Radiation Grafting/Crosslinking of Silk Using Electron-Beam Irradiation

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ABSTRACT: The radiation grafting of silk with methacrylamide (MAA) was studied using an electron-beam (EB) irradiation technique. Two irradiation processes, preirradiation and coirradiation, were compared, and some factors affecting the degree of grafting were investigated. The radiation crosslinking of silk with dimethyloldihydroxyethylene urea (DMDHEU) was preliminarily studied. The physical and mechanical properties such as whiteness, breaking strength, and resilience of the radiation-grafted/crosslinked silk fabrics were examined. The radiation grafting of silk with MAA increases the silk weight, while the radiation crosslinking of silk with DMDHEU imparts improved crease resistance to silk. X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR) analysis indicate the formation of peroxy and free-radical species on the EB-irradiated silk. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2028–2034, 2004

Key words: fibers; radiation; graft copolymers; crosslinking; electron beam irradiation

INTRODUCTION

Silk, a natural polymer, is so costly that many techniques have been devised for increasing the density of silk by artificial means. The weighting of silk with tin salt was the most popular process for producing heavily weighted silk fabrics, but not now due to the environmental problem caused by tin. Grafting of silk with an organic monomer is a new approach to silk weighting, and considerable work on the chemical graft copolymerization of vinyl monomers onto silk was reported.[1–3] Among various kinds of vinyl monomer grafting agents, methacrylaminde (MAA) and 2-hydroxyethyl methacrylate (HEMA) are the most useful silk grafting agents, which enable one not only to achieve heavily weighted silk at low cost but also to improve the characteristics of silk.[4–6]

Chemical and radiation grafting are two approaches used in the grafting modification of polymers. Compared to chemical grafting, radiation grafting exhibits a number of advantages where no chemical initiators are required and the grafting degree can be easily controlled by adjusting irradiation conditions. Therefore, radiation grafting of silk appears more attractive to silk research in recent years. This present research focused on the grafting modification of silk with MAA by electron-beam (EB) irradiation and XPS and ESR analyses of the irradiated silk.

Cotton radiation crosslinking has been reported to improve the crease resistance,[7,8] but little work on silk radiation crosslinking has been reported. In this article, we also present our preliminary work on the radiation crosslinking of silk with dimethyloldihydroxyethylene urea (DMDHEU), with a view to improving the crease resistance of silk fabrics.

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EXPERIMENTAL

Materials

A mill-degummed 100% silk twill, produced in Hangzhou, was used in all the experiments; MAA was a Aldrich analytical reagent, and the other chemicals reagents used were of laboratory grade (Shanghai, China).

Pretreatment of silk fabrics

The mill degummed silk twill was treated before irradiation using 0.5 g/L Peregol O (nonionic surfactant, produced by Shangyu Auxiliary Ltd., Shangyu, China) at 90°C for 30 min, then rinsed thoroughly and dried in the room atmosphere.

EB irradiation

EB irradiation was performed in a GJ-1.5 high-frequency and high-pressure electron accelerator. The main property parameters of the EB equipment were as follows: maximum power, 1.5 MeV; maximum intensity of the EB, 1.5 mA; scanning width, 600 mm;

scanning frequency, 50 Hz; and speed of the flat vehicle, 10 cm/s. The dose rate was adjusted by the intensity of the EB, while the radiation dose was the product of the dose rate multiplied by the irradiation time, which was controlled by the number of times the flat vehicle passed through the EB output.

Preirradiation grafting

Preirradiation grafting is a process in which silk was EB-irradiated first to produce free radicals on silk polymer molecules; then, the irradiated silk was put in an aqueous MAA solution to graft the silk with the monomer MAA. The detailed experimental method and process conditions were as follows:

Two groups of specimens were prepared. One group of specimens was put in plastic bags individually and purged with nitrogen for 10 min to remove oxygen, and then the bags were filled with nitrogen and sealed. The two groups of specimens, one of which was in a nitrogen atmosphere and the other in air conditions, were irradiated by an EB. After EB irradiation, unless otherwise stated, the specimens were immediately treated in an aqueous grafting bath containing 30% (o.w.f) of MAA and acetic acid (adjusting the bath to pH 4) in a liquor ratio of 1:30 at room temperature (about 25°C) for 1 h.

