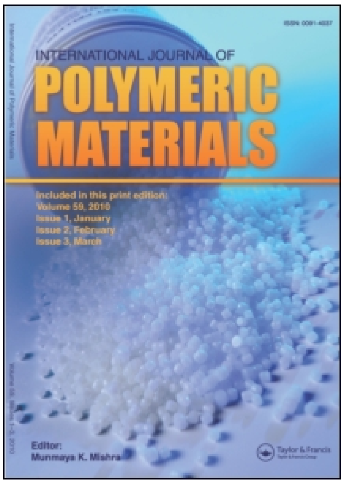

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Cellulose Phototransformation and Possibility of its Light Stability Increase

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This study clearly demonstrates that the variation of the accessible amorphous phase contents, the plasticizer concentration and the pH value affords to increase strongly (by a factor 10–100) the light stability for different kinds of cellulose.

KEYWORDS: Phototransformation, cellulose, amorphous phase, plasticizers, stability, pH-value

The world production of cellulosic material is evaluated by hundreds, millions and tons. There are many kinds of cellulose with the different properties (from cotton, linen, wood, modified celluloses). Some other types of cellulosic materials with new properties will be undoubtedly created in the future because cellulose is a renewed source for polymer production. However a little information is available about the cellulose properties needed for its high light stability.

The aim of this work is to determine the quantitative characteristics of cellulose phototransformation and on this basis to elucidate the principal factors having considerable effect on the light stability of cellulose.

RADICAL ACCUMULATION KINETICS

Different types of cellulose have been found to show different kinetic curves of radical accumulation under the conditions of irradiation (25°C, 60–80% of room humidity, in air, the wavelength and intensity of light 253.7 nm and $2.9 \cdot 10^{15}$ photons/sm^{2}s respectively, film masses of 1 sm^2 of surface $m = 4$–5 mg). Results are shown in Figure 1. Among four samples studied the α-fraction of cellulose I exhibited the highest value of the initial radical accumulation rate and the highest value of radical stationary-state concentration, whereas those of hydrocellulose and microcristalline cellulose were the smallest.

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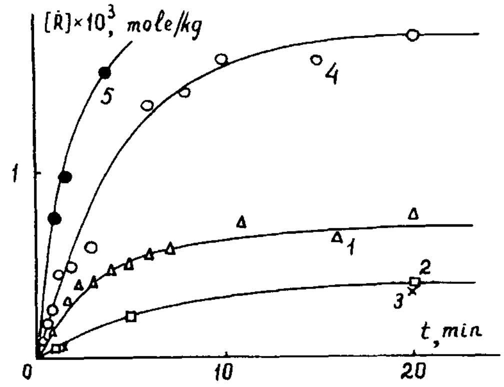

FIGURE 1 Experimental (points) and theoretical (lines) curves of radical accumulation for cellulose I (1, 5), microcristalline cellulose (2), hydrocellulose (3) and α-cellulose (4) irradiated with light of wavelength 253.7 nm in air at 25°C (1–4) and 77 K (5).

Under the experimental conditions a correlation between the contents of impurities and the initial rate of radical accumulation is absent due to a very small amounts of impurities in the purified cellulose samples used. It implies that the photolysis of cellulose is direct under these conditions.

There is no doubt that the photodegradability of cellulose is dependent upon its morphology. But the degree of cristallinity for given samples (Figure 1) was nearly the same (70–80%). It means that in this case any other factors will have greater effect than the degree of cristallinity on the photodegradability of cellulose.

In order to obtain more complete information we studied the radical decay kinetics and compared it with the radical accumulation kinetics for a number of cellulose samples with different structure and molecular mobility.

RADICAL DECAY KINETICS

Cellulose macroradical decay kinetics is known to be "polychromatic" when ensemble of free radicals has not a single rate constant but a broad spectrum of rate constants from k_{min} (minimum value) to k_{max} (maximum value). The kinetic law of radical decay for cellulose is described by Eq. (1):

$$(\dot{R})/(\dot{R})_0 = 1 - (\ln(k_{\mathrm{max}}/k_{\mathrm{min}}))^{-1}\ln(k_{\mathrm{max}}t + 1), \tag{1}$$

where $(\dot{R})$ and $(\dot{R})_0$ are the concentrations of radicals $\dot{R}$ at time t and $t = 0$ respectively.

The values of parameter $\ln(k_{\mathrm{max}}/k_{\mathrm{min}})$ determined by Eq. (1) for the samples of cellulose with different structure and molecular mobility are shown in Table I. Some additional samples of cellulose have been prepared by saponification of triacethylcellulose (TAC) films with subsequent treatment of the films at different temperatures in the presence of plasticizers (water and glycerine). Such treatment produces a transparent thin film of cellulose with the same absorption coefficient

TABLE I

Quantum yields ϕ_R of formation of radicals R and parameters $\ln(k_{max}/k_{min})$ for radical decay under cellulose photooxidation in air at 25°C

