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Photochemical reactions in poly(vinyl chloride)/poly(vinyl alcohol) blends

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Abstract

Poly(vinyl chloride) and poly(vinyl alcohol) (PVAL) blends with various molar ratios were UV-irradiated ($\lambda = 254$ nm) at room temperature and in air atmosphere. Photochemical reactions were monitored by FTIR and UV–vis absorption spectroscopy. Changes of average molecular weights, indicating chain scission, were measured by gel permeation chromatography. Simultaneously, the amount of insoluble gel formed resulting of photocrosslinking was gravimetrically estimated. The influence of solvent traces (*N*,*N*-dimethylformamide) on blend photodegradation was also discussed. It was found that sample composition and macromolecular interactions play an important role in photochemical reactions in PVC/PVAL.

Keywords: Poly(vinyl chloride); Poly(vinyl alcohol); Polymer blends; Photochemical reactions

1. Introduction

Although mechanisms of photochemical reactions in pure polymers are well known [1–3], the behavior of UV-irradiated polymeric blends is often difficult for prediction. The main reason of this fact is great complexity of interactions between components and products of their photodestruction. Studies of photodegradation of polymer blends supply evidences that some polymers hamper, but some of them accelerate degradation of second component. The stabilizing or destabilizing effect on photochemical reactions has been proved in case of specific interactions between mixed polymers, whereas, in case of lack of mutual molecular interaction, the additivity of most physicochemical properties can be expected.

The polymers studied in this work are broadly used in practice. Poly(vinyl chloride) (PVC) is one of the most popular, cheap and easy processed polymer applied in many industrial branches, agriculture and household goods production [4–6]. Its properties can be modified chemically and physically. The main disadvantage of PVC is low thermal and photochemical stability, thus, plastics based on this polymer have to be stabilized [5]. However, PVC photo- and thermal degradation is not enough fast for classification this polymer as degradable. Poly(vinyl alcohol) (PVAL), which is used to manufacture the water-soluble films and adhesives, has similar chemical structure to PVC but properties of both polymers differ significantly [7]. PVAL is water soluble and biodegradable, contrary to PVC (which is soluble in solvents such as organic halides or ketones). The various properties arise mainly from different macromolecular interactions in both polymers.

UV-irradiation causes great changes in chemical structure of polymers, which strongly influence their physical and mechanical properties. The main photoinduced reactions in macromolecules are main chain scission, branching, crosslinking, oxidation, side group abstraction and polyene formation. All of them occur in vinyl polymers such as PVC and PVAL [1–3,8].

UV-radiation can cause plastic damage but it is also used for modification of surface properties, thus, knowledge of photochemical reactions in complex polymeric systems is very important from practical point of view.

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The aim of our work was to study the reactions induced by short wavelength UV radiation (254 nm) in PVC/PVAL blends with different component ratio and to explain if macromolecular interactions influence the blends photostability.

2. Experimental details

2.1. Samples

Commercial polymers: poly(vinyl chloride) (PVC Polanvil S-67ZS, $K = 67.7$, Włocławek, Poland) and poly(vinyl alcohol) (PVAL, Loba Chemie Austria)—were used in this work. The blends in whole concentration range (from 0/100 to 100/0 PVC/PVAL molar ratio) were prepared by mixing of proper volume of 2% PVC and 1% PVAL solutions in *N*,*N*-dimethylformamide (DMF, pure for analysis), which is common solvent for both polymers. The thin polymeric films (thickness of 10–25 μm) were prepared by solution casting onto PE film (which facilitates taking off the samples from support). The solvent was evaporated at elevated temperature (323–333 K) and then samples were dried at vacuum. Films of the same thickness were chosen for each experiment. Content of residual acetic groups in PVAL (or deacetylation degree, which equals hydrolysis degree) was estimated by titration of acetic acid (evolved during hydrolysis) in NaOH solution.

2.2. Irradiation

The samples were UV-irradiated at room temperature and in air atmosphere upon low pressure mercury vapor lamp (TUV-30W, Philips, Holland) emitted mainly 254 nm radiation. The distance between sample and irradiation source was 5 cm; incident light intensity, measured by IL 1400A Radiometer (International Light, USA) was 3.12 mW/cm^2. Times of irradiation were 1–6 h, which correspond to 112–673 kJ/m^2 doses. After each hour of exposure, samples were analyzed.

2.3. Analysis

FTIR and UV–vis spectroscopies were done using Mattson Genesis II Spectrometer (USA) and UV-1601PC Shimadzu Spectrometer (Japan), respectively.

IR spectra were recorded as average of 100 scans; the resolution was 2 cm^{-1}. Band intensity and integral intensity (area of absorption band) was calculated after baseline correction using WinFirst 3.57 computer program (Mattson Instruments). The spectra of unexposed samples were used as references and relative changes of absorbance were calculated. Complex carbonyl band was separated onto components by mathematical resolution applying the least square fitting method and mixed Gaussian–Lorentzian function.

The changes of absorbance at chosen wavelengths, corresponding to different polyenes, were calculated from UV–vis spectra.

