Properties of Radicals Formed by the Irradiation of Wool Fibers

Huiyong WANG1*, Ruiqin LIU1, Tiechen TU1, Leidong XIE1, Kanglong SHENG1, Yali CHEN2 and Xin TANG2

Wool fiber/γ-Ray irradiation/ESR.

Wool fibers of different sample conditions were irradiated in different atmospheres by 60Co γ-rays and were studied by electron spin resonance method (ESR). It was found that a large percentage of the α-carbon radicals of polymer main chain were more long-lived radicals. The ESR measurements of irradiated cortex samples of the wool fibers proved that most radicals from the cortex were long-lived ones. Low water content (as low as 27.5%) in the reaction system did not greatly affect the radical formation, but higher water contents would reduce the radical concentrations dramatically and accelerate their decaying process. The results will be of help in property modification of wool products by radiation graft copolymerization.

INTRODUCTION

Wool, as a natural protein called α-keratin, has been for centuries a kind of popular fiber for making warm garments. However, the worsted textile industries, and research institutions as well, are still seeking ways to improve woolen fabrics against the materials’ undesirable property of felt shrinkage, which is related to the surface of a natural wool fiber being covered by overlapping scales.

The property modification of natural wool with graft copolymerization techniques has been a subject of interest in this field of research since the early 1970s. Grafting suitable monomers to wool fibers can be of help to improve physical, mechanical, and biochemical properties of wool fabrics. Several laboratories grafted vinyl monomers onto wool fabrics in their efforts to improve some properties of the material, and others investigated fine structures and physicochemical properties of irradiated wool fibers.1)

We think it important, however, to study the mechanisms of the radiation effects on wool fibers before we can apply the method to improve the physicochemical properties of the wool fabrics materials. Radiation-induced grafting copolymerization onto wool fibers involves the generation of a great many active free-radical sites on the wool backbone. Investigating properties and structure of the radicals from γ-ray irradiated wool fiber samples would provide insights into the mechanisms of radiation effects. ESR offers us a powerful means to study the properties of free radicals created by radiations.2,3) In this paper, we present our ESR studies on wool fiber samples irradiated by 60Co γ-rays in different irradiation and sample conditions.

Furthermore, the microscopic structure of a wool fiber is quite unique, with wool scales on its outside and the cortex inside. It is known that chemical compositions of the two parts are different from each other. Therefore different alpha-carbon radicals of the polymer main chain will be generated by the ionizing radiations. It would be interesting, therefore, to separate wool scales from the cortex and investigate the properties of the radicals from the irradiated scale and cortex samples. However, this kind of sample preparation is difficult. Instead, we used a technique to remove the scales from the wool fibers for ESR study of the radicals from the cortex. The results of the experiment with the scale-removed wool samples are also reported in this paper.

EXPERIMENTAL

The employment of ESR spectroscopy to detect the formation of free radicals in wool keratin requires that the sample should be relatively dry, since the presence of water would cause a large nonresonant microwave power adsorption, hence a sizableable reduction in spectrometer sensitivity.

Samples of natural wool were purified by Soxhlet extraction with acetone for 24 h. After repeatedly being washed with distilled water, the samples were allowed to dry at room temperature.

Moreover, the following method was used to treat the wool samples and remove the scales. Ten grams of wool samples were immersed into 98–100% formic acid solution for 15 min, and a 24-h stirring of the samples was performed in a
pulsator. The treated samples were repeatedly washed with distilled water to remove formic acid.

Wool samples of different humidity were prepared under 25°C with the following saturated solutions, which retained the humidity of different levels, as shown in the parentheses, in airtight containers. The wool samples could be found in their invariant weight after keeping them in airtight containers of the different solutions for about three weeks.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Humidity (%)</th>
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<tbody>
<tr>
<td>LiCl·H2O (10.2%)</td>
<td>10.2%</td>
</tr>
<tr>
<td>KC2H3O2·1.5H2O (22.5%)</td>
<td>22.5%</td>
</tr>
<tr>
<td>MgCl2·6H2O (33.0%)</td>
<td>33.0%</td>
</tr>
<tr>
<td>K2CO3·2H2O (42.8%)</td>
<td>42.8%</td>
</tr>
<tr>
<td>Na2Cr2O7·2H2O (54.0%)</td>
<td>54.0%</td>
</tr>
<tr>
<td>NaNO2 (65.0%)</td>
<td>65.0%</td>
</tr>
<tr>
<td>NaCl (75.3%)</td>
<td>75.3%</td>
</tr>
<tr>
<td>KCl (84.3%)</td>
<td>84.3%</td>
</tr>
<tr>
<td>K2SO4 (97.0%)</td>
<td>97.0%</td>
</tr>
</tbody>
</table>