Co-irradiation grafting

Co-irradiation grafting is a process in which silk is treated with an aqueous MAA solution first; then, the monomer-treated silk is EB-irradiated. Because the silk polymer and the MAA monomer are irradiated together, the formation of free radicals and the graft copolymerization of silk with MAA takes place simultaneously. The detailed experimental method and conditions were as below:

All specimens were padded (two dips and two nips) using an aqueous pad-bath containing 30% (v/v) MAA and acetic acid (adjusting the bath to pH 4) with 100% of wet pickup. After padding and drying, the specimens were divided into two groups: One group of specimens was put in plastic bags individually and purged with nitrogen for 10 min per specimen to remove oxygen, and then the bags were filled with nitrogen and sealed. The two groups of specimens, one of which was in a nitrogen atmosphere and the other in air conditions, were EB-irradiated. In this co-irradiation grafting process, the grafting time was the same as the irradiation time, which depends on the required irradiation dose and the dose rate.

Aftertreatment of grafted silk

To remove all the ungrafted monomer (unreacted grafting agent) and copolymerized compounds on the silk, the radiation-grafted samples were after-treated in a liquor containing 3% (o.w.f) of soap at a liquor ratio of 1:50 at 90°C for 20 min, then rinsed in warm water for 10 min, rinsed in running water for another 10 min, and, finally, rinsed with distilled water and dried at 50°C until a constant weight.

Calculation of degree of grafting (*g*)

$$G(\%) = [(W_g - W_0)/W_0] \times 100$$

where W_g and W_0 are weights of dried samples after and before EB irradiation grafting, respectively.

Chemical crosslinking and radiation crosslinking of silk

- Conventional chemical crosslinking of silk: Silk fabric was padded twice though a finishing bath containing 6% (w/w) of DMDHEU (crosslinking agent), 25.6 g/L of $MgCl_2 \cdot H_2O$ (catalyst), and 3.8 g/L tartaric acid with a wet pickup of 95–100%. The padded fabric was dried at 85°C for 3 min and then cured at 175°C for 35 s.
- Radiation crosslinking of silk: Silk fabric was EB-irradiated with a 30-kGy irradiation dose at a 150-Gy/s dose rate, followed by a padding–curing treatment the same as that of the above chemical crosslinking process.

Measurement of crease-recovery angle

The crease-recovery angles (CRAs) were measured on an LFY–1A crease recovery tester, and the size of the specimen was 1 × 4 cm to fit the tester. The dry CRA was measured according to the AATCC Test Method 66-1990, while the wet CRA was measured following the method suggested by Lee and Sin.[9]

X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectra were obtained using a vacuum generator ESCALAB 1 spectrometer. The samples were attached to the spectrometer probe with double-sided adhesive tape and analyzed with MgKα radiation (1253.6 eV) operating at a working pressure of 10^{-8} mbar.

Binding energy values were calculated relative to the C (1*s*) photoelectron peak at 285.0 eV. The peak area used to obtain the surface composition and relative elemental ratios was corrected using Wagner's sensitivity factors.[10]

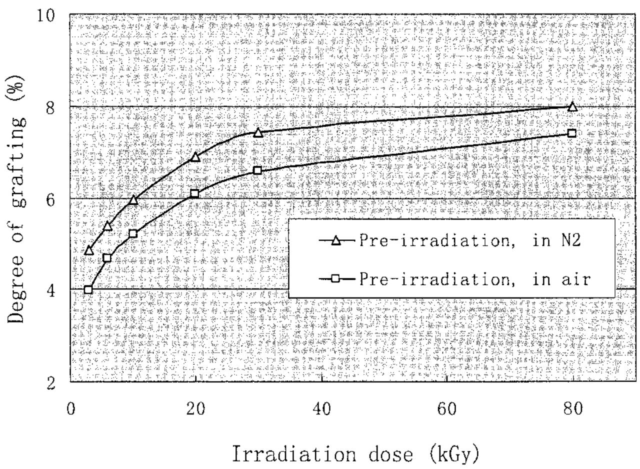
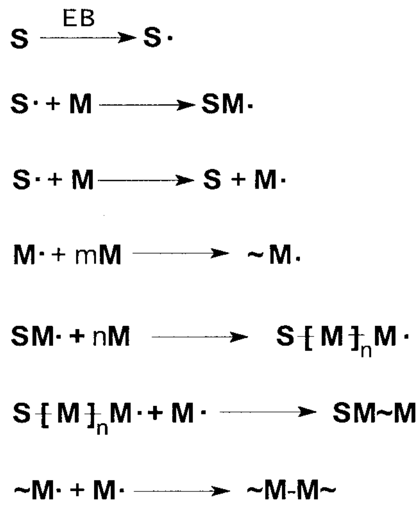


