Corona Treatment Changes Some Physical Properties of Cellulose

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Synopsis

Moisture absorption, dielectric properties, and x-ray crystallinity of cellulose handsheets and deacetylated cellulose acetate films have been determined. The moisture absorption of the treated samples was lower than that of the controls. Further, the changes of the electrical properties of the treated samples agreed with the observed decrease in the moisture absorptions of the treated samples: no significant change in their crystallinity was noted.

INTRODUCTION

The strong bond developed in paper after its formation on the paper machine is generally attributed to the hemicelluloses in wood. One way of increasing the bonding capability of cellulose fibers is to change the cellulose surface so that the new surface possesses properties similar to that of hemicellulose. Goring[1] treated cellulose, deacetylated cellulose acetate film, and birch wood in a corona discharge and found that the treatment increased the bond strength. However, the tensile strength increased only marginally, indicating that the corona treatment altered the surface only.

For various types of insulating cellulosic materials used in electrical applications, mechanical and electrical properties are important. Since the corona treatment increased the bond strength of handsheets, it would be of value to the electrical industry to know if this treatment altered the electrical properties of the material favorably. Accordingly, sorption, dielectric, and fine structure studies of the control and treated samples have been made and are reported in this paper.

EXPERIMENTAL

Materials

The corona-treated pulp handsheets and deacetylated cellulose acetate films were supplied by Dr. Goring of the Pulp and Paper Research Institute of Canada, Montreal. The details of the treatment are given in Table I. The handsheets were of commercial bleached sulphite pulp beaten to a Canadian Standard Freeness of 266. The films were prepared by deacetylation of a commercial secondary cellulose acetate sheet.

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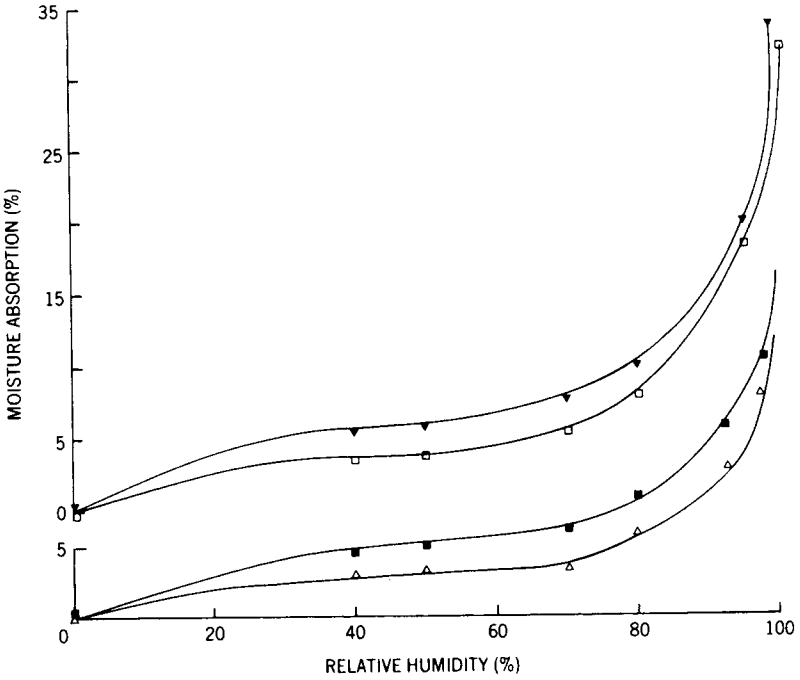


Fig. 1. Moisture absorption of samples. ■, A; △, B; ▼, C; □, D (see Table I).

TABLE I
Details of Corona Treatment of Samples

Sample	Treatment
Hand sheets—control (A)	None
Hand sheets—treated (B)	15 kV, 60 Hz, 5 min, one side only
Deacetylated cellulose acetate control (C)	None
acetate treated (D)	15 kV, 60 Hz, 5 min, one side only

Absorption Studies

The control and treated specimens of handsheets and films were humidified at relative humidities between 0% and 100%. The specimens were first vacuum-dried ($<10^{-3}$ Pa) at room temperature to determine the dry weight. They were then subjected to 40%, 50%, and 65% relative humidities in rooms of controlled humidity. At higher humidities, suitable saturated salt solutions were employed. From the vacuum-dry weight and the equilibrium weight of a specimen at each relative humidity, the moisture absorption at that relative humidity was calculated.

