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Development of Flame Retardant Polyphosphoric Acid Coating Based on the Polyelectrolyte Multilayers Technique

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Abstract

Polyelectrolyte multilayer (PEM) thin films were deposited on silk by sequential deposition of Chitosan and polyphosphoric acid. This PEM composition takes advantage of synergetic effect of the phosphorus and the nitrogen to provide an efficient coating, which prevents fiber decomposition at high temperature. Prior to the PEM assembly on silk fibers, the growth of the film was initially monitored using an atomic force microscopy (AFM). Films formed on silicon wafer after 10, 20, 30, 40 and 60 layers showed somewhat linear increase, which is consistent with the PEM technique. A total thickness ranging from 10 to 107 nm for the 10 to 60-layers films were found. Thermo-gravimetric analysis (TGA) was used to monitor the fiber decomposition as a function of increasing temperature. While the 10 layers coating was not show any improvement when compare with bare silk, the 30 and 60 layers coating showed significant difference in the thermograph. The decomposition of the fiber was significantly reduced which can be seen by the weight loss reduction even at 800 degrees. In conclusion the polyphosphoric based PEM coating seems a good candidate for the further development of flame retardant coating on silk fiber.

Key words : Polyphosphoric acid, layer-by-layer, film, chitosan

Introduction

Most flame retardant chemicals for textiles products are mainly designed to reduce the ignition and the rates of flame propagation. Heat resistant textiles, on the other hand, are not only expected to reduce ignition and flame propagation, but also form a barrier to heat and flame penetration to the underlying materials or surfaces. Untreated natural fibers such as cotton, linen and silk are more readily flammable than wool, which is more difficult to ignite and burns with a low flame velocity. In terms of flammability, silk might be the worst fiber with a high burning rate, which can be further, increased by dyes and other additives. Cotton and linen also have a high burning rate but this can be alleviated by the application of flame-retardant chemical. In contrast, most synthetic fabrics, such as nylon, acrylic or polyester can resist ignition.(1) Textiles can be rendered flame retardant for example by chemical treatment, addition of flame retardant during production, use of inherently flame retardant synthetic fibers or by combination of these methods. Chemical commonly used as flame retardant for cotton and wool fabrics include, ammonium polyphosphates, antimony III, oxide-organic halogen-resin systems or organophosphorus compound.(2) One of the concerns in flame retardant application is the high level of toxicity inherent to the chemicals used to coat the fiber. A lot of effort has been given to design flame resistant systems, which rely on clay or phosphoric acid. Previously prepared flame retardant from polyurea with microencapsulated ammonium phosphate showed interesting potential. The resulting fibers were coated with polyurea, which contained the ammonium phosphate microcapsules having the advantage to be wash resistant.(3) Another interesting improvement was the design of a planar microwave device for thermal treatment of textile material. The microwave treatment textile on cellulose had for effect to provide: durable press, water and oil repellent as well as flame retardant properties.(4) but might this process might be difficult to transfer into an industrial process.

The technique presented in this article is based on the self-assembled polyelectrolyte multilayers (PEM) technique. This method developed

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by Decher and coworkers in the early 1990s has received a great attention in the last decade. The PEM technique presents the advantage of allowing the coating of virtually any surface by simple dipping in dilute polyelectrolyte solutions without the need for further treatment.[6] Also the layer-by-layer process allow the construction of PEM with well-defined thickness, composition, and chemical functionalities by a very simple adsorption process, is highly inexpensive as well as environmental friendly.[7] Recently, our research group has demonstrated the possible Layer-by-Layer deposition of polyelectrolyte layers on cotton and silk fibers.[8] Using this technique, the deposition of PEM was found to improve the color fastness of silk. The wash fastness of a pre-dyed fiber with a scarlet dye was improved by the deposition of a polymer thin film preventing desorption of the dye in standard soap solution.[10] The layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibers was also studied and showed good anti-bacterial activity against Staphylococcus aureus.[11] Silk is the one of fibers for which flamed retardant properties would be greatly beneficial. Reports of flame retardant finishes with an organophosphorus compounds on silk fabrics have already been published.[12] The main idea deals with the application of a commercial organophosphorus flame retardant [N-hydroxymethyl (3-dimethyl phosphono) propionamide (HDPP), using the pad-dry-cure-wash method. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis show that the flame retardant causes silk fabrics to decompose below its ignition temperature (600°C) and formed carbonaceous residue or char when exposed to fire. The char behaves as a thermal barrier to fire providing the silk fabrics with good flame resistance.

