

Assembly of Polyelectrolyte Multilayers on Nylon Fibers

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ABSTRACT: Non-woven nylon fibers were investigated as a new type of substrate for the deposition of polyelectrolyte multilayers (PEM) thin films. PEM assembled from cationic poly(diallyldimethylammonium chloride) PDADMAC, and anionic Scarlet dye (λ_{\max} absorbance = 510 nm) were deposited directly on Nylon fibers and characterized using a reflectometer spectrophotometer. Evidences of the film assembly are presented as well as a study of the factors controlling the growth of the PDAMAC/dye PEM film on the fiber. The relation between the sorption coefficient (K) and the scattering (S) extracted from the reflectance data is commonly used to represent the dye fixation or the dye content of a given textile fiber. The increase in K/S value at 510 nm was correlated with the dye deposition and was found to increase linearly with the number of layers. The

effect of increasing number of layers, ionic strength of the solutions, concentration of chemicals, and dipping time on the film growth was investigated. Our results show that while increase in dye and PDADMAC concentrations from 0 to 1 mM enhance the deposition process, further increase in PDADMAC concentration to 50 mM led to a decrease in K/S value. The optimum salt concentration for the PDAMAC/dye film growth was found to be 0.5M and dipping times as short as 15 s were found to be sufficient for the deposition of the PEM. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3286–3290, 2006

Key words: polyelectrolyte; multilayers; coating; nylon; fiber

INTRODUCTION

The surface modification and finishing of textile fibers is a widely used method to improve the quality and properties of fabrics.^{1,2} A variety of chemicals, including polyelectrolytes, are used as finishing agents for their antiwrinkle, color fastness, light fastness, or even antimicrobial properties.^{3–6} Polyelectrolytes can be easily deposited on textile fibers by taking advantage of the electrostatic nature of some natural fibers such as silk or wool. For instance, carboxylic groups present at the surface of wool fibers permit, under certain conditions, the deposition of oppositely charged polycationic chitosan.⁷ The resulting modified fabric possesses the antimicrobial and antiwrinkle properties provided by the chitosan coating. Neutral fibers can also be coated but require chemical modification, etching, or grafting of the desired functional group onto the fibers.^{8,9} Because of an always-increasing need for environment-friendly production methods, more research is needed to develop the use of “green chemi-

cal” such as biocompatible polyelectrolytes to be used as finishing agent for textile fabric.¹⁰

While polyelectrolytes are widely used in several industrial applications, the last decade has seen the development of the polyelectrolyte multilayers (PEM) technique as a method of choice for the preparation of polymer thin films.^{11,12} PEM, with a thickness often in the range of few tens of nanometers, have led to a large range of applications such as superhydrophobic, antimicrobial, catalytic, or luminescent coatings.^{13–16} In most of these studies, the PEM films were deposited on flat substrates including silicon, metals, glass, or quartz slides.^{17,18} In more elaborate assemblies, sub-micron particles were used as sacrificial templates for the preparation of nanocapsules to be used in targeted drug delivery applications.^{19,20} Only recently, Hinstroza et al.²¹ have demonstrated that it was possible to deposit PEM directly onto a cotton fabric by successive dipping in oppositely charged polyelectrolyte solutions. Using the X-ray photoelectron spectroscopy (XPS) technique, they have demonstrated that the ratio of nitrogen to sulfur present at the surface of the cotton fabric varies with successive deposition of either poly(allylamine hydrochloride) or poly(sodium 4-styrene sulfonate) polyelectrolyte layers. Moreover, using transmission electron microscopy (TEM) they have shown the uniform coating provided by the PEM

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onto the cotton fabric. It seems possible that by following the same PEM deposition method, a wide range of molecules, nanoparticles, and other functionalized polyelectrolyte could be deposited on textile fabric leading to the development of new applications for technical textile. In this article, we have investigated the deposition of PEM thin films directly onto the textile fiber before being woven into textile cloth. The pre-coating of the fibers will allow the preparation of fabrics coated with different kind of PEM each of them bringing new properties to the finished product. One can imagine the design of woven fabrics containing fibers coated with antimicrobial film and other coated with nanoparticles, which could be assembled together into one single piece of cloth.

