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Photooxidative degradation of carboxylated poly (vinyl chloride)

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Abstract Thin films of poly(vinyl chloride), PVC, and carboxylated poly(vinyl chloride), C-PVC, containing 1.8% of carboxyl groups were exposed to high energy ultraviolet radiation ($\lambda = 254$ nm) in laboratory conditions. The photochemical reactions in irradiated samples were studied by FTIR and UV–Vis spectroscopy, gel permeation chromatography and gravimetric estimation of insoluble gel. It was found that photodegradation and photocrosslinking in C-PVC is accelerated, whereas photodehydrochlorination is retarded comparing to these processes in PVC. Photooxidation investigated on the base of reaction leading to formation of hydroxyl groups is also more efficient in modified PVC. However, the total amount of carbonyl groups is much lower in UV-irradiated C-PVC than that in PVC. It indicates that competitive reactions (destruction of carboxyl groups and formation of new carbonyls) occur simultaneously in C-PVC chains. The influence of carbonyl groups on photochemical processes can be explained by an efficient Norrish I and II reactions as well as by energy transfer from absorbing species to weak chemical bonds.

Keywords Poly(vinyl chloride) · Polymer modification · Irradiation · Photooxidative degradation

Introduction

Poly(vinyl chloride) is one of the most widely used polymers in many industrial applications and its production is maintained at very high level for many years. However, the disposal of PVC-based plastics is a serious ecological problem today. PVC macromolecules are not biodegradable because they cannot be assimilated by

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microorganisms. The possible way to transform this synthetic polymer into environmentally friendly material is its modification leading to enhancement of its photodegradation susceptibility. The accelerated polymer decomposition can be achieved by physical polymer modification, for instance by blending with appropriate low or high molecular weight compounds [1–4]. The second possibility is the chemical modification, such as copolymerisation with carbon monoxide or dioxide leading to the introduction of chromophoric groups in main chains [5–12]. It allows to obtain the photosensitive polymer, characterized by faster decay in natural environment comparing to traditional plastic. Besides of the intensive works describing the various types of degradable polymers, there are still a lot of unsolved questions and unproved hypothesis concerning this subject [1, 13].

The recent works devoted to PVC photodegradation consider the various problems [14–18], for example oxidation profiles i.e. concentration of oxidised products versus distance from exposed surface [19], the influence of radiation and water [20], the effect of degradation conditions [21] and the correlation between artificial and natural weathering [22].

The vinyl chloride-acrylic acid copolymer found practical application as selective membranes in (bio)sensors. Such membranes are suitable for enzyme immobilization or inorganic ion binding [23–26].

The aim of this work was to study the effect of UV-irradiation on the carboxylated PVC (C-PVC) in comparison to the unmodified poly(vinyl chloride) (PVC) using the spectroscopic (FTIR, UV–Vis) and chromatographic (GPC) methods. The photocrosslinking efficiency was estimated by the gravimetric measurement of insoluble gel. The structure of C-PVC, which is the copolymer of the vinyl chloride and the acrylic acid, is shown on Scheme 1.

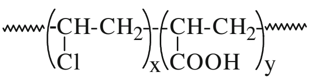
Carboxylated PVC should be more photosensitive than PVC hompolymer because carboxylic groups absorb UV-irradiation, thus can undegro photolysis (e.g. Norrish I and II reactions).

Experimental

The polymers: carboxylated PVC and reference PVC were purchased from Sigma-Aldrich. The carboxylated PVC ($M_w = 220{,}000$) contained 1.8% carboxyl groups, which was confirmed by the elemental analysis.

For the purpose of obtaining polymer films, 2%(v/m) solutions in tetrahydrofuran (THF) were poured onto leveled glass plates. After solvent evaporation, the thin films were taken off the plates and dried in vacuum. The samples of both polymers were then exposed to UV. The samples of the same thickness and surface area were placed at 6 cm distance from the light source which was the low pressure mercury

Scheme 1 The chemical structure of carboxylated poly(vinyl chloride)



$$\sim\!\left(\underset{\text{Cl}}{\text{CH}}\text{-CH}_2\right)_x\!\left(\underset{\text{COOH}}{\text{CH}}\text{-CH}_2\right)_y\!\sim$$

vapour lamp, emitting mainly 253.7 nm radiation. The intensity of incident light was 1.85 mJ cm^{-2}.

