Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 354, pp. 381-389
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Radiation Stimulation of the Reactivity of Different Types of Cellulose Pulps

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Institute of Nuclear Chemistry and Technology, Pulp and Paper Research Institute and Institute of Chemical Fibres carry out a joint research project in order to develop the radiation methods for modification of cellulose pulp to produce useful cellulose derivatives such as cellulose carbamate, carboxymethyl cellulose and methylcellulose. It is expected that radiation treatment should yield a final product with average degree of polymerization in the range 250 – 350 limiting the amount of chemicals activators used in classic methods and providing environmental benefits.

In this paper the effect of 10 MeV electron beam on degree of polymerization of various cellulose pulps has been studied. The role of free radicals in degradation process is also discussed.

Keywords: cellulose radicals; cellulose pulps; EB irradiation

INTRODUCTION

Cellulose fibres are important raw material for the production of textile and sanitary goods. The viscose technology has been not changed much for more than 100 years resulting in serious environmental hazards. New alternative technologies for the manufacture of cellulose fibers are currently under research and

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development. Two main methods - Lyocell and Cellca are used at present for production of cellulosic fiber without CS_2 use.[1, 2, 3]

Institute of Chemical Fibres (IWCh) in Łódź has been carrying out research since 1988 to develop technology for the production of cellulose carbamate as a raw material for production of fibers and films in order to eliminate the ecological problems associated with viscose method.[4, 5] Recently in the cooperation with the Institute of Nuclear Chemistry and Technology in Warsaw the effects of electron beam irradiation on various type of cellulose pulps have been studying in order improve the reactivity of raw material for production of cellulose carbamate.

EXPERIMENTAL

Three different type of textile pulp: Ketchikan, Alicell and Borregaard, labelled K, A and B, respectively and Kraft softwood pulp labelled S have been irradiated with 10 MeV electron beam from LAE 13/9 linear accelerator. Kraft softwood sheets selected to study the effects on radiation dose were irradiated in dry and wet form with doses of 10, 15, 25 and 50 kGy. Textile pulps were irradiated only in dry form with dose of 25 kGy.

The average viscosity and DP_v of cellulose pulps, unirradiated ones and irradiated with different doses, were measured in dilute solution of copper ethylenediamine (CED). [6, 7]

The content of α - cellulose was determined by gravimetric methods as percent of pulp insoluble in 17.5 % NaOH solution. [6, 7].

After electron-beam irradiation the samples of cellulose pulps have been examined by electron paramagnetic resonance (ESR) spectroscopy method.

For ESR study the irradiated pulps sheets were cut into narrow strips and placed in quartz ESR tubes (4 mm OD).

band Bruker spectrometer using microwave power of 1 mW and modulation amplitude of 0.4 mT. Dry samples were measured directly after EB irradiation, whereas the wet ones have been dried at ambient temperature for about 3 hours before ESR measurements. The relative radical concentrations were estimated by double integration of ESR spectra. No attempts were undertaken to determine absolute number of free radicals.

RESULTS AND DISCUSSION

Previous studies proved that cellulose fibres undergo degradation by ionizing radiation.[1, 2, 3] The chain scission can occur as a result of primary radiolytic reactions – electron capture or detachment but also in secondary reactions by attack of mobile free radicals formed in earlier stages of radiolysis[8, 9]. Besides chain scission free radicals can be also involved in the opening of the glucopyranose ring, formation of smaller chain sugars and elimination of H_2O, CO and CO_2. All these reactions affect the properties of cellulose pulps and may increase cellulose reactivity.

The ESR spectra of Ketchikan cellulose irradiated with dose of 25 kGy are shown in Fig. 1. Just after irradiation the spectrum consists of dominant triplet $A:A_{iso}$ = 3.0 mT, g_{iso} = 2.003 and quintet $B:A_{iso}$=1.8 mT and g_{iso}= 2.003 which lines appear only as the shoulders on the triplet. We tentatively assigned triplet to a radical in which unpaired electron located on carbon at position 1 interacts with C - 1 proton and C - 2 hydroxyl proton. Quintet B hyperfine structure is due to the interaction with four equivalent protons – one C - 1 proton, one C - 3 hydroxyl proton and two C – 5 methylene protons, represents free radical with unpaired electron on carbon at position 4. This interpretation implies chain scission at C-1 position.

