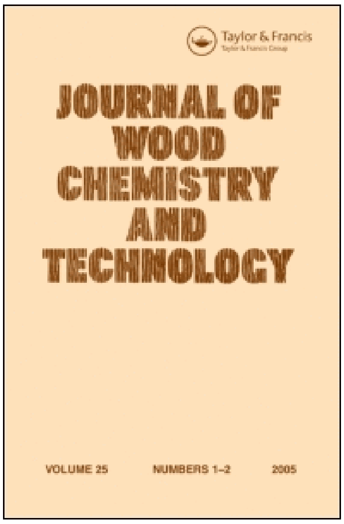

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HYDROXYL RADICAL INDUCED VISCOSITY LOSS IN CELLULOSE FIBRES

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ABSTRACT

Irradiation of pulp by ionizing radiation causes large viscosity drops, which are almost independent of consistency. Hydroxyl radical scavengers present during irradiation offer virtually no protection against depolymerization. These observations suggest that the major degradation of cellulose is due to direct ionization of the fibre, rather than to hydroxyl radicals extraneously produced in the surrounding water.

INTRODUCTION

In order to develop TCF bleaching various "active oxygen" species have been utilized. In these "active oxygen" driven processes there is always the possibility of hydroxyl radical formation. During both hydrogen peroxide[1,2] and ozone bleaching[3,4,5], hydroxyl radicals have been found to be intermediates. They have also been shown to play a important part in microbial degradation of wood.[6] Hydroxyl radicals are known to react with both aromatic substances and sugars.[7] The rate constants for hydroxyl radical addition to aromatics are around 10^{10} M^{-1} s^{-1}, while its rate constants for hydrogen abstraction from sugars are close to 10^9 M^{-1} s^{-1}. Thus the selectivity is low and due to the high concentration of cellulose in pulp almost all of the hydroxyl radicals will react with cellulose.[8] To the extent of ca 75 % hydroxyl radicals abstract hydrogen from cellulose to eventually form carbonyl groups. The remaining 25% will cause depolymerisation. In a series of experiments on pulp we tried to study the bleaching efficiency of γ-radiolytically generated one electron oxidants. To our dismay we found considerable viscosity losses even when ClO_2, an extremely lignin-selective bleaching agent, was produced in the γ-source. Our findings as well as those of Chirat and Lachenal[2,3] prompted us to scrutinize the effect of γ-irradiation and hydroxyl radicals on pulp.

EXPERIMENTAL

γ-Irradiations were performed in an AECL^{60}Co g-cell, the dose rate being 1kGy/h. The unbuffered solutions (pH 6 to 7) of pulp or cotton linters were saturated with nitrous oxide (N_2O) and the solutions were continuously stirred during γ-irradiation at 24 ^{0}C. Measurement of viscosity was performed according to SCAN-CM 15:88. Modified cooked and oxygen prebleached softwood kraft pulp (kappa number=12.9) or cotton linters were suspended in Millipore purified water.

RESULTS AND DISCUSSION

Cellulose Damage by hydroxyl Radicals Produced Outside the Fibres

Hydroxyl radicals can be produced in a controlled manner by γ-irradiation of water. The primary radicals are hydroxyl radical (45%), solvated electron (45 %) and H· (10%). In the presence of N_2O, solvated electrons are converted into hydroxyl radicals[9] through reaction 1.

$$e^-_{aq} + N_2O + H_2O \rightarrow OH\cdot + N_2 + OH^- \qquad (1)$$

The primary energy deposition is proportional to the mass of the irradiated components. Thus, in dilute aqueous solution <0.1 M the direct effect on the substrate is negligible. This is true for all substrates, except for macro molecules, like cellulose, where a single ionization can cause a chain break.

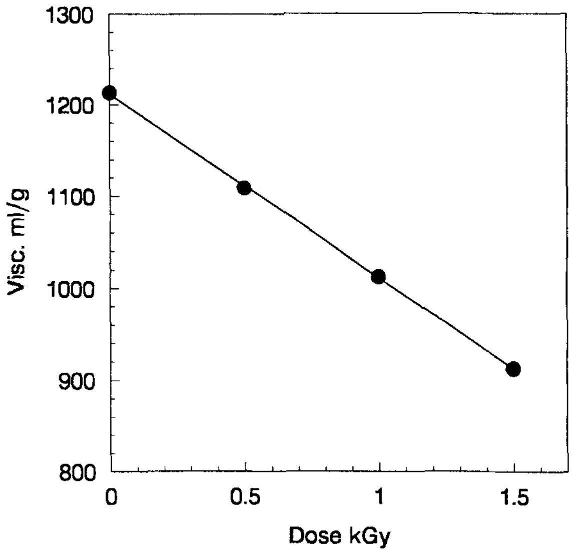

Fig 1. Viscosity of pulp as a function of imparted irradiation dose.

We have performed a series of experiments probing the effect on cellulose fibres of homogeneously generated hydroxyl radicals. The change in viscosity is proportional to the delivered dose as shown in fig. 1.

In table 1 the effect on viscosity of pulp consistency and scavenger addition are summarized. As can be seen from table 1, irradiation of 10 g pulp for 1 h causes a drop in viscosity by 180 units. It is also seen that a similar irradiation of 2 g pulp causes a drop in viscosity by 200 units. In both of these cases 5×10^{-4} moles hydroxyl radicals have been produced in the aqueous solvent. On a per mass basis this corresponds to 0.05 moles/kg and 0.25 moles/kg hydroxyl radicals being delivered to the pulp in the two cases. The major drop in viscosity can thus not be ascribed to homogeneously produced hydroxyl radicals. An estimate of the effect of the latter can be gained by ascribing the additional decrease in viscosity, 20 units, to the difference of 0.2 moles hydroxyl radicals/kg pulp. As the error in the viscosity analysis is around 10 units, the effect of hydroxyl radicals produced outside fibres would seem to be all but negligible.