Crystallinity Measurement by X-Ray Diffraction

To determine if corona treatment altered the fine structure of cellulose, x-ray diffractograms of specimens were recorded using a Phillips x-ray unit operating with parafocussing geometry. The collimated beam was defined by a divergence slit of 1° angular aperture at the x-ray post. The diffracted beam was defined by 0.61 mm receiving slit and 1° angular aperture scatter slit. The signal of the

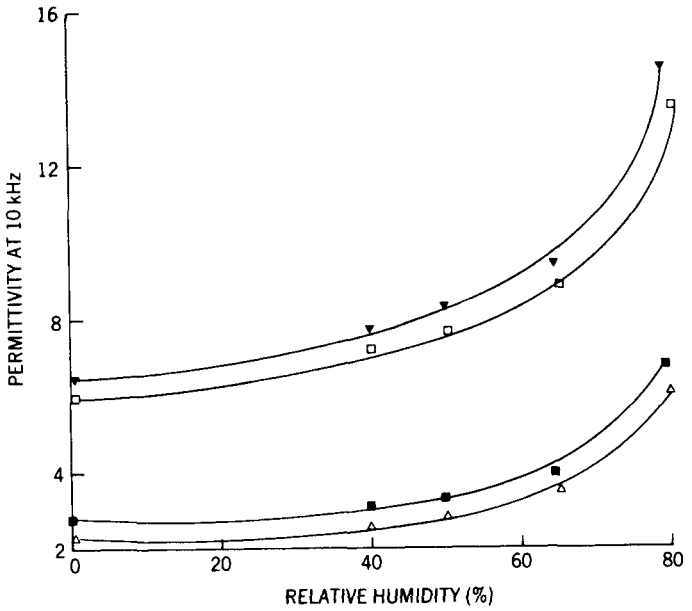


Fig. 2. Permittivities of samples. ■, A; △, B; ▼, C; □, D (see Table I).

TABLE II
Crystallinity of the Control and Treated Cellulose

Sample	No. of Tests	$I_{(002)}$ (arbitrary units)	I_{am} (arbitrary units)	Crystallinity (%)	
Untreated cellulose sheet	1	37.0	7.0	81.0	mean
	2	71.0	14.0	80.2	
	3	51.0	10.0	80.3	80.7
	4	70.0	13.0	81.4	
Treated sheet	5	43.5	9.0	79.3	
	6	45.5	10.5	76.9	78.2
	7	41.5	9.0	78.3	

beam was received by a Geiger counter and recorded by a Brown recording potentiometer.[2]

Rectangular specimens (20 × 15 mm) were clipped in the sample holder of the x-ray unit and then mounted on the goniometer. The diffraction intensity was measured from $2\theta = 10°$ to $2\theta = 30°$ to include the three main diffraction maxima of the cellulose lattice structure: the (101), (10$\bar{1}$), and (002) planes. The percent crystallinity is defined by[2]

$$C\gamma = 100\ (I_{(002)} - I_{am})/(I_{(002)})$$

where $I_{(002)}$ is the intensity of the diffraction from the (002) plane at $2\theta = 22.6°$ and I_{am} is that of the background scatter measured at approximately $2\theta = 18°$.[2] To eliminate any error due to misalignment the specimens were tested again after rotating them through 90° in the holder.[2]

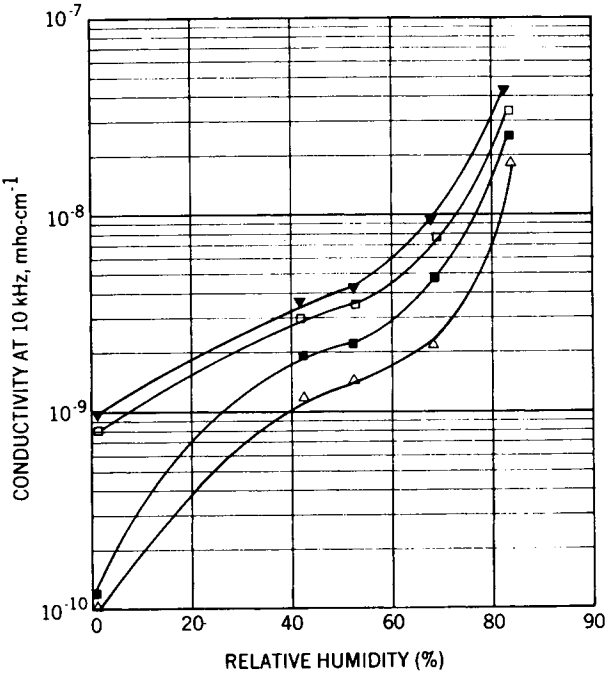


Fig. 3. AC conductivities of samples. For symbols, see Fig. 1.

