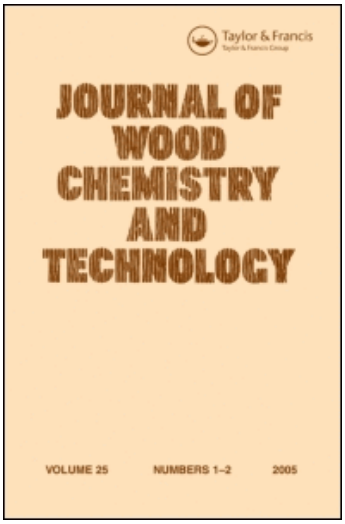

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Chen, Hope Y. and Zavarin, Eugene(1990) 'Interactions of Cold Radiofrequency Plasma with Solid Wood I. Nitrogen Permeability along the Grain', Journal of Wood Chemistry and Technology, 10: 3, 387 — 400
To link to this Article: DOI: 10.1080/02773819008050247
URL: http://dx.doi.org/10.1080/02773819008050247

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 10(3), 387-400 (1990)

INTERACTIONS OF COLD RADIOFREQUENCY PLASMA WITH SOLID WOOD I. NITROGEN PERMEABILITY ALONG THE GRAIN.

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ABSTRACT

Exposure of 1.5 cm diameter x 1.2 cm long white fir and Douglas-fir heart- and sapwood samples to the action of cold radiofrequency oxygen, nitrogen, and helium plasmas strongly increased wood permeability to nitrogen flow along the grain. Oxygen was most effective, followed by nitrogen and helium. While an increase in radiofrequency energy level increased the effect, the opposite was true for an increase in reactant gas flow rate. With white fir the rate of permeability increase was higher at the beginning of the plasma treatment. This was attributed to differing ablation rates of cellulose, hemicelluloses, and lignin. No significant time difference in the rate of permeability increase was observed with Douglas-fir. Extractives suppressed the plasma-induced permeability increase; thus extraction with water and ethanol, followed by oxygen plasma treatment increased permeability of Douglas-fir heartwood 32 times, while plasma treatment of the unextracted Douglas-fir increased permeability only 8 times. The permeability of extracted and oxygen plasma-treated wood did not vary much across the grain, but did decrease with distance from the ends of the samples due to incomplete removal of extractives from the center.

INTRODUCTION

Plasma is generally defined as a gas composed of free electrons, atoms, molecules, ions, free radicals, and metastables in excited and non-excited states, such that the total plasma volume is neutral. Plasmas in which the Boltzmann temperature of the atomic and molecular species is not far above the ambient while the temperature of electrons is ten to hundred times greater are termed cold plasmas. Cold plasmas can

be produced by glow discharges in gas media at reduced pressures, either by applying D.C. or low frequency A.C. voltages across electrodes, or by using radio- (RF) or microwave frequencies[1].

Plasmas represent rather reactive media. The reactions taking place with materials brought in contact with plasma result in two opposing processes - polymer formation (deposition of polymers) and polymer ablation (removal of polymers) and depend upon the nature and concentration of the reactive species, which in turn depend upon the nature of the gas used, method of plasma generation, gas pressure, gas flow rate, construction of the reactor, electrical power used, time of contact, location in the reactor, etc.[2].

Plasmas have been used for some time in the general field of polymers for synthesis, grafting, altering the surface chemistry (surface oxidation), etching, and ashing. Many excellent reviews are available on these subjects[2-4]. The attention given to plasma in the field of lignocellulosic polymers has been one-sided, however. While a fair amount of information is available on the interaction of plasma with cellulose and its derivatives, little is known about interactions between plasma and lignin or solid wood. Thus, it has been demonstrated that plasma treatment can lead to substantial modifications of the properties of cellulosic polymers by grafting or other surface interactions, resulting in increased dimensional stability, fire resistance, bonding ability, strength, water absorption, alkali resistance, and wrinkle recovery[5]. Probably the only work dealing with lignin is that of Simionescu et al[6] who were able to graft methylmethacrylate and acrylonitrile to a lignin of undefined nature. Relatively little has been done with solid wood and that has dealt mainly with the influence of corona discharge on the adhesive properties of wood or wood fiber, as summarized by Goring[7] and by Back[8].