Figure 1 Effect of preirradiation dose on the degree of MAA grafting (dose rate: 150 Gy/s).



Scheme 1 Radical reaction mechanism of silk grafting with EB irradiation.

Electron spin resonance (ESR) spectroscopic study

ESR spectra were obtained using a JES-FEIXG spectrometer in the X band. The conditions of the measurement were as follows: temperature, 20°C; frequency, 9.244 GHz; magnetic field intensity, 3300 ± 250 G; sweep time, 2 min; modulation width, 4G; gain amplitude, 20; and power, 4 mW.

RESULTS AND DISCUSSION

Effect of irradiation dose on the degree of grafting

Figures 1 and 2 indicate that the degree of grafting increases with an increasing irradiation dose, particularly in the case that the irradiation dose is lower than 30 kGy. Obviously, the higher grafting degree is attributed to the more radicals formed when a higher irradiation dose is absorbed.

Radiation grafting is based on a radical reaction mechanism.[11] In the EB grafting of silk, the bombardment of high-energy electrons induces radicals on the silk substrate, and this then results in graft copolymerization taking place by a radical mechanism. Scheme 1 outlines the possible radical reaction mechanism, where S represents silk polymer molecule and M represents monomer MAA.

Although a higher degree of grafting is accompanied by a higher irradiation dose used, it is noticeable that when the irradiation dose is over 30 kGy a further increase in the irradiation dose results in only a small increase in the degree of grafting. This suggests that an irradiation dose of 25–30 kGy should be suitable for the EB grafting of silk with MAA.

It is also clear that, from Figures 1 and 2, co-irradiation grafting produces a higher degree of grafting than does preirradiation grafting in every irradiation dose level. This might be due to the different utilization efficiency of radicals (the ratio of the effective radicals initiating the graft reaction to the total radicals generated during irradiation) in different processes. In the case of co-irradiation grafting, the radicals generated by EB irradiation can directly initiate the graft reaction, whereas in the preirradiation grafting process some radicals are quenched by oxygen and moisture during irradiation and decay in water rapidly during subsequent monomer treatment (see the section ESR Analysis). In the preirradiation grafting process, it is also unavoidable that some radicals decay in the time interval between the EB irradiation and the monomer treatment (see the section Effect of Storage Time %), although this was kept to a minimum. In addition, the observed higher degree of graft-

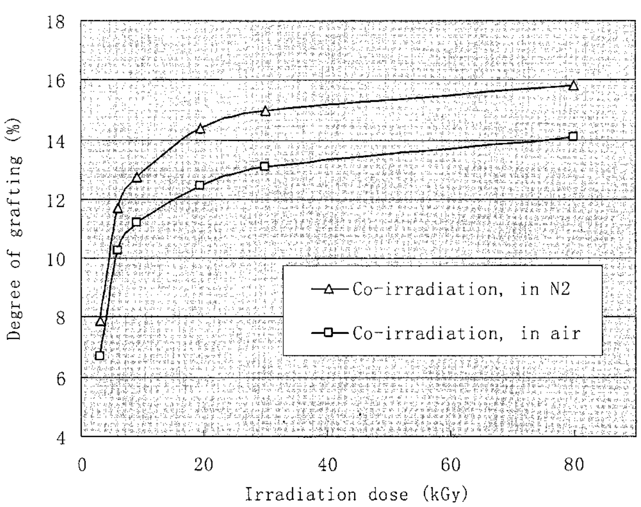


Figure 2 Effect of co-irradiation dose on the degree of MAA grafting (dose rate: 150 Gy/s).