Gel permeation chromatography (GPC) was done using Viscotek chromatograph (Texas, USA) equipped with two detectors-refractometric (Shoedex RI-71) and viscometric (Viscotek Model T50A) as well as two columns (of GMH$_{HR}$-MS type made by TSK-GEL) connected in line. The following parameters of measurements were applied: flowing speed 1 ml/min, temperature 30°C, concentration of polymer solution 0.5–3 mg/ml, and sample volume of 100 μl. Prior to measurements, the polymer solutions were filtered through the Titan Syringe Filter made from PTFE of 25 mm in diameter and pore size of 0.45 μm. Number and weight average molecular weights as well as molecular weight distributions were obtained after dissolution of irradiated blends (and after gel separation) in selective solvents: tetrahydrofurane (THF, chromatographic purity, Aldrich) for PVC and deionized water for PVAL. Column used for PVC in THF was calibrated with narrowly distributed PS standards but for calibration of column for PVAL in water – dextrane standards were applied (both types supplied by Aldrich).

Gel amount was estimated by separation of insoluble part from sol using common solvent (DMF), drying and weighing. Each estimation was repeated minimum three times.

3. Results and discussion

3.1. FTIR spectroscopy results

Absorption spectroscopy supplies information about changes in chemical structure of polymers during UV-irradiation. FTIR spectra of initial, unexposed samples are shown in Fig. 1. Characteristic bands assigned to methyl/methylene/methine (CH_3/CH_2/CH) stretching and deformation vibrations are clearly seen either in PVC or in PVAL at 2800–3000 cm^{-1} and 1300–1500 cm^{-1} ranges, respectively [9–11]. In PVC, additionally bands of C–Cl vibrations appear at 500–780 cm^{-1}. The intensive band at 3010–3680 cm^{-1} in PVAL spectrum is due to hydroxyl group existing in each polymeric unit. Carbonyl bands (at

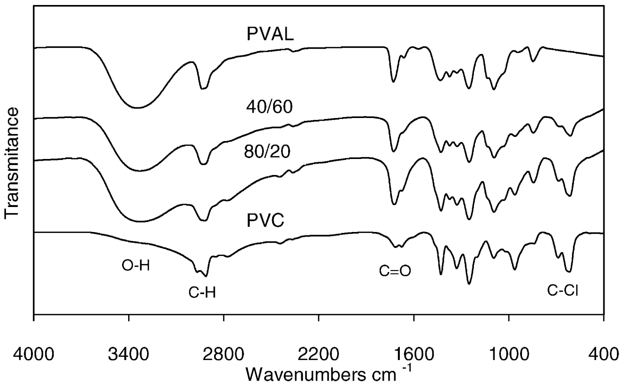
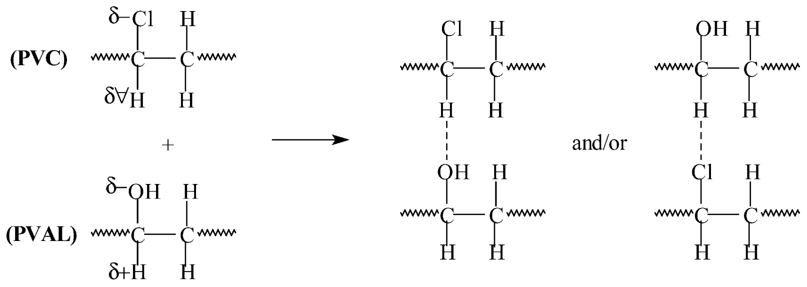


Fig. 1. FTIR spectra of initial samples (before UV-radiation):PVC, PVAL and their blends (40/60 and 80/20 describe the molar ratio PVC to PVAL).



Scheme 1. Interactions between PVC and PVAL.

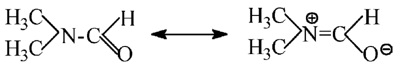
1600–1800 cm^{-1}) are detected in all polymeric films, which indicates the presence of impurities.

In PVAL, the presence of C=O is the results of non-complete removing of acetic groups because PVAL is made by indirect method from polyvinyl acetate (PVAC) by hydrolysis. As was estimated, deacetylation degree in our PVAL is 91%, which means that significant content (9%) of acetic groups still exist in this polymer. In fact, we have copolymer, in which carbonyl groups from PVAC fragments also participate in photochemical reactions. These reactions [12–14] and their influence on PVC were previously described in literature [15].

In spectra of PVC/PVAL, some small shifts of absorption bands were found, which suggest macromolecular interactions between blend components. Chlorine atoms in PVC and oxygen atoms from OH in PVAL are strongly electronegative, thus, mutual interactions between both polymers can be expected (Scheme 1).

3.2. Solvent residues in PVC/PVAL blends

In all samples solvent residues are present because DMF (having a high boiling temperature = 153 °C and high viscosity $\eta = 0.924 \times 10^3$ Pa s [16]) is difficult to remove from films even after long drying at elevated temperature and in vacuum. Further increase of drying temperature is dangerous because simultaneously thermal decomposition of polymers can start. Owing to its chemical nature (polar, aprotic) DMF is good solvent for polar and non-polar substances and exhibit unlimited solubility with water and organic solvents. It exists in two resonance forms [17]:



Because of unsharing electron pair on nitrogen atom, it acts (similarly to amines) as electron donor. It cannot form hydrogen bonds because it has no a hydrogen atom that is attached to an electronegative element (N or O). Moreover, DMF is known as quencher of singlet oxygen. Recently, one found that DMF behaves unexpectedly in process of fluorescence quenching in various donor–acceptor systems [17]. Because of absorption of 254 nm radiation, DMF photolyses [18], therefore, the influence of it decomposition products on PVC/PVAL blends have to be considered.