Since wood is an open-porous polymeric material, the lumina of its cell structures can be easily evacuated to the low pressures (<1 Torr) required for RF plasma generation. Thus it was deemed possible to generate plasma inside the cell lumina, opening the way for ablative attack on the surfaces of cell walls and the structures controlling flow of gases and liquids through wood, thus increasing its permeability.

This paper, which deals with the effect of plasmas on permeability of wood to nitrogen gas along the grain[9], is the first in a series on the influence of cold RF plasmas on the surface-related chemical and physicochemical properties of wood.

EXPERIMENTAL

Permeability of wood was calculated using Darcy's law:

$$K = \frac{dQ}{dt} \frac{\mu L P}{A \Delta P \bar{P}} \quad \ldots\ldots \quad (1)$$

where: dQ/dt = volume flow rate of the gas (ml/sec); μ = viscosity of the gas at the temperature of measurement (cp); L = length of the specimen (cm); A = cross-sectional area of the specimen (cm^2); ΔP = pressure differential (atm.); P = pressure at which gas volume was measured (atm.); and $\bar{P}$ = pressure at the midpoint of the specimen (atm.). The viscosity of nitrogen was taken as 0.01752 cp at 20 C° [10]. Wood used for the experiments was air-dry, defect-free white fir (Abies concolor (Gord. & Glend.) Lindl.) and Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco). Both woods -- particularly Douglas-fir -- are difficult to penetrate [11]. The specimens used for permeability measurement were cylinders, 1.2 cm long and 1.5 cm in diameter, whose axis was parallel to the grain.

For measurement of the rate of weight loss of wood constituents, about 1 g of cellulose, xylan, or lignin powder was compressed under vacuum into 0.5 mm X 5.6 cm diam. disks. Cellulose powder was obtained from commercial filter paper by defibration, grinding and screening to <200 mesh. Xylan was the commercial material (Sigma Chem. Co.), and lignin was prepared from brown cubical rot, as described before[12].

For measurement of permeability a sample was placed in a plastic tube and clamped with a steel clamp. One end of the plastic tube was attached via pressure regulators to a nitrogen cylinder. The other end of the tube was connected to an Erlenmeyer flask filled with water, which was gradually displaced into a measuring cylinder as nitrogen flowed through the sample.

The plasma treatment apparatus was an LFE Model LTA-604 low temperature asher operating at 13.56 MHz and 0-600 W. It included 4 cylindrical chambers, 10 cm in diameter and 21.5 cm long. Reactant gas was supplied from a gas cylinder, and the exhaust was led through a cold (-60°C) trap before entering the two stage vacuum pump.

The reproducibility of the permeability measurements at constant pressure (0.136 atm.) and constant displaced volume (250 ml) amounted to an average C.O.V. of 0.0055 (C.O.V. = coefficient of variation = standard deviation/mean) and at various volume settings (50 - 250 ml) to 0.012. Increasing the pressure differential to 0.34 and 0.68 atm increased the C.O.V. to 0.035 and 0.042, respectively, due to inconveniently short flow times. Therefore all measurements were performed at 0.136 atm. pressure differential and in the great majority of cases at time and volume settings of >10 sec and >50 ml, respectively.

Removal of extractives was accomplished by Soxhlet extraction, 72 hr. with water and 72 hr. with ethanol.

The experiments were generally run at 300 W power (power density of 0.08 W/ml). Although increasing the power to 600 W (N_2 reactant flow - 10 ml/min, 30 min treatment) increased the permeability of white fir 2.45 fold for heartwood and 2.08 fold for sapwood, vs 1.62 fold for heartwood and 1.50 fold for sapwood at 300 W (untreated wood basis), the power generator could not maintain 600 W output for a prolonged time and 300 W was chosen as the best compromise.

RESULTS AND DISCUSSION

The change in permeability of white fir and Douglas-fir heartwood and sapwood upon treatment with oxygen, nitrogen, and helium plasmas is summarized in Fig. 1 and in Table 1. In all cases the treatment produced substantial increases in permeability, with oxygen being most effective. At a gas flow rate of 10 ml/min nitrogen was appreciably more effective than helium, while at 50 ml/min the two gases produced about the same effect.

TABLE 1.

Effect of Cold Radiofrequency Plasma on Permeability of White Fir and Douglas-Fir Wood.

