Study on Free Radicals of Cotton and Wool Fibers Treated with Low-Temperature Plasma

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SYNOPSIS

Natural fibers, such as cotton and wool, were treated with low-temperature plasmas of O_2, N_2, Ar, H_2, CO, and CF_4. The intensity of the free radicals of the plasma-treated fibers was measured using electron-spin-resonance (ESR) spectroscopy. The result indicates that the reaction of low-temperature plasmas generates free radicals in the fiber matrix. The intensity of the free radicals is related to fiber matrix, fine structure, the kinds of plasma gases, and the condition of treatment. The thermal stability and variation with time of the free radicals were also inspected. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Low-temperature plasma treatment is a useful dry process technique to modify a polymer surface and leads to polymerization, grafting, crosslinking, and implantation. Treating fibers and polymeric materials with low-temperature plasma will generate free radicals in the matrix, which play an important role in these reactions.[1] Researchers have measured free radicals in fibers created by plasma treatment using ESR spectroscopy and have discussed the application of free radicals to textile finishing.[2-5] It is considered that the free radicals are active atomic groups, in which unstable free radicals recombine rapidly and some of stable free radicals remain in the polymer matrix.

The purpose of this study was to confirm free-radical production by a low-temperature plasma reaction and to discuss the factors affecting the intensity of the free radicals. The study promotes the application of the low-temperature plasma technique in textile finishing. The intensity of the free radicals in the fiber matrix was determined by ESR after a natural cellulose fiber cotton and a natural protein fiber wool were, respectively, irradiated with the low-temperature plasmas of O_2, N_2, Ar, H_2, CO, and CF_4. The effect of the fiber matrix, microstructure, plasma gas, and condition of treatment upon the intensity of the free radicals is discussed. The thermal stability and variation with time of the free radicals were also inspected.

EXPERIMENTAL

Cotton and wool fibers were dewaxed with carbon tetrachloride in a Soxhlet extraction for 8 h, followed by repeated washing with distilled water and drying in air. The low-temperature plasma reactor system used is schematically represented in Figure 1.

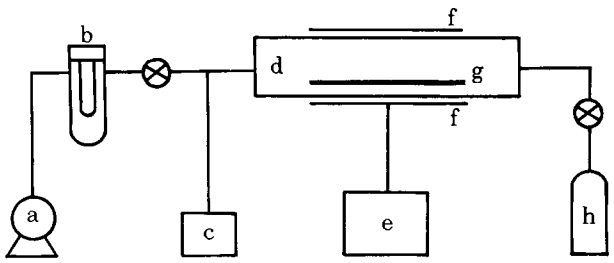

Figure 1 Plasma reactor system: (a) vacuum pump; (b) cold trap; (c) pressure gauge; (d) reaction chamber; (e) radio-frequency source; (f) electrodes; (g) sample plate; (h) gas bomb.

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The conditions of the low-temperature plasma reaction were the following: gas sources, O_2, N_2, Ar, CO, and CF_4; pressures in the reaction chamber, 0.3–1.5 Torr; power, 300 W; frequency, 13.56 MHz; and irradiating time, 10–300 s. The presence of free radicals was measured using ESR spectroscopy. MnO was used as a standard material. The conditions of the measurement were as follows: temperature, 18°C; magnetic field intensity, 3300 ± 500 G; sweep time, 4 min; amplitude modulation, 100 kHz with 20 G; gain amplitude, 5.0 × 100; and power, 4 mW. The intensity of the free radical of the samples is given by the following equation:

$$\text{Relative free radical intensity} = \frac{\text{ESR absorption intensity of fiber sample}}{\text{ESR absorption intensity of standard material}}$$

The samples pretreated with plasmas of O_2, CO, and CF_4 were retreated in hot air from room temperature 25°C to 200°C for 10 min, and the intensity of the free radical was measured. The samples pretreated with plasmas of O_2, CO, and CF_4 were treated in air at room temperature and the intensity of the free radicals was measured once every 5 days.