The two kinds of wool samples were weighed and packed into glass tubes of 4 mm in diameter. The tubes were sealed for γ-ray irradiation. According to different experimental requirements on irradiation conditions, some tubes were filled with N2, whereas the others remained aerated.

The wool samples were irradiated in a 60Co γ-ray facility of 3.7 × 1015 Bq at the Shanghai Institute of Applied Physics. The samples were exposed to the γ-rays at room temperature at irradiation positions of known dose rate. Dichromate dosimeters were deployed at the samples and read by a DMS-80 photospectrometer for dosimetry monitoring.

The irradiated samples were measured immediately after the irradiation by a Varian E X-band ESR spectrometer. And ESR measurements were performed periodically with some of the samples to investigate time-related properties of the radicals from the γ-ray irradiated wool fiber samples. Most ESR scans were traced with a 100 kHz field modulation of 8 G, and 1 mW of microwave power. Radical concentrations from the irradiated wool samples were integrated from the ESR spectra by a computer code using strong pitch as a reference.

**RESULTS AND DISCUSSION**

**ESR spectra of different irradiation atmospheres**

Typical ESR spectra are shown in Fig. 1 for the wool fiber samples irradiated to 50 kGy in different atmospheric conditions at a dose rate of 5.2 kGy/h.

Figure 1a is ESR spectra of the wool sample irradiated in N2. It consists of a strong doublet, which can be attributed to radicals formed at α-carbons of the polymer main chains.2,5)

![Figure 1](image)

However, the peaks in Fig. 1c, the ESR spectra of the wool samples irradiated in air, are much weaker than in Fig. 1a. This result might be explained because a large portion of the radicals had been destroyed by oxygen molecules diffused into the wool fiber samples. An oxygen molecule may react with the radical and cause the following reactions.5)

![Reaction](image)

When sample tubes containing substantial water were irradiated, the ESR spectra became complex, as shown in Fig. 1b. The peaks are weaker than in Fig. 1a, but stronger than in Fig. 1c. This indicates that the keratin proteins reacted very efficiently with primary water-free radicals. It is known that eaq− and OH•-free radicals could react with many targets.5) These effects caused the changes in the spectra. The humidity effects will be further discussed in “Humidity effects on radical concentration of the wool samples” on next page.

**Radical concentration under different irradiation or sample conditions**

**Radical concentration of different doses.** Wool samples were irradiated to different doses of 0.5–100 kGy in N2 at 5.2 kGy/h dose rate for ESR measurements. The radical concentrations increased with increasing doses, as shown in Fig. 2. In the dose range of up to 50 kGy, the radical concentration increased sharply with the dose, whereas in the dose range of 50–100 kGy, the radical concentration became saturated gradually.

**Radical concentration of different dose rates.** Wool fiber samples were irradiated to 30 kGy in N2 at the different dose rates from 3.6 to 25.2 kGy/h. The ESR measurement data are given in Table 1. The results show that there was no dose rate...
Humidity effects on radical concentration of the wool samples. Wool fibers of different humidities were irradiated to 50 kGy at 5.2 kGy/h dose rate. The final dose was chosen to facilitate observations of the reduced radical concentrations, which were calculated from their ESR spectra measured immediately after the irradiation. The results are given in Fig. 3. It is interesting to find that low water contents did not cause measurable changes in concentration of the radicals. Then as the humidity of the wool sample tubes increased to 27.5% and higher, the radical concentrations decreased dramatically.