Wood	Plasma	Gas Flow (ml/min)	Permeability Increase[1]	Number of Samples
White Fir, Sap	N_2	10	1.48	5
White Fir, Heart	N_2	10	1.63	5
White Fir, Sap	0_2	10	1.67	4
White Fir, Heart	0_2	10	2.22	4
White Fir, Heart	He	10	1.44	4
White Fir, Sap	N_2	50	1.41	4
White Fir, Heart	N_2	50	1.41	4
White Fir, Heart	0_2	50	1.81	4
White Fir, Heart	He	50	1.50	4
Douglas-Fir, Sap	N_2	10	2.05	8
Douglas-Fir, Heart	N_2	10	2.04	4
Douglas-Fir, Sap	0_2	10	3.13	4
Douglas-Fir, Heart	0_2	10	8.00	16

[1] K/K_o, with K - permeability after 30 min with plasma at 300 W power. K_o - Original permeability.

In all cases permeability kept increasing with time with no indication that the increase was leveling off. However, with white fir the rate of permeability increase was higher at the beginning of each run (Fig. 1 A and B) than later. Thus during the first 10 min the rate of permeability increase was between 41.0 X 10^{-4} and 123.0 X 10^{-4} Darcies per min, while between 10 and 30 min it amounted to 28.5 X 10^{-4} to 70.0 X 10^{-4} Darcies per min. Several reasons can be advanced for the higher initial rate of permeability increase: a) surface accumulation of materials condensed by plasma and more difficult to ablate; b) initial removal of more delicate wood anatomical elements of higher surface-to-mass ratio, such as bordered pit membranes; c) different rates of ablation of various wood constituents, resulting in the accumulation of harder-to-ablate materials on the surface.

In order to investigate the rates of ablation of individual wood constituents, discs composed of compressed cellulose, xylan, or lignin powder were exposed to oxygen and nitrogen plasmas and the weight loss determined as a function of time. The results, given in Table 2 and Fig. 2, indicate that cellulose and xylan ablate more than twice

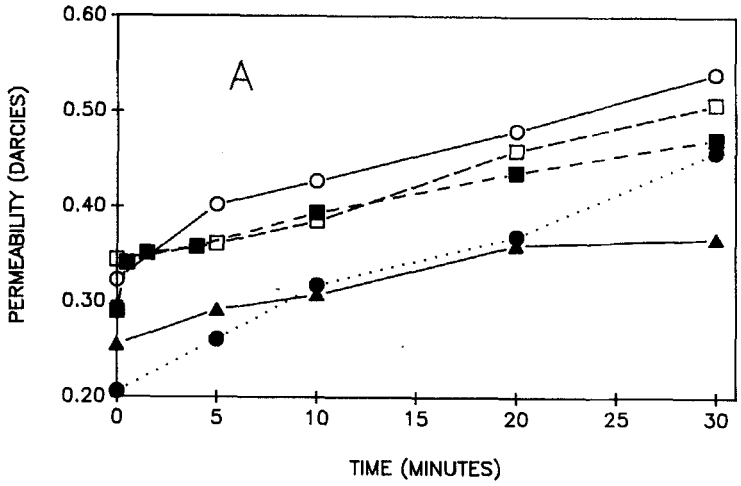

Figure 1. Increase in wood permeability (K) with time of plasma treatment (300 W). ○ - Oxygen, sapwood; □ - nitrogen, sapwood; ■ - nitrogen, heartwood; ● - oxygen, heartwood; ▲ - helium, heartwood. A - white fir, gas flow 10 ml/min; B - white fir, gas flow 50 ml/min; C - Douglas-fir, gas flow 10 ml/min. The data are averages for 4 samples, except: nitrogen, white fir, 10 ml/min, heart- and sapewood - 5 samples; nitrogen, Douglas-fir, 10 ml/min, sapwood - 8 samples.

as fast as lignin in either nitrogen or oxygen plasma. This suggests that mechanism c) is at least partly responsible for the higher initial rate of permeability increase in white fir.

Surprisingly, Douglas-fir did not behave like white fir, showing no time change in the rate of permeability increase.

The observed increase in permeability is most likely due to widening of the internal passages of the wood, i.e. by ablation of material from the surface of tracheid walls and particularly from the bordered pits. According to Yasuda[2] such ablation can take place by two different mechanisms: physical sputtering, i.e. by knocking out atomic or molecular fragments from the surface; and chemical etching, e.g. by oxidative processes taking place in an oxygen plasma. Noble gas plasmas ablate solely by the first mechanism, while both mechanisms can be active with chemically reactive gases. This, as well as lower energies required for the formation of reactive species (dissociation, ionization), could explain why chemically reactive nitrogen, and particularly oxygen plasmas are more effective in increasing the permeability of wood.

