INVESTIGATING THE CHROMOPHORE COMPOSITION OF WOOD PULPS IN THERMOAGING BY DIFFUSE REFLECTION

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Key words: wood pulp, composite paper, lignin, thermoaging, reflection spectrum, absorption spectrum.

The application of wood pulps (WP) to produce a wide assortment of paper products is hindered by their increased tendency to the process of photo- and thermoaging due to a high lignin content. It was shown in [1] that thermoaging of WP occurs on account of reactions which proceed through a chemiluminescence step (the most rapid component of the process) as well as the step of decomposition with the formation of multicomponent systems of volatile products and altering optical properties (the slowest step). It is evident that we can get a comprehensive idea of the interrelationship of these processes from knowledge of the mechanisms of each one. Different viewpoints of the mechanism of photo- or thermoinduced yellowing of mechanical WP are put forward. In the investigation of [1] by the method of chemiluminescence analysis, it was shown that significant yellowing of defibrator WP (DWP) or thermomechanical pulp (TMP) is preceded by peroxide and hydroperoxide formation and decomposition. The investigation of the chromophore composition and experiments with model lignin compounds led Forsskahl and Janson [2] to the assumption of similarity of the photo- and thermoaging mechanisms. At the same time, a conclusion was reached about the difference of these mechanisms in a number of works. Most likely, a similar uncertainty also occurs in the ideas about the mechanisms of photo- and thermoinduced yellowing in chemical WP.

The aim of the present investigation is to obtain more detailed information on the processes of change in the chromophore composition of WP during oxidation with a combination of a number of procedures within the framework of the spectroscopy of diffuse reflection in the near UV and visible regions; this work is devoted to a study of the changes in the WP chromophore composition in thermoinduced aging.

We took specimens of the initial composite paper (CP) based on TU 13-7309005-478-88 chemimechanical WP and WP subjected to thermoinitiated oxidation by the air oxygen at 170°C for 5 h. We measured the diffuse reflection spectra for WP on a Specord M400 (Carl Zeiss Jena) instrument, which is a two-beam spectrometer with a wide range of capabilities due to the presence of a built-in controlling computer and a large set of plug-in attachments. To record the spectral dependence of the diffuse reflection coefficient, we used an attachment from the Specord M400 set that ensures a measurement geometry of 45/0. The spectral width of the output slit of the illuminating monochromator was 0.1 nm.

From the results of studying the reflection spectra measured in the 200-800-nm interval, we calculated spectra of the ratio of specific absorption k, cm²/g, and scattering s, cm²/g, coefficients (Fig. 1), proportional to the spectra of the absorption coefficients in the indicated spectral interval [3].

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Both for the initial and thermally treated specimens, the basic absorption in the investigated spectral interval falls on the near UV region with characteristic maxima at 250 and 280 nm (the absorption band of ketone and aldehyde structures of the WP lignin associated with a carbonyl group [4])**

As the above spectra show, the process of thermoaging involves an increase in absorption over the entire spectrum as a branch appears in the 320-360-nm region.

More accurate information on the changes in the chromophore composition can be obtained by considering the absorption difference of the thermally treated and initial specimens \(A(k/s)_t = (k/s)_t - (k/s)_i\) (Fig. 1, curve 3). The basic band in the difference spectrum that has a maximum at 330 nm (coniferyl aldehyde, ferulic acid, dioxystilbene [5], a phenol-conjugated carbonyl group [6], double bonds, and phenylcumarone structures [7]) and a pronounced shortwave branch at 280 nm suggest a predominant absolute increase in the content of chromophores absorbing in the 280-400-nm region. At the same time, the maximum relative increase in \((A(k/s)_t)/(k/s)_i\) that falls on \(\lambda = 455\) nm (Fig. 1, curve 4) is, apparently, associated with a larger formation rate for the structures absorbing in the 400-560-nm band (ortho- and parahincons, biphenyl and stilbene structures [8, 9]).

It is common knowledge [5] that NaBH4 and KBH4 are selective reducers of carbonyl groups, which enables us to establish their contribution to the total absorption in subtracting the absorption spectrum of the reduced form from the unreduced one, \(\Delta(k/s)_r = (k/s)_r - (k/s)_i\). Use was made of KBH4 in this investigation. The specimens were prepared according to the procedure of [10] (the KBH4 consumption was 10%, pH 10.5, 60°C, \(t = 1\) h). Difference \(A(k/s)_r\)-spectra are given in Fig. 2.

The basic maxima (branches) in the \(\Delta(k/s)_r\)-spectra are located at 240, 275, and 325 nm (dioxystilbene, phenylcumarone, isoeugenol [5]). The process of thermoaging involves an increase in absorption in a band with \(\lambda_{max} = 325\) nm and a decrease in shortwave bands. The difference of \(\Delta(k/s)_r\)-spectra for the specimens of the initial and thermally treated CP \(\Delta[(k/s)_r] = (k/s)_r - (k/s)_i\) (Fig. 2, curve 3) points to the predominant increase in the content of chromophores that absorb at \(\lambda = 365\) nm (stilbene structures [5, 11]) in thermoaging. The largest relative change \(\Delta[(k/s)_r]/\Delta(k/s)_i\) in the concentration of carbonyl-free lignin chromophores is observed in a band with \(\lambda_{max} = 515\) nm and a branch in the 630-nm region (Fig. 2, curve 4).

**Hereinafter the absorption bands are correlated on the basis of positions of the absorption band maxima for individual monomer compounds that are known from the literature, with no account taken of overlapped spectra.