In this study, we chose to use Nylon instead of natural fibers to demonstrate that the PEM assembly is not limited to a certain type of fibers and can potentially be applied to a wide range of natural as well as low charge density synthetic fibers. For the PEM constituents, we chose to use cationic poly(diallyldimethylammonium chloride) (PDADMAC), and anionic Scarlet red dye, which presents a strong absorbance at 510 nm to be able to use reflectance spectrophotometry to monitor the layer-by-layer deposition. Evidences of the possible deposition of a dye-based PEM directly onto nylon fibers are given as well as a study of the parameters controlling the growth of the film. The effect of the number of layers, ionic strength of the solution, concentration of the constituents, and dipping time on the deposition of PEM was also investigated.

EXPERIMENTAL

Materials

The Scarlet G (C.I. Acid A.R. 97) was provided by the Department of Materials Science, Chulalongkorn University, Bangkok, Thailand. Poly(diallyldimethylammonium chloride) (PDADMAC) $M_w = 200,000$ – $350,000$ was purchased from Aldrich. Solutions of various pH between 3 and 7 were prepared by mixing the appropriate amount of acetic acid with sodium acetate salt and 1M sodium hydroxide solution was used to adjust the pH to 11. Analytical grade sodium chloride residue less than 0.1% was purchased from Aldrich. Nylon 6 fibers (partially oriented yarn: no twist) ref : POY 88D/24F lot 38 were donated by Asia Fiber Company, Bangkok, Thailand. All chemicals, solvents, and nylon fibers were used as received without any further purification or treatment.

Deposition of the PEM on nylon fibers

Nylon fibers were wrapped around a rectangular aluminum holder ($2.5 \times 3.5 \text{ cm}^2$) and spun in various

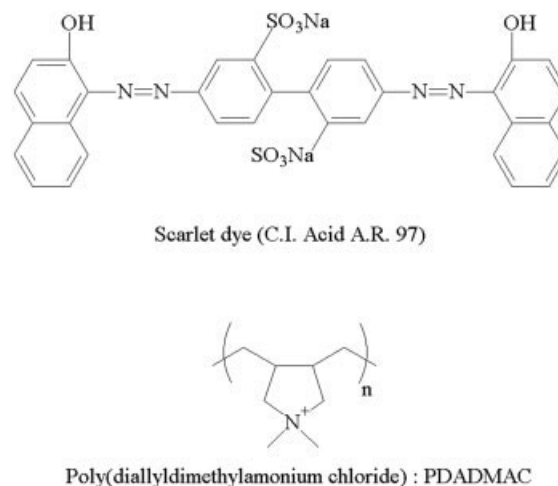


Figure 1 Chemicals used for the build-up of the polyelectrolyte multilayers.

solutions using a small dc motor. A home-built robotic platform, accommodating eight 100-mL beakers, was programmed to successively expose the fibers to either polyelectrolyte or Scarlet dye solutions followed by three water rinses of 1 min each as many times as the number of layer needed. At the end of the deposition process, the samples were allowed to dry overnight and then were wrapped on a plastic holder before analysis with a spectrophotometer. In a typical experiment setup, the PEMs were composed of 20 layers by alternatively dipping the nylon fiber in 1 mM PDADMAC and 0.5 mM dye solution for 30 s. The ionic strength of the solution was adjusted to 0.1M NaCl and the pH of all solution was set to 11. In our study, the number of layers was varied from 4, 8, 12, 16, 20, 30, and 40 and the ionic strength of the solutions was varied from 0M to 1M NaCl. The effects of increasing PDADMAC concentration from 0.001 mM to 50 mM, and dye concentration from 0.005 mM to 50 mM were also studied. Finally, we investigated the effect of the dipping time on the deposition process by varying the time of exposure of the fiber to PDADMAC and dye from 15 s to 5 min.

