Photooxidation of poly(vinyl chloride)
Changes in physical properties due to the exposure to corona discharge

J. POLAVKA and L. LAPČÍK

*Department of Physical Chemistry, Faculty of Chemical Technology,
Slovak Technical University, CS-812 37 Bratislava*

Dedicated to Academician V Kellö, in honour of his 70th birthday

The influence of exposure of poly(vinyl chloride) (PVC) to corona discharge on physical properties was investigated. It has been found that transport process of diffusion of the cyclohexanone into the PVC obeys the second Fick's law. The measured average apparent diffusion coefficients of the studied system vary in the interval $(0.9—2.5) \times 10^{-10} \, \text{m}^2 \, \text{s}^{-1}$ and increase with exposure in an equal manner as the activation energies of diffusion which vary in the interval $(27.6—32.8) \, \text{kJ} \, \text{mol}^{-1}$ There have been determined: limiting angle of wetting Θ, temperature of glass transition T_g, and absorption in the UV region. The dependence of the physical properties on time of exposure of PVC to corona discharge is described. The changes in the physical properties after the low-temperature plasma application are similar and much faster than the photochemical changes caused by ultraviolet radiation.

Исследовано влияние воздействия коронного разряда на физические свойства полихлорвинила (ПХВ). Обнаружено, что транспортный процесс диффузии циклогексанона в ПХВ подчиняется второму закону Фика. Измеренные средние величины кажущихся коэффициентов диффузии в изучаемой системе лежат в интервале от 0,9 $10^{-10} \, \text{м}^2 \, \text{с}^{-1}$ до 2,5 $10^{-10} \, \text{м}^2 \, \text{с}^{-1}$ и возрастают в результате воздействия разряда подобным образом, как и величины активационной энергии диффузии, которые находятся в интервале от 27,6 кДж моль$^{-1}$ до 32,8 кДж моль$^{-1}$. Проведено определение: лимитного угла смачивания Θ, температуры застеклевания T_g и поглощения в УФ области. Описана зависимость физических свойств от продолжительности воздействия коронного разряда на ПХВ. Изменения физических свойств под действием низкотемпературной плазмы подобны, но происходят значительно быстрее, чем фотохимические изменения, вызываемые ультрафиолетовым облучением.

The basic process in photooxidation of poly(vinyl chloride) (PVC) is dehydrochlorination and most authors dealing with the process believe it obeys a radical mechanism [1—7]. 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 high plasma effectiveness — solid surface energy transfer by electrons, exited atoms and ions collisions. During the past few years there has been a steady growth in the use of plasmas for the modifications of the surface properties of various solid materials [8—11]. This interest has been motivated by the ability of plasmas to produce a large variety of changes on solid surfaces such as desorption of gases, degradation, removing of layers, crosslinking, 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 the PVC. The polymer was modified by using the low-temperature plasma of corona discharge and studied by measuring transport properties, critical angle of wetting, 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 crosslinking.

Experimental

The cyclohexanone (CYH) used as a solvent was anal. grade chemical. It was distilled before use and its purity was checked by refractive index measurements.

The fractionated PVC was prepared by fractionation of the industrial product (W Pieck Chemical Works, Nováky) (it was the amorphous PVC of the emulsion type, the syndiotactic portion of which amounted to 60 %) and used as a basic polymer. The individual fractions were obtained by precipitating the 1 % solution of the polymer in tetrahydrofuran with water. The polydispersity of the investigated fraction was characterized by the ratio of average mass to average number molar mass (M_w/M), *i.e.* by the value of the coefficient of polydispersity. The value of this coefficient was 2.54 ($M_w = 126 \text{ kg mol}^{-1}$).

The samples in the form of films were prepared by casting from a 2 % solution of polymer in tetrahydrofuran which was deprived of peroxides by the standard procedure consisting in refluxing with solid KOH in darkness in nitrogen atmosphere [12]. The average width of films varied in the range 0.4—0.6 mm. For the plasma-thin polymer film

interaction a plasma with a low temperature was used. 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-temperature plasma of corona discharge from the nought second to 900 (the time of irradiation — t_{irr}). The irradiation was performed in air at the laboratory temperature (294 K) and atmospheric pressure.

