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RF-plasma vapor deposition of siloxane on paper. Part 1: Physical evolution of paper surface

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ABSTRACT

An alternative, new approach to improve the hydrophobicity and barrier properties of paper was evaluated by radio-frequency (RF) plasma octamethylcyclotetrasiloxane (OMCTSO) vapor treatment. The interaction between OMCTSO and paper, causing the increased hydophobicity, is likely through covalent bonding. The deposited thin silicone-like polymeric layer from OMCTSO plasma treatment possessed desirable hydrophobic properties. The SEM micrographs showed uniformly distributed grainy particles with various shapes on the paper surface. Deposition of the silicone polymer-like layer with the plasma treatment affects the distribution of voids in the network structure and increases the barrier against water intake and air. The water absorptivity was reduced by 44% for the OMCTSO plasma treated sheet. The highest resistance to air flow was an approximately 41% lower air permeability than virgin paper.

1. Introduction

Plasma is a state of ionized gas containing excited atomic, ionic, molecular, and free-radical species. In this manner, the plasma state is different than the solid, liquid and gas phases of matter, and is recognized as the fourth state of matter. A non-equilibrium plasma treatment, usually called cold plasma, can be used for surface modification of solid materials [1–3].

In the typical cold plasma state the electrons have high kinetic energies to induce ionization, excitation and molecular fragmentation processes in low pressure gas environments [2]. As free radicals, excited state species, and fast neutrals are available in the plasma state, a number of different processes can occur simultaneously.

Among various surface treatment techniques, gas plasma treatment offers numerous advantages over other conventional methods. All modifications and surface functionalization steps can be done in one step with a desired gas. The plasma process is performed in a closed system and all process parameters are controllable [1,2].

Cold-plasma treatment was used to treat wood [4,5], pulp [6,7], paper [8] and cellulose derivatives [9]. This technique is commonly used to improve wettability, either increase or decrease, and increase adhesion of different coating lacquers and binders to materials.

It has already been reported that plasma chemical vapor deposition (CVD) is a useful technique for preparation of thin polymeric films [3]. By choosing specific chemicals for different processing, it is possible to be very selective in the type of chemical surface obtainable from plasma chemical vapor deposition [1–3].

Finson and Felts [10] investigated the characteristics of plasma–silicone deposited transparent thin layers on polyethylene terephthalate and polyethylene surfaces and found it to be effective for creating barrier properties. Sapieha et al. [11] reported the deposition of organosilicone plasma polymers on the surface of paper, and noted that the effect of filling the pores on the surface and thickness of the film were influenced by treatment time. Cho and Sjoblom [5] also reported that plasma treatment of wood with hexamethyldisiloxane (HMDSO) resulted in contact angles over 130° from almost zero on fresh wood.

Silicone containing surfaces are usually described as having the lowest surface energies and, therefore, the least wettability of any class of material. In this investigation, the hydrophobicity of paper was improved with octamethylcyclotetrasiloxane "$Si_4O_4C_8$" (OMCTSO) plasma treatment. This chemical was used to coat paper with a very thin plasma polymeric layer which was expected to possess desirable hydrophobic and barrier properties. The OMCTSO is also one of the most hydrophobic polymer (polydimethylsiloxane) monomers. Thus, the main objective associated with such treatment is to increase the hydrophobic character of the paper,

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Table 1
Surface oxygen (O/C) and silicone (Si/C) to carbon atomic ratio and affects on contact angle and brightness changes of OMCTSO plasma treated papers (300 mTorr).

	25 W				100 W			
	O/C	Si/C	Θ (Deg.)	Bright (%)	O/C	Si/C	Θ (Deg.)	Bright (%)
Unt. Paper	0.85	0	0	83.2	0.85	0	0	83.2
1 Min	1.1	0.82	105	82.9	1.1	0.69	84	79.3
5 Min	0.52	0.50	114	83	0.62	0.55	105	77
10 Min	0.75	0.73	108	83	0.84	0.72	73	78.8

to produce paper grades suitable for special applications in which water proof properties are required.