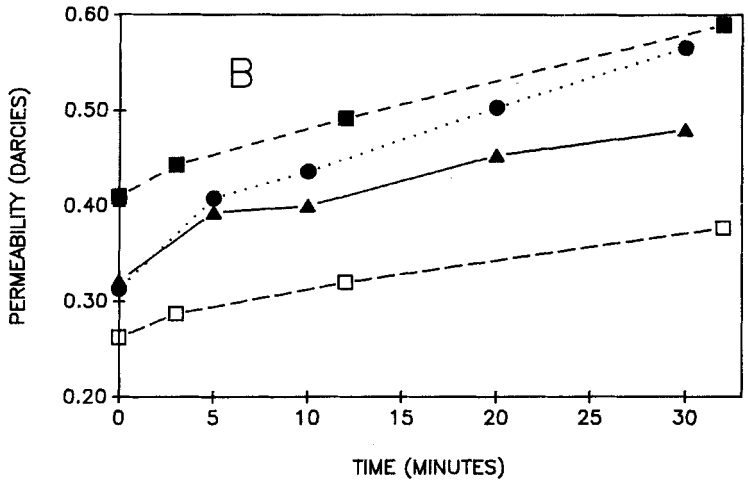

Figure 1B.

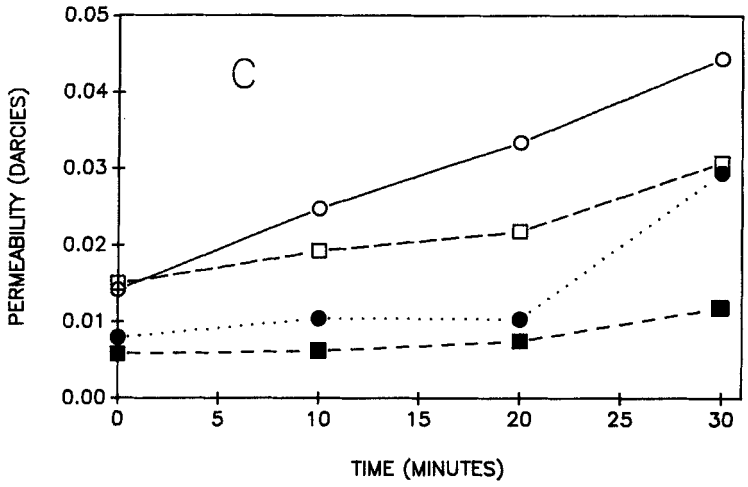

Figure 1C.