In this study, PEM we have developed a PEM coating built from cationic chitosan, which is a biopolymer derived from chitin and the anionic polyphosphoric acid, as shown in Figure 1. The polyphosphoric acid contains two phosphate groups in the end chain, which can electrostatically interact with the positively charged chitosan and therefore can be used to prepared polyelectrolyte multilayer. To the knowledge of the authors no reports of the assembly of Chitosan and polyphosphoric acid on fiber for flame-retardant applications has been made. Prior to the assembly on fibers, we have studied the growth of the film by layer-by-layer deposition of polyphosphoric acid in alternance with Chitosan thin films on silicon wafer. Atomic force microscope imaging was used to evaluate the thickness of the resulting films as a function of the number of layers. Later, a PEM assembled from polyphosphoric acid and Chitosan was deposited on silk thread in order to improve flame retardant property. Thermo-gravimetric analysis provided information on the efficiency of coating with various numbers of layers against to prevent the fiber decomposition against increasing temperature.

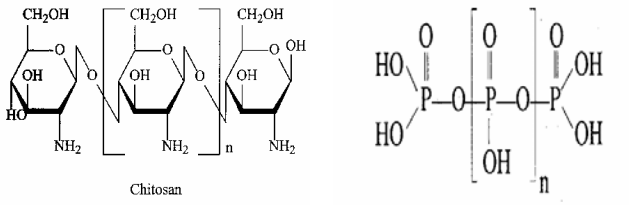

Figure 1. Chemical structure of Chitosan and Polyphosphoric acid used in the preparation of polyelectrolyte multilayer thin films.

Experimental section

Chemicals and materials

The polyphosphoric acid was purchased from Aldrich. Chitosan (Mw = 800,000) with 84% deacetylation was purchased from Fluka. Solutions of various pH between 3 and 6 were prepare by mixing 1M HCL and 1M NaOH. Analytical grade sodium chloride was purchased from Carlo Erba. All chemicals were used as received without any further purification. Silk multifilaments were donated by Chul Thai Silk Company Limited, Petchaboon, Thailand. Single side polished Silicon wafers with a (1,0,0) orientation were used as substrate for the AFM experiments. Double distilled water was used in all experiments.

Preparation of Polyelectrolyte Multilayer Thin Films

PEM with a variable number of layers were assembled on to silicon wafer for atomic force microscopy measurements. All PEMs were assembled by following the same procedure described hereafter. Before beginning the PEM deposition, silicon wafer substrates were cleaned from organic contaminants by a 30 minutes dipping step in an oxidizing “piranha solution” prepared by mixing a 2:1 volume ratio of concentrated sulfuric acid

and concentrated hydrogen peroxide and then rinse thoroughly in pure water.

For the PEM thin films build up, the substrate was first immersed for 2 minutes in a solution containing 1 mM of Chitosan based on the monomer repeat unit. The sample was then rinsed three times in de-ionized water for 1 minute. The purpose of the rinse bath is to remove the excess and loosely bound polyelectrolytes from the surface. These steps resulted in the deposition thin layers of Chitosan, which had for effect to reverse the charge at the surface of the sample from negative to positive. The surface with the Chitosan top layer was then immerse for 2 minutes in a solution containing 10 mM of polyphosphoric acid followed by three rinses in water. These steps resulted in the deposition of a bi-layer of Chitosan-polyphosphoric acid and were repeated as many times as needed. The pH of Chitosan, polyphosphoric acid and all rinses was adjusted at pH 4 and the added salt concentration in both dilute polyelectrolyte solutions was 0.3 M.

Thermogravimetric Analysis Measurement

Thermogravimetric Analysis Measurement is carried out using a TGA/SDTA851, METTLER TOLEDO apparatus in the air, with the sample that coated silk masses of about 4 mg and a heating rate of 10°C/min.

Atomic Force Microscopy Measurements

Topographic images were recorded using am atomic force microscope (AFM) model NanoScope® IV, from Digital Instrument. Measurements were performed in air on dry film using tapping mode with a silicon tip having a 280 KHz tuning frequency . To measure the thickness of the film using the AFM a scratch was initially made on the silicon wafer with a sharp pair of tweezers. The AFM image of the step edge allowed the later measurement of the thickness.