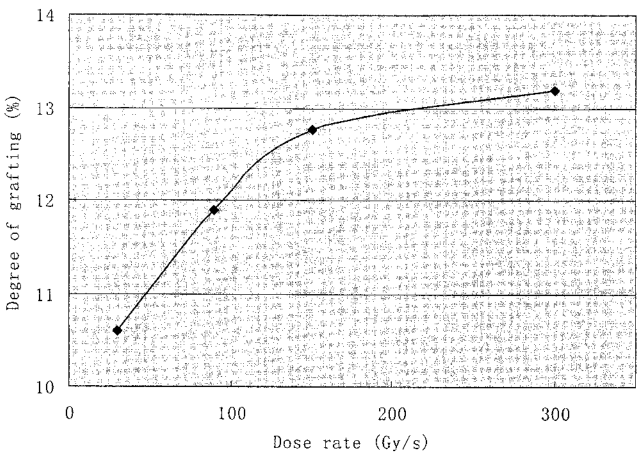


Figure 3 Effect of dose rate on the degree of MAA grafting (co-irradiation grafting in N_2 atmosphere; irradiation dose: 30 kGy).

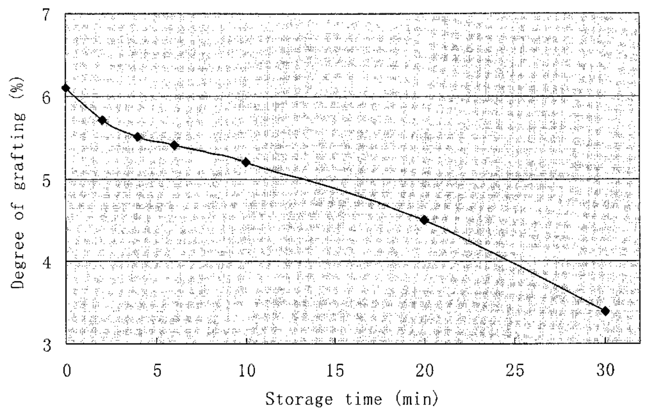


Figure 4 Effect of storage time on the degree of MAA grafting of preirradiated silk (irradiation dose: 30 kGy; dose rate: 150 Gy/s).

ing produced by co-irradiation grafting might be partially due to the higher self-polymerization of grafting agents because the monomers were also EB-irradiated.[11]

Effect of dose rate on the degree of grafting

Figure 3 shows that, in this experimental range of dose rate, the degree of grafting increases as the dose rate increases, but it levels off when the dose rate is beyond to 150 Gy/s. Obviously, a greater dose rate must induce more radicals on the silk substrate in a given time, resulting in a higher degree of grafting. However, if the radicals have been sufficient to initiate a grafting reaction, a further increase in the dose rate will produce exceeded radicals that decay by impacting each other. Therefore, a dose rate of around 150 Gy/s is a suitable level for MAA grafting of silk with EB irradiation.

Effect of irradiation atmosphere on the degree of grafting

From Figures 1 and 2, the effect of the irradiation atmosphere on the degree of grafting is evident. Regardless of co-irradiation grafting or the preirradiation process, the irradiation in a nitrogen atmosphere produces a higher degree of grafting compared with irradiation in air. This can be explained in terms of a lower concentration of radicals captured by oxygen when irradiated in a nitrogen atmosphere.

Effect of storage time on the degree of grafting of preirradiated silk

The degree of grafting of preirradiated silk decreases with the extension of the storage time after irradiation (Fig. 4), suggesting that the radicals induced by preirradiation decay rapidly. Therefore, the MAA grafting treatment should immediately follow the EB irradiation treatment to achieve a higher degree of grafting on preirradiated silk.

