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Photooxidation of Hydroxyethylcellulose Changes in Physical Properties due to Corona Discharge

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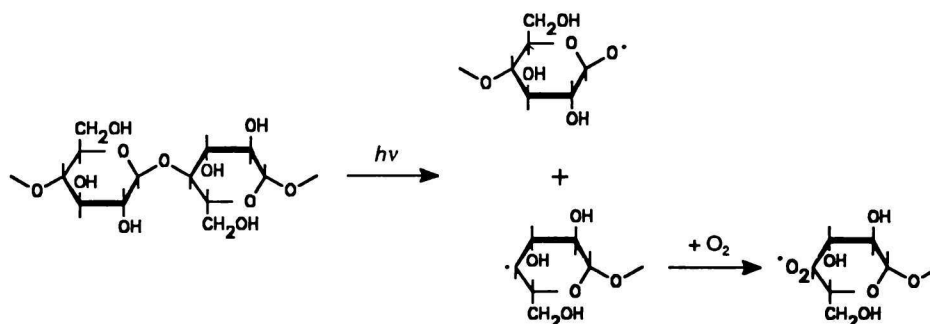
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The photooxidation of hydroxyethylcellulose by the action of corona discharge in air was studied at 25 °C. The influence of exposure on physical properties of polymer film was examined. It has been found that the transport process of diffusion of the distilled water into the polymer obeys the second Fick's law in the first period of one. The measured average apparent diffusion coefficient of the studied system varies in the interval $(2.1\text{--}15.2) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and decreases with exposure in an equal manner as the activation energies of diffusion which vary in the interval $(23.3\text{--}57.5) \text{ kJ mol}^{-1}$. On the basis of limiting contact angle measurements the temperature of glass transition was determined. It has been found that the preponderance of the cross-linking process over photodestruction of the polymer is significantly influenced by the time of irradiation by low-temperature plasma of corona source.

The photodegradation of cellulose materials has been extensively investigated [1–5]. The primary process is chain scission which occurs during UV irradiation (at $\lambda = 253.7 \text{ nm}$) of cellulose yielding many different compounds, e.g. xylose, D-glucose, and cellobiose. Many volatile products such as acetaldehyde, acetone, methanol, ethanol, ethane, water vapour are formed. These compounds are the results of the secondary degradation process. The composition of the photodegradation products depends on the system used. The following mechanism for the primary process has been proposed (Scheme 1).

Formation of free radicals during irradiation of cellulose with light has been verified by EPR spectroscopy [1, 2].

As obvious, the study of both kinetics and the mechanism of photochemical reactions in polymer materials has lately made a great progress and is very important from the viewpoint of polymer application. The low-temperature plasma treatment of polymer surface has been recently studied because of the ability to modify a polymer surface without great affecting its bulk properties. It can be presumed that the high speed of plasmochemical surface reactions results from the plasma effectiveness — solid surface energy transfer by electrons, excited atoms and ions collisions. During the past few years there has been a steady growth in the use of plasma for the modification of the surface properties of various solid materials [6–9]. This interest has been motivated by the ability



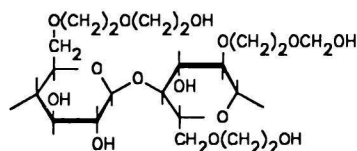
Scheme 1

of plasma to produce a large variety of changes on solid surfaces such as desorption of gases, degradation, removing of layers, cross-linking, chemical reactions, graft copolymerization, etc. In the case of polymers these changes improve the wettability, the adhesion, the increase of roughness and polar groups.

The aim of this study is to investigate the influence of photooxidation, due to corona discharge on the physical properties of hydroxyethylcellulose (HEC). The polymer was modified by using the low-temperature plasma of corona discharge in air and studied by measuring transport properties, contact critical angle of wetting by oleic acid, and optical properties. The great changes in the physical properties are assumed to be caused by the formed hydroperoxides, by carbonyl and carboxyl groups, as well as by surface cross-linking.

EXPERIMENTAL

The experimental measurements were carried out with NATROSOL (Hercules Trademark) — hydroxyethylcellulose (HEC). The sample type (NATROSOL 250 MHBR) is characterized by Brookfield viscosity (the Brookfield viscometer, type LVF, 2 % solution at 25 °C) equal to 15 Pa s and with moles of substituent combined — $MS = 2.5$. An idealized structure of NATROSOL 250 ($MS = 2.5$) is shown in Formula 1.