RESULTS AND DISCUSSION

The ESR spectra for cotton and wool treated and untreated with a low-temperature plasma of CO gas are shown in Figure 2. There are six lines of equal height in the ESR spectra of MnO. The ESR absorption spectrum of the free radicals of the fiber appears between the third and fourth line of the MnO spectra, which is nearly parallel to the ESR spectra of the untreated material, but the intensity is obviously different. This is shown in Figure 2(a) and (b); the relative intensity of the free radical of the untreated samples is very weak; 0.2 of the line height of the MnO. After being treated with CO plasma, the relative intensity of the free radical of wool fiber reaches 0.7 [Fig. 2(c)]. Compared with untreated wool fiber, it is 3.5 times larger. The relative intensity of the free radical of cotton fiber

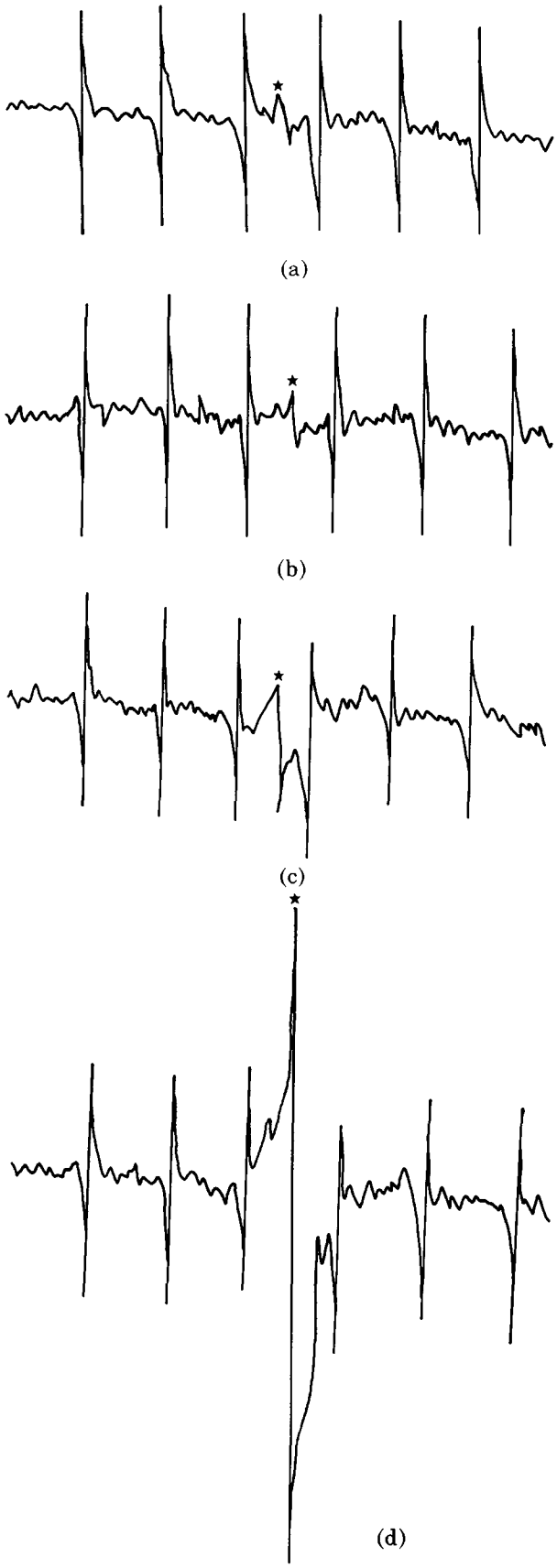

Figure 2 ESR spectra of cotton and wool treated with low-temperature plasma of CO: (a) wool/untreated; (b) cotton/untreated; (c) wool/CO; (d) cotton/CO. Time of plasma irradiation: 180 s; pressure of plasma treatment: 1 Torr. (*) ESR signal of samples.

Table I Relative Free Radical Intensities of Cotton and Wool Fibers Treated with Low-temperature Plasma of Various Gases[a]

Plasma Gas	Relative Free Radical Intensity	
	Cotton	Wool
O_2	0.5	0.4
N_2	0.6	0.5
Ar	1.6	0.6
H_2	1.8	0.6
CO	2.9	0.7
CF_4	3.1	0.9

[a] Plasma treatment was at a pressure of 1 Torr for 180 s.

reaches 2.9 [Fig. 2(d)], which is 14.5 times greater than that of untreated cotton or wool.

After being treated with low-temperature plasmas in various gases, such as O_2, N_2, Ar, CO, and CF_4, the different relative free-radical intensities of cotton and wool fibers detected by ESR are given in Table I. The result of the ESR detection confirms that the reaction of the low-temperature plasma with the wool and cotton generates free radicals in the fiber matrix, indicating that the chemical modification on the fiber surface is a free-radical reaction.