Physical and mechanical properties of radiation-grafted silk fabrics

The breaking strength of radiation-grafted silk decreases slightly with an increasing degree of grafting (Table I), which is in agreement with the phenomenon observed in the chemical grafting of silk.[12] The loss in the breaking strength might be attributed to the increasing uneven distribution of stress caused by grafting in silk molecule chains. However, a severe bombardment of an electron beam should also be responsible for the loss in the breaking strength in terms of the fact that when the irradiation dose is over 30 kGy

TABLE I
Breaking Strength lost of EB-irradiated Silk and Co-irradiation-grafted Silk

Measurement	Irradiation dose (kGy)						
	0	3	6	10	20	30	80
Degree of grafting in co-irradiation process[a] (in air)	0	6.7	10.3	11.2	12.4	13.1	14.1
Strength loss of EB-irradiated silk (%)	0	0	0	0	1	3	10
Strength loss of co-irradiation-grafted silk (%)	0	2	3	5	7	8	16

[a] Dose rate: 150 Gy/s).

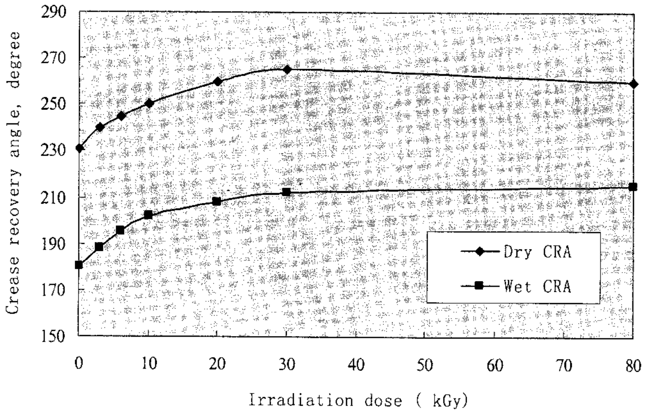


Figure 5 Dry and wet CRAs of co-irradiation-grafted silk.

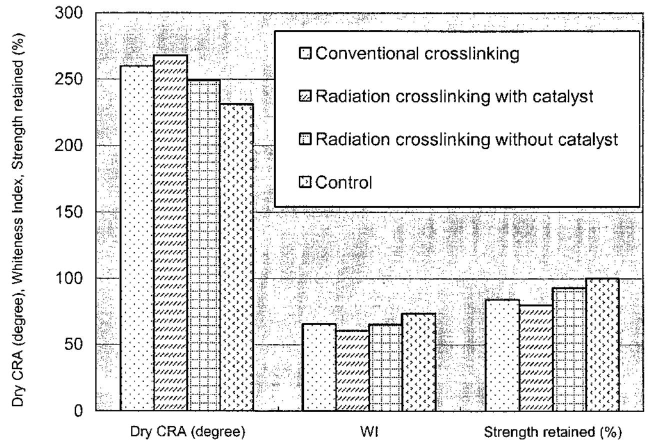


Figure 6 Comparison of radiation crosslinking of DMDHEU with conventional chemical crosslinking of silk.

a further increase in the irradiation dose is accompanied by a considerable decrease in the breaking strength of irradiated silk.

The resilience of silk fabrics was examined by dry and wet CRAs. The radiation grafting of silk with MAA increases both the dry and wet CRAs of silk considerably (Fig. 5). A permanent crease of the fabric results from the relative slippage of fiber molecules under an external force and the formation of new bonds in new fiber positions. Generally, the crosslinking between fiber molecules can reduce or prevent fibers from slippage and achieve an improved crease resistance.[13–15] However, the grafting of silk with MAA introduces some polymerized branch chains on the silk's main chains, and the resultant tangles with the main chains and branch chains act similarly to crosslinks, leading to the observed improvement in the crease resistance of silk. Both the increase in the silk weight and the improvement in the silk resilience are valuable to the silk industry.

Immediately after EB irradiation, the silk had a greenish color, which gradually changed to yellow on standing. The greenish color might be related to radicals that decay with an extension of the storage time. Coupled with an increasing irradiation dose was an increase in yellowness.