Formula 1

The HEC films were prepared by fast plaster casting on Petri dishes from 1 mass % solution of HEC heated to 80 °C. The solution was filtered through a fritted disk S-3. The films thus prepared

were of 0.13–0.15 mm width. They were dried for 24 h at 50 °C.

The films were interacted with a low-temperature plasma. The plasma was formed between two plate electrodes with clearance 2 mm of the plasma high-frequency generator (2 kHz). The polymer samples were exposed to the low corona discharge from 0 s to 1620 s (the time of irradiation t_{irr}). The irradiation was performed in air at the laboratory temperature (25 °C) and atmospheric pressure. The determination of a gel fraction was carried out by the standard filtration procedure. Simultaneously, the concentration of the noncross-linked polymer in the filtrate was determined. The results obtained in both cases were in agreement. The viscosity of the filtrate was measured with the Ubelohde viscometer U 2 at constant temperature (25 ± 0.1 °C).

The total thickness of the swollen surface layer (SSL) δ was measured in a simple experimental optical device which was described earlier [10]. The kinetics measurements in the system HEC—distilled water were performed at the temperatures $\theta/^\circ\text{C}$: 20, 25, 30, 35, and 40 (± 0.1). The values of the average apparent diffusion coefficient D were obtained from the following formula [11]

$$\delta = (2Dt)^{0.5} \quad (1)$$

the relative error being $\pm (3\text{--}5)$ %. The values of the activation parameters were determined with the relative error $\pm (5\text{--}10)$ %. The infrared spectra were recorded with a spectrometer 599 (Perkin—Elmer).

The limiting contact angle of oleic acid was measured with a reflex goniometer (Kernco Instrument, U.S.A.) temperature-controlled by means of a double thermostating equipment accurate to ± 0.1 °C. The precision of determining the limiting contact angle was for the measuring liquid (oleic acid) $\pm (0.12\text{--}0.16)$ rad. The volume of an applied measuring drop was constant and equal to 3 nm³. The procedure based on the temperature dependence was used for the determination of the temperature of glass transition T_g [9, 12].

RESULTS AND DISCUSSION

Remarkable changes of exposed samples of HEC were found in the infrared spectra. The examples of the most important changes in the detailed infrared spectra are represented in Fig. 1. The absorption band at $\tilde{\nu} = 1640 \text{ cm}^{-1}$ can be assigned to vibration of the water entrained in sample or water of crystallization. An increase of the number of carbonyl groups with time of irradiation (absorption band at $\tilde{\nu} = 1700 \text{ cm}^{-1}$) is observed during the photooxidative degradation of the HEC. During the photodegradation of cellulosic materials chain scission takes place which results in a complex of chromophores with the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions ($-\text{O}-$, $-\text{CO}-$, $-\text{COOH}$, ...). The luminescence of the materials has been attributed to the excitation of carbonyl groups [13, 14]. The degradation process is related to a rapid change in the degree of polymerization [1] which reduces the mechanical strength of cellulose materials. The quantum yields for the photodegradation of cellulose were determined to be 7×10^{-4} [15] and 2.5×10^{-3} [16]. Besides the breaking of the main chain, a cross-link sets in and results in the changes of physical properties. The photooxidation is accompanied by a colour change of the exposed foils into yellow. These changes also manifest

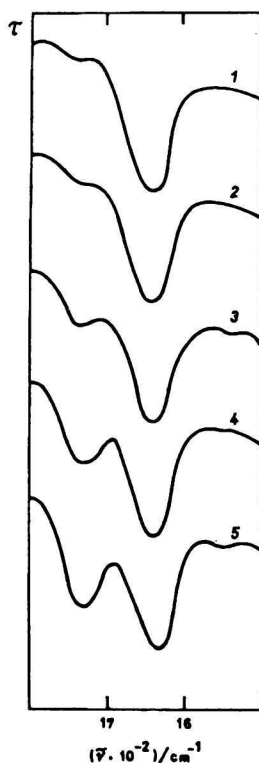


Fig. 1. Detail of the infrared spectrum of HEC films. The time of irradiation t_{ir}/s : 1. 0, 2. 60, 3. 180, 4. 540, 5. 1620.