After six weeks the sample had been exposed, the total thickness of the swollen surface layer (SSL) δ was measured in a simple experimental optical device which was described earlier [13]. The kinetic measurements in the system PVC—CYH were performed at the temperatures $\theta/°C = 20, 25, 30,$ and (35 ± 0.1). The values of the average apparent diffusion coefficient D were obtained from the following formula [3]

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

the relative error being $\pm (3—5) \%$. The values of the activation parameters were determined with the relative error $\pm (5—10) \%$. The ultraviolet and visible spectra were taken with a spectrograph Specord UV VIS (Zeiss, Jena) while the infrared spectra were recorded with a spectrophotometer Perkin—Elmer, Model 599.

The limiting angle of wetting was measured with a reflex goniometer (Kernco Instruments, U.S.A.) temperature-controlled by means of a double thermostatting equipment accurate to ± 0.1 °C. The precision of determining the limiting angle of wetting was for the measuring liquid (formamide) $\pm (0.12—0.16)$ rad. The volume of an applied measuring drop was constant and equal to 3 nm^3 The measurement of Θ was always performed at least six times in the medium of saturated vapour of the measuring liquid. The photographic records were used for reading in the region of low angles Θ and higher temperatures. As evident from Fig. 4, a procedure based on the temperature dependence of limiting angle of wetting was used for T_g determination [2]. The points of inflection of the curve $\Theta = \Theta(T^{-1})$ were determined by the numerical procedure (providing the validity of the Gaussian curve).

Results and discussion

The instance of kinetic curve representing the dependence of the total SSL thickness on time in case of varying value of the exposure time is given in Fig. 1. The course shows 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 1) increases with the time of irradiation of polymer which is due to photooxidative dehydrochlorination of PVC [2—4]. The mobility of polymer chains must increase with irradiation time and simultaneously the height of potential barrier for molecules of the solvent at the interface liquid—solid phase decreases. That is the fundamental factor determining the moveableness of macromolecule chains. Formally, all these influences are reflected in the values of D, i.e. in the values of the thermodynamic factor and hydrodynamic factor of the diffusion coef-

ficient [14]. The values of D in the systems studied calculated from eqn (1) vary within the range $(0.9—2.5) \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ (Table 1) whereas the corresponding values in crystalline phase are rather lower.
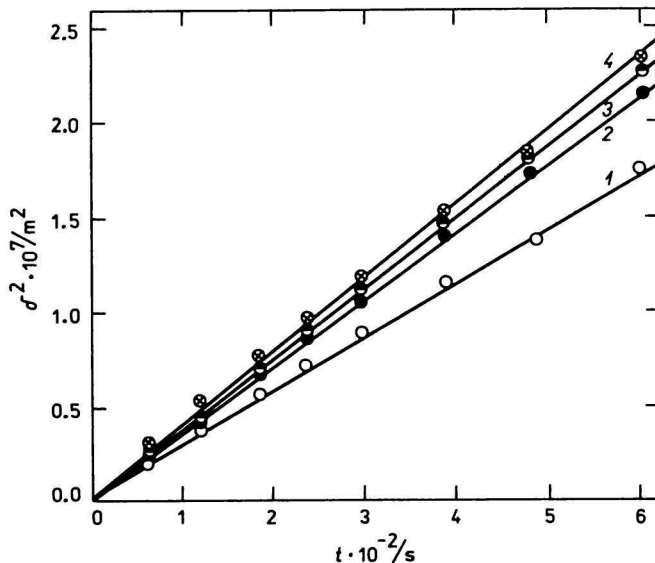

Fig. 1. Dependence of the squared thickness of the swollen surface layer δ^2 on time for the system PVC—CYH at 303.2 K. The time of irradiation: *1.* 0 s; *2.* 300 s; *3.* 600 s; *4.* 900 s.