Radiation crosslinking of silk with DMDHEU

The preliminary results of the radiation crosslinking of silk with DMDHEU (Fig. 6) demonstrates that only EB irradiation initiates a crosslinking reaction between the silk molecules and DMDHEU, as indicated by the improved crease resistance and the change in solubility (to be presented in the next section), but radiation crosslinking without a catalyst is not as effective as is conventional chemical crosslinking. EB irradiation followed by DMDHEU crosslinking with a catalyst can achieve greater crease resistance than can conventional chemical crosslinking. Further research on optimizing the conditions of the radiation crosslinking of silk with DMDHEU and BTCA was detailed in another article.[16]

Solubility of radiation-crosslinked silk fabrics

A potassium sulfocyanide solution is an excellent solvent for silk, with the breaking of the hydrogen bonds between the silk molecule chains. The insolubility of silk in a potassium sulfocyanide solution is an indicator of crosslinkages in silk fabrics.[17] Figure 7 indicates that radiation crosslinking of DMDHEU with a catalyst results in a similar solubility of silk to conventional chemical crosslinking, suggesting similar crosslinkages formed in the above radiation and chemical crosslinking treatments. Radiation crosslinking without a catalyst produces higher solubility than that with a catalyst, but much lower than that of the control sample. This is a good agreement with the

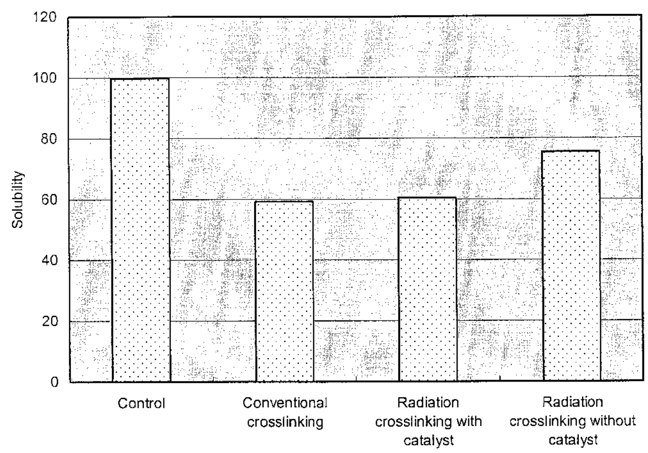


Figure 7 Solubility of silk in potassium sulfocyanide solution.

TABLE II
Surface Elemental Compositions of EB-irradiated Silk Fabrics

Sample	Composition (%)			
	C	O	N	S
Nonirradiated	64.2	22.1	13.4	0.3
20 kGy EB-irradiated	59.9	26.6	13.5	—
80 kGy EB-irradiated	56.8	29.3	13.9	—

crease-resistance results presented in the above section.

XPS analysis of EB-irradiated silk surface

XPS is a surface-sensitive technique allowing the chemical analysis of a sample surface to a depth of 3–5 nm. It is capable of providing both qualitative and quantitative information about the fiber surface.[18]

The surface elemental composition of EB-irradiated silk fabrics (Table II) indicates that EB irradiation produces an increase in the surface oxygen content. It was reported that EB irradiation in an air atmosphere results in the formation of peroxy side groups on the polymer chains, which will dissociate/convert to radicals.[11] An intense EB irradiation may also breakdown the silk's main chains and thus produce more carboxylic acid groups as indicated by Figure 8. The formation of both peroxy side groups and more carboxylic acids may account for the observed increase in the oxygen content. The decrease in surface carbon with an increasing irradiation dose suggests the probable modification/removal of the tyrosine-rich layer in the silk surface.[19]

Figure 8 shows that the EB irradiation of silk produces an increase in the higher binding energy intensity of the C (1*s*) peak. Previous XPS studies have assigned the component bands of the C (1*s*) spectrum as 285.0 eV for C—C/C—H, 286.5 eV for C—O/C—N, 288.0 eV for C═O/N—C═O, and 289.0 eV for O—C═O.[20,21] The effect of the EB irradiation is a decrease in the relative intensity of the C—C/C—H component at 285.0 eV accompanied by an increase in the intensity of the C—O component at 286.5 eV and the intensity of the O—C═O component at 289.0 eV. The increase in the C—O signal may suggest the formation of peroxy groups (C—O—OH), while the increase in the O—C═O signal may reflect the breakage of the silk's main chains, which is agreement with the strength loss of silk fabrics in severe EB irradiation.