Spectrophotometric analysis

The increase in absorbance at 510 nm of nylon fibers was monitored using a reflectance spectrophotometer. The nylon fibers after being coated with the dye containing PEM were wrapped onto a holder and analyzed using an ICS Macbeth Color Eye® 7000 spectrophotometer. The instrument analyzes the light being reflected from the sample and produces an absorption spectrum. The ratio between the sorption coefficient (K) and the scattering (S) can be extracted from the reflectance data using eq (1) where R is the reflectance of the fabric at 510 nm. The K/S value is commonly

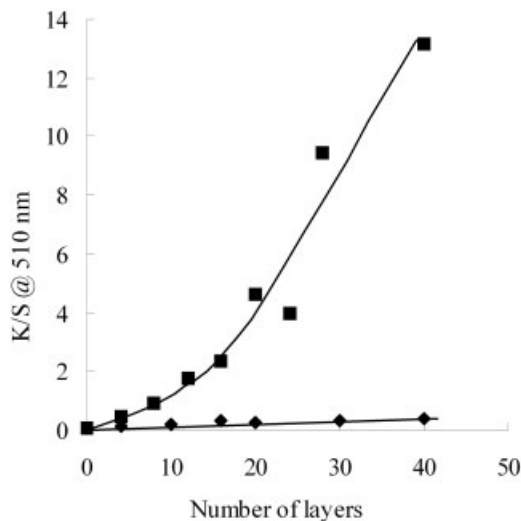


Figure 2 K/S value of the nylon fiber as a function of the pH of the Scarlet dye bath. The nylon fibers were dipped for 1 h in a 0.5 mM dye solution, rinsed three times in pure water and let dried overnight before measurements.

used to represent the amount of dye fixation or dye content of a given textile fiber. We can therefore, use the increase of the K/S value as a characteristic of the layer by layer deposition of the dye on the nylon fiber. The measurement parameters of the spectrophotometer were selected as follow: 10° from the observer, D65 illuminant, specular and UV-vis reflectance included. The reflectance of the coated fiber was measured in the 360–750 nm range and the K/S values were instrumentally determined from the reflectance measurements. Since the Scarlet dye presents a maximum absorbance at 510 nm, the K/S values were determined at this wavelength.

$$K/S = \frac{(1-R)^2}{2R} \quad (1)$$

RESULTS AND DISCUSSION

PEM growth on nylon fiber

In our study, among the different types of fibers, we chose to use nylon as substrate for the PEM deposition. This choice was motivated by the need of a fiber, which, under certain pH conditions, would not directly absorb the dye during the PEM buildup. Figure 2 shows the K/S value of the nylon fibers when dipped in a solution of Scarlet dye with pH values ranging from 3 to 12. Since lower K/S value corresponds to lower dye content or dye fixation, it can be seen that the amount of absorbed dye decrease as a function of pH. This decrease is due to the appearance of intrinsic negative charges at the surface of the nylon fiber at high pH from the deprotonation of the carbox-

ylic ending groups, which tend to repel the anionic Scarlet dye. This switch from positive surface charge to negative as a function of the pH has been reported in several studies and confirmed by zeta potential measurements.^{22,23} As a result of this effect, we can see that for solution having a pH above 9, a minimal amount of dye sticks to the fiber.

PEM thin films of Scarlet dye and PDADMAC (Fig. 1) were built by following the layer-by-layer deposition method described earlier. Pictures of the nylon fibers coated with 4, 8, 12, 20, 30, and 40 PEM layers are shown in Figure 3 where the increase in color can be seen as a result of the PDADMAC/dye PEM film growth. Figure 3 (curve A) shows the corresponding K/S value of the nylon fiber as a function of the number of deposited layers. For the initial 10 layers, a nonlinear growth can be observed, which is typical of the PEM deposition process and is explained elsewhere as a wall effect of the substrate limiting the diffusion of the polyelectrolytes.²⁴ Nevertheless, as expected for higher number of layers, the deposition process displays a linear relationship between the K/S value and number of layers, which is characteristic of the PEM growth. Up to 40 layers were deposited resulting in a strongly colored Nylon fiber. To confirm that the color was only due to the PEM buildup and not to the natural absorption of the dye in the fibers, we repeated the same experiment but we replaced the beaker containing the PDADMAC solution by a beaker containing pure water. As seen in Figure 3 curve B, no increase in K/S was observed when increasing the number of dipping steps. From these experiments we can conclude that the dye could not be absorbed onto