The FTIR and UV–Vis absorption spectra of irradiated samples were measured at regular time intervals using the FTIR Genesis II (Mattson, USA) and UV-1601PC (Shimadzu, Japan) spectrophotometers, respectively. Gel permeation chromatography was performed using GPC chromatograph made by Viscotek (Texas, USA) equipped with two detectors: reftractometric (Shoedex RI-71) and viscometric (Viscotek Model T50A). Tetrahydrofuran (chromatographic grade) was the eluent. The conditions of GPC analysis were following: flow rate, 1 ml min^{-1}; temperature, 30°C; polymer concentration, 0.5–2 mg ml^{-1} and solution volume, 100 ml. The calibration was carried out using PS standards (Aldrich).

The amount of gel was determined by extraction of insoluble part of polymer in THF. The gel was then separated from sol, washed by solvent and dried to a constant weight. The given value is an arithmetic average obtained for three repetitions.

Results and discussion

The FTIR spectra of both polymers are compared in Fig. 1. In the spectrum of PVC, the typical bands for this polymer at 2,700–3,100 cm^{-1} (attributed to stretching vibrations of CH/CH_2/CH_3 groups), 1,429 and 1,328 cm^{-1} (deformation) as well as 1,300–700 cm^{-1} range (skeletal) are observed. The bands at 623 and 690 cm^{-1}, due to C–Cl vibrations, are also present. In C-PVC spectrum, PVC bands are slightly shifted; additionally an intensive band of carbonyl groups at 1,711 cm^{-1} is clearly seen. The great changes in spectrum shape in C-PVC (comparing to PVC spectrum) are observed in 500–800 cm^{-1} region.

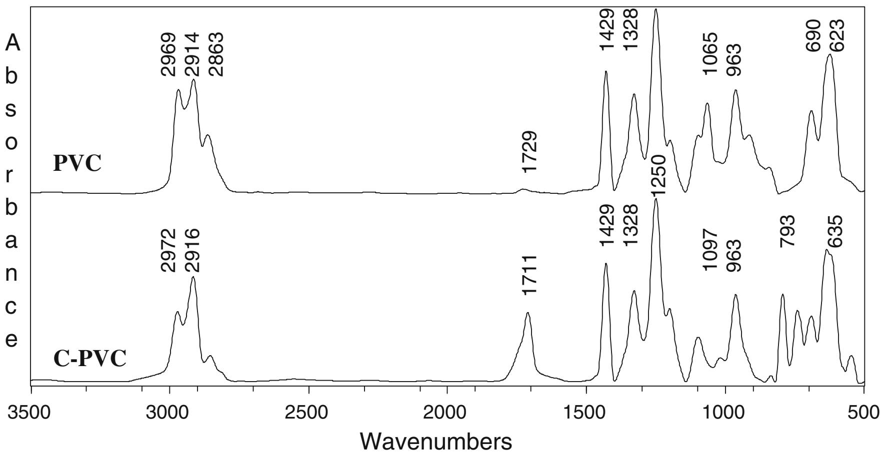


Fig. 1 FTIR spectra of carboxylated poly(vinyl chloride) (*bottom*) and origin PVC (*top*)

The main changes in FTIR spectra in both samples after UV-irradiation were detected in hydroxyl (3,100–3,600 cm^{-1}) and carbonyl (1,500–1,700 cm^{-1}) regions. An examples of mentioned parts of spectra of UV-irradiated PVC and C-PVC are presented in Figs. 2 and 3, respectively. Calculated relative integral intensities of bands attributed to C=O and OH groups were plotted versus irradiation time (Fig. 4). As can be noticed from these curves, in PVC mainly photooxidation leading to carbonyl groups formation occurs, whereas the creation of hydroxyl groups is much less efficient.

The photooxidation with formation of hydroxyl groups in C-PVC dominates but not so high efficiency of carbonyl generation is observed. It can be caused by their simultaneous decay. C=O intensities in FTIR spectra of C-PVC change irregularly, particularly at the early stages of exposure.

