Free-Radical Formation in Jute from Argon Plasma Treatment

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Ground jute (*Corchorus capsularis*), cellulose, ethanol lignin, and holocellulose from jute strands were treated with an argon plasma under various conditions to estimate the free-radical generation (ESR) and chemical changes (ESCA) at the surface of the various samples. The influences of radio frequency power, reaction time, and gas pressure during plasma irradiation were evaluated. On the basis of plasma treatments of isolated preparations, it was shown that lignin is the primary site of free-radical formation; however, the carbohydrate fraction also shows considerable relative free-radical intensity. The extractives appeared to inhibit free-radical formation. The stability of the plasma-generated free radicals under atmospheric conditions was also investigated by ESR. The experimental data suggest new possibilities for in situ and second-stage surface modification or grafting of lignocellulosic fibers for potential application to new composite materials.

INTRODUCTION

An increasing concern and awareness for the environment has given an impetus to research on lignocellulosic fibers for total or partial substitution of petroleum-based synthetic fibers which are neither biodegradable nor renewable. However, the great advantage of the ability to tailor synthetic fibers to suit particular end-use requirements and the high strength of the fibers are key factors for their large-scale use. Lignocellulosic fibers, on the other hand, pose a challenge for their modification to suit specific uses because of their complex morphological and chemical features and variability.

The literature abounds with references on the surface modification of synthetic fibers by chemical, physical, and physicochemical means. The past few years have seen increasing interest in the use of plasmas for in situ polymer synthesis and surface modification of synthetic fibers. A plasma is defined as a partially ionized gas composed of electrons, ions, atoms, and molecules in excited and ground states. Formation of these states may be achieved by very high temperatures, strong electric fields, or magnetic fields. Plasmas produced by electrical discharges can generally be divided into two types. The first type of plasma is characterized by high gas temperature and an approximately equal electron temperature known as an equilibrium or "hot" plasma. A second type has the characteristics of low gas temperature and high electron temperature known as a nonequilibrium or "cold" plasma. The latter type of plasma has proven to be suitable for modification of organic materials because the substrate remains at or near ambient temperature.

Two major types of reactions possible with nonequilibrium plasmas are (1) surface modification of polymers and (2) polymerization of monomers in the plasmas. The basic difference between plasmas and other forms of ionizing radiation is that the radiation effect is limited to the surface. The depth of the layer affected by the plasma is much smaller, and the intensity at the surface is generally stronger than that from other more penetrating radiation.

Plasma treatment, therefore, provides an ideal means of modifying surface properties of human-made and natural fibers. Most reactions initiated by thermal energy, light, γ-radiation, mechanical forces, and cold plasmas involve the formation of free radicals. Therefore, understanding the formation and nature of free radicals has been pursued with avid interest. Free radicals are usually very reactive because of the strong tendency of their unpaired electrons to interact with other electrons and form electron pairs (chemical bonds). The qualitative and quantitative estimation of free radicals on the surface of lignocellulosic fibers may indicate the possibility of grafting with appropriate monomers. Also, controlled bond cleavage with plasmas to form free radicals could possibly enhance delignification processes. The use of radio frequency cold plasmas of various gases for the surface modification of synthetic fibers is well-known (Wakida et al., 1986; Yasuda et al., 1984; Wrobel et al., 1976).

Extension of this application to modification of wood has occurred fairly recently. Appreciable enhancement in permeability and changes in external and internal morphology of wood treated with radio frequency oxygen and nitrogen gaseous plasmas have recently been reported (Chen, 1989). Considerable improvement in the water repellency of wood has been achieved by treatment with CH_4, C_2F_4, and hexamethyldisiloxane (HMDSO) plasmas (Cho and Sjoblom, 1990).

