EPR study of free radicals in cotton fiber for its potential use as a fortuitous dosimeter in radiological accidents

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Abstract. Electron paramagnetic resonance (EPR) spectroscopy was applied to characterize radiation-induced free radicals in the cotton fiber in order to determine the possibility for using cotton as a fortuitous dosimeter in accidental exposures to radiation. Cotton fabrics were irradiated at 0.1, 0.5, 1, 2, 10, 50 and 500 Gy using a ^{137}Cs gamma source. The irradiated samples were then stored in the dark under controlled environmental conditions for 1, 15, 35 and 60 days. The EPR spectra were observed in samples using a Bruker EMX X-band spectrometer equipped with a TE_{102} rectangular cavity. The EPR signal intensities of irradiated samples were determined from peak-to-peak amplitudes of EPR spectra and compared to those of unirradiated samples. The following optimum parameters were used: 100 kHz modulation frequency, 9.84 GHz microwave frequency, 1.8 mT modulation amplitude, 1.0 mW microwave power, 655 ms time constant, 41 ms conversion time and 41.98 s sweep time. The EPR spectra of unirradiated samples showed a singlet line with g = 2.006 due to pre-existing stable organic radicals in the cotton fibers, whereas those of irradiated samples showed the same pattern with different signal intensities according to the doses. Irradiation increased the signal intensity in a dose dependent manner. The signal intensity exhibited an exponential decay with storage time from 1 to 60 days. Obviously, the degree of fading of EPR intensity did not depend on the absorbed dose from 0.1 - 50 Gy. The maximum fading was about 60% at 60 days of storage for irradiated samples at all doses. However, this post-irradiation signal appeared to be detectable for up to 60 days. The EPR study results indicated the potential of using cotton as a fortuitous dosimeter in radiological accidents.

1. Introduction

Ionizing radiation is utilized and applied worldwide in many areas including medicine, industry, agriculture and research. The risk of radiological accidents might generally be increased and consequently the radiation emergency preparedness is of great concern in most countries. Following a radiological or nuclear incident, determination of the absorbed dose to individuals exposed to critically high radiation doses is of importance for initial medical treatment decisions. Therefore, the search for fortuitous dosimeters is currently needed especially when the accident happens in a local suburb area where people do not generally have a personal dosimeter, or the dosimeter is not properly worn at the appropriate position.

Electron paramagnetic resonance (EPR) spectroscopy is applicable to paramagnetic molecules with one or more unpaired electrons, i.e. radicals and transition metal ion complexes [1]. EPR spectral studies

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on several materials having potential to be used as a fortuitous dosimeter have been reported, such as mineral glasses from watch [2-3] and mobile phone LCDs [4], wallboards [5], sugar [6], eggshells [7] and cotton from clothing fabrics [8]. Among these materials, clothing fabrics have been shown to be suitable as a fortuitous EPR dosimeter due to their advantages in availability and practicality to provide dose mapping throughout the body. Viscomi *et al* [8] reported the preliminary EPR study in untreated cotton yarns following a high dose (500 Gy) and intermediate doses (50 to 10 Gy) of irradiations. The results highlighted the presence of a specific post-irradiation signal distinguishable from the pre-irradiation signal at all doses studied. In this work, the EPR signals in cotton fabrics were investigated covering the dose ranging from 0.1-500 Gy to explore the possibility of using cotton existing in the clothing fabrics as a fortuitous dosimeter. The parameters of EPR spectrometer were initially optimized. The dose-response relationship was obtained by using the optimized parameters. The fading of free radicals was demonstrated by studying the stability of EPR signals during storage.

2. Materials and methods

2.1. Cotton samples

Cotton fabrics used in this study were obtained from a textile company (anonymous). They were cut into small pieces and put into plastic bags for irradiation.

2.2. Gamma irradiation

Irradiation of cotton fabrics was carried out using a ^{137}Cs gamma source (Mark I) at a dose rate of 3.7 Gy min^{-1} confirmed by a Fricke dosimeter, giving doses of 0.1, 0.5, 1.0, 2.0, 10, 50 and 500 Gy. The irradiated samples were sealed in plastic bags and maintained in the dark at room temperature until EPR readings.