Permittivity and Conductivity Measurements

An accurate three-electrode system[3] was employed for electrical measurements. Permittivity and conductivity of the specimens between 100 Hz and 100 kHz and the dc resistance were measured over a moisture content range from 0% to 15%. For ac measurements a GR 1615A capacitance-conductance bridge and conventional accessories were used. Measurements in the dc field were made by means of a 610 C Keithley Electrometer. The diameter of the electrode was 5 cm and the electrode gap varied between 0.3 and 0.375 mm.

The electrical measurements were first made on vacuum-dry ($<10^{-3}$ Pa) specimens at room temperature. These were then exposed to various relative humidities either in rooms of controlled humidity and temperature or by the use of suitable saturated salt solutions.

Oil-Impregnated Samples

Dissipation factor and dielectric breakdown were determined with oil-impregnated specimens, since they are most valuable in electrical applications when so treated. Inhibited transformer oil, 10-C, obtained through the courtesy of the G.E. Company in Toronto, was used for this purpose.

Specimens were thoroughly vacuum-dried at room temperature for 72 hr. The dissolved air in the oil was removed by evacuation. A Karl Fischer titration showed a moisture content of 20 ppm in the oil. The vacuum-treated specimens were impregnated with oil without exposing them to the atmosphere. The vacuum was then broken with dry nitrogen. The impregnated specimens were then allowed to stand for 6 hr before measurement.

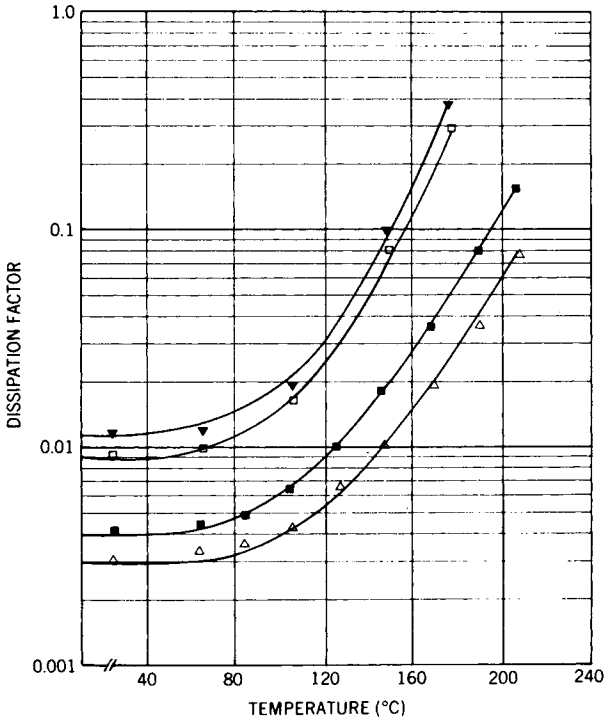


Fig. 4. Dissipation factor of samples at various temperatures. For symbols, see Fig. 1.

Dissipation factor measurements were made at 1 kHz and for temperatures between 20° and 200°C using a GR 1615A capacitance bridge. Measurements were made in duplicate using a test fixture comprising two flat steel disk electrodes, 5.1 cm in diameter, with a specimen clamped between them. Dielectric breakdown of the impregnated specimens was determined following American Society for Testing and Materials (ASTM) method D 149T-55.