The first attempt to understand whether wood is paramagnetic was made in 1960 (Rex, 1960). He reported that no signal was detected by ESR spectroscopy of air-dried, undamaged fresh wood shavings collected from a number of species. A small signal was detected (Kleinert and Marton, 1962) in undamaged black spruce by using a more sensitive spectrophotometer. These authors also found that after the wood was passed through a Wiley mill, a more intense signal was obtained. The signal could be further enhanced by subsequent ball milling. High-purity bleached pulp, however, gave a very small signal even after ball milling. It was suggested that either the radicals are formed by the effect of grinding upon the rigid lignin network in wood or more radicals are trapped in the ground lignin than in ground cellulose. According to Hon (Hon et al., 1980), the customary observed intrinsic free radicals in wood may well be an artifact. Free radicals on wood are feasibly created during mechanical preparations as well as from exposure to electromagnetic radiation such as terrestrial sunlight and indoor fluorescent light.

The majority of free-radical studies conducted on wood have been made to understand degradation of wood by light and ionizing rays (Fengel and Wegener, 1984). These

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Table I. Chemical Analysis of Mature Jute (Extracted) and Holocellulose

content, %[a]	mature jute	holocellulose
Klason lignin	11.8	0.2
acid-soluble lignin	2.7	4.0
arabinan	0.1	0.1
galactan	0.5	0.3
glucan	61.9	72.3
xylan	11.8	12.2
mannan	0.9	1.0
ash	0.6	0.9

[a] Based on oven-dry material.

studies have primarily concentrated on softwoods and to a lesser extent on hardwoods. Studies on nonwoody dicot angiosperms (a category containing jute) are practically nonexistent. The woody and nonwoody lignocellulosic plants have common major chemical components: cellulose, hemicellulose, lignin, and extractives. However, there are further differences in both chemical structure and morphology.

In recent years, nonwoody plants have been receiving considerable attention for a plethora of applications due to their exceptional abundance (2.28 billion tons/annum worldwide), light weight, and renewable and biodegradable nature (Atchison, 1983). However, the application of radio frequency cold nonreactive plasma treatment for generation of free radicals on lignocellulosic fibers has not been reported. The present investigation, therefore, is a first attempt to evaluate the use of cold radio frequency argon plasmas for generation of free radicals on nonwoody lignocellulosic fibers. Identification of these free radicals may prove to be beneficial for selection of suitable monomers for grafting on the fibers and the major polymeric components. Also, a better understanding of the free-radical generation in lignin will not only help in the development of suitable processes for grafting but also help our understanding of the lignin breakdown process, which is key to controlled delignification for the production of pulp and paper.

EXPERIMENTAL PROCEDURES

Jute (*Corchorus capsularis*) strands extracted from the stem by a retting process in India and approximately 1 m in length were used in the investigation. The strands were cut into 10-cm lengths and were ground in a Wiley mill. The ground sample passing through 40 mesh and retained on 60 mesh was used for all experiments. Part of the sample was extracted using a standard procedure which is often used for the preparation of extractive-free wood. The sample was first extracted with ethanol–benzene (1:2, 4 h) followed by extraction with boiling water. The extracted sample was analyzed for its chemical composition (Table I) by using Tappi standard methods. Holocellulose was extracted by the chlorite method (Wise et al., 1946). Three instead of four treatments with sodium chlorite were given because of the much lower relative lignin content (12–13%) in jute fibers as compared to wood (20–30%). The yield of holocellulose was 84.8% on the basis of over-dry jute sample. The chemical composition of holocellulose determined by Tappi standard methods is also shown in Table I. The lignin was extracted by an ethanol method (Browning, 1967). The yield of lignin was 2.3% on the basis of oven-dry jute. Ground Whatman standard cellulose was used in our experiments.

