسيل) أكثر سمكا.