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Uncovering the Best Way to Turn Dull Wood Pulp into Bright Paper

When making paper, manufacturers typically use hydrogen peroxide to bleach the processed wood pulp, thus brightening the final product. To avoid delignifying the pulp — reducing the pulp yield and destroying the fibers that provide strength — the industry uses thermomechanical pulp, which is steamed during processing, and a bleach slurry that has a pH of -11.

Pulp bleaching, however, can be pricey; therefore, manufacturers are trying to reduce costs by adding a higher-acidity first stage of bleaching.

To determine what a two-stage peroxide bleaching technique should entail, investigators led by Adam Wójciak of Agricultural University of Poznań and Marek Sikorski of Adam Mickiewicz University, both in Poznań, Poland, have used several spectroscopic techniques to track the structural changes that occur in thermomechanical pulp as it is processed.

The group also included researchers representing Universidade do Algarve in Faro, Portugal; Instituto Superior Técnico in Lisbon, Portugal; and Jagiellonian University in Krakow, Poland.

Using an x-ray photoelectron spectrometer made by VG Scientific (now part of Thermo Fisher Scientific Inc.), the researchers examined changes in the surface of the pulp fibers caused by hydrogen peroxide after treatment in alkaline and acidic conditions. They confirmed that the treatment uncovers the superficial lignin molecules that act as chromophores in the untreated pulp. Removing any chromophore increases overall brightness.

They performed time-resolved dif-



Researchers used multiple spectroscopic techniques to characterize alkaline and acidic versions of bleaching wood pulp with hydrogen peroxide. Courtesy of Marek Sikorski, Adam Mickiewicz University, and Adam Wójciak, Agricultural University of Poznań.

fuse reflectance laser flash photolysis experiments using a 266-nm Nd:YAG laser made by B.M. Industries (now part of Thales Group in Orsay, France) for excitation and a gated intensified CCD camera made by Oriol (now part of Newport Corp. of Irvine, Calif.) for detection of the resulting emissions.

This technique enabled the researchers to elucidate the differences in the photochemical behavior of the treated and untreated pulp. The recorded spectral shapes from the two forms were nearly identical, showing that both maintained the same transient chemical species, but that the absorption spectra of

the peroxide-treated samples decayed much faster after laser excitation than did the untreated samples.

The investigators also detected Fourier transform infrared (FTIR) spectra, using a spectrophotometer made by Mattson (now also part of Thermo Fisher Scientific) that scanned the range from 550 to 4000 cm^{-1} with a resolution of 2 cm^{-1} . In addition, they acquired spectra using a Fourier transform Raman device made by Bio-Rad Laboratories Inc. of Hercules, Calif., a nitrogen-cooled germanium detector and a Spectra-Physics Nd:YAG laser for excitation at 1064 nm.

The latter techniques allowed the scientists to judge the influence of treatment conditions on the lignin and carbohydrate content of the pulp. According to Wójciak, FTIR Raman analysis confirmed the removal of the pulp's chromophoric structures related to coniferaldehyde, a lignin precursor that is the product of lignin-degradation reactions. "Identification and quantification of coniferaldehyde end-units is important from the technological point of view," he said.

The researchers concluded that using a two-stage approach to peroxide-based bleaching is beneficial because the high-acid first stage prepares the pulp fibers so that the alkaline second stage is more efficacious than when an alkaline stage is used exclusively.

They plan to continue refining their knowledge of pulp-bleaching processes, including testing novel bleaching reagents under delignifying conditions and using other analytical techniques such as nuclear

magnetic resonance imaging and model systems.

According to Wójciak and Sikorski, wood pulp samples represent

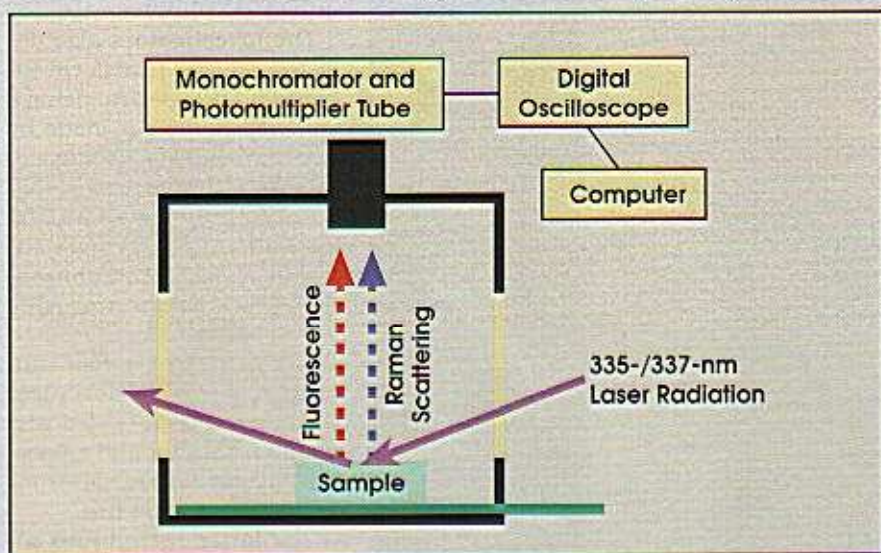
complex chemical and physical structures, and only the combined application of a range of spectroscopic methods may produce mean-