Cellulose samples	Cellulose characteristics				
	Type	a.a.ph., %	(H_2O), %	$\phi_R \cdot 10^3$	$\ln(k_{max}/k_{min})$
Cellulose I	I	9.5	4–5[a]	5 20[b]	6.6 ± 0.1
α-Fraction	II	12.1	[a]	8 34[b]	8.8 ± 0.3
Hydrocellulose	II	16.7	8–9[a]	1	6.8 ± 0.1
Microcristalline cellulose	I	7.0	[a]	2	6.1 ± 0.2
Cellulose from TAC	II	19.6	0	7	9.7 ± 0.8
			8	3	4.2 ± 0.4
			15.6	0.2	0.5
Cellulose from TAC	II	10.4	0	11	8.5 ± 0.6
			8.4	2	4.0 ± 0.4
			12.4	0.5	1.8 ± 0.2
Cellulose from TAC	IV	8.7	0	5	5.7 ± 0.2
			8	2.5	4.5 ± 0.3
			13	0.5	2.0 ± 0.2

[a] At 60–80% room humidity.
[b] At 77 K.

($\varepsilon_{254} = 1.6\,M^{-1}\,sm^{-1}$) but with the different structure in a large scale. Cellulose structure has been characterized by iodine adsorption. The ratio of iodine adsorption for a given sample to iodine adsorption for amorphous cellulose (412 mg of I_2 per 1 g of cellulose) represents the contents of accessible amorphous phase (a.a.ph.) for a given cellulose sample. The a.a.ph. values for all samples are summarized in Table I.

The width of hyperbolic function of distribution on radical reactivities (k_{max}/k_{min}) is proportional to life time of radicals which is heavily dependent upon cellulose molecular mobility. So the width of radical distribution is a quantitative characteristic of molecular mobility. As shown in Table I, due to structure and plasticization with water the width of radical distribution is changed by a factor 10^2–10^3.

STRUCTURE AND MOLECULAR MOBILITY EFFECTS ON RADICAL ACCUMULATION AND DECAY KINETICS

The quantum yield of radical formation is one of the most important characteristics of the photodegradability. The quantum yields of radical formation ϕ_R have been determined from the initial rates of radical accumulation for the different samples of cellulose. At the initial stages of reactions the termination of radicals R is absent and has no effect on the initial rate of radical accumulation which equals to the radical formation rate in this case. The values of ϕ_R are shown in Table I.

One can see from Table I that the decrease of the water contents in cellulose increases the value of ϕ_R and the width of radical distribution $k_{\max}/k_{\min}$. The increase of ϕ_R is also observed with the decrease of temperature of u.v. irradiation. The linear correlation has been found between the values of $\phi_R^{1/2}$ and $\ln(k_{\max}/k_{\min})$ which is valid for all cellulose samples used. It indicates that the quantum yield of radicals R is heavily dependent upon the molecular mobility of cellulose. This dependence may be the main source of difference among the values of ϕ_R for cellulose samples with different structure.

The radical accumulation kinetics under u.v. irradiation of cellulose can be explained by Scheme 1.

$$\text{Cell.} + h\nu \rightarrow \dot{r} \tag{0}$$

$$\dot{r} \rightarrow \dot{R} \tag{1}$$

$$\dot{R} \rightarrow \dot{r} \tag{2}$$

$$\left.\begin{array}{r}\dot{r} + \dot{r} \rightarrow \\ \dot{r} + \dot{R} \rightarrow \\ \dot{R} + \dot{R} \rightarrow \end{array}\right\}\text{termination} \qquad \begin{array}{r}(3)\\(4)\\(5)\end{array}$$

SCHEME 1

According to Scheme 1, the radicals $\dot{R}$ determined by the ESR measurements at room temperature are not a primary radical but they are the most stable radicals under the experimental conditions. In the solid phase k_3 and $k_4 \gg k_5$ due to high reactivity of primary radicals $\dot{r}$. So the stationary-state concentration of $\dot{r}$ achieves its level very rapidly and $(\dot{r})_{st} \ll (\dot{R})$ at the initial stages of radical accumulation process. As a result the initial rate of radical accumulation equals to the rate of formation of radicals $\dot{R}$ by reaction (1). But the rate of reaction (1) can be much more lower than the rate of overall photoinitiation via reaction (0), being dependent on the value of k_1^2/k_3.

The theoretic curves calculated on the basis of Scheme 1 are represented in Figure 1 and are in a good accordance with the experimental results.

Thus the increase of ϕ_R with the decrease of molecular mobility can be explained by strong dependence of the reactions (1) and (4) on structure and molecular mobility of cellulose. It implies that the stabilization of primary radicals by reaction (1) plays an important role and has effect on the photodegradability of cellulose. It should be also noticed that the quantum yield of initial radical accumulation in cellulose is not the quantum yield of all radicals formed but it is the quantum yield of formation of only stabilized radicals which is heavily dependent upon the conditions of radical stabilization (structure and molecular mobility of cellulose).

