Photostabilization of mechanical pulps by polyvinylpyrrolidone

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ABSTRACT: Free phenolic hydroxyl groups in lignin are largely responsible for the formation of colored structures in mechanical pulps. Polyvinylpyrrolidone (PVP) has been reported to interact with the phenolic hydroxyl groups in lignin via hydrogen bonds. Results presented here show that mechanical spruce pulps were stabilized against photoyellowing by treatment with PVP. The most efficient PVP compounds were the monomer (n-vinyl-2-pyrrolidone) and the lowest-molecular-weight (10,000) polymer. The polymers increased initial brightness and functioned as stabilizers against photoyellowing.

KEYWORDS: Brightness, high yield pulps, hydroxyl groups, mechanical pulps, phenol groups, Picea, polyvinyl pyrrolidone, stabilization, yellowing.

High-yield mechanical pulps are being used increasingly as components in high-value paper products, and this trend is expected to continue. A major drawback to the use of mechanical pulps is their tendency to yellow upon exposure to light. High-yield pulps contain basically the same components as wood: cellulose, hemicellulose, and lignin. Of these, lignin is mainly responsible for the yellowing.

The basic mechanisms of photo-yellowing were recently reviewed by Heitner and Schmidt (*1*), who reported at least three reaction pathways:

1. Direct absorption of UV light by conjugated phenolic groups to form phenoxyl radicals
2. Abstraction of phenolic hydroxyl hydrogen by aromatic carbonyl triplets
3. Cleavage of nonphenolic phenacyl-α-*o*-arylethers to phenacyl–phenoxyl free-radical pairs.

Hydroxyl radicals generated during irradiation also have been proposed to be a major cause of discoloration (*2*). Furthermore, oxygen—which reacts with phenoxyl and other free radicals as well as, or in combination with, reactive intermediates of the quinone and hydroquinone type—has been proposed to participate in the overall photoyellowing process (*1, 3*). Carbonyl groups and free phenolic hydroxyl groups in lignin are largely responsible for the formation of colored structures in high-yield pulps. Thus brightness stability is increased by reactions (e.g., esterification and alkylation) that eliminate the free phenolic groups (*4–7*).

The search for new methods of preventing photoyellowing of paper has prompted researchers to examine studies of discoloration in other types of biological materials. The browning reactions of vegetables and other plant materials have been studied in detail. Endogenic enzymes, particularly polyphenol oxidases, often are involved in the reactions. Browning reactions caused by polyphenol oxidases are mainly the result of oxidation of phenolic groups to quinones in the plant materials (*8*). Polyphenol oxidases can be inhibited by specific inhibitors acting either on enzymes or on substrates. In the substrate-level inhibition, the phenolic groups can be blocked by specific adsorbents.

Polyvinylpyrrolidone (or its monomeric constituent) has been found to be an efficient substrate-level inhibitor (*8*). According to the suggested reaction mechanism, the phenolic hydroxyl groups form hydrogen bonds with the substituted amide groups of the polymer (*9*). The phenol-adsorbing capacity of polyvinylpyrrolidone (PVP) also has been utilized to protect plant enzymes from inhibition by phenolics (*9*).

PVPs are commercially available from many manufacturers in different grades and under a variety of trade names. The basic monomer is *n*-vinyl-2-pyrrolidone. PVP products differ mainly with respect to their molar masses, varying from 10,000 D to

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360,000 D. PVP is used in various products in the cosmetic, perfume, and pharmaceutical industries. It also is used as a detergent in the washing industry (*10*).

PVP has been used to investigate polymer adsorption on cellulosic materials in studies to obtain fundamental knowledge about the adsorption process (*11*). It is strongly adsorbed to unbleached kraft pulp, weakly adsorbed to mechanical pulp, and not adsorbed at all to bleached kraft pulp (*12*). It has been suggested that the polymer segments interact with the lignin of unbleached kraft and mechanical pulps by hydrogen bond formation of the catechol and phenol groups.

PVP also has found application in the forest-products industry in the manufacture of resin adhesives, as a binder for silica, as a filler in papers, as a flocculating agent in the production of paper, as an additive in printing inks, and as a slip-prevention agent for paper (*13*). Furthermore, PVP has been used to stabilize cellulosic materials for electrical insulation and as a preservative polymer component to increase the dimensional stability of wood (*14*). The use of PVP in paper coatings also has been found to improve whiteness and gloss (*15*). Despite the variety of applications in the forest-products industry, PVP has not yet been studied as an agent for preventing photoyellowing. The present work analyzes the capacity of *n*-vinyl-2-pyrrolidone and its polymers to prevent brightness reversion in two types of mechanical pulps.