ingful research results. □

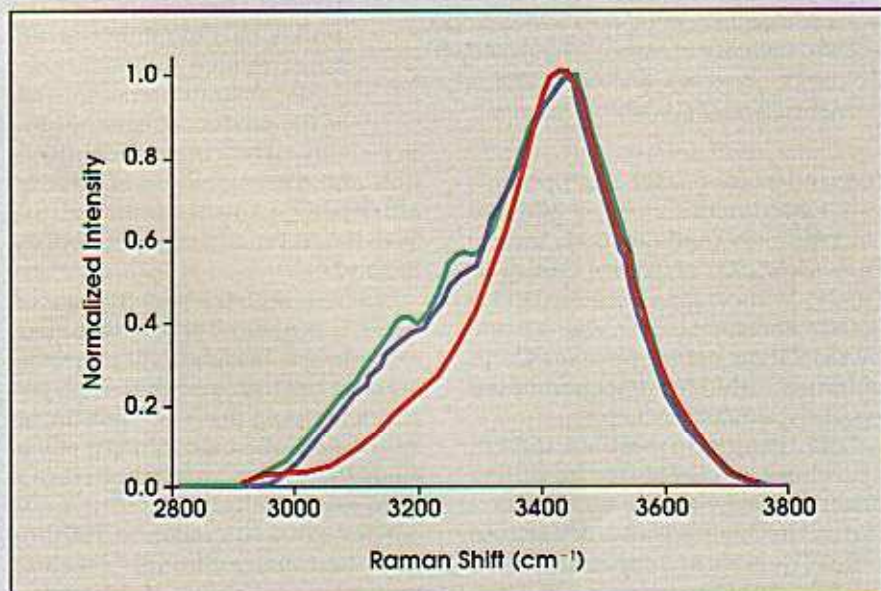
Lynn M. Savage

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Different Chemistry at an Icy Edge



Researchers studied the interface between air and ice using two techniques simultaneously. Ultraviolet laser beams enter through quartz windows, providing the light for both glancing-angle Raman (355-nm excitation) and laser-induced fluorescence (337-nm excitation) spectroscopy. A single detector picks up both signals. Images courtesy of Tara Kahan, University of Toronto.



This image shows the Raman spectra of the OH-stretch band of a pure ice surface (blue trace); the same ice surface after the deposition of gaseous HCl (green trace); and the surface of a frozen 0.01-M aqueous NaCl solution (red trace).

Clearing up the atmospheric impact of salting roads and sidewalks is one possible outcome of recent research exploring the quasiliquid layer found at the interface between air and ice. Another possible outcome could be a better understanding of the chemistry inside high-altitude cirrus clouds, which has important implications for atmospheric science.

Investigators from the University of Toronto and from the University of Bristol in the UK used glancing-angle Raman and laser-induced fluorescence spectroscopy to study the air-ice interface and found evidence of enhanced hydrogen bonding of the surficial water molecules.

Previous work by the group had shown a dramatic difference in the photochemical degradation rates, and other scientists have reported chemically strange behavior at the interface.

"We are trying to understand how chemistry differs at the ice surface from that which takes place at the liquid water surface or in aqueous solution," said D. James Donaldson, professor of chemistry at the University of Toronto.

He added that, in the course of such investigations, having a variety of probes to study what is happening is important. That is one reason that they used both glancing-angle Raman and laser-induced fluorescence spectroscopy, neither of which had been used widely for such research.

Applying these methods was not easy. Both fluorescence and Raman scattering signals generally are much stronger from the bulk substrate than from the surface. Several years ago, the researchers began using glancing-angle fluorescence to study chemical reactions on water. They