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ESR signals from silk fabrics irradiated by UV -rays

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Abstract ESR studies were done on UV-ray irradiated silk fabric samples at room temperature. Different types of UV lamps were used and similar ESR signals were observed. The results indicate that UV-rays can produce free radicals for graft-copolymerization of monomer onto silk fibers without external additives or co additives, Also, radicals in silk fabrics irradiated by UV-rays are purer than that irradiated by γ-rays. The study suggests that UV-lights may be a better tool to improve properties of silk fabrics by grafting monomers onto the polymer chains.

Key words ESR, UV-ray irradiation, Silk fabrics

CLC numbers O636, O629.73

1 Introduction

Silk fabric is known as "queen of fibers", but it does have undesirable properties that limit its applications. Various kinds of efforts have been made to improve crease recovery, dyeing property, color fastness and dimension stability of silk fabrics. For a couple of years, we were working on improving crease recovery of silk fabrics by grafting vinyl monomers onto silk fabrics with γ-ray irradiation. Despite encouraging achievements, however, building a ^{60}Co γ-ray facility did not look so practical in production premises of the silk industry, and an alternative way is to use UV-lights to graft silk fiber.

UV–rays have been extensively used in surface curing to improve the product in terms of their physical, chemical and mechanical properties. In some applications, the method can be free of additives and co additives, alleviating much pressure of environmental pollution. UV-irradiation is also advantageous in its easy and safe operation of the inexpensive UV-lights in comparison with γ-ray and electron beam irradiators.

It is well known that polymeric materials, either synthesized products or natural fibers, such as silk fabrics can be grafted with monomers via their reactions with free radicals generated by the γ-rays[1-3]. In this paper, silk fabric samples irradiated under different UV-lights were studied with an electron spin resonance (ESR) spectrometer. It was proved that UV-rays produce free radicals in the silk samples. The ESR signals that varied by different factors were examined. Since UV-irradiation can result in chemical degradation to form stable subsided-radicals, it is of great interest to investigate properties of free radicals in UV–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.

2 Materials and methods

The silk fabric used in the study was bleached Chinese crepe 12102, a mulberry silk product made by Wujiang Silk Industry Co., Ltd., Jiangsu Province, China. The silk fabric was degummed successively with ethanol solutions of analytical grade in order to remove fats and inorganic residues. After washing in distilled water, the silk fabric was dried at 70℃ until constant mass was reached. Silk fabric samples of 14cm×2cm were sealed in quartz tubes, with N_2 or air (referred as limited O_2), for UV- or γ-ray irradiation and ESR measurement at room temperature. In the

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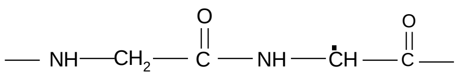
UV–irradiation, the dose was controlled by adjusting distance of the samples to UV lights. Different types of UV lamps with different wavelengths were used, i.e. 3kW iodine-gallium lamp of λ= 270~420 nm and 80W low pressure mercury lamp of λ=254 nm. The ESR measurements were conducted immediately after the irradiation on a Varian E X-band spectrometer. Most of the ESR scans were traced with a 100 kHz field modulation of 0.4mT amplitude, with the microwave power level being 1mW.

3 Results and discussion

3.1 ESR spectra of silk fabric samples irradiated by iodine-gallium lamp

Fig.1 is a typical ESR spectrum of the silk fabric irradiated in limited O_2 for 50 min at 30cm to the iodine-gallium lamp. The second peak of the doublet is much weaker than the first peak. However, ESR spectrum (Fig.2) of the silk fabric samples irradiated in N_2 differs from Fig.1, with a relatively strong doublet. From the fact that about 50% amino–acid–residues are glycine, the doublet can be attributed to [2-4]