Table I shows that the free-radical intensities are different for various gases with the general rule that $O_2 < N_2 < Ar < H_2 < CO < CF_4$. For cotton or wool fibers treated with CO or CF_4 plasma gases, the free-radical intensity is the strongest, while with a plasma of O_2 or N_2, it is the weakest. In fact, this is the same rule that has been observed for other natural and synthetic fibers.[6] This indicates that the activity differs for various plasmas. The plasmas were generated for the various gases by electric discharge in a vacuum condition. It is also observed from Table I that whichever fiber is treated with plasmas of any of the gases the ESR signal for cotton fiber is much stronger than that for wool fiber. In other words, the free-radical intensity of the natural cellulose fiber is stronger than that of the protein fiber. This is in accordance with the results of a former study on linen and silk.[7] It indicates that the stability of the free radicals produced by the low-temperature plasma reaction in the fiber matrix is connected to the chemical components of the fiber and the position of the broken chemical bond.

The relationship between fiber crystallinity and free-radical intensity is shown in Table II. Through a mercerizing treatment, the cotton fiber structure

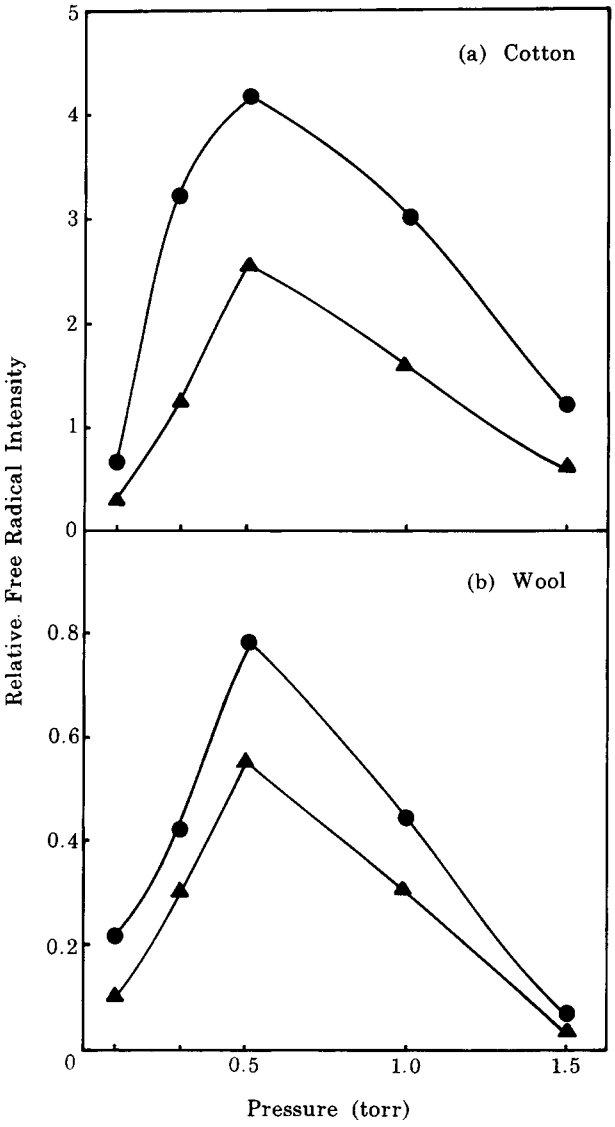

Figure 3 Effect of plasma gas pressure on relative free-radical intensity: (●) CF_4; (▲) CO. Time of plasma irradiation: 180 s.

Table II Effect of Crystallinity of Cotton Fiber on the Relative Free-radical Intensity after a Low-temperature Plasma Reaction[a]

Fiber	Crystallinity[8] (%)	Relative Free-radical Intensity		
		CF_4	CO	O_2
Cotton	70	3.1	2.9	0.5
Mercerzed Cotton	50	2.6	1.7	0.3

[a] Plasma treatment was done at a pressure of 1 Torr for 180 s.