It was not found another good common (for both polymers) solvent with higher volatility.

3.3. Influence of UV-irradiation

UV-irradiation of samples causes the changes in all FTIR spectra. Main differences were observed in carbonyl and hydroxyl range, which is an evidence of photo-oxidative degradation. Total amount of carbonyl groups calculated as integral intensity (area of C=O absorption band), changes irregularly with irradiation time in most samples. Thus, for better explanation of process observed, the mathematical resolution of complex band (at range 1600–1800 cm^{-1}) onto components was done. An example of such resolved spectrum is shown in Fig. 2 for exposed PVAL.

The number of band components was deduced from the second derivative of spectrum. The interpretation is based on the following assumptions:

(a) band at 1735 cm^{-1}, which is present only in PVAL and in PVC/PVAL blends, whereas is absent in PVC alone, is attributed to ester groups (residual from polyvinyl acetate);
(b) band at 1675 cm^{-1} is due to solvent residue—the spectrum of pure DMF contains the same peak;
(c) band at 1710 cm^{-1} is assigned to new carbonyl groups formed during photooxidation (ketone and/or aldehyde);

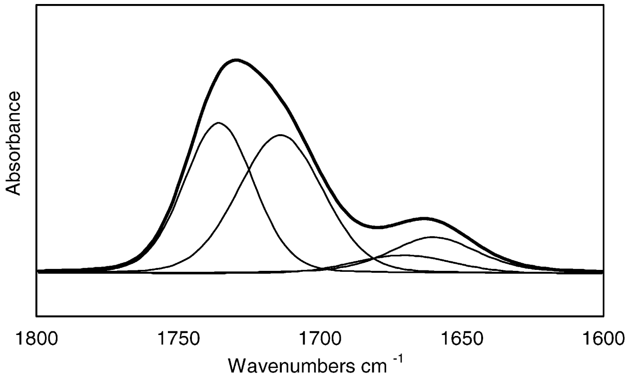


Fig. 2. Resolution of complex carbonyl band of PVAL after 6h UV-irradiation.

Table 1
The changes of area of carbonyl band component formed during photooxidation (maximum at 1700 cm^{-1}) and total area of carbonyl complex band (calculated at 1600–1800 cm^{-1} range) in PVC, PVAL and some of their blends after different irradiation time

Amount of PVC in blend (%)	Time of irradiation (h)	Relative area of 1710 cm^{-1}peak	Total area of C=O band
100	0	0.00	0.00
	1	86.14	103.25
	2	42.45	27.34
	3	73.07	83.68
	4	180.85	158.61
	5	251.12	236.39
	6	215.88	200.39
80	0	0.00	0.00
	1	21.65	26.52
	2	32.01	29.13
	3	46.78	39.46
	4	65.12	50.07
	5	122.02	121.78
	6	95.19	69.96
40	0	0.00	0.00
	1	17.09	12.26
	2	54.46	33.39
	3	34.90	3.26
	4	71.24	14.78
	5	98.93	10.22
	6	59.61	−2.18
0	0	0.00	0.00
	1	23.96	−15.83
	2	22.62	15.02
	3	18.09	−35.89
	4	13.86	−21.69
	5	35.71	−37.61
	6	−0.97	−46.10

(d) band at 1655 cm^{-1} is due to single or conjugated double bonds (also carbonyl coupled with C=C) formed as a result of photodehydrochlorination.

This assignment was supported by literature data [9–11,19].

The relative changes of total carbonyl band area (calculated on the base of integral intensity) and component attributed to carbonyl groups as a result of photo-oxidation are listed in Table 1.

As can be seen, photo-oxidation (concluded on the changes of absorption band at 1710 cm^{-1}) is most efficient in UV-irradiated PVC, whereas this process seems to be somewhat hampered in the blends after prolonged exposure (Fig. 3).

This retarding effect is clear in Fig. 4 for samples containing more than 50% PVC (negative deviation from predicted additive behavior – straight, dashed line).

It can be caused by fast recombination of macroradicals from both polymers by mobile small radicals formed either in PVC (H, Cl, HO$^\bullet$) or in PVAC ($CH_3COO^\bullet$, $CH_3CO^\bullet$, $^\bullet CH_3$), which leads to efficient termination of decomposition. Another reason of oxidation retarding in that case can be also simultaneous photocrosslinking because formed three-dimensional compact network makes difficult the oxygen diffusion to polymer bulk.

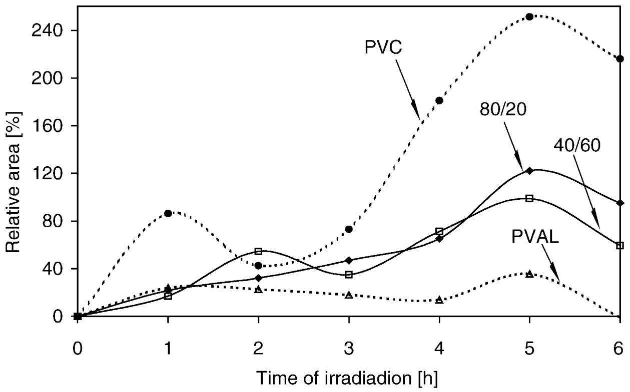


Fig. 3. Relative changes of carbonyl band component at 1710 cm^{-1} for PVC, PVAL and their blends versus irradiation time; 40/60 and 80/20 describe the molar ratio PVC to PVAL; relative are (%) was calculated according to formula: $\Delta S = [(S_t - S_0)/S_0] \times 100\%$, where S_t and S_0 are integral intensities of carbonyl band after t irradiation time and before irradiation, respectively.