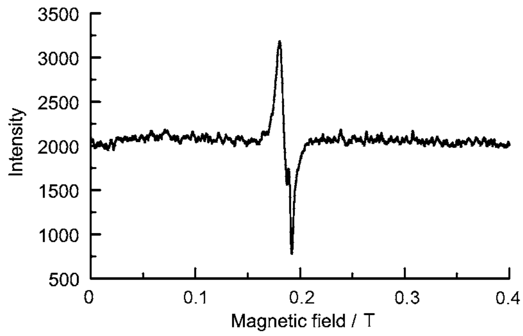
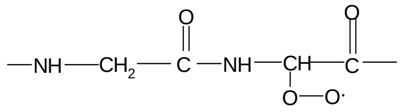


Fig.1 ESR spectrum of the silk fabric sample irradiated for 50min in limited oxygen with a 3kW iodine-gallium lamp, and measured at room temperatures, with scan range of 0.05T and receiver gain of 30000.

The second peak in Fig.2 is much stronger than that of Fig.1. 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 24 h after the irradiation, the doublet in Fig.1 became a singlet (Fig.3) with an intensity of only a few percent of the doublet, as most of the radicals were eliminated by O_2. The value of *g*–tensor is 2.0050, which nearly equals to that of the peroxide radicals formed by UV–irradiated silk fibers in O_2. The results suggest the formation of the following peroxide radicals:



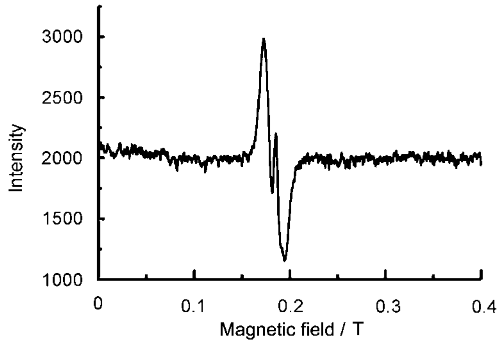


Fig.2 ESR spectrum of the silk fabric sample irradiated for 50min in N_2 with a 3kW iodine-gallium lamp, and measured at room temperatures, with scan range of 0.05T and receiver gain of 25000.

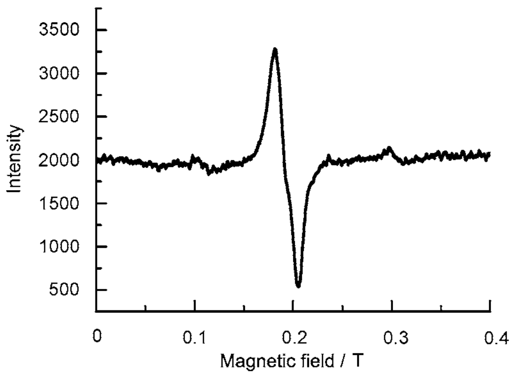


Fig.3 ESR spectrum of a silk fabric sample irradiated in limited O_2 with a 3kW iodine-gallium lamp, and measured at room temperatures three days after the irradiation, with scan range of 0.05T and receiver gain of 40000.

3.2 ESR spectra of silk fabric samples irradiated by low pressure mercury lamp

The ESR spectrum of the silk fabrics, irradiated in N_2 for 50min at 5cm to the low pressure mercury lamp is shown in Fig.4. It consists of a strong doublet and weak background absorption. And Fig.5 and Fig.6 (of 2.0056 in *g*-tensor) show the ESR spectra of silk fabric samples irradiated in limited O_2 and O_2, respectively, under the same UV-lights as Fig.4. Comparing the spectra in Figs.4, 5 and 6, one sees that the second peak in Fig.5 is weaker than that in Fig.4 and the doublet turned to a singlet in Fig.6. When the sample in Fig.5 was measured after three days of exposure to O_2, which was admitted into the sample tube, the doublet became a singlet (Fig.7, with a *g*-tensor of 2.0051) that is similar to Fig.6. From the result in section 3.1, it can be deduced that the radicals were formed at α–carbons of polymer main chains and its peroxide radical. The intensity of the singlet in Fig.7 is only a few percent of that of the doublet in Fig.5.