It is known that hydrated electrons react with the carbonyl groups of peptidic bone. The consequences of the reactions can be fragmentation and ammonia liberation in the polymer main chain. This cleavage is supposed to take place at the free radical level. Figure 4 shows the ESR spectra of irradiated wool samples in different humidities. With growing humidity, spectral changes from strong triple peaks in a reaction system of 10.2% humidity (Fig. 4a) to a single peak at 75.3% humidity (Fig. 4c) could be observed. In a water-containing reaction system, the energetic photons ionized the wool fiber proteins and also the water molecules. The latter would affect the formation and combination of the wool protein radicals. In a reaction system of low humidity, the primary free radicals of the water were not enough to break such a balance of the protein radical formation and decay. However, when the system’s humidity was higher (higher than about 30%, as shown by the experimental data), the probability for a keratin protein radical to react with the water radicals became larger enough to cause dramatic reductions of the protein radical concentration. Furthermore, the lifetime of the protein radicals of the high-humidity reaction system was shorter than that in dry systems of the reactions.

Radical decay of the irradiated wool fiber. Wool fiber samples were irradiated to 50 kGy in N₂ at 5.2 kGy/h dose rate. ESR measurements were performed immediately after the irradiation and in time intervals of several hours at first, and a few days or weeks thereafter, to observe the decay behavior of the wool protein radicals. Figure 5 shows hyperfine structure in the ESR spectra of the γ-ray-irradiated wool fibers. Figure 5a was measured immediately after irradiation, and Fig. 5b 14 days later. It can be seen that the spectral structure after a two-week decay of the radicals changed greatly from the beginning.

The radical concentrations were calculated from the ESR spectra. As shown in Fig. 6, the radical concentration decreased sharply within 24 h after the irradiation, then the radical decay rate became slower and slower. According to the ESR measurements, about 44.7 and 62.2% of the wool protein radicals had lifetimes shorter than 24 and 193 h, respectively, whereas more than 35.0% of the radicals had lifetimes longer than 400 h. The large percentage of longer life radicals will ensure a desirable efficiency of the graft rate when the postirradiation graft method is used to modify properties of the wool fibers.

Radical characteristics of the wool cortex. Wool fiber pro-
Proteins consist of a variety of amino acids, and the chemical compositions are different in the scale and cortex of a wool fiber. Generally, the scale part contains more cystine, whereas the cortex part contains more glycine, tyrosine, and phenylalanine. Therefore the \( \gamma \)-rays would produce \( \alpha \)-carbon radicals of the polymer main chain of quite different properties from the scale and cortex. Figure 7 shows scanning electron microscope (SEM) images of two wool fibers. In Fig. 7a is a wool fiber sample before the treatment and in Fig. 7b is a wool fiber sample that had been treated with the method described in Section 2 to remove the scales. ESR measurements of the irradiated samples revealed their spectral difference. However, what interested us the most is that ESR spectra of the untreated wool sample measured two weeks after irradiation (Fig. 8a) looked like very much like the ESR spectra of the treated wool samples measured just after the irradiation (Fig. 8b). This suggests that most of the radicals formed from the surface of wool fibers (mainly in scales) are short-lived radicals, whereas radicals from the cortex of wool fibers are...
mostly long-lived ones. The phenomena will be further investigated to facilitate experimental designs of postirradiation graft methods to improve the wool fabrics’ properties.

CONCLUSION

From ESR studies of the wool fiber samples irradiated in different atmosphere and sample conditions, we have had a better understanding of the properties and the behavior of radicals generated by the γ-rays. The radicals were formed at α-carbons of the polymer main chains. In a dose range of up to 50 kGy, the radical concentrations increased rapidly with the dose, whereas no dose rate effects were observed up to 25.2 kGy/h. The irradiation of the wool fibers should be better conducted in nitrogen to prevent reductive reactions. Low water content (up to 27.5%) in the reaction system did not greatly affect the radical formation, but higher water contents would reduce the radical concentrations dramatically and accelerate their decaying process. In a dry reaction system, the large percentage of more long-lived radicals would ensure a desirable efficiency of the graft rate when a postirradiation graft method is used to modify the properties of the wool fibers. ESR measurements of irradiated cortex samples of the wool fibers proved that most radicals from the cortex were long-lived ones, whereas most radicals formed from the scales were short-lived. The results will be of help in the property modification of wool products by radiation graft copolymerization.

REFERENCES