A schematic diagram of the radio frequency cold plasma installation used to treat jute samples is shown in Figure 1. In a typical experiment, the jute fiber sample was introduced into the plasma reactor (8) and the reaction vessel was connected through the capillary Pyrex ends (4) to both the argon supply (1, 2) and the pneumatic rotating system (9), which leads to the vacuum installation (10, 12) via elastic couplers (3). The gas pressure from the plasma reactor was monitored by means of a

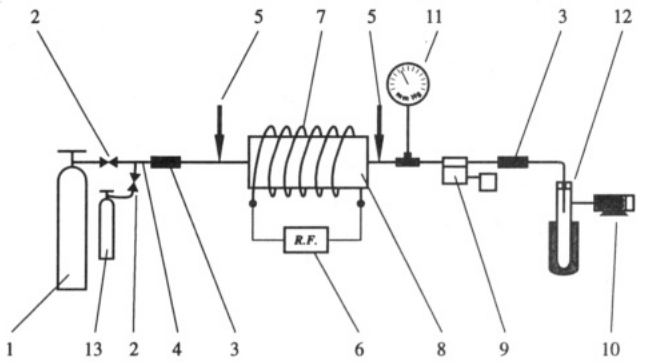

Figure 1. Schematic of plasma reactor.

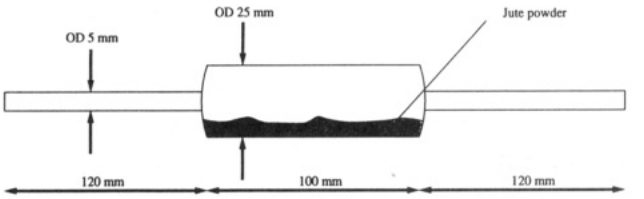

Figure 2. Diagram of capillary sample holder for plasma treatments.

Table II. Experimental Conditions for Argon Plasma Treatments

RF power, W	20, 60, 100
nature of coupling	inductive
frequency, MHz	13.56
inert gas	argon
ground pressure, mmHg	0.05
number of argon washings	4
pressures of argon, mmHg	0.3, 0,5 0.7
reaction time, min	0.5–10

DV-4D Hasting vacuum gauge (11). Experimental conditions selected for Ar plasma irradiation are presented in Table II.

To avoid contamination from the atmosphere, the plasma irradiations were preceded by evacuating the chamber to a pressure of 0.05 mmHg followed by washing with argon in four cycles up to 20 mmHg. The vessel was then brought to the selected pressure with the proper flow of argon through the chamber. Oscillation of the reactor was begun by flowing pressurized air through the pneumatic pressure rotation device (9). Plasma treatment was initiated by switching on the radio frequency generator (6) and inductive coupling coil (7). After treatment, the reaction vessel was sealed at both ends with a propane welding torch (5) and removed from the plasma chamber.

ESR spectra were recorded with a Bruker Analytische Messtechnik X-band ESR spectrometer. To avoid distortion of the spectra by power saturation, the ESR measurements were carried out at a microwave power of 10 mW.

For cold plasma treatments and ESR measurements, a specially designed Pyrex glass sample holder was used (Figure 2), which permitted the sealing of the plasma-treated samples under vacuum conditions by using a propane–oxygen flame welding torch. The ground jute samples were packed into one end of the capillary (12-mm length, 3-mm i.d. and 5-mm o.d.) by placing the sample holder in a vertical position and forcing the substrate down with a mechanical vibrator. The sample holder containing the sample was placed in the Pyrex envelope and rotated back and forth by 360° during plasma irradiation, which allowed a more uniform surface treatment. The tubes were then vacuum-sealed (0.05 mmHg) and inserted directly into the ESR for electron spin determination. Spectra were recorded at room temperature.

Plasma-irradiated samples were also investigated for free spin concentrations under open atmospheric conditions. The vacuum-

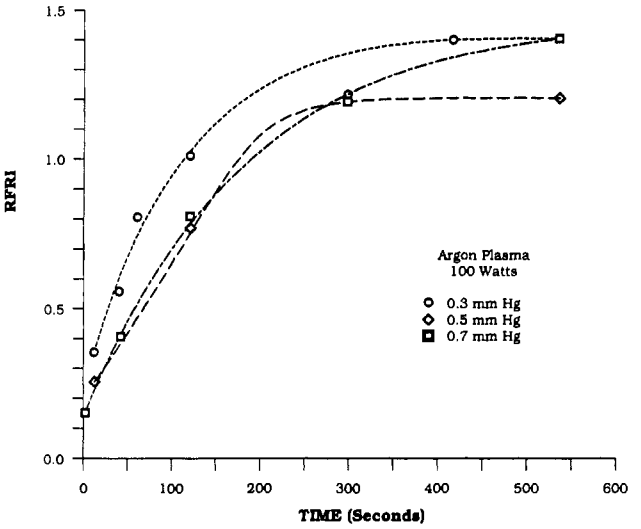

Figure 3. Influence of plasma treatment times on free-radical generation [relative free-radical intensity (RFRI)] for jute.

