Nanoscale Surface Roughening of Mulberry Silk by Monochromatic VUV Excimer Lamp

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ABSTRACT: Surface treatment of mulberry silk was carried out using a VUV excimer lamp (172 nm). The changes occurring in morphology and physical properties of silk were studied. The nanopores created on the surface of treated samples were quantitatively analyzed using a high resolution scanning electron microscope. The physical and chemical changes taking place in silk fabric on irradiation were studied through measurement of wetting and wicking time, weight loss, crystallinity, and strength. Effect of irradiation time and distance from the lamp on these properties was also studied. Results show that wettability and wickability of silk improved significantly on exposure before stabilizing at 5 min irradiation time while the weight loss continued to increase. The effect of irradiation was negligible when the distance of the sample from the lamp became >15 mm. The effect of irradiation on tensile strength was found to be insignificant. Presence of moisture in silk hindered the effect of irradiation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 4102–4106, 2007

Key words: nanoheterogenity; irradiation; morphology; surface, photochemistry

INTRODUCTION

Surface modification of fibers and polymers has been carried out by chemical means for a long time. However, more recently, surface treatments based on physical principles such as low temperature, low pressure plasma, and excimer laser[1–3] have also been used to introduce oxygen-containing functional groups on the polymer surfaces, mainly to improve adhesion, wettability, and printability.

UV lamps, which work on the dielectric barrier discharge principle,[4–6] and emit intense and nearly monochromatic light in the vacuum ultraviolet (VUV) region of the spectrum are known as excimer lamps. These lamps combine the relatively simple handling of a lamp with the photochemical properties of a monochromatic light source such as an excimer laser. Because of their simplicity of construction, large emission area, low cost, and availability of different wavelengths, excimer sources are an attractive alternative to plasma and lasers for large area industrial applications.

Organic materials with multiple bonds or atoms that have nonbonding electron pairs such as oxygen or nitrogen absorb light of wavelength less than 200 nm very strongly.[7] Therefore irradiation by these lamps modifies only the surface properties of textile fibers without affecting the bulk properties.

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Although studies have been reported on effect of UV irradiation on silk,[8,9] there is hardly any study conducted on effect of 172 nm VUV irradiation on silk using excimer lamp. In a study Chen et al.[10] have established that the morphological changes produced by the 126 nm VUV radiation are much more than those by 172 nm VUV radiation. However, use of such a very low wave length (126 nm) may be detrimental to the silk fiber surface and its luster. Therefore, in this study, it was decided to study the effect of 172 nm VUV excimer lamp irradiation on silk.

EXPERIMENTAL

Materials

Degummed mulberry silk fabric (GSM-96, EPI-122, PPI-68, warp count-3/7.5 Tex, weft count 2/2 Tex) was supplied by Nath brothers, New Delhi, India. It was washed in distilled water at 60°C for $^1/_2$ h and dried, conditioned at (20 ± 2)°C and (65 ± 2)% relative humidity before irradiation.

Excimer UV radiation chamber

Xenon Excimer UV lamp (XERADEX 20W/L40/120/SB-SX46/KF50), and the high voltage power supply (DBD 110 V/230 V 50 Hz/60 Hz) for the lamp were procured from Messrs Radium Lampenwerk Wipperfurth, Germany. The lamp emits almost monochromatic light in VUV region (λ-172 nm). A chamber for fixing the lamp was fabricated in-house.

Irradiation of the sample

To study the change in surface properties of silk, samples were irradiated for 1, 3, 5, 10, 15, and 30 min. Similarly, to study the effect of distance between the sample and the lamp, the samples were exposed at 5, 15, 30, and 50 mm distance from the lamp. For all other exposures, the sample was kept at 5 mm distance from the lamp.

To study the effect of moisture on the irradiation effect, silk samples were soaked in distilled water for 5 min and squeezed through a mangle to remove excess water.

Characterization

The SEM analysis was performed with a high resolution (up to 3 nm) scanning electron microscope (ZEISS EVO 50) at 23 k magnification. The average number of pores formed per square micron area of the fiber surface was measured as the intensity of pores.

Wetting time was measured as the time taken for the absorption of a (180 μl) water droplet by the fabric. Such measurements were made on four different parts of the fabric and the average wetting time thus was calculated.