One can point out that similar conclusion can be drawn on the base of total carbonyl group amount (Table 1) but changes in this case are less regular (positive and negative), which indicate the competitive reactions. Thus, the complex band decomposition is necessary to find the real behavior of system upon UV-irradiation.

The slowest and less efficient photo-oxidation was found in origin PVAL. Probably, the different types of hydrogen bonds in this polymer reinforce its structure and also impede the oxygen diffusion to macrochain (Scheme 2).

Another possible reason is protection of polymer by the carbonyl groups from vinyl acetate units, which absorb UV-radiation and can dissipate excitation energy in physical, non-harmful processes (such as luminescence or internal conversion).

Process of double bond formation is very efficient in PVC and its blends, which was concluded on the base of increase of 1655 cm^{-1} band component. These results are confirmed

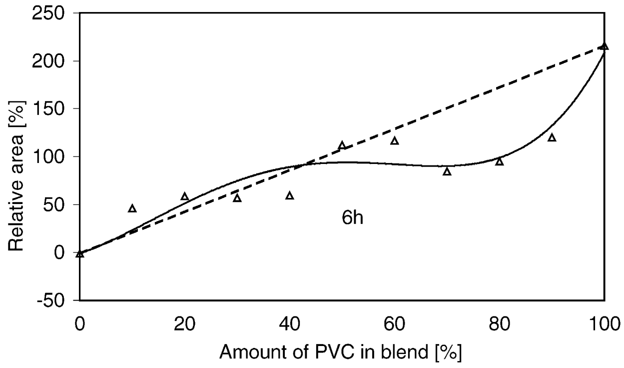
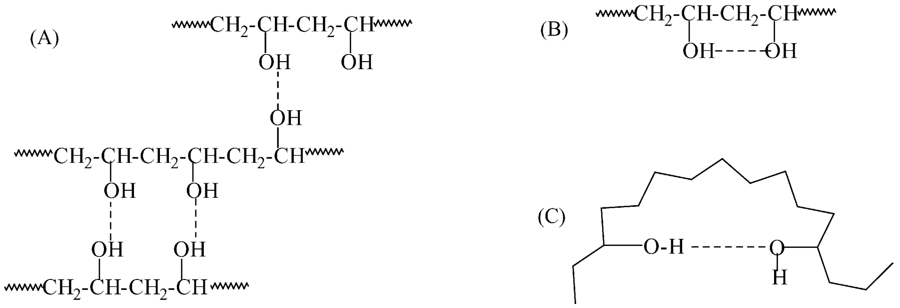


Fig. 4. Experimental dependence of carbonyl group amount (component band with maximum at 1710 cm^{-1}) formed after 6 h UV-irradiation vs. blend composition (—) and dependence predicted on the additivity rule (- - -).



Scheme 2. Different types of hydrogen bonds in PVAL (A—intermolecular, B—adjacent, intramoleular, and C—non-adjacent intramolecular).

by analysis of C–Cl bands at 500–780 cm^{-1} range but more detailed analysis of photodehydrochlorination was done on the basis of UV–vis spectroscopy (section 3.4).

The band assigned to C=O from solvent (1675 cm^{-1}) systematically decreases during sample exposure to UV, which indicates that DMF is slowly evaporated or decomposed. To check, if the DMF photolysis takes place, the experiments with pure solvent was carried out. For this purpose DMF (dissolved by water or methanol) was UV-irradiated and absorption spectra (both FTIR and UV–vis) were taken after each 10 min period. It was found that during DMF irradiation (in closed system) slow changes of absorbance of carbonyl band were observed in both FTIR and UV–vis spectra after some induction period. Thus, residual DMF can influence the photochemical processes in polymers, but its effect should be similar in all studied specimens, which were obtained by the same method (assuming the identical solvent concentration in films of the same thickness).

3.4. UV–vis spectroscopy results

The absorbance increase in whole UV–vis region was observed for all samples during UV-irradiation, but new clear bands are not created. It is caused by overlapping of various bands (more overlapping bands, less clear maxima). For comparison photochemical reactions leading to chromophores formation, the changes of absorbance at wavelengths of 257, 278, and 425 nm were chosen and plotted against irradiation time for PVC and its blends with PVAL. According to literature, these values can be assigned to polyenes containing three, four to five and nine conjugated double bonds, respectively [20]. For elimination of background, which is somewhat different in blends with various molar ratio, the absorbance at 800 nm was substracted from absorbance measured at given point.

The representative results for UV-irradiated samples are presented in Fig. 5.

The highest changes were observed for absorbance at lower wavelength values, i.e. for short polyenes. The reason is not only high concentration of groups—chromophores absorbing here can have higher molar absorption coefficient, moreover, in this region also carbonyl groups absorb (at 270–280 nm). The absorbance at longer wavelengths (>400 nm) is responsible for color changes (yellowing) observed visually.