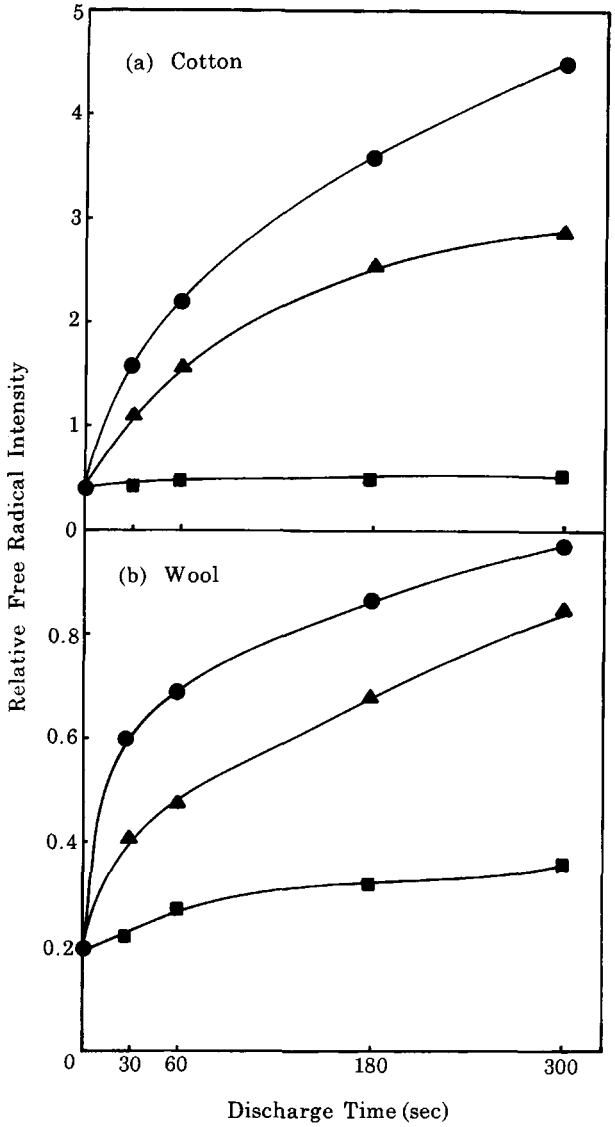

Figure 4 Effect of plasma discharge time to relative free-radical intensity: (●) CF_4; (▲) CO; (■) O_2. Plasma treatment was done at a pressure of 1 Torr.

becomes slack and crystallinity decreases. The free radicals produced in the noncrystal area of the slack structure more easily recombine with each other. The intensity of the free radicals in mercerized cotton is weaker than that in the original cotton fiber. These results indicate that the stability of free radicals which are produced by the low-temperature plasma reaction in a fiber matrix is strongly affected by the fine structure of the fibers.

The relationship between gas pressure of the plasma reaction and the relative free-radical intensity is shown in Figure 3. When cotton fiber is treated by plasmas of CF_4 or CO, the free-radical intensity increases rapidly with pressure when the pressure of the gas is less than 0.5 Torr. The intensity passes through a maximum when the pressure is approximately 0.5 Torr. The intensity of the free radicals decreases rapidly with increase in gas pressure, so that at a pressure of 1.5 Torr, it is only slightly different from what it was at the lowest pressure. The same rule applies for the wool fiber treated with CF_4 and CO plasmas; when the pressure reaches 0.5 Torr. The free-radical intensity is the strongest. A study by Mimoru indicated that under a special gasous pressure both the degree and speed of the plasma reaction reach a maximum.[9]

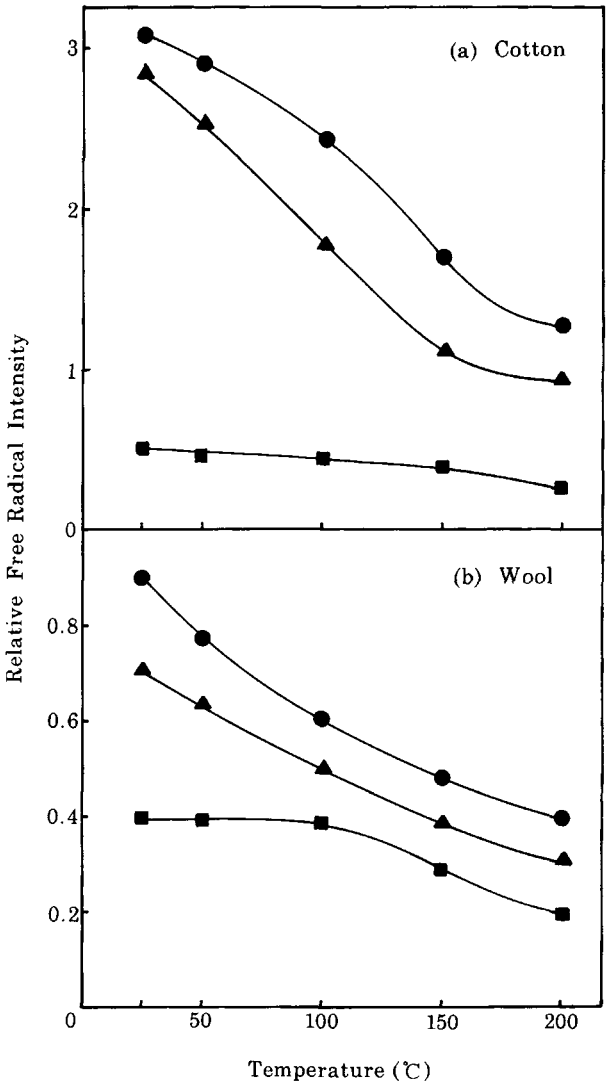

Figure 5 Effect of temperature of heat treatment to relative free-radical intensity: (●) CF_4; (▲) CO; (■) O_2. Plasma pretreatment was done at a pressure of 1 Torr for 180 s.