2.3. EPR measurements

EPR spectra were measured using a Bruker EMX X-band EPR spectrometer equipped with a TE_{102} rectangular cavity. The samples were cut into small pieces with suitable size to be put into the quartz tube. The ESR tube containing 100 mg of sample was adjusted to a fixed position to maintain reproducibility in the cavity. Initial EPR measurements were carried out using a 500 Gy-irradiated cotton fabric to optimize the parameters including microwave power, modulation amplitude and time constant. The optimal parameters used for the dose dependent study were: 100 kHz modulation frequency, 9.84 GHz microwave frequency, 1.0 mW microwave power, 1.8 mT modulation amplitude, 655 ms time constant, 41 ms conversion time and 41.98 s sweep time. The intensity of the EPR signal was measured by determining the peak-to-peak height from the minimum to the maximum of the spectrum. The fading characteristics of EPR signal for the storage time of 1, 15, 35 and 60 days were examined. All reported intensities represented the mean of three individual experiments.

3. Results and discussion

3.1. EPR spectrum optimization

As previously described, the magnitude of the microwave power affected the saturation of EPR signal intensity [9]. The initial value for microwave power was set at 0.01 mW, while the modulation amplitude was fixed at 1.8 mT. The EPR signal intensity was observed when the microwave power was increased from 0.01 to 5.0 mW. The relationship between EPR signal intensity and the square root of microwave power is shown in figure 1a. The signal amplitude increased with microwave power from 0.01 to 1.0 then gradually decreased. A microwave power of 1 mW was selected for all experiments to avoid saturation effects.

Next, the modulation amplitude was optimized by acquiring the spectrum at a set modulation varied from 0.1 to 2.5 mT. It was found that the intensity increased while the pattern of EPR spectra was not changed (figure 1b). The modulation amplitude at 1.8 mT was set since the best spectrum was obtained.

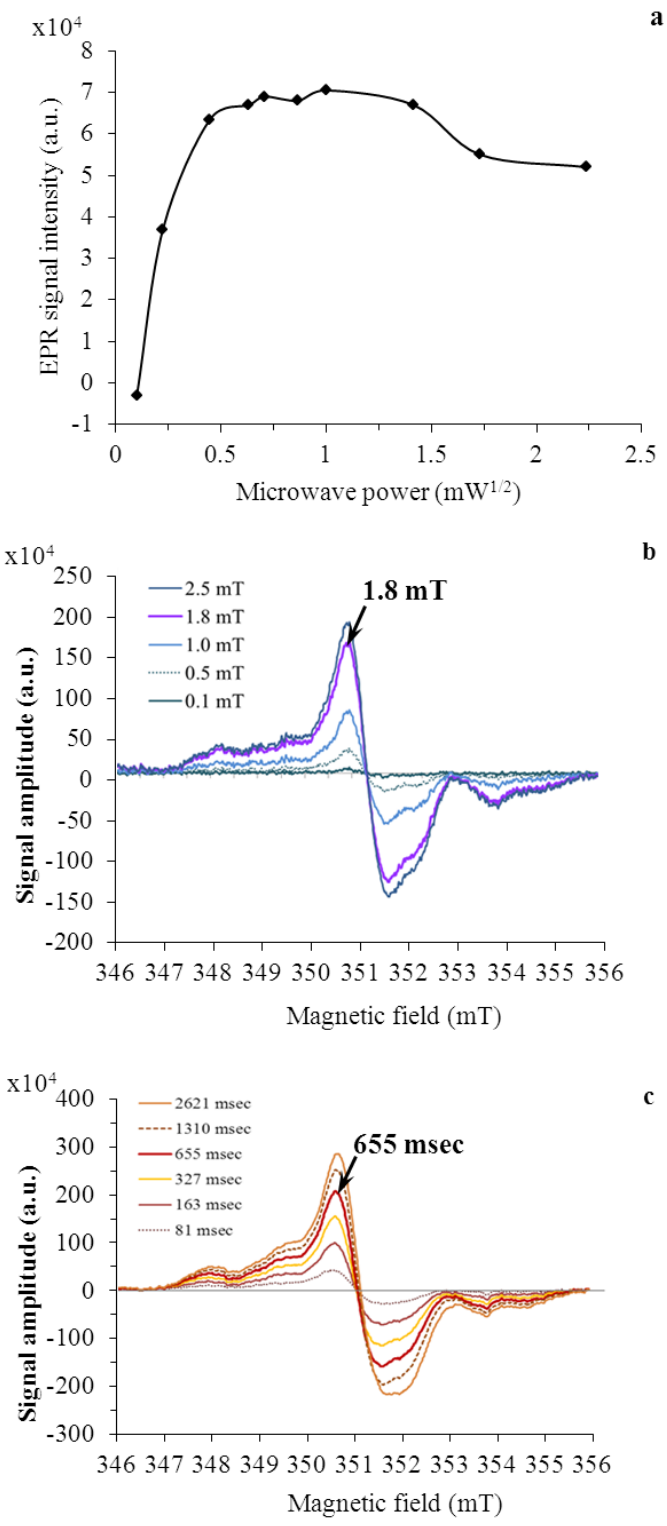


Figure 1. EPR spectrum optimization. (a) Variation of EPR signal intensity with microwave power for irradiated cotton (500 Gy). (b) EPR spectra with varied modulation amplitude. (c) EPR spectra with varied time constant.