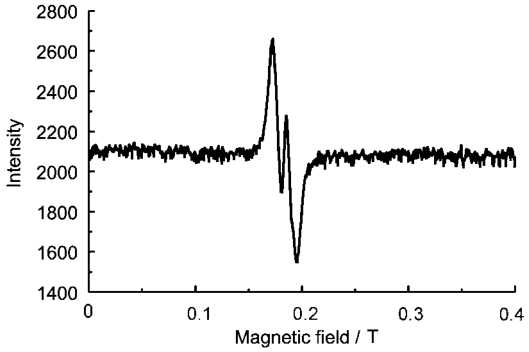


Fig.4 ESR spectrum of a silk fabric sample irradiated for 20min in N_2 with an array of four 20W low pressure mercury lamps and measured at room temperatures, with scan range of 0.05T and receiver gain of 12500.

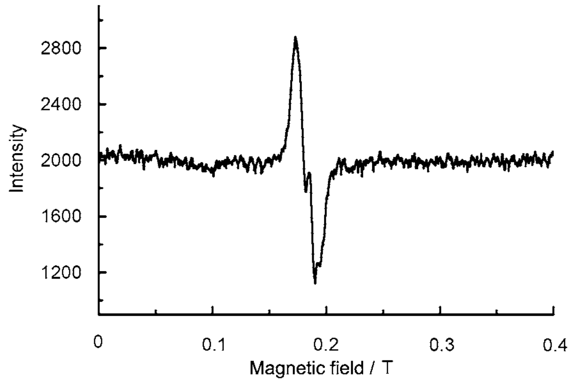


Fig.5 ESR spectrum of a silk fabric sample irradiated for 20min in limited O_2 with an array of four 20W low pressure mercury lamps and measured at room temperatures, with scan range of 0.05T and receiver gain of 30000.

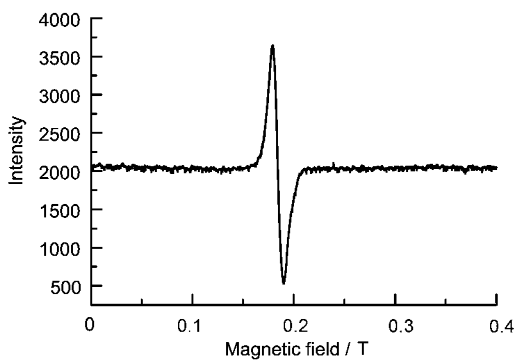


Fig.6 ESR spectrum of a silk fabric sample irradiated for 20min in O_2 with an array of four 20W low pressure mercury lamps, and measured at room temperatures, with scan range of 0.05T and receiver gain of 35000.

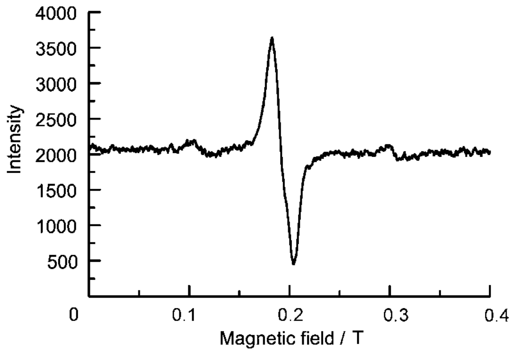


Fig.7 ESR spectrum of a silk fabric sample irradiated for 20min in limited O_2 with an array of four 20W low pressure mercury lamps. The sample had been exposed to O_2 before it was measured on the 3rd day after the irradiation, with scan range of 0.05T and receiver gain of 40000.