The other important photoreaction in PVC and C-PVC is dehydrochlorination, as a result of which the samples become coloured (from slightly yellow to brown after high UV doses). Photodehydrochlorination of studied samples was monitored by the UV–Vis spectroscopy (Fig. 5). The increase of the absorbance at the whole observed range (200–800 nm) indicates that the conjugated double bonds (polyenes

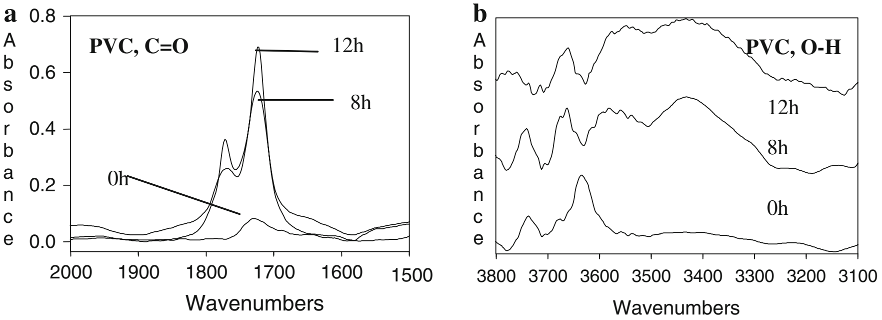


Fig. 2 Changes in carbonyl (**a**) and hydroxyl (**b**) region in FTIR spectra of PVC after 0, 8 and 12 h UV-irradiation

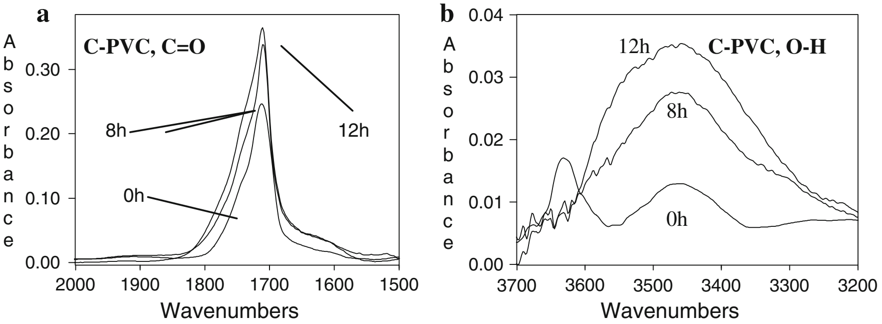


Fig. 3 Changes in carbonyl (**a**) and hydroxyl (**b**) region in FTIR spectra of carboxylated PVC after 0, 8 and 12 h UV-irradiation

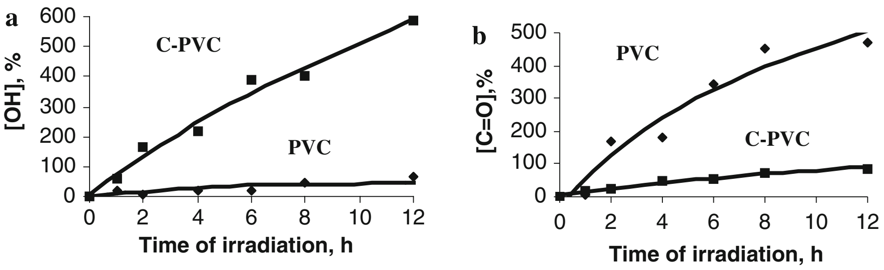


Fig. 4 Changes of the total amount of hydroxyl (**a**) and carbonyl (**b**) groups in PVC and carboxylated poly(vinyl chloride) during UV-irradiation (calculated on the basis of the surface area of absorption bands)

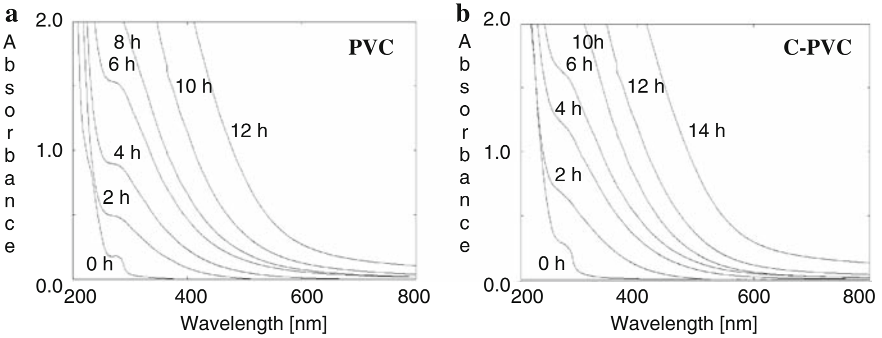


Fig. 5 Changes in UV-Vis absorption spectra of PVC (**a**), and carboxylated poly(vinyl chloride), (C-PVC), (**b**) during eposure to UV (time of irradiation: 0–14 h)