2. Materials and methods

The plasma treatments was performed on a standard white spruce bleached kraft paper, produced especially for this investigation, on the paper machine at the USDA Forest Products Laboratory, Madison-Wisconsin. There were no additives or fillers contained in the sheet which could affect the results. The specially cut paper samples were dried in an vacuum oven at 40 °C for 1 day prior to treatment. The dried paper samples were then subjected to the selected plasma treatments.

Octamethylcyclotetrasiloxane and other chemicals used in this study were purchased from Aldrich Chemical Co. (Milwaukee, WI) with a purity of at least 99%, unless otherwise noted.

The plasma-enhanced functionalization reactions were carried out in a cylindrical stainless steel, capacitively coupled (disc-shaped stainless steel electrodes; electrode diameter: 20 cm; gap: 3 cm) RF-plasma reactor equipped with a 40 kHz power supply. The discharge is mainly confined between the electrodes. Capacitive coupling to parallel electrodes inside the reactor enables the creation of uniform electric fields determined by the size of electrode. A detailed description of plasma reactor design and working procedure can be found elsewhere [11].

The relative surface atomic concentrations and the non-equivalent atomic linkages of plasma modified paper samples were carried out using a PerkinElmer Physical Electronics XPS system (Mg source; 15 kV; 300 W; pass energy: 89.45 eV; take-off angle: 45°).

The water contact angle test was performed by the projected sessile droplet method with deionized water (0.05 μml.). If the image of the drop remained stable, the measurements were done with a manual goniometer. A sustaining (60 s or longer) angle between water and paper surface is indicative of good hydrophobic characteristics.

Selected paper specimens were examined with a Hitachi 450 scanning electron microscopy (SEM). For analysis, specimens were allowed to air dry on the aluminum stubs. The specimens were then be coated with 40% gold and 60% palladium, and the micrographs obtained. Further investigation of surface morphology of the paper was evaluated by atomic force microscopy (AFM) to measure the chemical force interactions. A contact mode AFM microscopy, digital instruments III AFM was used.

The air permeation, tensile strength and brightness measurements were carried out according to Tappi test method T 460 (Gurley porosity), T 494, T 525, respectively.

'The paper smoothness test was carried out according to Tappi test method (Sheffield method) T 538. According to this approach, the measured flow rate of air across a sheet is an indirect measurement of surface smoothness. It measures the extent, which

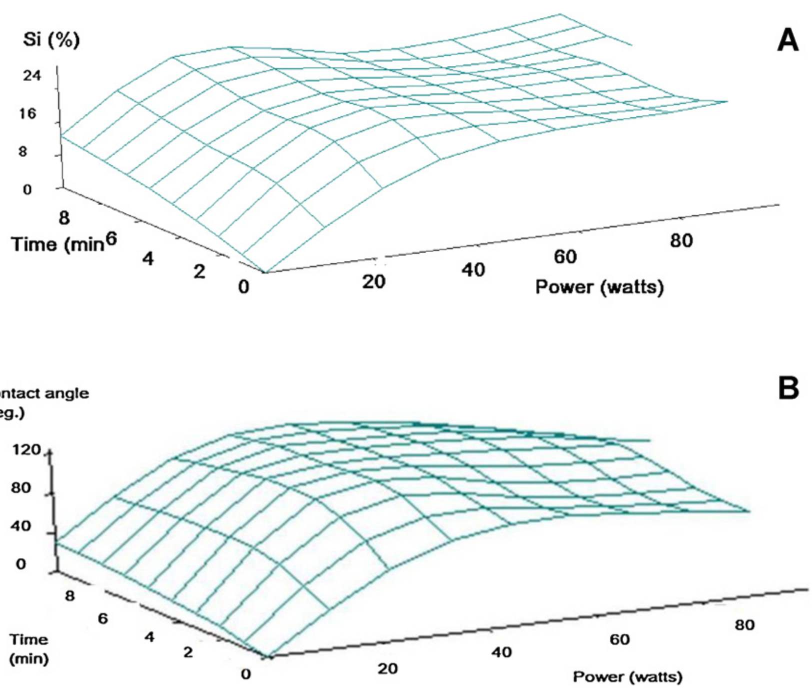

Fig. 1. Treatment time and RF-power effects on silicone concentration (a) and contact angle (b) on OMCTSO plasma treated paper (300 mTorr).