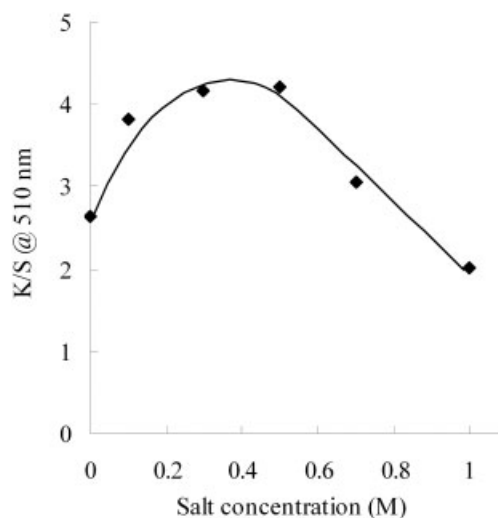


Figure 3 K/S value as a function of the number of PDADMAC-Dye layer (A), and number of dye layers (B). The sample was successively dipped in 1 mM PDADMAC or 0.5 mM dye solutions and the dipping time was set to 30 s followed by three rinses of 20 s each in pure water. The pH of each solution was adjusted to 11.

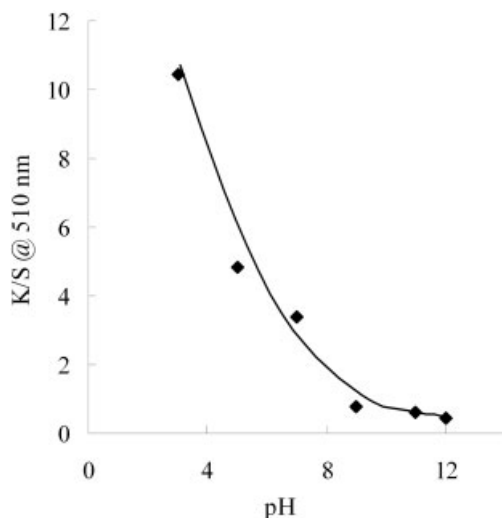


Figure 4 K/S value of the nylon fiber as a function of the ionic strength in the polyelectrolyte and dye solutions.

the fiber by itself and that the coloring of the fiber only occurs with the deposition of the PEM on the nylon fiber. These results strongly suggest that other type of PEM could be similarly deposited onto nylon or other textile fibers. As mentioned previously, the weaving of fibers coated with different type of PEM could open the way to interesting composite-coating fibers assembly.

Factors controlling the growth of PEM on nylon

After giving evidences of the possible PDADMAC/dye PEM deposition, we studied the effect of changing the experimental parameters on the growth of the film. First, the effect of the salt concentration on the PEM's growth was investigated by changing the ionic strength of the PDADMAC and dye solution from 0 to 1M NaCl (Fig. 4). The increase in K/S value with increasing NaCl concentration from 0 to 0.5M NaCl is due to enhancement of the deposition process by the salt present in solution. The effect of the salt ions is to screen the repulsive forces between polyelectrolyte as well as increase in diffusion through the PEM film as it has been reported elsewhere.^{25,26} Further increase in salt concentration to 1M led to a sharp decrease in K/S value. This decrease is due to the appearance of some precipitates of the dye in the solution, which prevents the dye from sticking to the PDAMAC and therefore limits the PEM growth.

The effect of the dye or PDADMAC concentration on the K/S value is presented in Figure 5. The dye and PDADMAC concentrations were increased from 0.005 to 50 mM and 0.001 to 50 mM, respectively. When the concentration of one constituent was varied, the concentration of the other was kept fixed at 1 mM for the PDAMAC and 0.5 mM for the dye solution. The curve