of different length) are formed. It is clearly perceived from the calculated absorbance values, that the photodehydrochlorination is somewhat hampered in C-PVC comparing to that process in unmodified PVC. This is due to the effect of carbonyl groups in macromolecules, restricting the chain reaction of HCl evolution (so called *zip* reaction).

The same conclusion can be drawn on the basis of the FT-IR analysis—the intensity of C–Cl absorption band decreases much faster in the spectrum of UV-irradiated PVC than in the C-PVC. The main chain scission, estimated by GPC on the basis of changes of the average molecular weight, is more efficient in C-PVC (Table 1). The calculated percentage changes are higher in C-PVC (above 20% after 12 h UV-irradiation) than those in PVC. The polydispersity (M_w/M_n) increases in both samples, which is an evidence of competitive photoreactions occuring simultaneously.

It is known that besides of photooxidative degradation, also crosslinking in PVC occurs during the exposure to UV radiation. This process, evaluated by the amount of insoluble gel (expressed in %), is more efficient in C-PVC than in PVC (Table 2). This is caused by faster recombination of free radicals formed in C-PVC occurring with higher efficiency comparing to the course of these processes in PVC alone.

Table 1 Weight average molecular weight and its percentage changes in PVC and C-PVC during UV-irradiation

Irradiation time (h)	PVC		C-PVC	
	M_w	Δ (%)	M_w	Δ (%)
0	200,000	–	220,000	–
4	175,000	−12.5	183,000	−16.8
8	168,000	−16.0	165,000	−25.0
12	161,000	−19.5	124,000	−43.6

Where: $\Delta(\%) = \frac{M_w(t) - M_w(0)}{M_w(0)} \times 100\%$, and $M_w(0)$, $M_w(t)$ are weight average molecular weights of polymer before irradiation and after t time of exposure, respectively

Table 2 The gel amount formed in PVC and C-PVC during UV-irradiation

Irradiation time (h)	Gel amount (%)	
	PVC	C-PVC
1	19.3	24.3
2	21.2	31.5
4	24.5	44.7
6	28.3	58.3

The enhancement of the photooxidative degradation in C-PVC can be explained by the effect of carboxyl groups undergoing direct photolysis (Norrish I and II) or sensitising the polymer to UV-radiation. The carbonyl groups conjugated with unsaturated bonds weaken the neighbouring chemical bonds and facilitate their scission. Although in PVC also some residues of carbonyl impurities are present (as can be seen on absorption spectra—Figs. 1 and 5), their amount is very limited. The accelerated photoodegradation in the modified polymer comparing to the original PVC can also arise from the transfer of excitation energy (absorbed by COOH) to other macromolecule sites, where the weak chemical bonds (i.e. structural defects such as branching points, internal unsaturation, labile chlorine or head-to-head units exist. The defected macromolecules, always present in polymer, are not able to photolyse if they do not have chromphoric groups. Energy transfer or migration make possible the breaking of such weak bonds.

Conclusions

The results indicate that the carboxylated PVC is characterized by higher sensitivity to the UV-irradiation than the unmodified PVC. The photooxidative degradation leading to hydroxyl groups formation is more efficient comparing to PVC. Significant reduction of the average molecular weight is observed in C-PVC. Photodestruction connected with decay of carbonyl moieties is a result of Norrish type reactions. Moreover, photocrosslinking process is significantly accelerated in C-PVC, whereas photodehydrochlorination is retarded in this polymer. It should be pointed out that hampered dehydrochlorination is advantageous, because smaller amounts of hydrogen chloride are evolved to atmosphere during the degradation of plastics based on C-PVC. It means that C-PVC can replace unmodified polymer in special applications where enhanced degradation is expected, for example in packaging industry or in single-use medical devices.

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