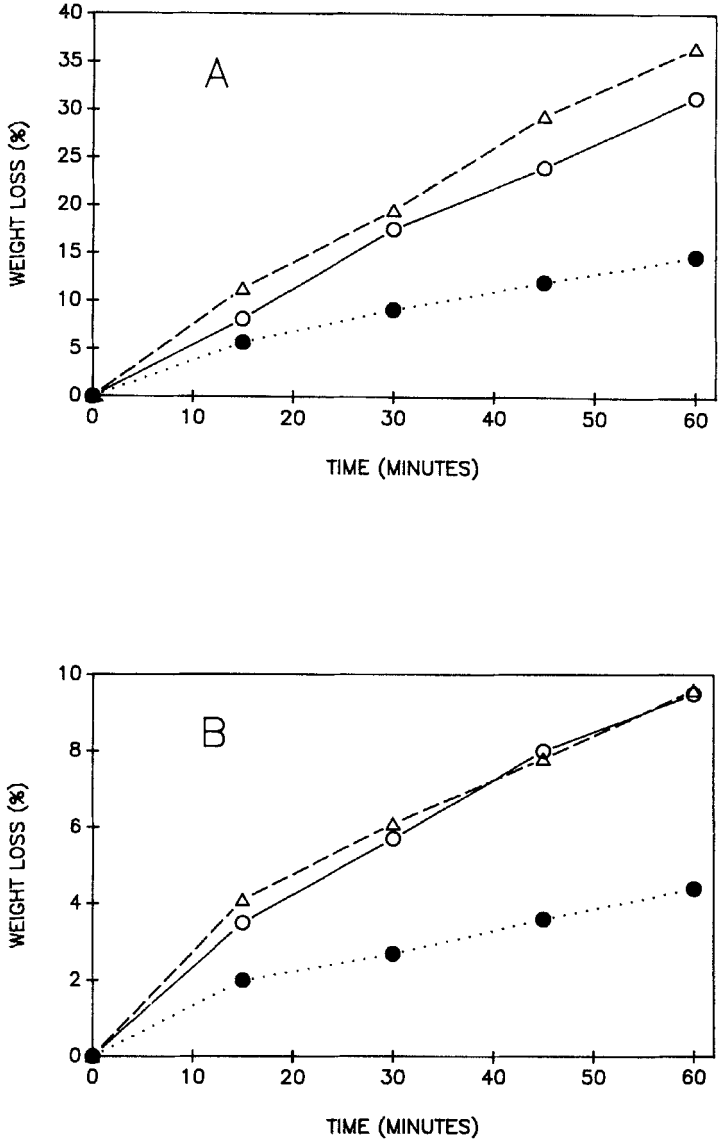

Figure 2. Percent weight loss for xylan (Δ), cellulose (○), and lignin (●) disks with time of plasma treatment, 300 W, 10 ml/min gas flow. A - oxygen; B - nitrogen.

TABLE 2.

Weight Loss of Cellulose, Hemicellulose, and Lignin Disks in Oxygen and Nitrogen Plasma.

Wood Constituent	Gas[1]	Weight Loss (%)
Cellulose	Oxygen	31.3
Cellulose	Nitrogen	9.5
Xylan	Oxygen	36.5
Xylan	Nitrogen	9.6
Lignin	Oxygen	14.7
Lignin	Nitrogen	4.4

[1]*60 min, 300 W, 10 ml/min flow.*

Increasing in the gas flow rate from 10 to 50 ml/min adversely affected the permeability increase of wood in the case of oxygen and nitrogen, but had no influence when helium was used. According to Yasuda[2] chemical etching depends upon the concentration of the reactive species which is in turn determined by the gas flow rate and by the discharge energy of the plasma generator. Thus the etching rate initially increases with gas flow rate, reaches a maximum, and then actually decreases with higher flow rates as RF energy becomes limiting. The relationships obtained by us place our experimental conditions in the higher flow rate region, where RF energy (see experimental section) rather than flow rate primarily determines the rate of ablation.

The influence of extractives on the plasma-induced increase in the permeability of white fir and Douglas-fir wood is summarized in Table 3. While extraction alone produced a marked increase in permeability of white fir heartwood, the effect was well below that produced by oxygen plasma treatment. The same was true for Douglas-fir, although the effect was much stronger in the second case. Particularly interesting was the combined effect of extraction and oxygen plasma treatment on Douglas-fir. When samples were first extracted and then plasma treated, the permeability increased nearly 32 times, approaching that of untreated white fir. Reversing the order of treatment, however, yielded a much smaller permeability increase (7.5 times). Since plasma treatment without extraction raised the permeability by about the same factor (Table 3), it appears that the extraction of plasma-treated wood has no effect on permeability. This could be due to plasma-induced polymerization and grafting of the extractives within the wood, rendering them insoluble in polar organic solvents like ethanol.

TABLE 3.

Effect of Extraneous Materials on Permeability of Oxygen Plasma-Treated Heartwood[1].

Species	Number of Samples	Plasma Treated	Extracted (Darcies)	K	Permeability Increase, K/K_o[2]
White fir	25	No	No	0.29	--
White fir	8	No	Yes	0.34	1.2
White fir	4	Yes	No	0.46	1.6
Douglas-fir	16	No	No	0.008	--
Douglas-fir	17	No	Yes	0.036	4.5
Douglas-fir	16	Yes	No	0.063	8.0
Douglas-fir	18	2. Yes	1. Yes	0.254	31.8
Douglas-fir	5	1. Yes	2. Yes	0.060	7.5

[1]Oxygen flow - 10 ml/min; power - 300 W; time of treatment - 30 min. Numbers in columns two and three indicate the order of treatment.
[2]K_o - Permeability of unextracted and untreated white fir and Douglas-fir, respectively.