TABLE 1
γ-Irradiation of 1 dm^3 N_2O Saturated Aqueous Solutions Containing Pulp or Cotton Linters with Initial Viscosities of 1213 ml/g and 856 ml/g, Respectively.

amount g/dm^3	irr.time h	visc. ml/g	OH·prod. moles	additive
pulp in 1 dm^3 of water				
10	1	1033	5×10^{-4}	
2	1	1013	5×10^{-4}	
2	0.5	1109	2.5×10^{-4}	
2	1.5	912	7.5×10^{-4}	
cotton linters in 1 dm^3 of water				
2	1	780	5×10^{-4}	
2	1	727	5×10^{-4}	0.1 M *t*-butanol
2	1	723	5×10^{-4}	0.2 M *t*-butanol
2	1	710	5×10^{-4}	0.4 M *t*-butanol
2	1	722	5×10^{-4}	0.7 M *t*-butanol
2	1	700	5×10^{-4}	1.0 M *t*-butanol
2	1	793	3×10^{-4}	5.0 M 2-propanol
2	1	865	3×10^{-5}	tri-ethylamine 95%
cotton linters in N_2O atmosphere				
2	1	740	4×10^{-7}	40 % consistency
2	1	616		vacuum dried fibres

The virtual lack of reaction between homogeneously produced hydroxyl radicals and cellulose is also evident from the irradiation of cotton linters in the presence hydroxyl radical scavengers. Within experimental error the viscosity loss of irradiated cotton linters (0.25 mol hydroxyl radical /kg) is unaffected by 5 M 2-propanol added. Interestingly, t-butanol not only fails to protect the cotton but contributes even slightly to viscosity losses.

The above observations can be understood in the light of the high and indiscriminate reactivity of the hydroxyl radical towards most functional groups, as a result of which the interior of the fibres should be inaccessible to the hydroxyl radicals generated homogeneously on the outside. This is corroborated by the following estimate. The effective rate of hydroxyl radicals reacting with cellulosic C-H groups is ca 10^9 s^{-1} in the fibre. The diffusion coefficient of the hydroxyl radical should be below

10^{-9} m^2s^{-1}. Thus, during its life-time the hydroxyl radical should not travel more than a few nanometers in the fibre.

The effect of homogeneous hydroxyl radicals will probably be limited to their peeling off water-soluble oligomers from surface cellulose, while leaving the bulk polymer intact, i.e., a certain loss of polymer will not be accompanied by substantial viscosity losses. In this context a rationale can be given to our finding that t-butanol somewhat enhances the viscosity losses. As hydroxyl radicals are converted to primary alkyl radicals ($\cdot CH_2C(OH)(CH_3)_2$), the latter manage to partly diffuse into the fibres, being much less reactive than hydroxyl radicals, and abstract hydrogen from cellulose. In the presence of 2-propanol secondary alkyl radicals are generated and the latter are not capable of abstracting cellulosic hydrogens. We note that in the presence of O_2 all alkyl radicals are transformed into peroxyl radicals[10]. For energetic reasons the latter are incapable of abstracting cellulosic hydrogen atoms.

It has to be concluded that the main cause of the viscosity loss upon γ-irradiation are not externally generated hydroxyl radicals. Two possibilities exist; direct ionization of the cellulose and/or hydroxyl radicals formed inside the fibres. The last two entries in the table refer to non-suspended fibres. At similar irradiation these fibres are seen to suffer greater viscosity losses than in suspension. Furthermore, dry fibres are degraded by irradiation even more than moist ones. On the face of it, internal water appears to protect the fibres. This suggests direct ionization of cellulose to be the main cause of depolymerisation. The internal water presumably acts as a channel allowing the ejected electrons to return to the site of ionization. Further support for the prime importance of direct ionization is provided by the finding that in the presence of triethyl amine virtually no viscosity loss is observed. This is rationalized by the fact that the ionization potential of triethyl amine[11], 7.5 eV, is well below that of cellulose[12], 9-10 eV, and therefore the ionized cellulose is expected to transfer all its charge to triethyl amine prior to degradation.

Direct ionization is a statistical process causing random chain breaks. It is then appropriate to correlate the latter to viscosity losses. From the data in table 1 it is seen that 1 h of irradiation results in a viscosity drop of ca 15%. From the effect of γ-irradiation of cellulose on the degree of its polymerisation, reported in ref. 13, we calculate that a dose of 1 kGy gives rise to ca 6×10^{-4} moles of chain breaks in 1 kg pulp or cellulose. From this value and the slope of fig 1. we estimate 4×10^{-5} moles of chain breaks to cause a viscosity loss of 1% in the viscosity range pertaining to our experiments.

CONCLUSIONS

When pulp is bleached with "active oxygen" species hydroxyl radicals appear to cause viscosity losses. However, hydroxyl radicals produced outside wood fibres will have negligible effect on the final viscosity. The high reactivity of hydroxyl radicals demands their site of generation to coincide with that of their consumption. Thus, during "active oxygen" bleaching, hydroxyl radicals appear to be produced inside the fibre.

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