Properties of radicals created by γ-ray irradiation of silk fabrics

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Abstract The properties of radicals from γ-ray irradiated silk fabrics were studied by electron spin resonance method (ESR). The ESR spectra of silk fabrics irradiated in N_2 showed a doublet at room temperature. The doublet became a singlet at g=2.0057 after placing the sample in air for 24 hours. This can be explained by formation of peroxide radicals. The radical concentration of the irradiated silk fabric and the decay rate of radicals are significantly affected by irradiation conditions, which include the absorbed dose, atmosphere, and water content of the silk fabric samples. However, no dose rate effect on the radical concentration was observed. The results are of help in our practice of property modification of silk products by radiation graft copolymerization.

Keywords Silk fabric, γ-ray irradiation, ESR

CLC numbers O631.3+4, O636, O644.2 A

1 INTRODUCTION

Developments in nuclear technology have made radiation techniques available to improve properties of natural fibers. High energy radiations, such as γ-rays, x-rays, and other shortwave lights, have proved to be a convenient source of free radicals that can be characterized by ESR spectra in silk fibers.[1-4] In recent years, there has been a growing interest in γ-ray radiation graft copolymerization of silk fabrics to improve the product in terms of their physical , chemical and mechanical properties.[5-8] Most papers have dealt with the graft copolymerization of vinyl monomers on silk fabrics to modify the crease recovery, dyeing property, color fastness and dimension stability, whereas others focused on the effects of the physicochemical properties and the fine structure of the irradiated silk fibers.[9] However, little attention has been paid to mechanisms of radiation effects on silk fabrics so far. Since γ-ray irradiation can result in chemical degradation to form stable subsided-radicals, it is of great interest to investigate the properties of free radicals in γ-irradiated silk fabrics in an attempt to add to our understanding of the radiation effects on silk fabrics, and to explore industrial applications of the technique.

Radiation graft copolymerization can be conducted in two ways. One is a direct method, by which monomer(s) and the polymeric materials are irradiated simultaneously, and graft copolymerization occurs during the irradiation. Another is an indirect method, or pre-irradiation method, by which just polymeric materials are irradiated to create

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long life radicals that react with monomer(s) after the irradiation (In the presence of oxygen, the radiation creates peroxidates that react with the monomers, too). In view of homopolymerization effect, which is unavoidable with the direct method, and heavy mass of the monomer(s) solution for irradiation, the pre-irradiation method is more desirable for applying the radiation graft copolymerization technique to the silk fabric industry. On the other hand, with the indirect method it is possible to irradiate the silk product with electron beams, which is more appealing to the industry and the public than a γ-ray facility over considerations on radiation hazards. Therefore, behaviors of long life radicals from irradiated silk fabrics are of particular interest.

In this paper, we report ESR studies on silk fabric samples irradiated in different atmospheric or sample conditions.

2 EXPERIMENTAL

The silk fabric used in the study was bleached Chinese crepe 12102, a mulberry silk product made by Wujiang Silk Industry Co., Ltd., Jiangsu, China. The silk fabric was washed in Peregol O and distilled water, and degummed successively with ethanol and acetone solutions of analytical grade. The treated silk fabrics was allowed to dry in air and cut into samples of 14 cm$\times$7 cm.

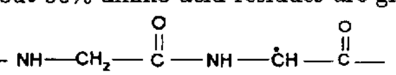
γ-ray irradiation of the samples were performed in a ^{60}Co source of 3.7×10^{15} Bq at Shanghai Institute of Nuclear Research. The samples, sealed in test tubes with N_2 or air, were exposed to the γ-rays at room temperature at irradiation positions of known dose rate. Dichromate dosimeters were used to monitor the absorbed doses of the samples.

ESR measurements were conducted immediately after the irradiations at room temperature on a Varian E X-band spectrometer. Most of ESR scans were traced with a 100 kHz field modulation of 4×10^{-4} T amplitude, with the microwave power level being 1 mW. Radical concentrations of silk samples were calculated by a computer code using strong pitch as a reference.

3 RESULTS AND DISCUSSION

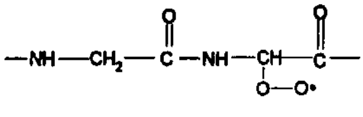
3.1 ESR spectra of different irradiation atmospheres

Fig.1.a is a typical ESR spectrum of the silk fabric irradiated in N_2 at a dose rate of 5 kGy/h for 3 hours. It consists of a strong doublet, which features similarly to the ESR spectrum of silk fibers irradiated in vacuum at room temperature in Ref.[4]. From the fact that about 50% amino-acid-residues are glycine, the doublet can be attribute to



radicals formed at α-carbons of the polymer main chains.

However, ESR spectra of the silk fabric samples irradiated in limited oxygen (the tube had been sealed with air) are different from Fig.1.a, as shown in Fig.1.b. The sample was irradiated to 15 kGy in 3 hours and measured right afterward. It is also composed of a strong doublet, but the second peak is much weaker than in Fig.1.a. This indicates that a considerable part of the radicals was destroyed by the oxygen diffused into the silk fibers of the samples. When the sample was measured again after 24 hours, the doublet turned to a singlet as shown in Fig.2.a. The intensity of the singlet became only a few percent of the doublet, with most of the radicals being eliminated by O_2. The value of g–tensor is 2.0057, which nearly equals to that of the peroxide radicals formed by the reaction of γ-irradiated silk fibers in vacuum with O_2. The results suggest formation of the following peroxide radicals.