Table 1. Values of Limiting Viscosity Numbers $[\eta]$, Interaction Constants k , Content of Gel Fractions (GF), and Temperatures of Glass Transition T_g for Different Times of Irradiation t_{ir}

t_{ir}/s	$[\eta]/(\text{m}^3 \text{ kg}^{-1})$	k	GF content/%	T_g/K
0	0.727	1.37	0.0	316
60	0.717	1.40	0.0	316
180	0.702	1.61	4.3	315
540	0.762	1.10	8.1	313
1629	0.719	1.45	13.1	313

themselves distinctly in mechanical properties of the film which, due to increasing exposure, become tougher.

After dissolving the irradiated films in water, it was possible, in accordance with the authors of [17], to observe formation of insoluble gel residues. The amount of the gel depends on the time of exposure of the irradiated sample (Table 1). The content of the gel fraction increases exponentially with exposure, which confirms the existence of the cross-linking process.

The viscometric measurements of the soluble portion of the HEC samples in water gave characteristic curves and confirmed applicability of the usual Huggins extrapolation procedure [18]. The Huggins equation was used

$$\eta_m/c = [\eta] + k[\eta]^2 c \quad (2)$$

The calculated values of limiting viscosity numbers $[\eta]$ and interaction constants k are listed in Table 1 and varied in the interval $0.702\text{--}0.762 \text{ m}^3 \text{ kg}^{-1}$ and $1.10\text{--}1.45$, respectively. The numerical value of these constants is a function of the molar mass of polymer, temperature, and probably of the degree of branching, as well [19]. A confrontation of the content of the gel fraction with limiting viscosity numbers of the soluble fraction enables us to allege that the preponderance of the cross-linking process over photodestruction of the polymer chain manifests itself with increasing time of irradiation. Desai [20] has reported that cross-linking of cellulose is induced by light irradiation. The treatment caused a decrease in water retention and moisture regain.

These conclusions are also in a good agreement with our kinetic curves giving the dependence of the overall width of SSL δ on time with a variable value of the temperature in Fig. 2. The courses show clearly that the diffusion follows the second Fick's law, while the sample surface is saturated immediately after both phases came into contact. The value of the average apparent diffusion coefficient D (Table 2) decreases with the time of irradiation of the polymer. The mobility of polymer chain must decrease with irradiation time and

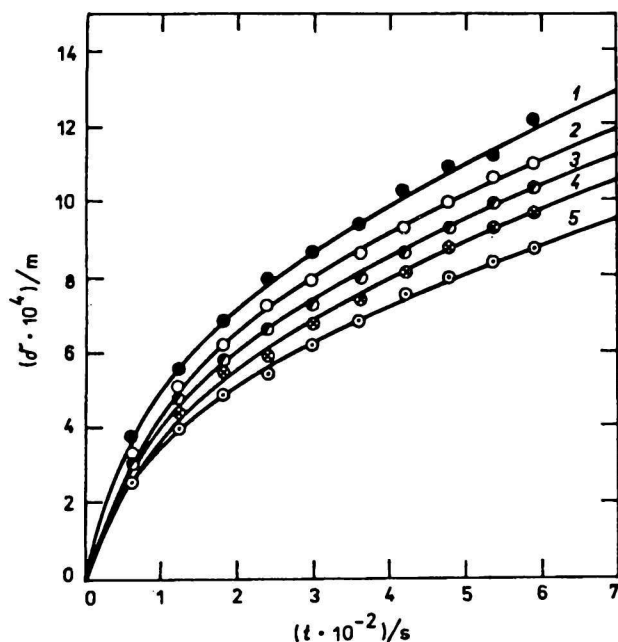


Fig. 2. Dependence of the thickness of the swollen surface layer δ on time for the system HEC—distilled water (the time of irradiation 180 s). 1. 40°C; 2. 35°C; 3. 30°C; 4. 25°C; 5. 20°C.

simultaneously the height of potential barrier for molecules of the solvent at the interface liquid—solid phase increases. That is the fundamental factor determining the moveability of macromolecular chains. Formally, all these influences are reflected in the values of the thermodynamic factor and hydrodynamic factor of the diffusion coefficient D [21]. The values of D in the systems studied calculated from eqn (1) vary within the range $(2.1\text{--}15.2) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Table 2).