Since RF radiation penetrates wood and the since the evacuation of cell lumina should present no difficulty, it would be expected that plasma will form both inside and outside the wood and attack the wood substance uniformly. The only factor that is likely to influence this uniformity is the possible difference in composition between the gas trapped in cell lumina and the outside atmosphere. In order to measure possible permeability gradients in plasma treated wood, extracted Douglas-fir heartwood samples were treated with oxygen plasma (30 min, 300 W, 10 ml/min), followed by (a) stepwise reduction of the diameter of the samples by 2 mm, or by (b) stepwise reduction of the sample length by removing 1 mm portions from each end, with permeability measurement after each step. The results were compared with those obtained by the same procedure using samples extracted but not plasma-treated (Fig 3).

Decreasing the cross-sectional area did not affect the permeability of either the extracted-only wood or the extracted/plasma-treated wood, with the exception of the sample with the smallest cross-sectional area, which had about 25% higher permeability than expected. The latter is most likely due to natural variations in the wood, which should become particularly noticeable in small samples.

Decreasing the sample length resulted in decreased permeability in both extracted-only and extracted/plasma-treated samples, particularly in the latter. This decrease was rather surprising, as Bramhall[13], and Fogg and Chung[14] have demonstrated that the

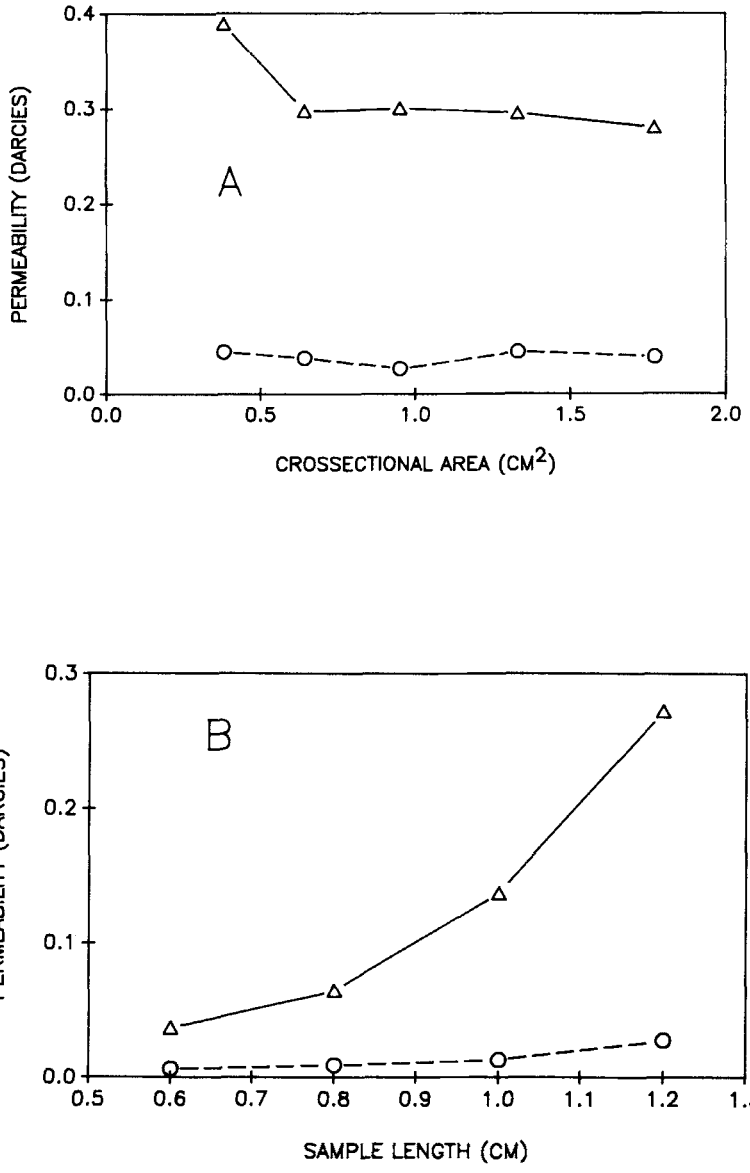

Figure 3. Change in wood permeability of extracted Douglas-fir heartwood samples following sequential reduction of the cross-sectional area by removal of exterior layers. Δ - plasma treated (30 min, 300 W, 10 ml/min oxygen flow); o - plasma-untreated. B. Same as A except reduction of sample length rather than diameter.