For wickability measurements a vertical wicking apparatus[11] was used. A rectangular (100×20 mm^2) silk sample was used for the wicking measurement. Three datum lines L1, L2, and L3 were marked along the longitudinal direction of the fabric, at a distance of 10, 20, and 40 mm respectively, from one end of the sample. The sample was immersed in water up to L1 and the time taken for the water level to travel upward between the lines L2 and L3 (20 mm) was measured as wicking time.

Weight loss was calculated by the difference in weight of the fabric before and after irradiation and expressed as percentage of the weight of the fabric before irradiation. After irradiation, the fabric was not exposed to open atmosphere until the weight of the fabric was taken. Then the irradiated sample was exposed to open atmosphere to study of there is any increase in weight due to moisture absorption. Thus the weight gain was calculated by the increase in weight of the fabric with time and expressed as percentage of the total weight loss.

Crystallinity of samples was measured by X′ Pert PRO PANalytical X-ray diffractometer. Tensile strength of the samples was measured using Instron 4301.

RESULTS AND DISCUSSION

Surface morphology

Scanning electron micrographs show that nanoroughening of silk fiber surface has occurred on irradiation [Fig. 1] because of formation of nanopores. Knittel et al.[12] have reported roll-like structure formation on silk because of excimer laser irradiation. No such effect is observed in our case, may be, because the severity of exposure is less in excimer lamp irradiation and the thermal effects are also absent. It is interesting to note that the size and intensity of pore appear to change as the irradiation time is increased, Table I. As the irradiation time increase from 1 to 30 min, the average pore size increases from 95 to 190 nm. The intensity of pore reaches a maxima of 32/μm^2 at 5 min and then decreases to 16/μm^2 at 30 min of exposure. It appears that during the initial irradiation period (up to 1 min), the incidence of high energy photons (7.2 eV) breaks the surface molecular chains leading to formation of micropores of less than 100 nm. On further irradiation (up to 5 min), two effects are observed namely, an increase in pore size of the already formed pores and creation of new pores on the fiber surface. Hence, an increment in both the pore size and pore intensity is observed. Beyond 5 min of irradiation the pore size increases whereas the pore intensity decreases possibly because the onset of new pores is saturated and so further irradiation causes only enlargement and merging of already formed pores. Consequently irradiation beyond 5 min causes increase in pore size and decrease in pore intensity.

Wickability

Wickability of silk was tested by a special set up described earlier. The effect of excimer radiation upon wickability is shown in Figure 2. It can be seen that irradiation of samples increases the wickability of silk. The effect is more significant up to 5 min of exposure time, beyond which the wickability stabilizes. This can be explained with respect to the capillary action of water which is defined as the upward movement of water against gravitational force within the spaces of a porous material. It is a function of the forces of adhesion (attraction between water molecules and the substrate because of intermolecular forces of attraction), cohesion (attraction between water molecules), and surface tension. Capillary action occurs when the adhesive intermolecular forces between the liquid and the substrate are stronger than the cohesive intermolecular forces within the liquid. Moreover, if the pore size is small and relatively uniform, water level can rise to higher level by capillary action than if the pore size is large or nonuniform.[13] SEM study shows that irradiation of silk with the excimer lamp has created nanopores over the silk fiber surface [Fig. 1]. Formation of nanopores along with increase in surface hydrophilic groups may significantly contribute to the adhesive forces between the silk fiber surface and water mole-