A represents the change in K/S value as a function of the dye concentration with fixed PDADMAC concentration. The change in slope after 0.5 mM suggests that the effect of increasing dye concentration is maximum between 0.005 mM and 0.5 mM and leads to an increase in K/S value of 2 orders in magnitude. Further increase from 0.5 to 50 mM of the dye concentration only increases the K/S value of 10%. Shown on curve B, the change in K/S value as a function of increasing PDADMAC concentration presents a much different behavior. The K/S value of the fiber increases with the PDADMAC concentration up to 1 mM but further increase of the PDADMAC concentration leads to decrease in K/S value. This decrease is to be correlated with the appearance of a red coloration in the PDADMAC solution due to the release of dye molecules from the fiber into the solution. This desorption phenomenon has already been reported by Schlenoff and coworkers²⁷ and is due to the molecular weight (M_w) mismatch between PDADMAC ($M_w = 300,000$) and the Scarlet dye ($M_w = 648$). In their work, they have demonstrated that during the PEM assembly, when two polyelectrolytes have very different molecular weight, the higher M_w polyelectrolyte is able to strip off the absorbed low M_w species from the surface, which prevents the PEM growth. In our system, the high M_w PDADMAC is able to strip the low M_w Scarlet dye from the surface leading to the red coloring of the PDADMAC solution.

Lastly, the effect of the dipping time on the overall PEM deposition was investigated. Nylon fibers were dipped in polyelectrolyte and dye solutions for time ranging from 15 s to 5 min. The results shown in Figure 6 demonstrated that dipping times as short as 15 s are sufficient to obtain a maximum deposition of

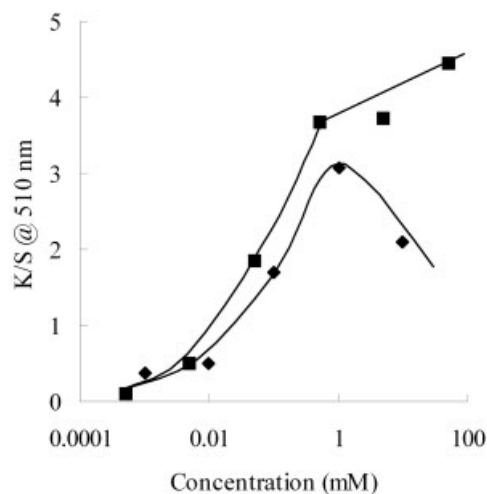


Figure 5 K/S value of the nylon fiber for increasing dye concentration (curve A ■) with fixed PDADMAC at 1 mM and increasing PDADMAC concentration (curve B ◆) with fixed dye concentration at 0.5 mM

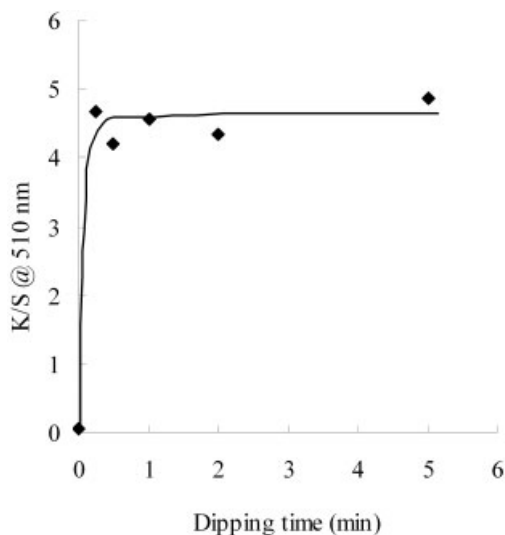


Figure 6 K/S value of the nylon fiber as a function of the dipping time of the fibers in the PDADMAC and the dye solutions.

the PEM film. Further increase in the dipping time did not lead to any increase in the overall K/S value suggesting that the deposition process was complete. The fast deposition is expected for low molecular weight species, which can diffuse faster to the surface and in the PEM. The fast kinetics of the PEM deposition on nylon fiber could be an interesting point for further industrial developments.

CONCLUSIONS

In conclusion, we have demonstrated and characterized the possible deposition of PEMs assembled from PDAMAC and Scarlet dye onto nylon fibers. The growth of PEM on this new kind of substrate follows very similar growth pattern to that of PEMs assembled on flat surface. The PEMs growth of PDADMAC/Scarlet dye on nylon fibers could be summarized as highly dependent on the number of layers, salt concentration, and concentration of chemicals but almost independent on the dipping time. It is clear that the PEMs deposition is not limited to nylon and that other type of natural or synthetic fibers could be used as

substrate. Future development of the PEM technique on textile fiber is a very promising method for the development of a new range of application for the textile and technical fiber industry.

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