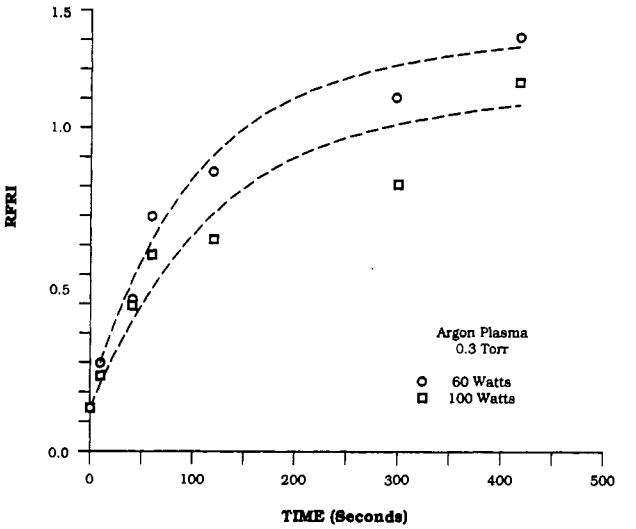

Figure 4. Influence of power on relative free-radical intensity (RFRI) for jute.

sealed vessels were cut open at one capillary end while in the ESR chamber. Electron spin measurements were measured over a series of time periods to estimate the lifetime of the generated free radicals.

X-ray photoelectron spectroscopy was used for comparison between the surfaces of argon plasma treated samples of unextracted vs extracted jute fibers. The instrument was a Perkin-Elmer Physical Electronics 05400 small area ESCA system (conditions: Mg source, 15 kV, 300 W). The ESCA measurements involved determination of the relative concentrations of carbon (C1s) and oxygen (O1s).

RESULTS AND DISCUSSION

Untreated jute strands did not show any paramagnetic properties as was evident from the absence of an ESR signal, which is consistent with an earlier report on the occurrence of free radicals in wood (Rex, 1960). Ground jute also failed to show any ESR response, although mechanical disintegration of high molecular weight substances was shown to produce free radicals (Steurer and Hess, 1944). Their findings were further substantiated (Assarason et al., 1959), and it was demonstrated that C–C as well as C–O linkages are ruptured during wood grinding and the degradation is entirely mechanical. The absence of an ESR response for both virgin jute fibers and ground jute samples may be explained on the basis of differences in the morphological characteristics of nonwoody compared to woody lignocellulosic materials.

Figure 3 shows the influence of treatment time and argon pressure during plasma irradiation on the formation of free radicals on the surface of ground jute at 100-W radio frequency power. This relation shows that higher free-radical concentration is obtained with longer treatment time. However, saturation is reached after 5 min regardless of the pressure. This saturation can be explained in part via intra- and interchain cross-linking through radical recombination mechanisms. With longer treatment times, the free-spin concentration is more dense, which favors interconnecting reactions due to the close vicinity of unstable radicals.

From Figure 3, it appears that lower pressures tend to generate higher free-radical intensities. The electron energy distribution function which is responsible for the plasma-induced modifications is mean free path dependent. Lower pressures intensify the higher energy tail of the distribution, leading to more significant electron–molecule interactions (Shanin, 1971). A higher concentration of "hot" electrons will induce more intense surface–molecular fragmentation. This same phenomenon may account for the appearance of lower free-radical concentrations at higher dissipated power levels as seen in Figure 4.