3.3 Comparison of ESR signals in silk fabrics irradiated by UV- and γ-rays

ESR spectra of γ-irradiated silk fabrics studied in our previous work[3], are shown in Figs.8, 9 and 10 (*g*=2.0056). From these spectra and *g*-tensor, it is thought that the type of radicals in silk fabrics irradiated by UV-rays is similar to that generated by γ-ray irradiation. The radicals may be formed at α–carbons of polymer main chains and its peroxide radicals. However, the width of the spectra in Figs.8-10 is larger than the spectra from silk fabric samples irradiated by the UV-rays. As UV-rays are far less powerful than the ^{60}Co γ-rays, and photo-chemistry is selected, the radicals in the UV irradiation would be purer than that by the γ-rays. And this would be beneficial to the graft-copolymerization of monomer onto silk fabrics by introducing no additives and co additives into the reactions.

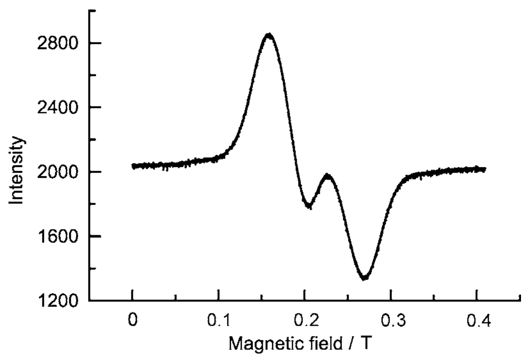


Fig.8 ESR spectrum of a silk fabrics sample irradiated in N_2 by ^{60}Co γ-rays and measured at room temperatures, with scan range of 0.01T and receiver gain of 1250.

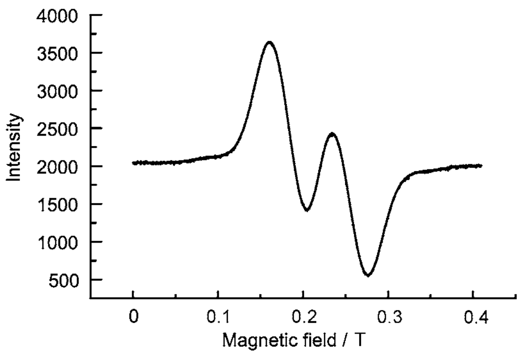


Fig.9 ESR spectrum of a silk fabrics sample irradiated in limited O_2 by ^{60}Co γ-rays and measured at room temperatures, with scan range of 0.01T and receiver gain of 1250.

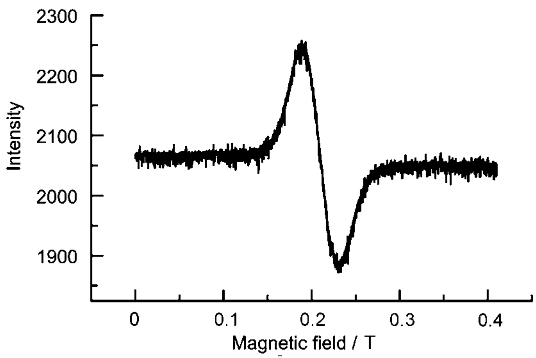


Fig.10 ESR spectrum of a silk fabrics sample irradiated in limited O_2 by ^{60}Co γ-rays and measured 24 h after the irradiation, with scan range of 0.01T and receiver gain of 1560.

4 Conclusions

ESR signals from silk fabrics irradiated by UV-rays can be summarized as follows:

The shapes and multiplicity of components of the spectra in the UV-irradiated silk fabrics (except small difference in ESR spectrum) are generally the same, though *g*-tensor of the singlet is slightly different. The line width and intensity depend on the type of UV-light. Radicals in silk fabrics irradiated by UV-rays are purer than that irradiated by γ-rays. The results also indicate that UV-lights can be a better tool for graft-copolymerization of monomer onto silk fabrics. Improvements in dyeing property and color fastness of the silk fabrics irradiated by UV-rays will be reported elsewhere.

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