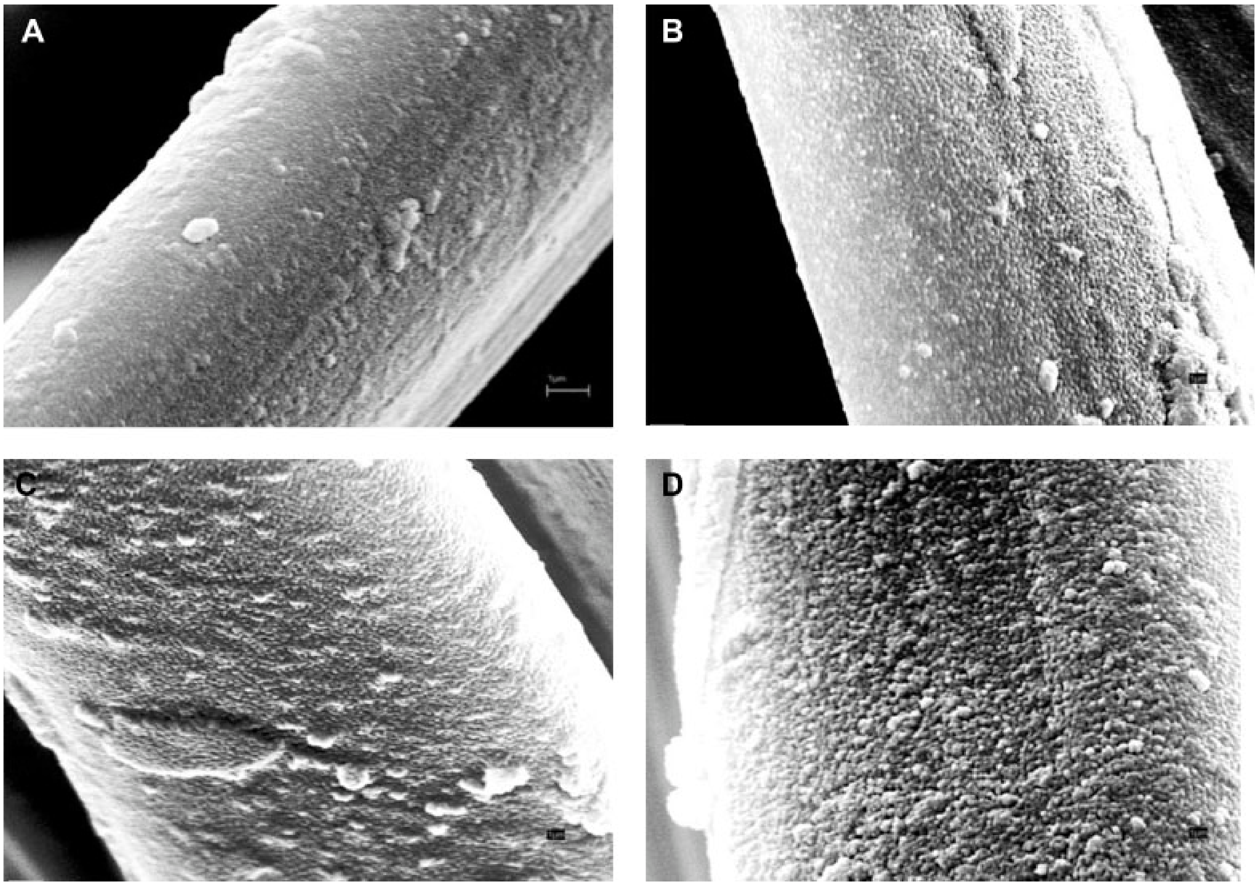

Figure 1 SEM micrographs of silk fiber irradiated with excimer lamp (a) untreated, (b) 5 min, (c) 15 min, and (d) 30 min.

cules, leading to increase in wickability. The saturation of wickability beyond 5 min of irradiation corresponds to the increase in pore size and decrease in pore intensity reported earlier in Table I. Similar effects have been reported by Wong et al.[14] on treatment of linen fabric with plasma.

Weight loss

The weight loss of silk as a function of irradiation time is plotted in Figure 3. It can be observed from the figure that the weight loss increases with irradiation time and is rapid up to 5 min of exposure. Loss of surface polymer molecules due to etching, and loss of water molecules due to rise of substrate temperature can be the two possible reasons for this loss in weight. To study the actual cause for the weight loss, a study was carried out by monitoring the weight gain of a sample, irradiated for 15 min, upon exposing to open atmosphere [Fig. 4]. Although the irradiated sample shows 2% weight loss [Fig. 3], the weight is regained in about 100 s when the sample is exposed to open atmosphere. It can thus be concluded that the observed loss of weight on irradia-

TABLE I
Effect of Irradiation Time on Fibre Morphology

Irradiation time (min)	Average pore size (nm)	Pore intensity (pores/μm^2)	Crystallinity % (X_n)
1	95	26	34
3	105	30	34
5	125	32	35
10	160	28	36
15	165	27	35
30	190	16	34

crystallinity of untreated silk is 38%.