Table 1

Values of the average apparent diffusion coefficients D, preexponential factors D_0, and the activation energy of diffusion E_D in the system PVC—CYH of the exposed films

t_{irr}/s	T/K				$D_0 \quad 10^5$	E_D
	293.2	298.2	303.2	308.2		
	$D \quad 10^{10}/(\mathrm{m^2\,s^{-1}})$				$\mathrm{m^2\,s^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
0	0.89	1.09	1.44	1.82	2.69	30.5
300	1.18	1.42	1.78	2.23	1.07	27.6
600	1.27	1.51	1.88	2.38	8.49	32.8
900	1.34	1.61	1.97	2.50	5.92	31.6

At the first moment of exposure, substantial changes appear in the organized structure of the solid PVC phase. These changes are accompanied by increase in absorptivity of the UV radiation (Fig. 2) owing to formation of the polyene chromophores which accelerate the process of chain breaking. This fact is the most conspicuous during the first seconds of irradiation and manifests itself in a characteristic course of the relationship between the activation energy of diffusion and time. Nevertheless the values of activation energy obtained with irradiated sample are not smaller than those obtained with nonirradiated sample for the times 600 and 900 s. The interpretation of the course is here impossible for the relative error in determining activation energies being $\pm$ (5—10) % and correlates with the results of *Hollahan* [8] (*i.e.* the changes of properties of the exposed sample are only in the solid surface layer with a depth of about 1 µm).
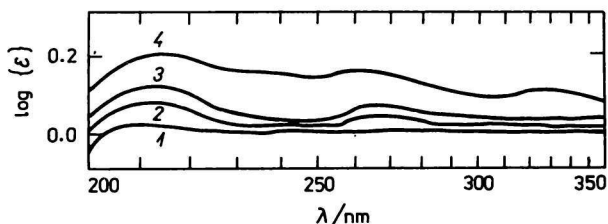

Fig. 2. Ultraviolet spectrum of the exposed samples of PVC. The time of irradiation: *1*. 0 s; *2*. 300 s; *3*. 600 s; *4*. 900 s.

As obvious from Fig. 3, the logarithmic dependence of diffusion coefficient on temperature of the solvent molecules in solid PVC may be described by an equation of the Arrhenius type

$$D = D_0 \exp(- E_D/RT) \qquad (2)$$

The values of diffusion coefficients D, preexponential factors D_0, and activation energies E_D are given in Table 1.

As evident from Fig. 4, the temperature dependence of the limiting angle of wetting sensitively reacts to the point of inversion of the second order of a transition region [2]. In the region of phase transition (in the region of T_g) a rapid decrease in the limiting angle of wetting appears, which is due to a change in a surface energy of the solid polymer phase.

As obvious from the results given in Table 2, the data of the glass transition temperature T_g and the data of the limiting angle of wetting Θ decrease with increasing exposure of PVC to corona discharge (t_{irr}) and simultaneously the transition interval of T_g (ΔT_g) becomes broader. The decrease in the angle of

wetting and glass transition temperature accompanying destruction may be explained by a formation of polar carbonyl, hydroxyl, and peroxidic groups in the surface of exposed polymer samples. These facts correspond with the measurements of the photooxidative degradation of PVC by the action of monochromatic ultraviolet radiation of the wavelength of 405 nm [2].
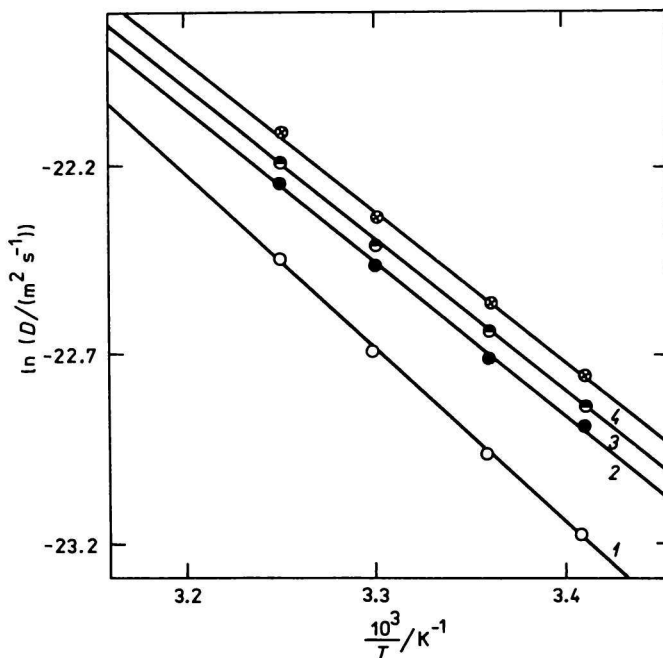