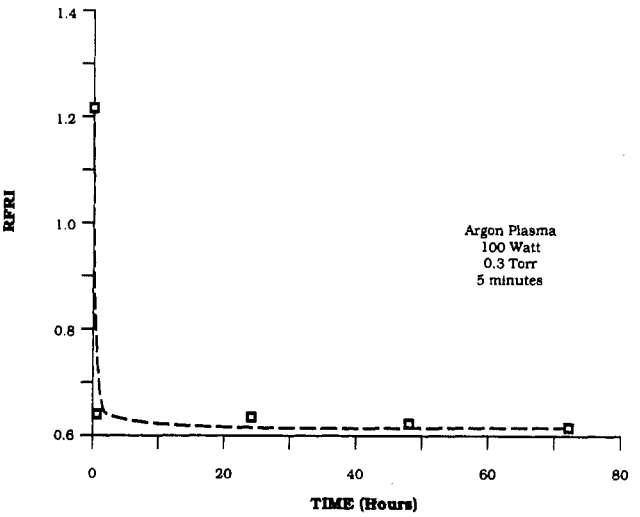

Figure 5. Effect of time on the stability of free radicals on jute in the atmosphere.

Saturation is reached within 5 min regardless of the other experimental conditions (Figure 4). This indicates that 2–3-min treatment times are sufficient for utilitarian purposes to avoid significant cross-linking reactions. Understanding the effect of the experimental conditions is essential for control over the recombination reactions and retention of free radicals for possible posttreatment grafting as well as for modification of surface properties such as wettability. Figures 5 and 6 exhibit the influences of atmospheric conditions and increased temperature (under vacuum conditions) on the stability of free radicals from plasma-treated jute fibers. From Figure 5, it is seen that exposure to atmospheric conditions dramatically reduces the free-radical intensity in less than a minute to the same value as the untreated materials. This phenomenon is very likely due to oxygen and moisture in the atmosphere combining with the free radicals and quenching the free spin concentration. The influence of the atmospheric conditions on the reduction of the free-spin concentration indicates that second-stage plasma modi-

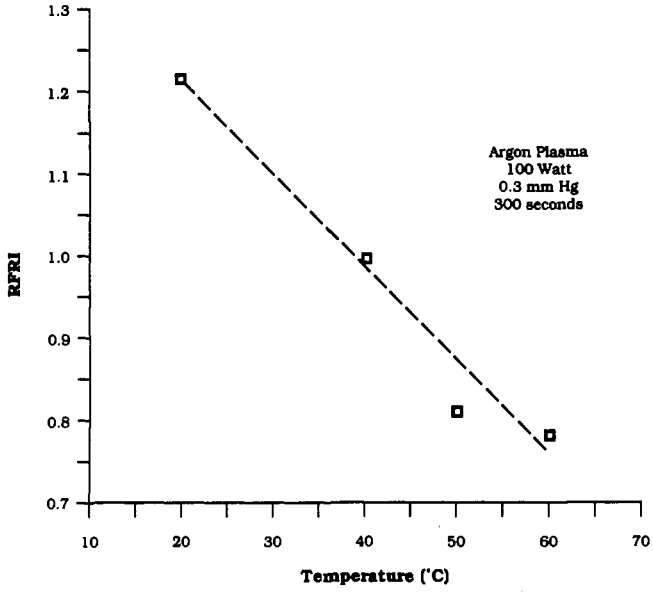

Figure 6. Effect of temperature on the stability of free radicals on jute in vacuum.

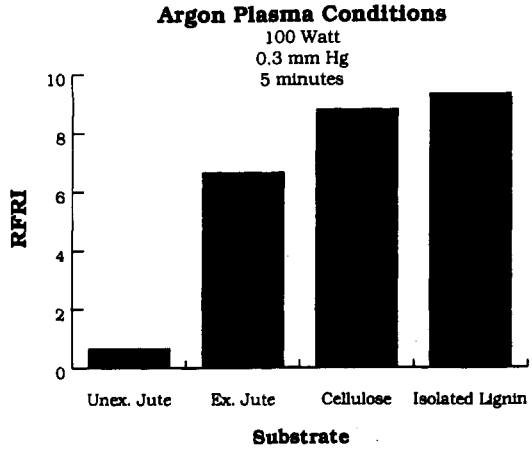

Figure 7. Comparative free-radical intensities for unextracted and extracted jute, cellulose, and lignin after argon plasma treatment.

fications would need to be carried out or initiated under an inert gas or vacuum environment.