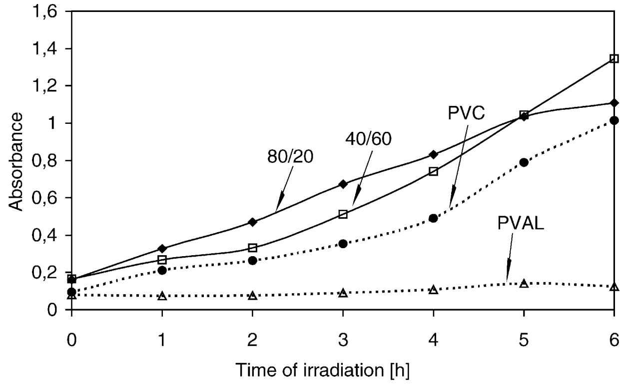


Fig. 5. Changes of absorbance at 278 nm (corresponding to four to five number of double bonds) in PVC, PVAL and their blends during UV irradiation.

Analysis of UV–vis spectra leads to conclusion that PVC is very susceptible to photodehydrochlorination but abstraction of OH groups in PVAL with simultaneous formation of double bonds is imperceptible. Unexpectedly, in all PVC/PVAL blends process of chromophores formation is more efficient than in PVC alone (Figs. 5 and 6).

Acceleration effect is especially efficient in blends containing 40% or more PVC. Probably, mutual interactions facilitate PVC dehydrochlorination (which is chain reaction) and induce formation of conjugated double bonds also in PVAL phase.

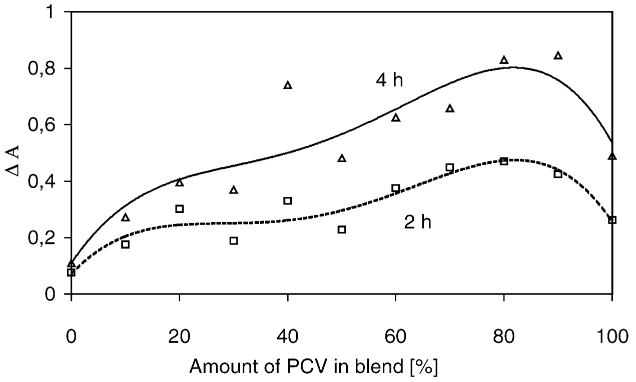


Fig. 6. Dependence of changes of absorbance at 278 nm after 2 h and 6 h UV-irradiation vs. blend composition.

Table 2
Number and weight average molecular weights ($\overline{M}_w$, $\overline{M}_n$) and polydispersity index ($P_d = \overline{M}_w/\overline{M}_n$) for PVC, PVAL and their blends before and after UV-irradiation

Time of irradiation (h)	Amount of PVC in blend (%)	$\overline{M}_n$	$\overline{M}_w$	P_d	$\Delta\overline{M}_n$ (%)[a]	$\Delta\overline{M}_w$ (%)[a]
0	100	24000	60600	2.52		
1	100	17300	56100	3.24	27.92	7.42
	90	17300	52100	3.01	27.92	14.03
	80	11600	39500	3.40	51.67	34.82
	70	15100	38200	2.53	37.08	36.96
	60	9700	32600	3.36	59.58	46.20
	50	13700	33600	2.45	42.92	44.55
2	100	11300	54400	4.81	52.92	10.23
	90	10300	42600	4.14	57.08	29.70
	80	9600	35900	3.74	60.00	40.76
	70	10700	39500	3.69	55.42	34.82
	60	9100	27400	3.01	62.08	54.79
	50	9800	33400	3.41	59.17	44.88
4	100	10700	43500	4.07	55.42	28.22
	90	9600	71300	7.43	60.00	−017.66
	80	11100	61000	5.50	53.75	−0.66
	70	12500	56000	4.48	47.92	7.59
	60	13300	52600	3.95	44.58	13.20
	50	9800	48000	4. 90	59.17	20.79
6	100	5400	37800	7.00	77.50	37.62
	90	8400	51300	6.11	65.00	15.35
	80	8000	87900	10.99	66.67	−45.05
	70	10000	107300	10.73	58.33	−77.06
	60	8100	54600	6.74	66.25	9.90
	50	11900	75400	6.34	50.42	−24.42

[a] Percentages changes of $\overline{M}_n$ and $\overline{M}_w$ were calculated as following: $\Delta\overline{M}(\%) = \left[\frac{\overline{M}(0)-\overline{M}(t)}{\overline{M}(0)}\right] \times 100$, where $\overline{M}(0)$ and $\overline{M}(t)$ are the average molecular weight before irradiation and after t time of irradiation.

The changes of absorbance at other wavelengths show the same trend and lead to the same conclusions.

3.5. GPC results

Two sets of GPC experiments with different chromatographic columns and solvents were carried out:

(a) PVC and blends with prevalent amount of PVC (minimum 50%)—in THF.
(b) PVAL—in water.

Molecular weights of both starting polymers differ significantly. In PVC—$\overline{M}_n$ = 24,000, whereas is two-fold in PVAL: $\overline{M}_n$ = 55,300. Moreover, PVAL is characterised by higher initial polydispersity (7.3) than PVC (2.5).

It was impossible to estimate average molecular weight of PVAL in blends even in case of dominant amount of PVAL (>50%) because of great amount of gel formed after irradiation. Even if some part of uncrosslinked PVAL remains in composition, macromolecules can be entangled and nonextractable. In pure PVAL, $\overline{M}_n$ decreases systematically during exposure to UV but $\overline{M}_w$ and polydispersity index increases, which is an evidence that radical recombination occurs also in sol part.