number of conducting tracheids decreases exponentially along the grain due to random blockage by aspirated pits, resulting in an inverse relationship between permeability and sample length. We suspected our results might be due to incomplete extraction of the wood due to the notoriously low permeability of Douglas-fir. To test this assumption, each of five extracted samples was separated into (A) two 2 mm end-sections, (B) two immediately adjacent 2 mm sections, and (C) a 4 mm center section. The corresponding wood sections were combined, ground to 80 mesh, and the extractive content of each of the three sawdust portions was determined by 8 hour extraction using ethanol and water. The extractive content of the three portions amounted to A - 2.2%, B - 7.4%, and C - 7.8%, with the extractive content of unextracted Douglas-fir being 8.0%. This shows that extraction was effective only in the outside third of the wood samples and that the observed decrease in permeability with decreasing length of the extracted-only samples was primarily due to incomplete extraction. This also explains the decrease in permeability towards the center of extracted/plasma-treated Douglas-fir samples, as it was shown earlier that extractives strongly interfere with the plasma-induced permeability increase. However, it is significant that although extraction was ineffective in the central portion of the samples, plasma treatment still increased the permeability in this region 5.7 times. This is of the same order of magnitude as the plasma-induced increase in permeability of unextracted Douglas-fir wood (8.0 times, Table 3) and demonstrates that plasma ablation takes place within wood samples. Furthermore, it can be estimated by simple calculation using the measured permeabilities and extractives values of the extracted and unextracted samples, and assuming an inverse linear relationship between permeability increase and extractives content, that the plasma-induced permeability of Douglas-fir could be raised from 32 fold (Table 3), to over 100 fold, if it were possible to completely remove all extractives from the wood samples.

Finally, in order to investigate the influence of the plasma-induced permeability increase on the rate and level of wood impregnation with commercial fungicides and related materials, plasma-treated wood samples (oxygen 10 ml/min, 300 W, 30 min) and untreated controls were brought in contact with Termin-8, a commercial liquid fungicide, and the weight gain at ambient temperature measured as function of time. The results are summarized in Fig. 4. As expected, the control samples absorbed the fungicide most slowly, but surprisingly, unextracted/plasma-treated samples gained weight only slightly faster. The absorption rate was appreciably higher in the extracted samples, with the extracted/plasma-treated samples absorbing Termin-8 fastest, as expected.

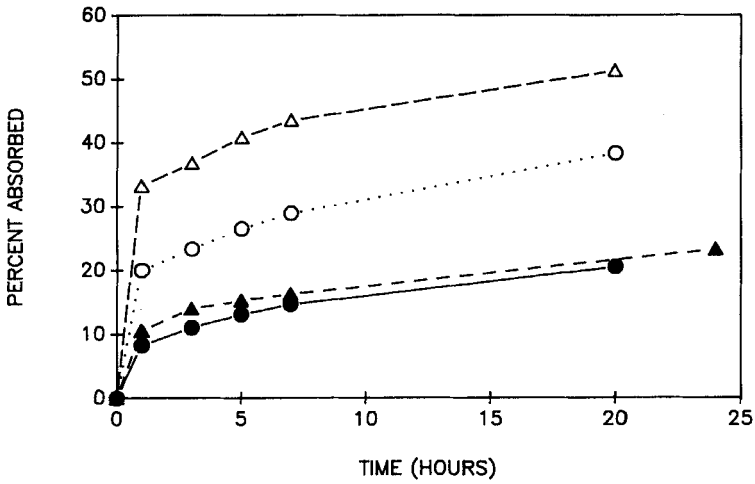

Figure 4. Effect of oxygen plasma treatment on absorption of Termin-8 fungicide by Douglas-fir wood samples. o - Control, untreated wood; ▲ - unextracted plasma-treated wood; o - extracted plasma-untreated wood; Δ - extracted, then plasma-treated wood.

Investigations into the mechanism of plasma-induced permeability increase are being pursued using scanning electron microscopy, and are also being extended into a study of water permeability.

ACKNOWLEDGEMENTS

This research is based on the doctoral dissertation of the senior author. The authors wish to express their thanks to the United States Dept. of Agriculture (grant No. 86-FSTY-9-0169) for supporting this research. The authors are also indebted to Prof. Donald G. Arganbright and Mr. Laurence Cool for various suggestions and discussions, and to Mr. Steven Jones for some of the experimental work.

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