Raising the temperature (Figure 6) also diminishes the free-radical concentration significantly. The free-radical concentration is rapidly reduced by elevated temperature and above 50 °C is negligible. Caloric energy-induced molecular translations and rotations from increased temperature facilitate recombination mechanisms.

A comparative experiment was run to provide more information on the plasma-generated free radicals. Both extracted jute and unextracted jute were treated and compared with pure cellulose and a lignin preparation (Figure 7). The experimental data clearly show that free-radical formation is inhibited in unextracted jute. It is possible that the presence of activated low molecular weight compounds present in unextracted jute quench the free radicals. It is also apparent that the free-radical concentration is significantly lower in extracted jute vs that in pure cellulose. The ethanol lignin preparation clearly shows a strong propensity for formation of free radicals. This phenomenon is probably due to the aromatic nature of the lignin and that of the lignin present in the jute. Lignin acts as an "electron sink" during plasma irradiation, leading to an elevated unpaired electron concentration. A similar phenomenon has been observed

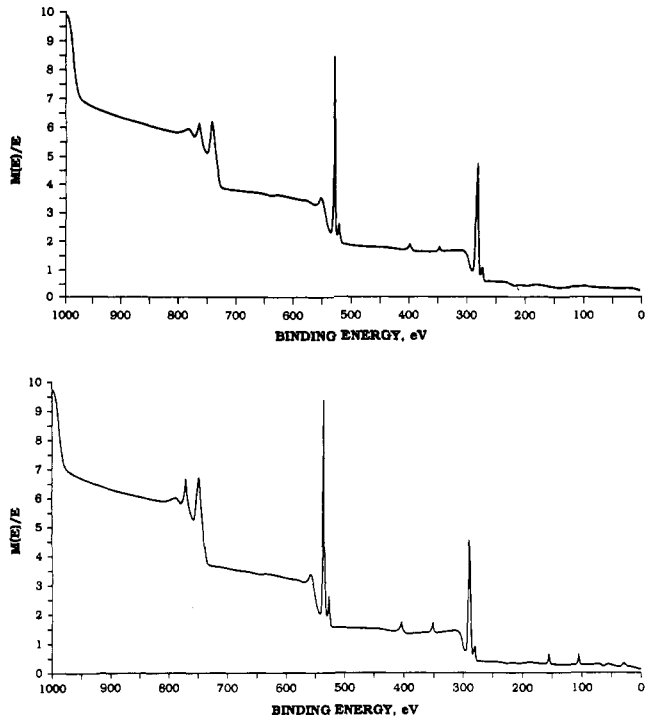

Figure 8. (Top, a) ESCA spectrum of unextracted jute. (Bottom, b) ESCA spectrum of extracted jute.