Finally, the time constant was varied to maximize the signal-to-noise ratio. It appeared that the intensity increased as the time constant was increased from 81 to 2,621 ms; however, distortion was not obviously present (figure 1c). Since the time constant is related to the scan time, the moderate time constant at 655 ms was selected to obtain the appropriate scan time to collect the spectra under this experiment.

3.2. EPR spectra of unirradiated and irradiated samples

EPR spectral investigations were carried out in unirradiated and irradiated samples. As shown in figure 2, the EPR spectrum of an unirradiated sample exhibited a singlet lines centered at $g = 2.006$ probably arising from stable free radicals originated from the processing of the cotton fabrics. This might be due to the effect of several parameters on cotton fibers during its fabrication such as chemical and physical processes. The results were in agreement with the previous work reported by Viscomi *et al* [8].

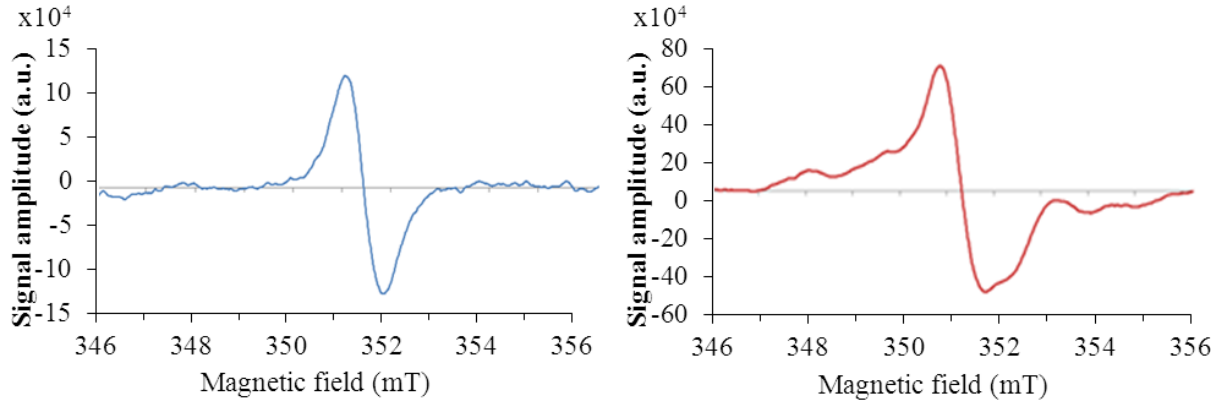


Figure 2. EPR spectra of unirradiated (left) and 500 Gy-irradiated (right) cotton samples.

After irradiation of the cotton samples, there was no difference observed except that the signal intensity of EPR spectrum was changed. It is generally known that cotton is nearly pure cellulose consisting of polysaccharide chains. This EPR signal originated from the carbon-centered radicals produced in the cotton cellulose by gamma irradiation and stabilized at room temperature. It was previously expected that 5 different types of radicals would be produced by H atom elimination from a C-H bond in the molecule of saccharides [10]. The yield of free radicals varied depending on the dose received. Even though these free radicals were detected in unirradiated cotton fibers, their EPR spectrum showed a weak signal compared to samples irradiated at the lowest dose of 0.1 Gy under this study. The EPR signal of 0.1 Gy-irradiated samples exhibited an increase of 40% relative to that of unirradiated samples.

The EPR spectra in relation to the doses of irradiated cotton are shown in figure 3. The pattern of EPR spectra did not change as the dose increased from 0.1 - 50 Gy. It was observed that the EPR signal intensity of irradiated cotton linearly increased with the absorbed dose (data not shown). The construction of the dose-response curve might be further developed in order to be used to estimate the dose received in unknown samples.