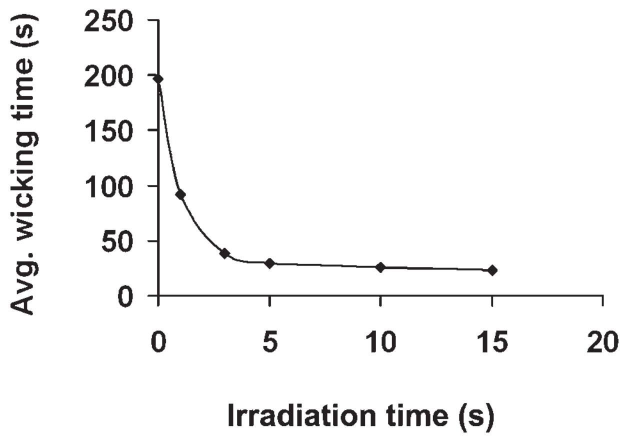

Figure 2 Effect of 172 nm excimer radiation on wickability of silk.

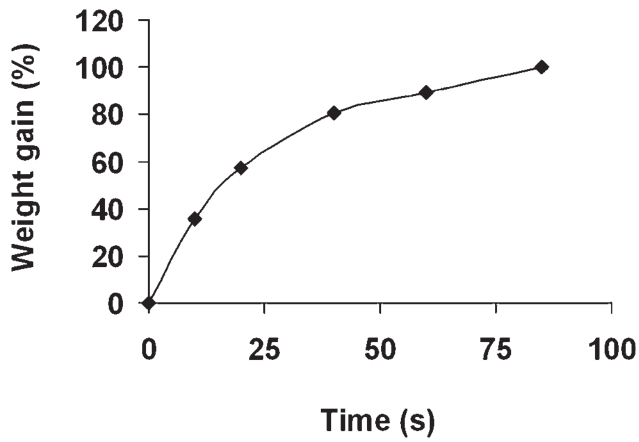

Figure 4 Weight gain of irradiated silk on exposure to open atmosphere.

tion is actually caused by loss of water molecules only. The weight loss due to etching if any is thus found to be negligible.

Wettability

Irradiation of silk with 172 nm excimer lamp reduces the wetting time significantly even at an exposure time of 1 min, Figure 5. The wetting time continues to decrease with irradiation time up to 5 min beyond which it stabilizes. This increase in wettability of silk can be attributed to the formation of polar groups on the fiber surface. The mechanism can explained as follows: the oxygen in air absorbs the high energy photon and forms highly reactive excited oxygen O (^{1}D) either directly or first forming O_3 (ozone) and then dissociating into O (^{1}D) and O_2. Thus the excited oxygen O (^{1}D) reacts with the fiber surface and forms oxygen containing polar groups such as hydroxyl (—OH) and carbonyl (—C=O) on fiber surface.[15]

Effect of distance between the substrate and the excimer source

The silk fabric for all the aforementioned results was exposed to the excimer lamp at a distance of 5 mm from the lamp. To study the effect of irradiation power, experiments were also conducted by varying the distance from the lamp, keeping the time of irradiation at 5 min. The effect of distance from the lamp upon wettability and wickability of silk substrate is shown in Table II.

Irradiation reduces both the wetting time and wicking time significantly up to a distance of 15 mm. If the substrate is kept at a distance of more than 15 mm, the change in wetting time and wicking time becomes less significant. This phenomenon can be explained by the fact that the effect of excimer radiation upon the substrate is twofold. Firstly, the direct incidence of high energy photon on silk surface may lead to chain scission of surface molecules leading to formation of oxygen containing hydrophilic groups. Secondly, the gas (oxygen in air) in the exposure chamber can absorb the 172 nm excimer radiation to

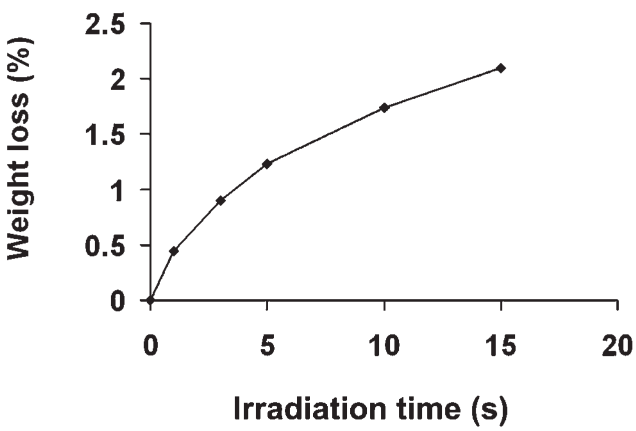

Figure 3 Effect of irradiation time on weight loss.