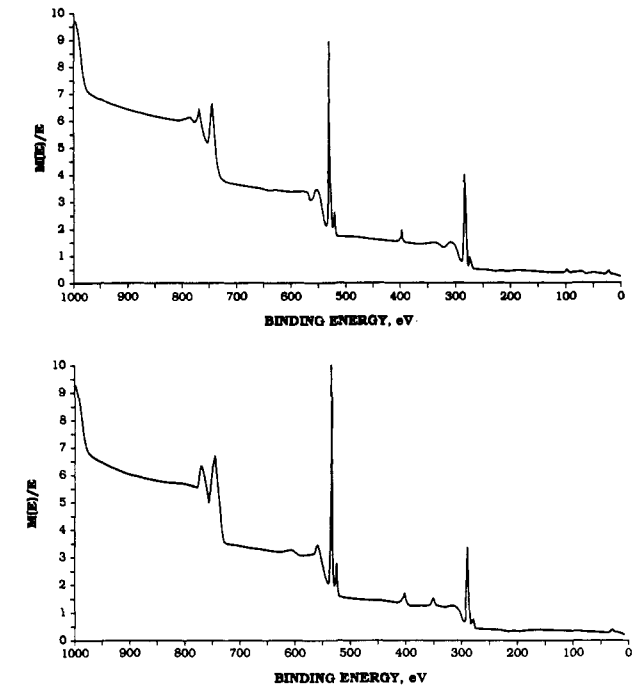

Figure 9. (Top, a) ESCA spectrum of plasma-treated unextracted jute. (Bottom, b) ESCA spectrum of plasma-treated extracted jute.

in the case of electromagnetic energy irradiated lignin (Nanassy and Desai, 1971).

Data obtained from ESCA analysis agree well with the ESR measurements. Figure 8 exhibits the survey spectra of unextracted and extracted jute. The corresponding ESCA spectra for the plasma-treated samples are shown in Figure 9. The two major peaks in the spectra represent the C1s and O1s concentrations.

From the ESCA spectra, it can be seen that extraction of the jute raised the oxygen/carbon ratio from 0.48 to 0.59, which indicates the removal of more nonpolar-type compounds characteristic of extractive material (Table

Table III. ESCA O1s/C1s Ratios for Jute Samples

jute sample	treatment	O1s/C1s
unextracted	control	0.48
unextracted	Ar plasma[a]	0.68
extracted	control	0.59
extracted	Ar plasma[a]	0.95

[a] Plasma conditions: power, 100 W; pressure, 0.3 Torr; time, 5 min.

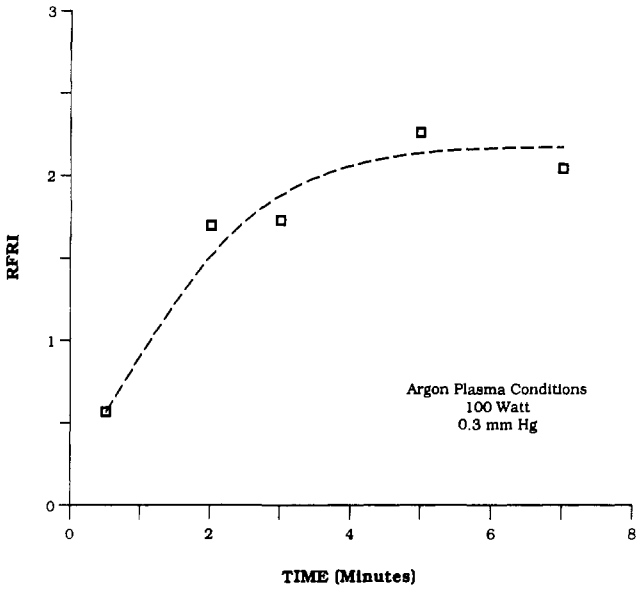

Figure 10. Relative free-radical intensity (RFRI) of plasma-treated cellulose at various reaction times.

III). Argon plasma treatment of the unextracted jute raised the oxygen/carbon ratio substantially to 0.68; however, the plasma treatment of the extracted jute showed an even more dramatic increase in the oxygen/carbon ratio of 0.95, a 28% higher oxygen concentration compared to that of the plasma-treated unextracted jute. There is a correlation between the higher free-radical intensity present in the extracted jute and the more intense oxidation of the substrate. Knowledge of these effects is important for second-stage grafting reactions. Possible peroxide or hydroperoxide formation would permit temperature-induced free-radical regeneration via peroxide linkage decomposition. This opens up practical possibilities for atmospheric grafting posttreatments.

The free-radical concentration of plasma-treated cellulose is presented in Figure 10. Saturation is reached in less than 6 min. Similarity between the behavior of cellulose and jute (Figure 4) is not surprising since cellulose is the major component of lignocellulosic materials. Cross-linking reactions probably also account for the decrease in free-radical intensity with longer reaction times in this case. Figure 11 exhibits the stability of plasma-generated free radicals on cellulose fiber surfaces. Disappearance of free radicals occurs in the first minute. Oxygen and moisture from the atmosphere are suggested as the primary factors causing the loss of the free radicals.