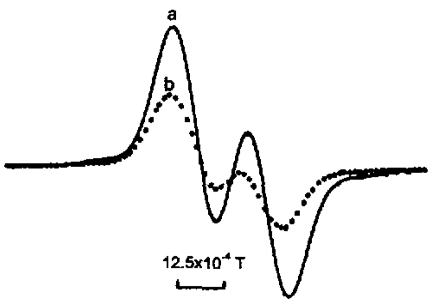


Fig.1 ESR spectrum of γ-irradiated silk fabrics
a. Irradiated and measured at room temperature in nitrogen, b. Irradiated in limited oxygen and measured at room temperature
Dose: 15 kGy, Dose rate: 5 kGy/h, Scan range: 100×10^{-4} T, Receiver gain: 1250

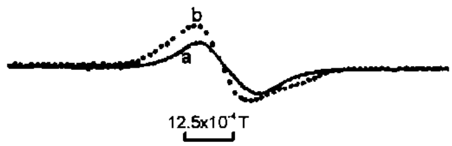


Fig.2 ESR spectrum of γ-irradiated silk fabrics
a. Irradiated in limited oxygen and measured 24 hours after irradiation at room temperature, b. Irradiated in open air at room temperature
Dose: 15 kGy, Dose rate: 5 kGy/h, Scan range: 100×10^{-4} T a. Receiver gain: 1560, b. Receiver gain: 1440

The silk fabric sample irradiated in open air, however, gave rise to even worse oxidation effect. Fig.2.b depicts the ESR spectrum of such a sample after 15 kGy irradiation.

3.2 Radical concentrations of different irradiation or sample conditions

3.2.1 Radical concentration of different doses

The silk fabric samples were irradiated in N_2 at the same dose rate to different doses of 1–50 kGy for their ESR measurements. Within the dose range measured, the radical concentration increases with increasing doses. As shown in Fig.3, the radical concentration increases sharply in low dose range, whereas the increase rate becomes smaller in high dose range. In this case, it is practical to perform radiation graft copolymerization of silk fabrics with suitable low dose. In addition, silk fabrics exposed to high doses would undergo physicochemical changes, as we partially observed at doses higher than 20 kGy, in their yellowing index, tensile properties, strength, elongation at break, thermal behavior, etc.

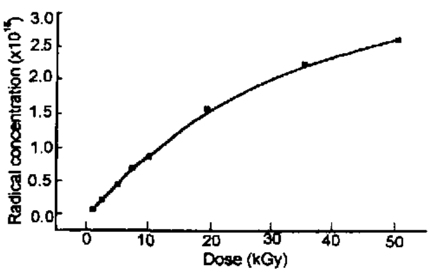


Fig.3 The effect of dose on radical concentration of γ-irradiated silk fabrics in nitrogen at room temperature

3.2 Radical concentrations of different atmosphere

The silk fabric samples were irradiated to 15 kGy at a dose rate of 5 kGy/h in N_2, limited O_2, and open air, respectively. Radical concentrations calculated from their ESR spectra are given in Table 1. Radical concentrations of the silk fabric samples irradiated in N_2 is 162% and 219% higher than the samples irradiated in limited O_2 and open air, respectively. The higher radical creation rate of irradiation in N_2 can ensure greater graft yields of monomers onto silk fabrics. And inferior properties of silk fabrics can be improved to desirable extent by low dose irradiation, without sacrificing their superior properties.

Table 1 Effect of atmosphere on radical concentration of silk fabric

Atmosphere	Relative radical concentration ($\times 10^{16}$)[1]
Nitrogen	3.68
Limited oxygen	2.27
Open air	1.68

[1]The relative radical concentrations were obtained by using strong pitch as a reference

3.3 Radical concentrations of different water content of the silk samples

Silk fabric samples of different water contents were irradiated in N_2 at a dose rate of 5 kGy/h for 3 hours. ESR measurements of the irradiated samples were done and radical concentrations were calculated. The results are given in Table 2. The radical concentration decreases sharply with increasing water content of silk fabrics. It is interesting that several percent of the moisture content resulted in huge losses of the radical concentration. This indicates that in pre-radiation graft copolymerization of silk fabrics, the material should be kept in dry conditions during the irradiation.

These silk fabrics were kept in N_2 at room temperature to measure half-life of the radicals. The results are listed in the right column of Table 2. The half-life shortened greatly with increasing water content of silk fabrics. It can be speculated that radicals react with water to accelerate the decay of free radicals in irradiated silk fabrics.

Table 2 Relationship between the properties and water content of silk fabric
(dose: 15 kGy, dose rate: 5 kGy/h)

Water content (%)	Initial concentration of the radicals ($\times 10^{16}$)[1]	Half-life of radicals (min)
0	2.7	>50000
5.8	1.6	9444
7.6	1.3	6278
11.9	1.2	3378

[1]Relative concentration, as noted in Table 1

3.4 Effect of dose rate on radical concentration

Silk fabric samples were irradiated at the different dose rates to 15 kGy in N_2. The ESR measurement results show that there was no dose rate effect on radical concentration up to the dose rate of 30 kGy/hr under investigation.

4 CONCLUSION

In conclusion, from ESR studies of the silk fabric samples irradiated in different atmosphere and sample conditions, we have had a better understanding of properties and behavior of radicals created by the γ-ray irradiation. The radical concentrations were greatly affected by oxidation during irradiation. And even a few percent of water contents of the samples reduced the radical concentration significantly. Besides, the samples' water content also accelerated the decay process of the radicals. In addition, no dose rate effects on radical concentrations were observed within the dose rate under investigation. The results are of help in our practice of property modification of silk products by radiation graft copolymerization.

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