Number and weight average molecular weights ($\overline{M}_w$, $\overline{M}_n$) and polydispersity index ($\overline{M}_w/\overline{M}_n$) obtained from GPC (in THF) for PVC and blends with its major content are listed in Table 2 (results concern soluble fraction after gel separation).

Data indicate that, in our conditions, very efficient chain scission takes place in PVC. In blends with high amount of PVC (50–90%), this process is even accelerated at short irradiation time (1–2 h). It is clearly seen on the base of $\overline{M}_w$ and $\overline{M}_n$ percentage changes (two last columns in Table 2).

Table 3
Gel amount formed during UV-irradiation in PVC, PVAL and their blends (estimated by extraction in DMF)

Amount of PCV in blend (%)	Time of irradiation (h)		
	1	2	6
	Amount of insoluble gel in blend (%)		
100	18	30	47
90	27	30	49
80	59	63	73
70	68	76	78
60	73	75	82
50	80	80	86
40	89	89	90
30	83	87	87
20	87	87	89
10	89	89	92
0	99	98	95

After prolonged exposure (>2 h), average molecular weights change irregularly ($\overline{M}_w$ sometimes even increases). Further decrease of $\overline{M}_w$ and $\overline{M}_n$ is observed in PVC alone (after 4–6 h) but in blends probably competitive reactions such as macroradical recombinations became important. This fact is confirmed by increase of polydisperity during irradiation—it means that besides of chain breaking also their lengthening takes place.

3.6. Insoluble gel

Insoluble gel is formed resulting of photocrosslinking. In this experiment samples were extracted in DMF, which is common solvent for both initial polymers. As can be seen from Table 3, almost all PVAL becomes insoluble just after 1 h UV-irradiation, whereas in PVC amount of gel increases systematically with exposure time but even after 6 h does not exceed 50%.

One can deduce that photocrosslinking in PVC/PVAL blends is accelerated comparing to pure components because all experimental points lies above straight line (dashed) calculated on the base of additivity rule (Fig. 7).

Efficient crosslinking in PVAL (Scheme 3A) and it blends (Scheme 3B) can be explained by privileged arrangement of macrochains facilitating intermolecular bonding with simultaneous elimination low-molecular products (preferentially water and hydrochloride).

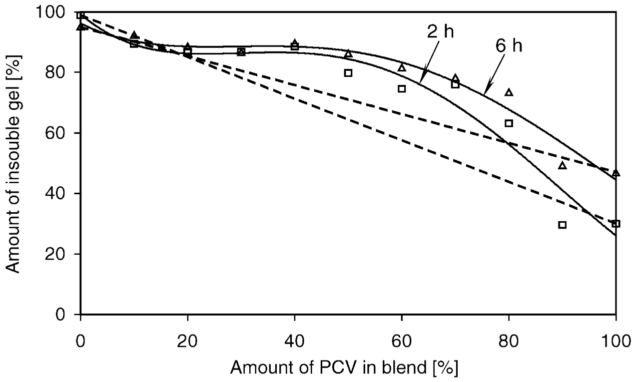
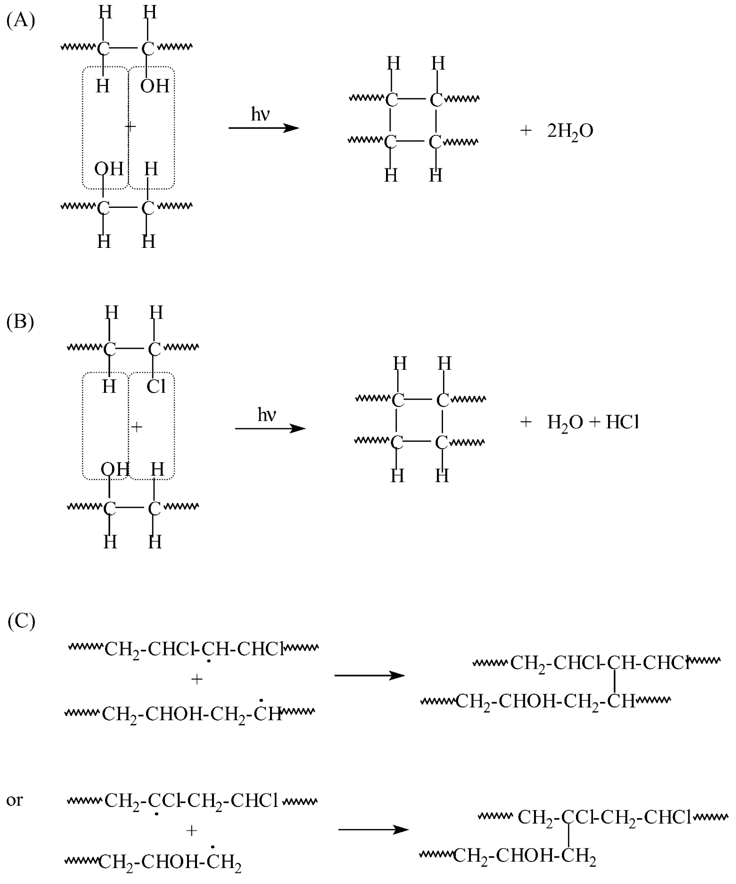
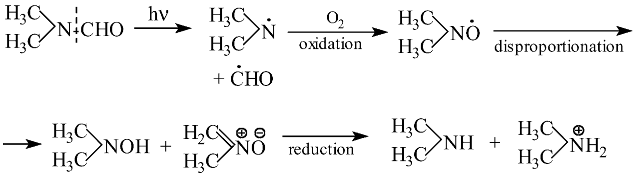


Fig. 7. Changes of gel amount formed after 2 h and 6 h UV-irradiation vs. blend composition.