After 23 days storage at room temperature the intensity of triplet decreases with a

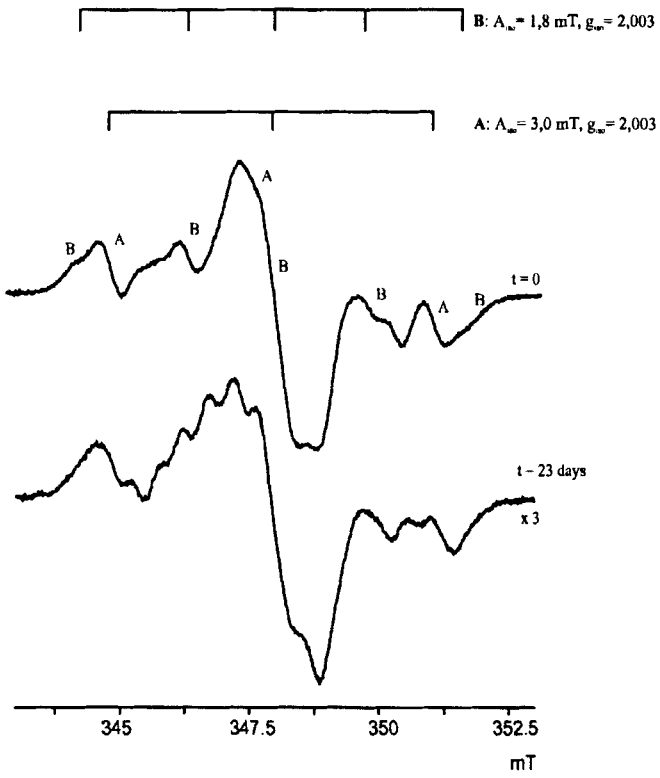

FIGURE 1 The ESR spectra of Ketchikan cellulose pulp EB irradiated at room temperature with a dose of 25 kGy measured directly after irradiation and after storage for 23 days

factor of 3 whereas lines B disappears nearly completely. At the same time a new spectrum appears in the field range 345-349 mT showing 7 lines with splitting of 0,5 mT. It is not clear whether the radicals represented by this spectrum arise directly after irradiation or they are formed by transformation of B radicals.

The character of the ESR spectra is similar for all studied cellulose samples.

The number of free radicals in Ketchikan, Alicell and Borregaard cellulose is practically the same as well as their decay rates (Table I). However, in Kraft

TABLE I The relative concentrations of free radicals in different cellulose pulps after 10 MeV irradiation with dose of 25 kGy

Cellulose samples	$[R^{\bullet}]$/a.u. t = 30 min	$[R^{\bullet}]$/a.u. t = 11 days
Alicell (A)	3.48	0.89
Borregaard (B)	3.86	0.85
Ketchikan (K)	3.65	0.82
Kraft softwood (S) dry	10.61	1.96**
Kraft softwood (S) wet	4.11*	2.22**

* time after irradiation 3 hours

** time after irradiation 10 days

softwood pulp the concentration of free radicals is higher with factor of about 3. The stabilization of free radicals can be due to the cellulose structure which control chain flexibility. The kinetic data presented in Figure 2 show that in textile pulps radical concentration decreases rapidly during first 12 hours and later remains nearly unchanged. In Kraft softwood pulp after fast decay stage was observed the second stage with moderate decay rate (1-3 day). In general in Kraft softwood pulp we can distinguish three types of radical sites:

1. reactive sites, possibility located on the surface,
2. sites with limited reactivity, placed in less rigid domains,
3. sites stable for days at room temperature trapped in rigid domains.

The second type of radical sites is not observed in textile pulps. Owing to this steady-state concentration of free radicals measured directly after irradiation is lower textile than in softwood pulp. In other words the equilibrium between formation and decay of radicals is reached at lower concentration level. It is worthy to mention that irradiation of Kraft softwood pulp in wet form does not affect much the radiation processes. The same radicals with similar concentrations are formed in

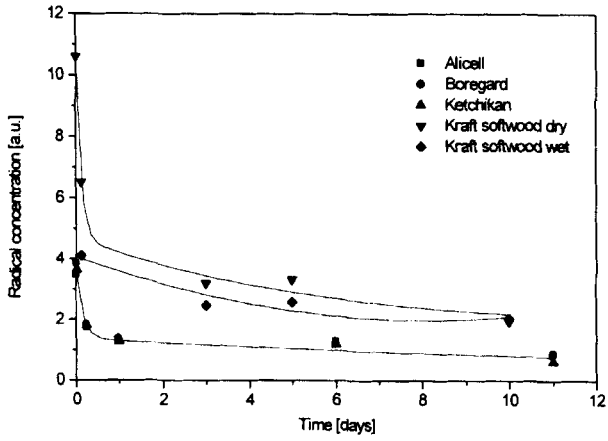

FIGURE 2 Decay of free radicals in different types of cellulose pulps irradiated with 10 MeV EB

dry and wet samples. The water presence does not influence radical kinetics also.