Fig. 3. Variation of the average apparent diffusion coefficient D with temperature for different times of irradiation of PVC in the system PVC—CYH. The time of irradiation: *1.* 0 s; *2.* 300 s; *3.* 600 s; *4.* 900 s.
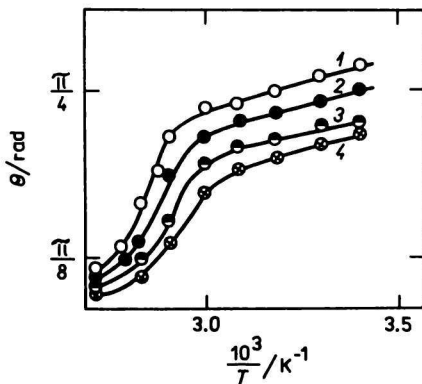

Fig. 4. Limiting angle of wetting of the exposed films of PVC with formamide. The time of irradiation: *1.* 0 s; *2.* 15 s; *3.* 30 s; *4.* 60 s.

Table 2

Values of the transition interval of temperature of glass transition ΔT_g, temperatures of glass transition T_g, and the limiting angles of wetting Θ of the exposed PVC surface with formamide at 298.2 K

t_{irr}/s	ΔT_g/K	T_g/K	Θ/grad
0	35.7	352.3	0.742
15	43.5	348.3	0.681
30	53.2	344.6	0.611
60	59.1	341.9	0.550

It seems quite likely that the changes of hydrophility 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 effect of UV light and active parts of plasma, the collisions with 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 [2, 9, 11]. 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 PVC, a more intensive sorption of different kinds of polar compound vapour (especially H_2O) easily takes place on the surface. Defect metastables (free radicals, discharge centres, *etc.*) can also be created by this mechanism.

It seems quite probable that the changes in surface hydrophility and transport properties after plasma application are similar to those in the measurements of the properties as a result of the UV radiation exposure [2, 3, 15, 16].

References

1. Kwei, K. P. S., *J. Polym. Sci., A-1 7*, 1075 (1969).
2. Lapčik, L., Štefanec, J., Valášek, J., Čeppan, M., Blažková, A., and Polavka, J., *Chem. Zvesti 35*, 359 (1981).
3. Polavka, J., Lapčík, L., and Valášek, J., *Chem. Zvesti 34*, 63 (1980).
4. Ranby, B. and Rabek, J. F., *Photodegradation, Photo-oxidation and Photostabilization of Polymers*. J. Wiley, New York, 1975.
5. Mori, F., Koyama, M., and Oki, Y., *Angew. Makromol. Chem. 64*, 89 (1977).
6. Scott, G. and Tahan, M., *Polym. J. 11*, 535 (1975).
7. Minsʵer, K. S. and Redoseeva, G. T., *Destruktsiya i stabilizatsiya polivinilkhlorida*. Khimiya, Moscow, 1972.
8. Hollahan, J. R. and Bell, A. T., *Techniques and Application of Plasma Chemistry*. Wiley—Interscience, New York, 1974.

9. Shen, M., *Plasma Chemistry of Polymers*. M. Dekker, New York, 1976.

10. Yasuda, H., Sherry, B., El-Nokaly, H. A., and Friberg, S. E., *Appl. Polym. Sci. 27*, 1735 (1982).

11. Blecha, J., Mastihuba, M., Lapčík, L., Lodes, A., and Krupa, P., *Acta Phys. Slovaca 32*, 333 (1982).

12. Vávra, J., Lapčík, L., and Sabadoš, J., *J. Polym. Sci., A-2 13*, 1305 (1967).

13. Lapčík, L., Panák, J., Kellö, V., and Polavka, J., *J. Polym. Sci. 14*, 981 (1976).

14. Polavka, J. and Lapčík, L., *Chem. Zvesti 38*, 721 (1984).

15. Baszkin, A., Deyme, M., Nishino, M., and Ter-Minassian-Saraga, L., *Prog. Coll. Polym. Sci. 61*, 97 (1976).

16. Cernia, E., Mantovani, E., Marconi, W., Mazzei, M., Palladino, N., and Zanobi, A., *J. Appl. Polym. Sci. 19*, 15 (1975).