The logarithmic dependence of diffusion coefficient on temperature of the solvent molecules in solid HEC may be described by an equation of the Arrhenius type

$$D = D_0 \exp(-E_D/RT) \quad (3)$$

Table 2. Values of the Average Apparent Diffusion Coefficients D , Preexponential Factors D_0 and the Activation Energy of Diffusion E_D in the System HEC—Distilled Water of the Exposed Films

Quantity	T/K	t_{irr}/s			
		0	60	180	540
$D \cdot 10^{10}/(\text{m}^2 \text{ s}^{-1})$	293.2	7.60	6.56	6.54	2.12
	298.2	10.20	8.60	8.07	2.87
	303.2	11.60	10.79	9.07	4.72
	308.2	13.19	12.54	10.07	7.44
	313.2	15.23	13.34	12.46	8.72
$D_0 \cdot 10^5/(\text{m}^2 \text{ s}^{-1})$		3.01	5.22	1.01	3.67×10^5
$E_D/(\text{kJ mol}^{-1})$		25.63	27.33	23.35	57.51

and the values of diffusion coefficients D , pre-exponential factor D_0 , and activation energies E_D obtained are given in Table 2. These results also confirm that some types of water-resistant, cross-linking bonds are formed in the polymer. Another interpretation is that observed changes are caused by arising of local crystallization after the irradiation.

As obvious from Fig. 3, the temperature dependence of contact angle sensitively reacts to the point of inversion of the second order. In the region of phase transition (in the region of T_g) a rapid decrease appears which is due to a change in a surface energy of the solid polymer phase. As evident from the data given in Table 1, there are not great T_g changes with increasing exposure of HEC to the radiation. The further decrease and glass transition temperature accompanying destruction may be explained by a formation of hydrophilic groups (e.g. carboxyl, carbonyl, hydroxyl, peroxidic groups) in the surface of polymer sample. The simultaneous formation of cross-links between chains results in increasing kinetic elasticity, which manifests itself by the decrease in T_g and broadening of the transition region about T_g . The obtained T_g values are in a very good agreement with the literature value 316 K [22].

It seems quite likely that the changes of hydrophilicity and the other physical properties, as a consequence of the effect of low-temperature plasma treatment on the polymer surface, are a common result of the photochemical effects of UV light and active parts of plasma, the collisions with

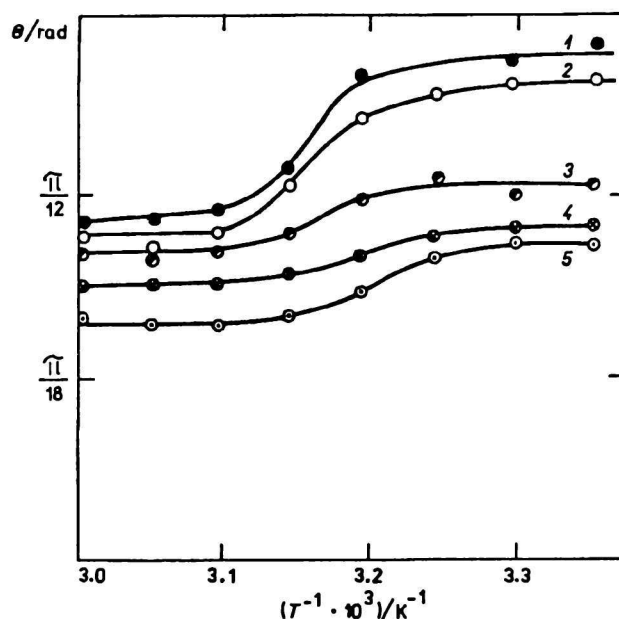


Fig. 3. Limiting angle of wetting of the exposed films of HEC with oleic acid. The time of irradiation t_{irr}/s : 1. 0, 2. 60, 3. 180, 4. 540, 5. 1620.

electrons, excited atoms and ions on the polymer surface. The most important should be the action of singlet oxygen causing intensive changes in the exposed materials [6—9]. The corona discharge leads to the perturbation in the energy distribution of the system and to its localization in the sample surface. Owing to the increased content of the surface polar hydrophilic groups of the studied HEC, a more intensive sorption of different kinds of polar compound vapour (especially water) easily takes place on the surface. Defect metastables (free radicals, discharge centres, etc.) can also be created by this mechanism.

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