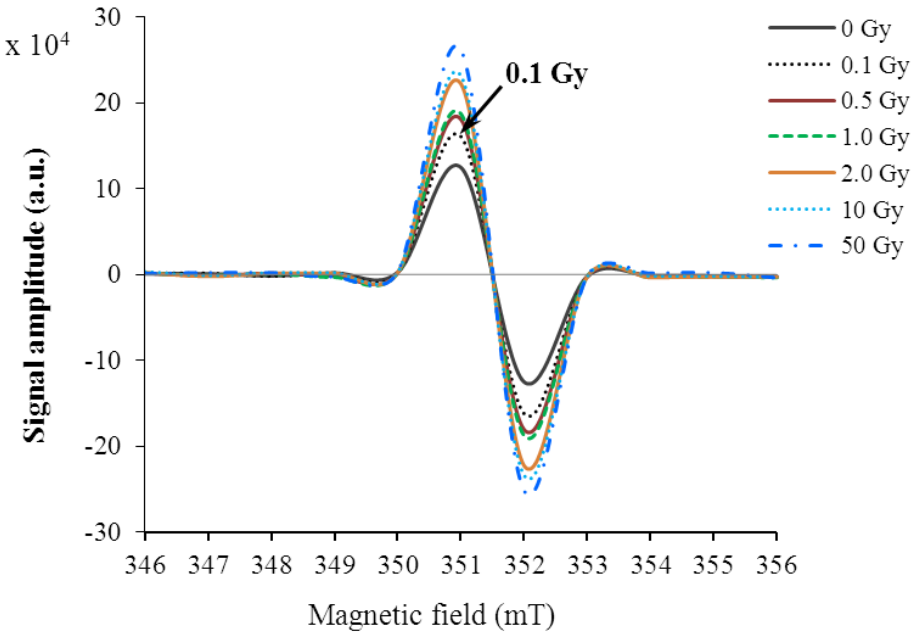


Figure 3. EPR spectra of unirradiated and irradiated cotton samples.

3.3. The stability of EPR signals

When irradiated samples were stored at room temperature in the dark, their EPR spectrum exhibited a broadened signal with a slight shift in the resonance signal and centred at $g = 2.234$. The signal intensity exhibited an exponential decay with storage time from 1 to 60 days (figure 4). However, the degree of fading of EPR intensity was not related to the absorbed dose from 0.1-50 Gy. The intensity of signal decreased between 55 and 60% after 60 days of storage of the irradiated samples at all doses. However, the post-irradiation signal was still detectable for up to 60 days. Further investigation should be performed to explore its persistence for periods longer than 60 days to assess the possibility of using the EPR signal as a marker of radiation exposure.

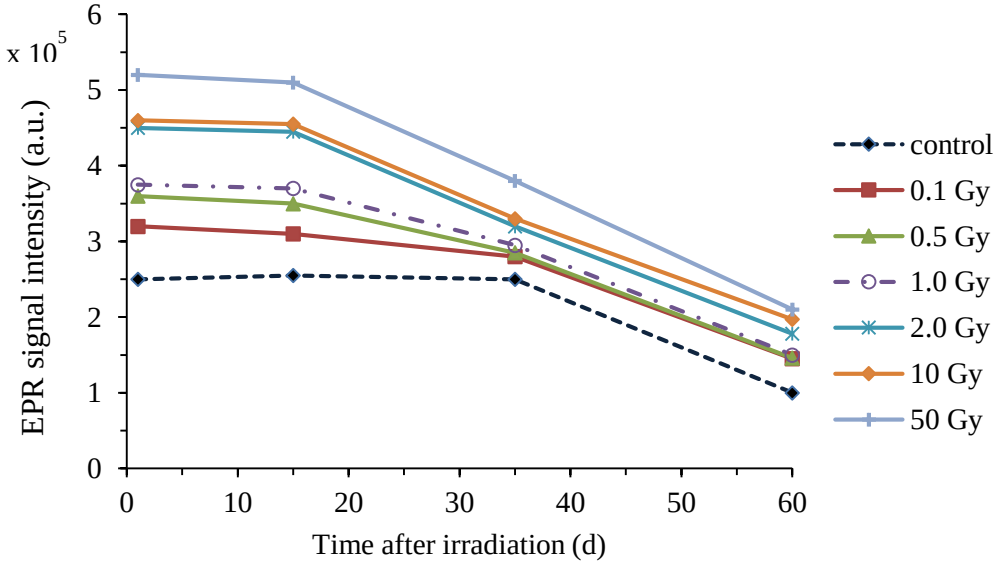


Figure 4. The stability of the EPR signals of cotton samples during the storage period.

4. Conclusions

The measurement of free-radicals in the cotton fabrics using EPR spectroscopy is possible for the determination of the radiation dose received by affected individuals in a radiological accident. The dose distribution obtained will provide useful information for medical treatments. As cotton is used to make a number of textile products and can be blended with other materials such as fibers, including rayon, and synthetic fibers such as polyester, further efforts are required to develop it a fortuitous dosimeter.

Acknowledgements

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