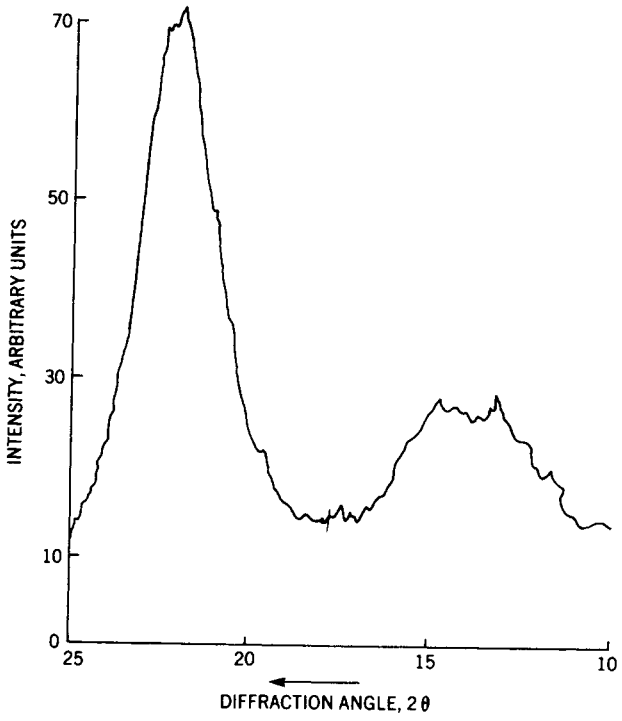
RESULTS AND DISCUSSION

The water-vapor absorption isotherms for the control and treated specimens (Fig. 1) show that the corona treatment decreased the moisture absorption of the treated specimens. In the humidity range studied, the difference of these values varies between 2% and 4%.

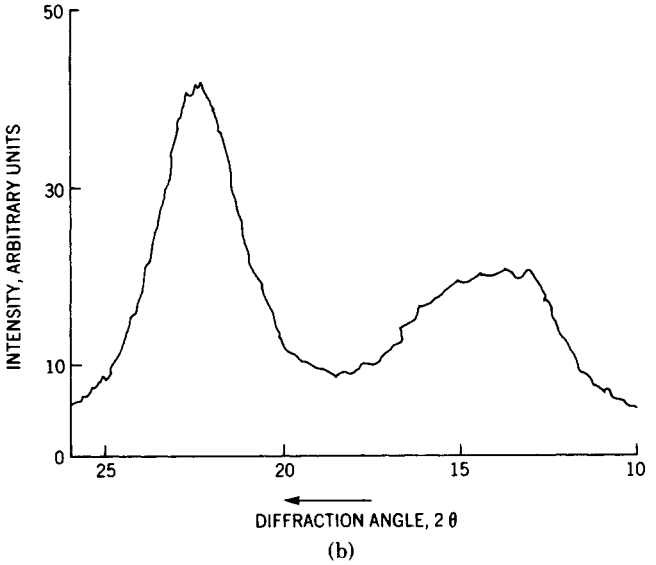
According to Goring,[1] in a corona treatment oxidation and degradation of the cellulose molecules by ozone generates a thin layer of low molecular weight oxycellulose on the surface. During this process it is possible that some crosslinking also occurs on the treated surface. Such a crosslinking would tend to decrease the moisture absorption of the treated samples.

The permittivity of the treated specimens is slightly higher than that for the corresponding controls (Fig. 2). The corona treatment (Figs. 3 and 4) decreases the conductivity and dissipation factor. The decrease in these two properties is much less for the films than that for the handsheets.

The higher permittivity for the film as compared to that for the handsheets



(a)



(b)

Fig. 5. X-Ray diffractograms of pulp sheets: (a) untreated; (b) treated.

TABLE III
Dielectric Breakdown of Control and Corona-Treated Samples

Material	Electrode gap (mils)	Breakdown voltage (kV)	Breakdown strength (kV/mil)
Untreated cellulose A	10.5	14.5	1.38
Treated cellulose B	10.0	15.0	1.50
Untreated film C	12.2	15.0	1.23
Treated film D	10.1	14.0	1.39

(Fig. 2) can be interpreted to mean that the handsheets contain fewer polar groups than the films.

The decrease in the conductivity and dissipation factor of the corona-treated specimens is in agreement with the observed decrease in the moisture pickup of the specimens on corona treatment. The smaller change in conductivity and dissipation factor for films than for handsheets can be attributed to the higher density of the films.

The partial x-ray diffractograms of the samples are given in Figures 5(a) and 5(b) and the crystallinities calculated from them are given in Table II. These indicate that x-ray diffraction measurements do not detect any significant changes in the crystallinity (of the control and corona-treated samples) possibly due to (i) the empirical nature of the formula used to calculate crystallinity; or (ii) the fact that the corona treatment produces only a surface effect.

Table III gives the dielectric breakdown voltages of oil-impregnated samples. The treated samples break down at higher voltages. This is to be expected since corona treatment decreases the moisture absorption.

CONCLUSIONS

This study shows that the corona treatment produces changes in some of the physical and electrical properties of cellulose of interest for practical applications in the electrical industry.

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