Materials and methods

The pulps were produced in laboratory scale at the Finnish Pulp and Paper Research Institute. Pressurized groundwood (PGW) was made from fresh spruce by grinding with overpressure in a 110-kW pilot grinder with a stone of 120-mm width and 500-mm diameter. Chemithermomechanical pulp (CTMP) was made from industrial spruce chips by steaming, cold impregnation with sodium sulfite solution (3 g Na_2SO_3/L, i.e., 2% on dry wood), heating at 125°C for 5 min, and refining in two steps (total energy about 1.7 MW·h/metric ton) in a 1000-mm double-disc refiner.

I. Light-induced color reversion of PGW treated with different concentrations of PVP K 15

PVP in solution, %	PVP in sheet, %	R_1	R_2	PC_1	PC_2	PC
			457 nm			
0	0	60.7	53.2	0	7.86	7.86
0.1	0.9	61.3	53.5	-0.50	7.99	7.49
1	6.1	62.1	55.4	-1.11	6.40	5.29
10	16.9	63.8	59.2	-2.45	3.79	1.34
			557 nm			
0	0	75.5	72.2	0	1.36	1.36
0.1	0.9	76.2	72.8	-0.27	1.38	1.11
1	6.1	77.2	74.3	-0.62	1.07	0.45
10	16.9	78.8	77.0	-1.14	0.59	-0.55

II. Light-induced color reversion of CTMP treated with different concentrations of PVP K 15

PVP in solution, %	PVP in sheet, %	R_1	R_2	PC_1	PC_2	PC
			457 nm			
0	0	60.1	51.8	0	9.20	9.20
0.1	5.3	58.7	51.1	1.24	8.87	10.11
1	10.6	60.5	54.1	-0.35	6.53	6.18
10	17.2	60.5	55.8	-0.35	4.62	4.27
			557 nm			
0	0	74.9	70.7	0	1.87	1.87
0.1	5.3	73.7	69.7	0.48	1.88	2.36
1	10.6	75.5	72.4	-0.24	1.27	1.03
10	17.2	75.9	73.6	-0.39	0.89	0.50

The PVPs used were: *n*-vinyl-2-pyrrolidone (Aldrich Chemicals), PVP K 15 (MW 10,000, Fluka), PVP K 25 (MW 24,000, Fluka), PVP K 30 (MW 40,000, Fluka), PVP K 60 (MW 160,000, Fluka), PVP 360 (MW 360,000, Sigma), and PVPP 6755 (Sigma).

The treatments with PVP were carried out by suspending the pulp (2 g) in PVP solutions (100 mL) of different concentrations and incubating at room temperature for 1.5 h. Handsheets (95 cm^2) were made on a Büchner funnel without washing the treatment liquor. After drying at room temperature, the sheets were irradiated at 27°C and 47% RH for 3 h in a Xenotest 150 S apparatus (Heraeus Hanau) equipped with a xenon lamp, total output 1.3 kW.

Before and after irradiation of the reference and PVP-treated samples, the reflectances of the samples were measured with an Elrepho reflectance photometer in blue and green lights with a 457-nm brightness filter and a 557-nm luminance filter, respectively.

The Kubelka–Munk relationship between light absorption, scattering, and reflectivity was used.

$$k_i/s_i = (1 - 0.01R_i)^2/0.02R_i \qquad (1)$$

where

R_i = reflectivity, %

k_i = specific absorption coefficient, m^2/kg

s_i = specific scattering coefficient, m^2/kg

i = 0 (untreated sample), 1 (PVP-treated sample), or 2 (irradiated sample).

Post-color (PC) values were calculated according to Giertz (*16*).

$$PC_1 = 100(k_1/s_1 - k_0/s_0)$$

III. Light-induced color reversion of PGW treated with polyvinylpyrrolidones of various molecular weights (1% solutions)

PVP	Molecular weight	PVP in sheet, %	PC no. 457 nm	PC no. 557 nm
None	...	...	7.86	1.36
Monomer*	111	1.3	5.12	0.66
PVP K 15	10,000	6.1	5.29	0.45
PVP K 25	24,000	3.8	7.42	0.77
PVP K 30	40,000	0.3	8.31	1.21
PVP K 60	160,000	1.3	8.81	1.47
PVP 360	360,000	0.9	9.49	1.56
PVPP 6755	high MW	47	3.86	0.32