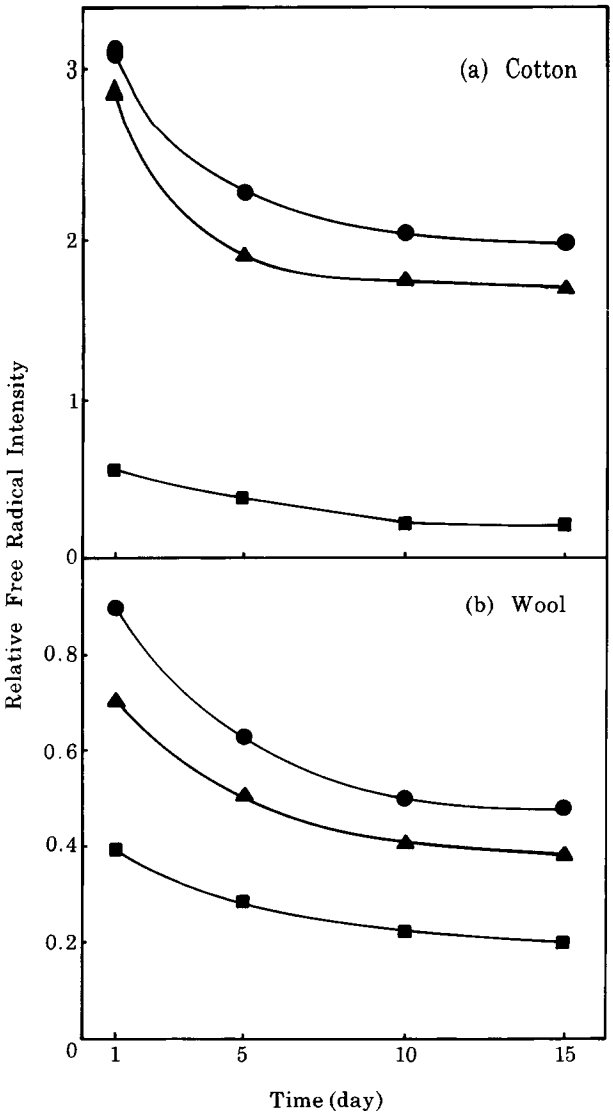

Figure 6 Variation with time of free radicals generated in cotton and wool by O_2, CO, and CF_4 plasmas in air at room temperature. Plasma treatment was done at a pressure of 1 Torr for 180 s: (●) CF_4; (▲) CO; (■) O_2.

Changes in the free-radical intensity of cotton and wool fibers with different discharging times (10, 30, 60, 180, and 300 s) are shown in Figure 4(a) and (b). The free radicals are produced by treatment with CF_4, CO, and O_2 plasmas. From Figure 4(a) and (b), it is seen that for both fiber types and whichever gas is used in the treatment the free-radical intensity increases with discharging time. This indicates that the degree of the free-radical reaction is enhanced with increase in the discharging time.

The fibers of cotton and wool treated with O_2, CO, and CF_4 plasma were heated to 200°C in air for 10 min in a dry-heat condition. The variation with temperature of the heat treatment on the relative intensity of the free radical is shown in Figure 5(a) and (b). When the temperature increases, the free-radical intensity of cotton and wool fibers becomes weaker after being treated by any gas plasma. This observation attests to the fact that at high temperature the free radical becomes more active and the active free radicals are able to recombine more rapidly.

The samples of cotton and wool treated with O_2, CO, and CF_4 plasmas after exposure to air at room temperature exhibited the variation of free-radical intensity with time given in Figure 6(a) and (b). The variations with time of the free-radical intensity of cotton and wool fibers treated with three types of gas plasmas exhibited the same decreasing rule. Up to an exposure of 5 days in air, the free-radical intensity reduces rapidly. From 5 to 10 days, the intensity reduces slowly. After 10 days, the intensity is quite stable. As discussed previously in this article, the reaction of low-temperature plasmas on fibers and polymer surfaces is based on free radicals. The intensity of the free radical in the fiber matrix reduces rapidly with time. It can be supposed that it is one of the important reasons of poor variation with time for surface modification of fibers or polymers with low-temperature plasma and will be more studied and tested.

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