Moreover, the recombination between various macroradicals formed in primary photoreactions also leads to three-dimensional insoluble network (including branching), where fragments of both polymers can be built. This way, grafted copolymer is formed (Scheme 3C).



Scheme 3. Some possibilities of photocrosslinking in PVAL (A) and PVC/PVAL blend (B and C). A and B—bimolecular reactions; C—recombination of macroradicals.



Scheme 4. Photolysis mechanism of dimethylformamide [18].

It should be added, that sometimes even linear, uncrosslinked polymers defy dissolution. It can take place in case of very long and entangled macrochains. Thus, crosslinking is only one reason of the lack of solubility.

3.7. Discussion of mechanism of photo-oxidative degradation and effect of solvent residues

The starting point for discussion of mechanism of photochemical reactions in PVC/PVAL blends is behavior of origin components during UV-irradiation. The photo-oxidative degradation either PVC or PVAL is based on free radical mechanism [1–3]. The residual impurities (solvent traces) and structural defects present in both polymers are responsible for initiation of their decomposition.

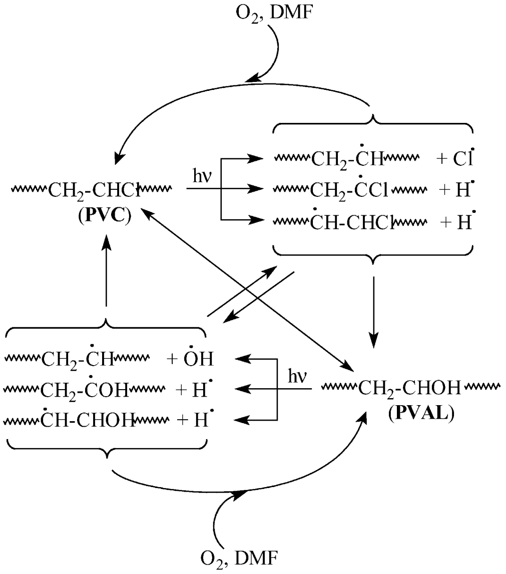
The detailed reactions occurring in UV-irradiated PVC [1,2,21] and PVAL [22,23] individually were described previously and it is not necessary to repeat them here. We want only to explain the reason why photochemical reactions in PVC/PVAL blends are not additive processes.

First main factor influencing the course of photoinduced processes is PVC/PVAL is mutual interactions between macromolecules of both types. As was suggested, resulting of mixing of polymeric components, the hydrogen bonds in PVAL (Scheme 2) are partially destroyed and new bindings are formed resulting of interactions (Scheme 1). More or less regular arrangement of macrochains makes easy the abstraction of side substituents: Cl atoms from PVC, OH groups from PVAL and H atoms from both polymers (Scheme 3A and B). It can explain higher efficiency of some photochemical reactions (such crosslinking, PVC dehydrochlorination).

The influence of solvent residues cannot be neglected. The photolysis mechanism of DMF was proposed (Scheme 4) [18].

The breaking of N–C bonds and formation of aminyl radicals is the first step of DMF decomposition. Then, in reaction with atmospheric oxygen, nitroxyl radicals are formed and secondary products appear (in traces of water) resulting of disproportionation, dimerization and reduction processes. Simultaneously, formation of hydroxy ($HO^\bullet$) and hydroperoxy ($HO_2^\bullet$) radicals, which further initiate degradation of polymers, can take place. However, nitroxyl radicals ($>NO^\bullet$) should rather play stabilizing role [3,24,25]. The traces of DMF present in film can also plasticize of composites and somewhat improve the compatibility of both polymers.

Finally, the influence of viny acetate units (9% in PVAL) should be considered. In thermal and photodegradation of PVC and PVAC blends or copolymers mutual destabilization was observed [15,26,27]. It was explained by catalysing effects of acids (HCl from PVC and CH_3COOH from PVAC) evolved during degradation. In our blends, the effect of vinyl acetate units is most important in blends with higher amount of PVAL. In blends with lower PVAL amount, also vinyl acetate concentration is very low. However, even very low content of absorbing groups is enough for photosensitizing processes. It is necessary to remind that PVC and PVAL are immiscible polymers, in which separated domains of both components are present. Residual PVAC units can improve miscibility of PVC and PVAL because its solubility parameter (δ_{PVAC} = 9.59 (cal/cm^3)$^{1/2}$) is near value for PVC (δ_{PVC}=9.38–9.45 (cal/cm^3)$^{1/2}$). Solubility parameters of PVAL (δ_{PVAL} = 12.60 (cal/cm^3)$^{1/2}$) differs from δ_{PVC} and δ_{PVAC} but is close to DMF (δ_{DMF} = 12.1 (cal/cm^3)$^{1/2}$) [28].