Result and Discussion

In order to confirm the possible growth of the PEM, we first studied the growth of film assembled from polyphosphoric acid and Chitosan on silicon wafer. This important preliminary study has to objective to ensure that the growth of a PEM from these polyelectrolytes is possible and find the optimum condition. A pH of 4 for all dipping solutions was chosen to insure the de-protonation of the hydroxyl groups of the polyphosphoric acid to maximize its negative charge linear density. Also the pH 4 is low enough to ensure a good protonation ($NH3^{+}$) of the amino groups present on the Chitosan pendant groups. Multilayers assembled from Chitosan and Polyphosphoric acid were then deposited by following Layer-by-Layer deposition method on silicon wafers described earlier. The number of layers was varied from 10, 20, 30, 40 and 60 layers deposited on silicon wafers. The ionic strength of the solution was adjusted with a NaCl concentration of 0.3 M to screen polyelectrolyte repulsion and enhance the deposition process. Once the film was prepared in was scratched and analyses by atomic force microscopy.

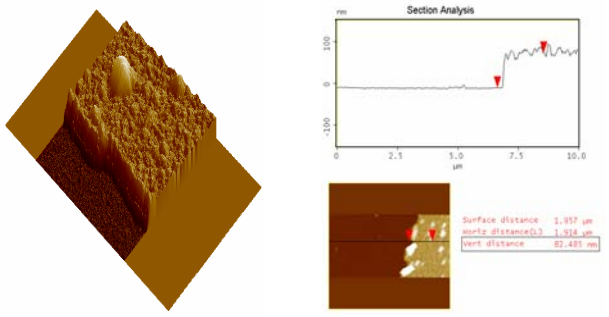

Figure 2. 3-dimension view of the scratched PEM on the silicon wafer (picture A) and cross section analysis of the film thickness (picture B)

The thickness analysis of the film was conducted as follow. The freshly prepared film was first scratched with a sharp tool and then atomic force microscope was used to image the step edge of the scratch. Picture A from the figure 2 shows a 3D image of the scratch with the dark area representing the lower elevation of the silicon wafer and the brighter part represents the PEM film. Data analysis tools from the AFM software were used to measure the thickness of the film. Picture B in figure 2 shows the profile along the dark line crossing the silicon wafer area and the PEM film area. Red markers are used to define the thickness to be measured and the Vertical distance of 82.4 nm can be measured. This vertical distance represents the thickness of the film. This procedure was repeated for all samples assembled from 10, 20, 30, 40 and 60 layers. The resulting thicknesses are plotted in figure 3.

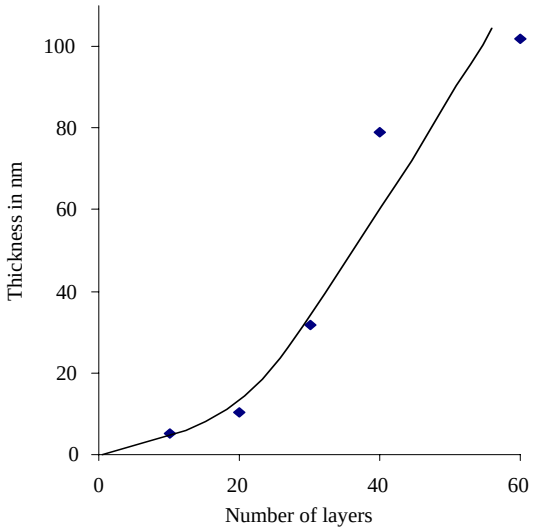

Figure 3. Thickness as a function of the number of layers for Chitosan/Polyphosphoric acid multilayers.

When a solution of Chitosan is brought into contact with a negatively charged solid surface, Chitosan adsorb on the substrate. The adsorption process is under certain conditions irreversible and leads to charge overcompensation, so that the surface charge becomes positive. When this coated surface is brought into contact with a polyphosphoric acid solution, the polyphosphoric acid interacts with the adsorbed Chitosan. This leads again to charge overcompensation and, thereby, to the appearance of a negative surface charge. From the Figure 3, higher layer numbers shows the increased adsorbed amounts due compensation process as a function of the number of layers. The ionic strengths of polyelectrolyte solutions solutions constitute a particularly important parameter because counterions from added salt reduce the repulsion between charges along the chain leads to a decrease in repulsion forces allowing the adsorbsion of the polyelectrolyte chain within PEM. Also, pH of polyphosphoric acid and Chitosan solutions was adjusted to increase the charge density and provided the increasing efficiency of electrostatic interaction. The thickness of the film increase linearly with the number of layers, which is typical for such layered systems. The overall thinkness of the film was found to be 107nm after 60 dipping cycles (30 Chitosan layers- 30 polyphosphoric acid layers), which is relatively thin. Further work should be done to optimized the growth mode of the PEM film and therefore reach such thickness with a lower number of layers.