*n-vinyl-2-pyrrolidone

IV. Light-induced color reversion of CTMP treated with polyvinylpyrrolidones of various molecular weights (1% solutions)

PVP	Molecular weight	PVP in sheet, %	PC no. 457 nm	PC no. 557 nm
None	...	...	10.27	1.89
Monomer*	111	1.4	6.20	1.00
PVP K 15	10,000	10.6	6.18	1.03
PVP K 25	24,000	3.8	8.93	1.63
PVP K 30	40,000	5.5	9.83	1.64
PVP K 60	160,000	0.2	11.53	1.79
PVP 360	360,000	0.5	12.25	2.19
PVPP 6755	high MW	55	4.55	0.37

*n-vinyl-2-pyrrolidone

$$PC_2 = 100(k_2/s_2 - k_1/s_1)$$

$$PC = PC_1 + PC_2.$$

Results and discussion

The effect of PVP on photoyellowing was studied using PGW and CTMP, two commercially important papermaking pulps. The PC values were calculated for the untreated reference samples, the PVP-treated samples, and the irradiated samples. The amounts of absorbed PVP compounds were estimated by weighing the dried handsheets. In these preliminary tests, the pulps were mixed with the chemicals without further optimization of the treatment.

The PVP with the lowest molecular weight (PVP K 15) was the first one chosen for studying the effect of the polymer concentration in the treatment. **Table I** shows the results obtained for PGW. **Table II** shows results for CTMP. The results indicate that the polymer affected the pulps in two ways. Treatment with PVP increased the brightness of the pulps and also prevented brightness reversion. The effect of PVP on brightness and on brightness reversion was obvious both in blue light (457 nm) and in green light (557 nm). The effect of PVP treatment on pulp brightness is apparent in the negative PC_1 values. The photostabilization effect is evident at the higher concentrations of PVP, where the PC_2 values for the irradiated handsheets were reduced by about 50% for both PGW and CTMP. For PGW, the total effect (treatment and irradiation) at 557 nm on the pulp was even an increase in reflectivity (from 75.5% to 77.0%). Using the highest concentration of the polymer, the dry weight of the handsheet was increased by about 17% for both pulps.

The effect of PVP molecular weight was determined by treating both pulps with 1% solutions of the various PVPs used in this study. The monomeric compound (*n*-vinyl-2-pyrrolidone) was also included in the experiments. Results for PGW and CTMP are presented in **Tables III** and **IV**, respectively. The lowest PC values were obtained for the pulps treated with the high-molecular-weight polyvinylpolypyrrolidone (PVPP 6755). However, in this case, the PVPP was adsorbed totally on the pulps and, accordingly, the dry weight of the handsheets increased by about 50% for both pulps. The monomer (*n*-vinyl-2-pyrrolidone) and the lowest-molecular-weight polymer (PVP K 15) were about equally efficient, as judged by the final PC values. Apart from these, no systematic connection between molar mass and stabilizing effect was detected. However, the various samples may have had different types of molar-mass distribution and different purities. Adsorption of PVP K 15 on the pulp was greater than for the other PVPs, even the higher-molecular-weight preparations, except for the PVPP.

Conclusion

This report examines the effectiveness of polyvinylpyrrolidone (PVP) as an agent for improving the brightness stability of mechanical pulps. PVP has previously been studied for various applications in the pulp and paper industry, but there are no published reports about their beneficial effect on the photostabilization of mechanical pulps.

The brightness values of the polymer-treated PGW and CTMP pulps were superior to the original brightness values, even after irradiation. The most efficient compounds were the monomer (*n*-vinyl-2-pyrrolidone) and the lowest-molecular-weight polymer (MW 10,000). The increased brightness was due to two effects. The polymers increased initial brightness and functioned as stabilizers against photoyellowing. The photostabilization was found to correlate with the con-

centration of the polymer in the pulp slurry, which also affected the amount of polymer adsorbed on the pulps.

In the search for specific inhibitors against photoyellowing, vinyl pyrrolidone (*n*-vinyl-2-pyrrolidone) and its polymeric forms represent an interesting group of compounds. The free phenolic groups of lignin have been reported to be largely responsible for the brightness reversion of mechanical pulps. PVP has previously been suggested to interact with the phenolic groups of lignin via hydrogen bonds (*12*). Thus, vinyl pyrrolidones can be expected to be specific adsorbents preventing the oxidation of phenol or catechol groups to quinones.

Other polymers, such as polyethylene glycol, have been studied as potential agents for improving photostabilization (*7, 17*). However, polyethylene glycol has not been reported to be specific for any of the chemical groups responsible for brightness reversion. The mechanism of the interaction of the PVP and pulp is being studied further.

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