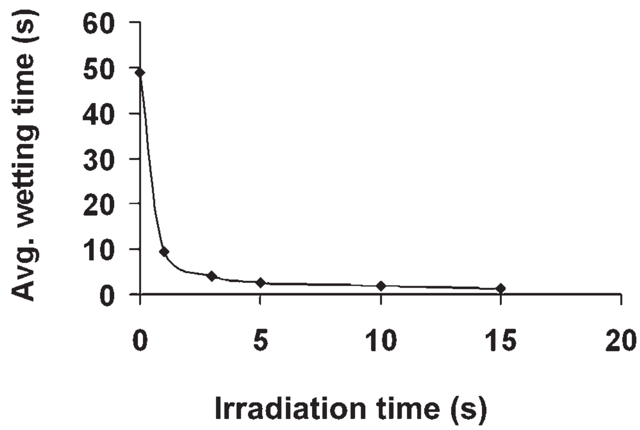

Figure 5 Effect of irradiation on wettability of silk.

TABLE II
Effect of Distance from the Lamp on Wettability and Wickability of Silk

Distance from the lamp (mm)	Average wetting time (s)	Average wicking time (s)
Untreated	79.00	197
5	2.56	32
15	29.84	74
30	43.58	155
50	47.76	189

form ozone and excited oxygen. By the action of these excited oxygen species and ozone, the fiber surface may get further activated. As the distance between the substrate and the lamp is increased, apart from the natural decrease in irradiation power, the reach of excimer radiation to the substrate is limited by the strong absorption of the high energy photons by atmospheric oxygen. So, beyond a certain limit the surface modification will be purely by the action of ozone and excited oxygen atoms. However, there will be higher concentration of ozone and excited oxygen atoms closer to the lamp only. It is because of these reasons that the irradiation effect is found to be noticeably less beyond distance of 15 mm from the lamp.

Effect of prewetting

Another series of experiments was conducted to study the effect of irradiation on silk that had been prewetted. The wetting and wicking time of the sample without prewetting is 2.56 and 32 s respectively. Interestingly, wet silk sample shows a slight increase in both the wetting time (3.48 s) as well as wicking time (37 s) indicating that radiation effect is hindered by the presence of water in silk. This can be because water also absorbs the 172 nm radiations strongly; a part of irradiation is absorbed by water. The water layer may also hinder the action of ozone and excited oxygen over the substrate. Thus it can be inferred that the silk should be free from moisture for effective surface modification.

Fine structure

Crystallinity of silk fiber decreases slightly on irradiation, Table I. As the change on exposure to excimer irradiation is restricted only to the surface of the fiber, the decrease in crystallinity is probably on account of decrease in the surface crystallinity. Similar results have also been reported by Nadiger and Bhat[16] when they treated mulberry silk with plasma.

Tensile strength

Effect of irradiation upon tensile strength of silk was studied. As the weight loss was found to be negligible, it could be expected that strength loss would also be insignificant. Irradiated samples showed slight decrease in strength that can be ascribed to the surface degradation effect due to etching. However the 't' test for significance showed that there was no significant difference between the mean strength of the treated and untreated samples even at 1% level of significance.

CONCLUSIONS

The study showed that irradiation of mulberry silk with 172 nm excimer lamp causes nano roughening of its surface. At 1 min irradiation time pores of 80 to 100 nm with average pore intensity of $26/\mu m^2$ were formed on the surface of silk on exposure. As the irradiation time increased, the pore size increased but the pore intensity reached a maxima of $32/\mu m^2$ at irradiation time of 5 min, and then started decreasing.

Because of the physical and chemical modification of the fiber surface, wickability, and wettability of silk fabric improved significantly. The effect was significant even with an irradiation time of 1 min. These positive changes were accompanied by negligible loss in weight, crystallinity, and strength. Treatment was found to be ineffective beyond a distance of 15 mm from the source of irradiation. Presence of moisture in the sample hindered the effect of irradiation on silk.

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