QUANTITATIVE CHARACTERISTICS OF CELLULOSE PHOTOTRANSFORMATION

Oxygen consumption kinetics

The kinetic curves of oxygen consumption has been found to have a small "induction" period (about 20 min) where the initial rate of oxygen consumption is

TABLE II

Quantum yields of cellulose phototransformation (25°C, dry air, 354 nm)

Cellulose samples	ϕ_R[a]	ϕ_{O_2}[b]	ϕ_{CO_2}	$\phi_{\text{—CHO}}$
Cellulose I	0.020	0.015	0.0010	0.050
Hydrocellulose	—	0.012	0.0006	0.021
α-Cellulose	0.034	—	0.0010	—
Microcristalline cellulose	—	0.008	0.003	—

[a] Measured at 77 K.

[b] At $I_0 = 2.9 . 10^{15}$ photons/sm^2 s.

4 times less than the steady-state rate. The oxidation products have no effect on the steady-state rate. The induction time equals to the time of growth of the radical concentration to a stationary-state level. Thus the increase of the photooxidation rate at the initial stages of reaction should be explained by the increase of radical concentration up to the stationary-state level under irradiation.

Accumulation of aldehide groups

The rate of aldehide accumulation is proportional to the light intensity I_0 at the initial stages of u.v. irradiation. The decrease of initial aldehide concentration by means of reduction of aldehide groups to hydroxyl groups and the increase of aldehide concentration during the irradiation have no effect on the rates of accumulation of aldehides and free radicals. It implies that aldehide groups are not the photosensitizer of cellulose phototransformation under the experimental conditions.

The coloured products of cellulose phototransformation are shown to act only as u.v. screen. It confirms the direct photolysis of cellulose under the experimental conditions.

The quantum yields have been calculated for some processes of cellulose phototransformation: formation of radicals (ϕ_R), oxygen consumption (ϕ_{O_2}), formation of aldehides ($\phi_{\text{—CHO}}$) and carbon dioxide (ϕ_{CO_2}). Its values are shown in Table II.

The quantum yield of oxygen consumption is less than that of radical formation. It indicates that the photooxidation of cellulose is a non-chain process under the experimental conditions. Nevertheless the quantum yield of aldehides exceeds that of radical formation. It demonstrates the chain transformation of cellulose macroradicals without O_2 under the photooxidation. The possible effect of cellulose structure on the photochemical transformation of cellulose has been also demonstrated by data of Table II.

CORRELATION BETWEEN STRUCTURE AND PHOTOTRANSFORMATION OF CELLULOSE

This correlation has been established by the parallel measurements of the contents of accessible amorphous phase (a.a.ph.) and the rate of cellulose

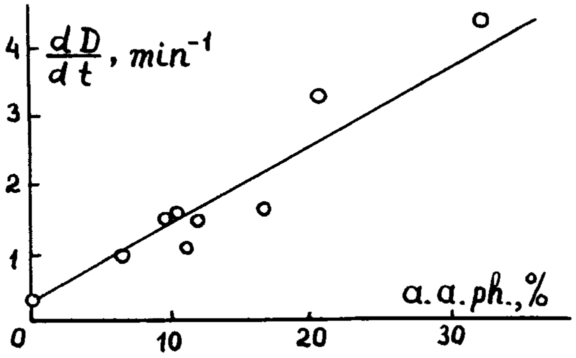

FIGURE 2 Dependence of the rate of cellulose photoyellowing on the cellulose structure characterized by a.a.ph. value.

photoyellowing for a large number of different cellulose samples (some of these samples were mentioned in Tables I and II). As can be seen (Figure 2) the rate of yellowing (dD_{360}/dt) is increased by a factor ~14 with the increase of a.a.ph. value from 0 to 32%. Thus the special modification of cellulose structure is one of the most possible ways for effective photostabilization of cellulose.

MOLECULAR MOBILITY EFFECTS ON CELLULOSE PHOTOTRANSFORMATION

For the cellulose samples of the same structure the rate of yellowing has been found to be dependent on the water concentration: the increase of the water contents from 0 to 100% decreases the rate of photoyellowing by a factor ~6. Simultaneously the life-time of radicals is decreased. It demonstrates the effect of molecular mobility due to plasticized action of water on the cellulose phototransformation.

The partial acetylation of cellulose has also been shown to decrease the life-time of free radicals and to increase the light stability of cellulose. On the basis of these data it has been supposed that the decrease of radical life-time is responsible for the light stabilization by partial acetylation. The decrease of radical life-time may be due to plasticized action of acetyl groups and acetic acid formed by the photolysis of ester groups.

BASE CATALYSIS OF CELLULOSE PHOTOTRANSFORMATION

The presence of base has been found to increase strongly (by a factor 10^2–10^3) the rate of cellulose phototransformation. Alkaline environments catalysis the photoyellowing of all cellulose samples studied and model compounds—cellobiose and sacharose. Therefore a polyene system needed for absorption in visible range of light can be formed by a phototransformation of carbohydrates themselves and not only by a transformation of aromatics as it had been supposed earlier. The dependence of the photoyellowing rate on pH value of solution indicates the range of pH values where the rate of carbohydrate phototransformation is the lowest. Thus the optimal pH values for cellobiose are in the range of 4–5 and a change to pH 7 increases the rate of photoyellowing substantially (by a factor 13). Therefore the optimal pH values may be selected for the effective increase of cellulose light stability.