Free Radicals of Fibers Treated with Low Temperature Plasma

JIE RONG CHEN

Department of Textile Chemistry, Northwest Institute of Textile Science and Technology, Jin hua Rd. Xi'an City, People's Republic of China

SYNOPSIS

Cotton, linen, polynosic rayon, standard rayon, nylon 6, and poly(ethylene terephthalate) (PET) fibers were treated with low temperature plasmas of O_2, N_2, Ar, CF_4, and CO. The relative free-radical intensities obtained by ESR spectra increased in the following order: linen > cotton > polynosic rayon > standard rayon > nylon 6 $\approx$ PET and CF_4 > CO > Ar > N_2 > O_2.

Low temperature plasma treatment is a useful technique to modify a polymer surface and leads to polymerization, grafting, crosslinking, and chemical incorporation. Free radicals generated in the treatment play an important role in these reactions, and it is likely that some of unstable free radicals recombine rapidly and some of stable free radicals remain in the polymer matrix as living radicals.

In this study electron spin resonance (ESR) spectra of cotton, linen, polynosic rayon, standard rayon, nylon 6, and PET fibers treated with plasmas of various gases were measured. Furthermore, to gain an insight into the stability of the free radicals trapped in the plasma-treated fiber, heat treatment was carried out after the plasma treatment. The effect of heat treatment at various temperatures on the free-radical intensity was examined.

Cotton, linen, polynosic rayon, standard rayon, nylon 6, and PET fibers dewaxed with carbon tetrachloride were treated with low temperature plasmas of O_2, N_2, Ar, CF_4, and CO gases at a pressure of 1 torr at a power level of 300 W for 10–300 s.[1] After the treatment the fiber was taken out in air and then subjected to ESR measurements after keeping the treated fiber in a desiccator for 24 h. Furthermore, with some cotton fibers heat treatment was carried out at 120, 160, and 200°C in air and at 28, 50, and 80°C in water for 5 min and at 160°C in air for 1–20 min after the plasma treatment. The presence of free radicals was measured by means of ESR spectroscopy (JES-FEIX, JEOL). The conditions of the measurement were as follows: temperature, 18°C; field, 3300 ± 500 G; sweep time, 4 min; modulation, 100 kHz and 20 G; amplitude, 5.0 × 100; power, 4 mW. MnO was used as a standard material. The relative free-radical intensity was calculated by the ratio of ESR absorption intensity of free-radicals in fiber to that of MnO.

ESR spectra of cotton treated with O_2 and CO plasmas are shown in Figure 1 as typical examples. The treatment with CO plasma exhibits larger absorption intensity of free radicals than that with O_2 plasma. Also the free-radical intensity of CO plasma-

Table I Effect of Discharging Time on Relative Free-Radical Intensity of Cotton Treated with Low Temperature Plasma

	Relative Free-Radical Intensity, Discharging Time of Plasma				
Plasma Gas	10 s	30 s	60 s	180 s	300 s
O_2	0.2	0.3	0.3	0.3	0.4
CO	0.7	1.3	1.9	2.9	3.0

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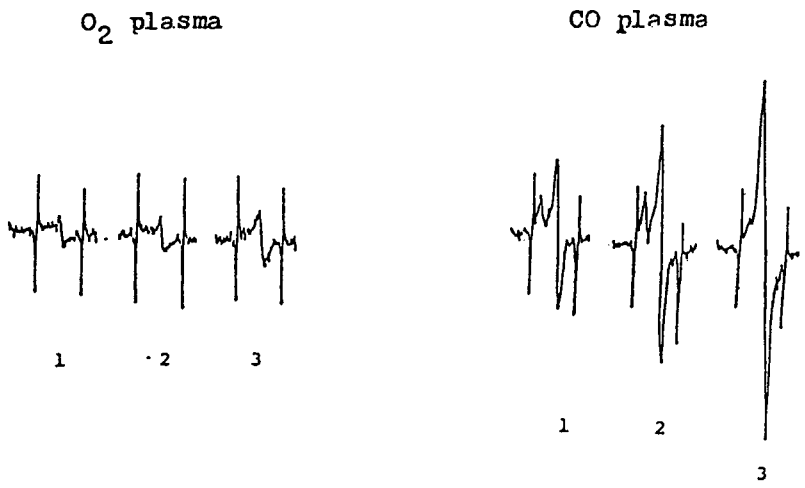

Figure 1 ESR spectra of cotton treated with low temperature plasmas of O_2 and CO. Time of plasma treatment (s): (1) 30; (2) 60; (3) 300.