The relationship between dose and the concentration of radicals in dry Kraft softwood pulp after EB irradiation at room temperature is shown in Figure 3. Up the 25 kGy radical concentration grows linearly with dose (curve-b). For higher doses the number of radicals increases much slower which is typical for radiolytic saturation effect. Curve-a on the same with radiation figure shows decrease of degree of polymerization dose for the same type of softwood pulp.

The smallest applied dose - 10 kGy makes chain scission process very effective and as a result the degree of polymerization decreases about 46 %. The effectiveness of cellulose degradation is much lower for higher doses and for 25 kGy degree of polymerization is only 30 % indicating that doses around 10 kGy are optimal from economical point of view. Similar dose dependence of degree of polymerization was observed in irradiated Ketchikan textile pulp (see Table II) suggesting that this

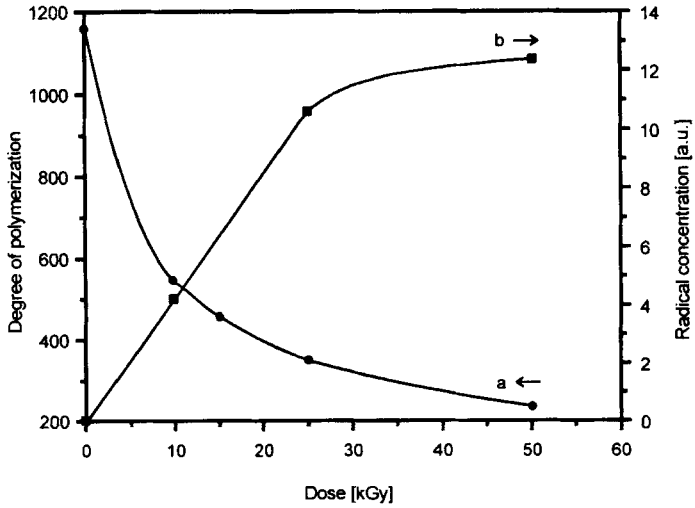

FIGURE 3 Dose depedence of degree of polymeryzation (a) and free radicals concentration (b) for dry Kraft softwood cellulose pulp EB irradiated with a dose of 25 kGy.

relationship has a general character for cellulose polymer chains.

The effect of 10 MeV electrons on viscosity, degree of polymerization and content of α - cellulose for Ketchikan and Kraft softwood is shown in Table II.

The curve-a in Fig. 3 to some extent is a mirror reflexion of curve-b. However, correlation between the changes of free radicals number and degree of cellulose degradation is not perfect. In dose range 10–25 kGy decrease of polymerization degree is rather moderate whereas the concentration of radicals increases with factor of 2. It should be mentioned, however, that the scission of the chain at its side part does not change much the degree of polymerization in spite of producing similar number of radicals as the scission in the central part of chain. Additionally, the small radicals produced in this case can be involved in secondary scission reactions causing observed differences. We think, however, that in general

TABLE II The effect of 10 MeV EB irradiation on viscosity, degree of polymerization (DP) and α - cellulose content for Ketchikan and Kraft softwood cellulose pulps

Cellulose samples		EB dose [kGy] 0	10	15	25	50
Ketchikan	viscosity [ml/g]	601	347	307	246	139
	DP	856	467	408	319	170
	α - cellulose [%]	93.4	91.4	88.9	88.6	76.0
Kraft softwood	viscosity [ml/g]	797	399	341	268	188
	DP	1169	544	458	350	237
	α - cellulose [%]	86.6	85.6	84.3	84.4	80.9

the number of free radicals recorded by ESR is related to degree of cellulose degradation.

CONCLUSIONS

The results of primary investigations show that EB irradiation with a dose of 10 kGy leads to decrease the degree of polymerization of textile as well as softwood pulps for about 50 %. For Ketchikan pulp and Kraf softwood pulp the degree of polymerization decay to 467 and 544, respectively. At the same time the content of α - cellulose decreases in meaningless way. The results are very promising clearly indicating that production of cellulose carbamate using as a raw material the cellulose modified radiolyticaly should be much more effective. It was proved by analyzing the ESR spectra that similar radicals are formed in different types of textile and softwood pulps. However, the number of radicals stabilized in Kraft softwood pulp at room temperature is three times higher than in Ketchikan, Alicell and Borregaard textile pulps. It is speculated that the differences in radical stability

are associated with cellulose chain flexibility which is controlled by cellulose structure.

Acknowledgments

This project was supported by the Polish State Comittee for Scientifitic Research (KBN) under Grant No.7 T08 E 033 17.

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