Scheme 5. The main interactions in PVC/PVAL blends during photo-oxidative degradation.

Summarizing our results, we can propose the mechanism of photo-oxidative degradation of PVC/PVAL blends (Scheme 5).

All macroradicals and small radicals formed in one polymer can induced reaction in the same or in the second component. Moreover, mutual reactions (cross-reactions) between degradation products are also possible. The small excited molecules or radicals are very active because of their great mobility. Thus, they can easily diffuse to deeper layers of polymer film and cause further secondary reactions. The excited macromolecules and macroradicals react at the same place where were created (cage effect) or in the close neighborhood (it depends on segmental flexibility).

4. Conclusions

On the basis of above results, one can conclude that photochemical reaction in PVC/PVAL blends depends on sample composition. Because of different behavior of both polymers during UV-irradiation, the blends with dominant amount of PVC component differ from blends with PVAL prevalent content. Generally, photoreactions such as chain scission, crosslinking and polyenes formation are accelerated in all blends but oxidation is somewhat retarded in samples with greater PVC content (>50%).

The PVC/PVAL is a complex system and photochemical reactions in blends depend not only on the chemical nature of PVC and PVAL but also on macromolecular interactions. Hydrogen bonds in PVAl are destroyed during blend preparation and new dipole-dipole co-interactions between PCV and PVAL occur. It facilitates crossing reactions, for instance, recombination of macroradicals and reactions of PVC and PVAL with small, active radicals or excited particles formed in both phases. The products of photodegradation of PVC/PVAL can further participate in subsequent chain reactions.

These blends, specially with major PVAL amount, are potentially biodegradable composites, although, only PVAL decay is expected in natural environment. Similar behavior is observed in case of blends of synthetic polymers with starch or cellulose, where decomposition caused by microorganisms is limited to natural component.

References

[1] J.F. Rabek, Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers, Wiley, Chichester, 1987.
[2] J.F. Rabek, Polymer Photodegradation, Chapman and Hall, London, 1995.
[3] J. Pączkowski (Ed.), Fotochemia Polimerów. Teoria i Zastosowanie (Photochemistry of Polymers. Theory and Application), UMK, Toruń, 2003.
[4] E.D. Owen, Degradation and Stabilisation of PVC, Elsevier Applied Science Publishers Ltd., London, 1984.
[5] J.L. Philippart, J.-L. Gardette, Polym. Degrad. Stab. 71 (2001) 189.
[6] W.H. Starnes, Prog. Polym. Sci. 27 (2002) 2133.
[7] Z. Floriańczyk, S. Penczek (Eds.), Chemia Polimerów (Chemistry of Polymers), Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa,1997.
[8] G. Geuskens, M. Borsu, C. David, Eur. Polym. J. 8 (883) (1972) 1347.
[9] Hummel, Schol, Atlas der Kunststoff – Analyse, Verlag Chemie GmbH, Weinheim/Bergstr, 1968.
[10] L.J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hall Publishers Ltd., London, 1975.
[11] N.B. Colthup, L.H. Daly, S.E. Wiberleg, Introduction to Infrared and Raman Spectroscopy, Academic Press Inc., New York, 1975.
[12] K.J. Buchanan, W.J. McGill, Eur. Polym. J. 16 (1980) 309–319.
[13] H. Anders, H. Zimmerann, Polym. Degrad. Stab. 18 (1987) 111.
[14] E.Y.L. Vaidergorin, M.E.R. Marcontes, V.G. Toscano, Polym. Degrad. Stab. 18 (1987) 329.
[15] H. Kaczmarek, R. Drąg, M. Świątek, D. Ołdak, Surf. Sci. 877 (2002) 507–510.
[16] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, second ed., Marcel Dekker, Inc., New York, 1993, p. 285.
[17] S. Chatterjee, S. Basu, N. Ghosh, M. Chekrabarty, Chem. Phys. Lett. 388 (2004) 79.
[18] K. Papadopoulos, T. Triantis, D. Dimotikati, J. Nikokavouras, J. Photochem. Photobiol. A: Chem. 124 (1999) 85.
[19] L. Seibles, J. Polym. Sci. Part A: Polym. Chem. 28 (1990) 2179–2186.
[20] P. Kohn, P.C. Marechal, J. Verdu, Anal. Chem. 51 (1979) 1000.
[21] A. Torikai, H. Hasegawa, Polym. Degrad. Stab. 63 (1999) 445.
[22] K. Maruyama, Y. Kuramota, Y. Tanizaki, Polymer 30 (1989) 1419.
[23] Aoki, Eur. Polym. J. 16 (1980) 571.
[24] H. Zweifel, Stabilization of Polymeric Materials, Springer, Berlin, 1998.
[25] S.H. Hamid, Handbook of Polymer Degradation, second ed., Marcel Dekker, Inc., New York, 2000.
[26] I.C. McNeill, The thermal degradation of polymer blends, in: N. Grassie (Ed.), Developments in Polymer Degradation—Part 1, Applied Science Publishers, London, 1977, p. 171, Chapter 6.
[27] J. Pospisil, Z. Horak, Z. Krulis, S. Nespurek, S. Kuroda, Polym. Degrad. Stab. 65 (1999) 405.
[28] J. Brandrup, E.H. Inmmergut, Polymer Handbook, third ed., John Wiley and Sons, New York, 1989.