Table II Relative Free-Radical Intensities of Fibers Treated with Low Temperature Plasma of Various Gases[a]

	Relative Free-Radical Intensity					
Plasma Gas	Linen	Cotton	Polynosic Rayon	Standard Rayon	Nylon 6	PET
CF_4	4.5	2.9	1.2	0.9	0	0
CO	3.2	2.9	0.8	0.4	0	0
Ar	1.9	1.4	0.7	0.3	0	0
N_2	0.5	0.4	0.3	0.1	0	0
O_2	0.1	0.3	0.1	0.1	0	0

[a] Plasma treatment was carried out for 180 s.

treated cotton increases considerably with an increase in the discharging time of plasma (Table I). The relative free-radical intensities of various fibers treated with a variety of gases are summarized in Table II. The intensity varies greatly with fiber and plasma gas and increases in the following order: linen > cotton > polynosic rayon > standard rayon > nylon 6 $\approx$ PET and CF_4 > CO > Ar > N_2 > O_2.

Table III Effect of Heat Treatment in Air on the Relative Free-Radical Intensity of Plasma-Pretreated Cotton[a]

	Relative Free-Radical Intensity, Temperature of Heat Treatment			
Plasma Gas	Untreated	120°C	160°C	200°C
O_2	0.3	0.3	0.2	0.2
CO	2.9	1.6	0.9	0.7
CF_4	2.9	2.3	1.5	0.7

[a] Plasma pretreatment was carried out for 180 s. Heat treatment was made for 5 min.

Table IV Effect of Heat Treatment in Water on the Relative Free-Radical Intensity of Plasma-Pretreated Cotton[a]

	Relative Free-Radical Intensity, Temperature of Heat Treatment			
Plasma Gas	Untreated	28°C	50°C	80°C
O_2	0.3	0.1	0.1	0.1
CO	2.9	2.0	1.7	1.5
CF_4	2.9	2.4	2.0	2.3

[a] Plasma pretreatment was carried out for 180 s. Heat treatment was made for 5 min.

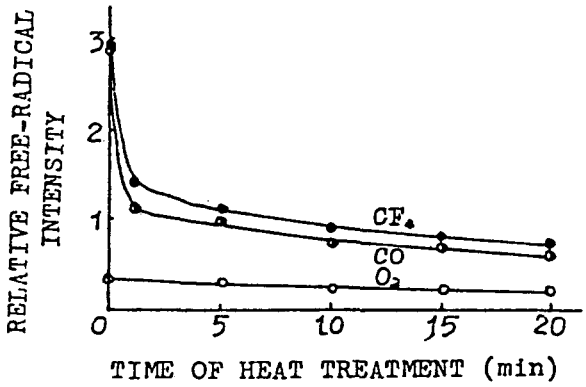

Figure 2 Effect of time of heat treatment at 160°C in air on the relative free-radical intensity of plasma-pretreated cotton. Plasma pretreatment was carried out for 180 s.

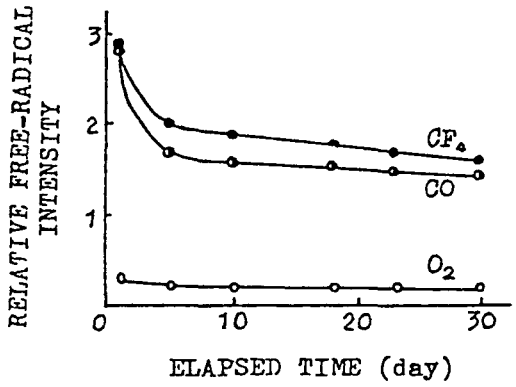

Figure 3 Effect of elapsed time at room temperature (20°C) on relative free-radical intensity of cotton treated with low temperature plasma. Plasma treatment was carried out for 180 s.

Although the cellulose fibers, in particular, plant fibers, produce much more stable free radicals, the synthetic ones do not appreciably.

It is evident from O_{1s} and F_{1s} intensities of ESCA measurements that both O_2 and CF_4 plasma treatments cause surface modification considerably: These two treatments incorporated oxygen and fluorine atoms to the PET[1,2] and cotton[3] surfaces. Nevertheless, the radical intensity of O_2 plasma detected by the ESR measurements is significantly low compared to that of CF_4 plasma. Thus it is likely that unstable free radicals with short lifetime are generated by O_2 plasma treatment and their rapid recombination occurs. In contrast, CF_4 plasma treatment produces stable free radicals in the polymer matrix. In order to investigate the stability of the living free-radicals trapped in cotton fibers, the fibers pretreated with O_2, CF_4, and CO plasmas were heat-treated in air and water at various temperatures. The results are shown in Tables III and IV. The relative free-radical intensities of CF_4 and CO plasma-pretreated fibers decrease markedly with an increase in the temperature of heat treatment in air. Also the intensity is affected by the time of heat treatment and elapsed time at room temperature (Figs. 2 and 3). It seems very likely that various kinds of free radicals are generated, depending on the fiber and the plasma gas, and that their stability is also influenced by the constitution and the fine structure of the fiber.

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