Flame retardant behavior of coated silk

The deposition of the PEM was reproduced on silk fiber and although it is not expected that the same thickness would result from the deposition, the negatively charged silk fiber appear to be a good substrate for PEM assembly. Once coated the silk fibers were dried and tested using thermo-gravimetric analysis. The weight loss associated with the temperature increase is a common tool to investigate the potential flame retardant properties of a certain chemical on textile fibers. The temperature of the decomposition and the thermal stability of different coated silk in comparison with the uncoated silk were evaluated.

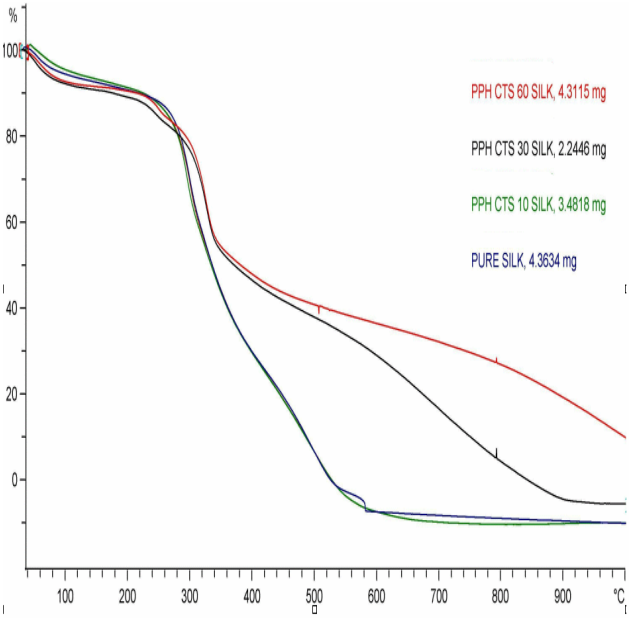

Figure 4. TGA curve of coated silk with Chitosan and Polyphosphoric acid 0-60 layers, heating rate 10°C/min in the air.

From the result of TGA analysis shown in figure 4 we can observe that the thermal stability behaviors of the fibers coated with various number of PEM layers are quite different. Clearly the 10 layers coated silk and uncoated silk start to decompose at about 280°C while the 30 and 60 layers coated silk decompose near 320°C. The uncoated and 10 layers PEM coated silk fiber exhibit a 100% weight loss at around 550 degree while the 30 and 60 layers coated retained 40% weight up to nearly 600 degrees. The 60 layers coated even retained 20% weight at 1000 degrees C. Clearly the number of Chitosan – polyphosphoric acid coating has a direct effect on the flame

resistance of the fiber. While the 10 layers films is very thin and has little effect on the fiber resistance to heat the higher number of layers is quite efficient to protect the fibers. A synergic effect between Phosphorus and Nitrogen has already been reported and is very likely to be responsible for the heat resistance of the fibers. Also examination of a uncoated silk sample and a 60 layers sample after exposure to 600 degrees for 10 min showed significant differences. The uncoated silk was completely decomposed and a black powder was found in the sample holder. This confirms the complete decomposition of the uncoated fiber. On the other hand the 60 layers coated silk fiber was found almost intact but covered with a layer of char on its outside. These char formation is well known and appear a very powerful tool to act against fiber decomposition at high temperature.

Conclusion

We have demonstrated using atomic force microscopy that the assembly of Chitosan with polyphosphoric acid was possible under controlled conditions. When assembled on silicon wafer the thickness increase linearly with the number of layer, which is consistent with the PEM assembly theory. TGA analysis of the silk samples coated with various number of layers showed good potential with high number of layers (30 and 60 layers). Nevertheless a high number of dipping cycles is not yet practical for the textile industry and further will be necessary to achieve such efficiency with a lower number of layers.

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