ESR analysis

ESR is the most direct and sensitive technique to detect and characterize paramagnetic free-radical species. The ESR spectrum of EB-irradiated silk shows an intense signal at $g = 2.004$ together with an unresolved shoulder at $g = 2.017$ and a medium strong signal at $g = 1.993$ (Fig. 9). The signal at 2.004 has been previously assigned mainly to glycine and alanine radicals.[19,22] The ESR spectrum of the EB-irradiated silk supports the radical mechanism of the radiation grafting of silk. After rinsing in water, the radical signals were seen to decay markedly. This is agreement with the previous ESR study on wool and silk.[19] Water molecules can diffuse into the silk fibers faster than can the monomer molecules due to its smaller molecular size, so that some free radicals in silk fibers might have been quenched by water before the monomer molecules diffused into the silk fibers in the preirradiation grafting process. Hence, the significant decay of radical signals after rinsing may partially explain the lower degree of grafting and the relatively higher surface grafting in the preirradiation grafting process than in the co-irradiation grafting processes.

CONCLUSIONS

The MAA grafting of silk with EB irradiation can increase the silk weight effectively. The co-irradiation grafting process produces a higher degree of grafting than does the preirradiation grafting process; the degree of grafting increases significantly with an increasing irradiation dose, while it changes slightly with the variation of the dose rate used in this project. A N_2-enriched atmosphere is beneficial to produce a higher degree of grafting.

EB radiation crosslinking of silk with DMDHEU improves the crease resistance of silk, and the radiation crosslinking with a catalyst produces better a crease resistance of silk than without a catalyst.

XPS analysis indicated the oxidative modification of silk and the formation of peroxy groups on silk with EB irradiation, while ESR spectroscopy demonstrated

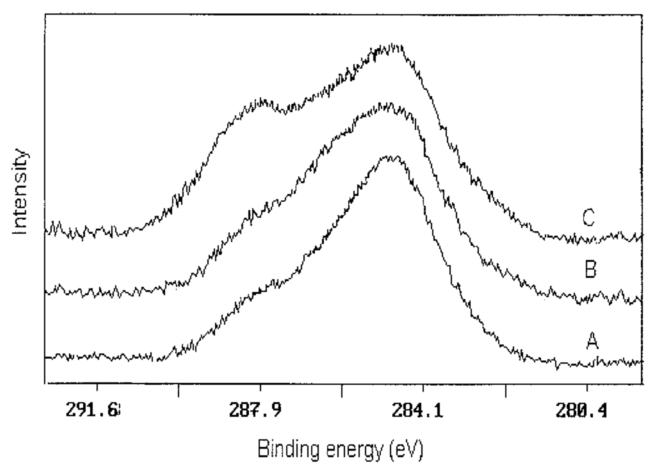


Figure 8 C (1*s*) spectra of EB-irradiated silk fabrics.

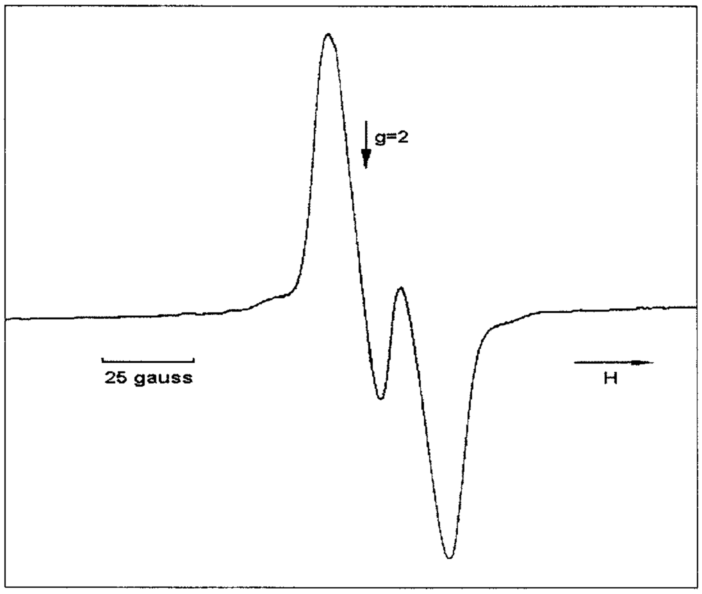


Figure 9 ESR spectrum of EB irradiated silk.

the generation of free radicals on silk with EB irradiation and the decay of the radicals in water.

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