The holocellulose fraction of the jute strand, which comprises 75% of the weight, was also argon plasma irradiated under a similar set of conditions as employed for isolated lignin and pure cellulose. The stability of free radicals in atmospheric conditions is shown in Figure 12. The free radicals from holocellulose appear to be more stable than those from jute, although after 6 h, the free-radical intensity was almost negligible. The free radical lifetime for holocellulose indicates a much slower quenching mechanism than that of cellulose. Steric hindrance,

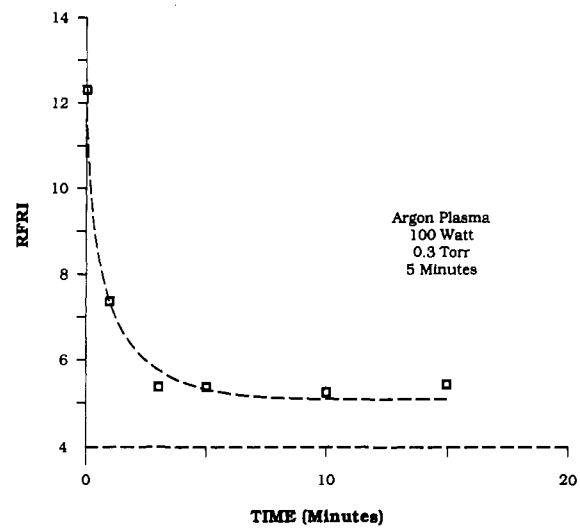

Figure 11. Stability of free radicals for plasma-treated cellulose in atmospheric conditions.

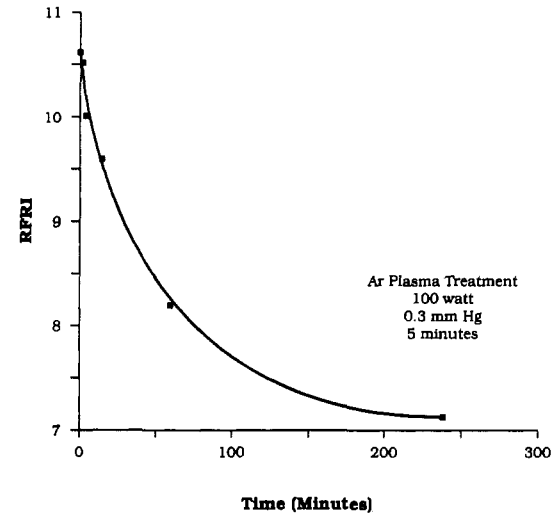

Figure 12. Stability of free radicals for plasma-treated holocellulose in atmospheric conditions.

both from molecular and from supramolecular structures, might play a role. More experimental work is needed to understand this anomolous behavior.

CONCLUSIONS

Free-radical generation for plasma-treated ground jute reaches a plateau under a given set of conditions of power, pressure, and time. Lower pressure appears to favor the generation of higher free-radical intensities. It has been determined that 2–3 min of treatment time is sufficient to maximize free-radical production and avoid quenching reactions. Free-radical intensity is dramatically reduced in less than a minute under atmospheric conditions, thereby making it essential to carry out proposed second-stage free-radical-initiated graft polymerization reactions under an inert gas or vacuum. Raising the temperature (in a vacuum) also diminishes free-radical concentration. Unextracted jute exhibited lower free-radical generation as compared to extracted jute. Extensive free-radical formation was observed in the case of isolated jute ethanol lignin, which is apparently a free-radical "sink". For the pure cellulose the free-radical intensity reached a maximum in less than 5 min but decreased rapidly when exposed to the atmosphere, while an unusually long lifetime was observed for free radicals generated in the holocellulose

fraction. The cause of this difference in behavior is under further investigation.

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