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The effect of UV-irradiation on poly(vinyl alcohol) composites with montmorillonite

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Abstract

Poly(vinyl alcohol), PVA, microcomposites with montmorillonite, MMT, were prepared by their mixing in aqueous colloidal solution. Thin films of composites obtained by solvent evaporation were exposed to 254-nm radiation. The course of photochemical reactions leading to various products was monitored by FTIR and UV–vis spectroscopy. The chain scission reaction was confirmed by measurement of average molecular weights and polydispersity using gel permeation chromatography (GPC) method. The crosslinking was minor process whereas oxidation and degradation appeared more efficient in exposed PVA/MMT. It was found that the presence of clay filler (MMT) has slight influence on PVA photooxidative degradation.

Keywords: Poly(vinyl alcohol); Polymer composites; Montmorillonite; Ultraviolet-irradiation

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1. Introduction

The polymeric composites have increasing interest in recent years [1–3]. The polymers reinforced by various fillers found numerous applications in household, industry and military. Especially interested are nanocomposites containing low amount of nanometric-sized additive in polymer matrix [4–10]. The main advantages of nanocomposites are improved thermal and mechanical properties, reduced flammability and better barrier properties comparing to unfilled polymer. The composite studies focus on the method of their preparation, structure characterization, mechanical and thermal properties as well as processing.

Poly(vinyl alcohol) (PVA) is a water-soluble polymer, which is widely used in industry because of its high capability of water absorption [11,12]. Owing to hydroxyl groups present in each unit, PVA is characterized by strong hydrophilic and hydrogen bonding character, thus, it forms hydrogels applied in medicine and pharmacy [13–15]. The next important feature of PVA is biodegradability [16,17]. This polymer was used for preparation of nanocomposites with graphite oxide [18,19], silica [20], chitin whisker [21] and montmorillonite (MMT) [22–24].

MMT, which occurs in natural clays, is popular filler for various polymers. It is composed of joined silica and alumina sheets stacked on top of each other [25,26]. The chemical composition is described by general formula: $(Na,Ca)_{0.3}(Al,Mg)2(Si_4O_{10})(OH)_2nH_2O$, however, the cation amount ratio can vary dependently on the mineral source and its treatment. MMT have ability to exchange ions [27,28] and this process is used for structure modification necessary to its mixing with hydrophobic polymers. MMT exhibits tendency to agglomeration, thus, in some polymeric matrixes it forms microcomposites with larger particles. Although the structure and properties of PVA composites are intensively studied [23,24,26,29], there is a lack of information on the influence of electromagnetic radiation on their stability.

The aim of this work was to investigate the effect of short wavelength UV-irradiation on PVA/MMT composite properties. One knows that doping of polymer by layered filler changes the macromolecular interactions, which can affect composite resistance to UV-radiation.

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2. Experimental part

2.1. Materials

PVA and MMT, were supplied by Sigma Aldrich. Polymer weight average molecular weight was about 100,000 and hydrolysis degree, 98%. Surface area of clay was 220–270 m^2/g. MMT was purified according to recipe [4,6,30].

2.2. Composite preparation

MMT immersed in water was sonicated in ultrasonic bath, and then, the PVA aqueous solution (1%, w/v) was added. The obtained colloidal dispersion was mixed by magnetic stirrer and heated at 80 °C for 4 h. Such prepared PVA solutions, containing different amount of MMT (0.1–5.0%), were poured out onto leveled glass plates. Thin solid films with various compositions were obtained after water evaporation and drying of sample in vacuum oven.

2.3. UV-irradiation

PVA/MMT films were exposed to UV at room temperature and air atmosphere using low-pressure mercury vapor lamp (TUV30W, Philips, Netherlands), which emits 254-nm radiation. Exposure time was 1–10 h, which corresponds to 115–1150 kJ/m^2 doses. Distance between sample and light source was 5 cm, at which irradiation intensity equals 3.12 mW/cm^2.

2.4. Analysis

Infrared (FTIR) and ultraviolet–visible (UV–vis) spectra were recorded using Genesis II (Mattson, USA) and UVPC 1600 (Shimadzu, Japan) spectrometers, respectively. IR spectra were obtained by averaging 100 scans at 2 cm^{-1} resolution. The integration of carbonyl bands and mathematical decomposition of this complex band on to constituents was done applying the curve fitting by Gauss-Lorentz mixed function.

Average molecular weights ($\overline{M_n}$, $\overline{M_w}$) were evaluated by gel permeation chromatography method. Viscotek chromatograph with two detectors (refractometer, Waters 410, and light scattering, Viscotek T60A) and TSPKgel PWXL column was used. The temperature was 40 °C; eluent: 0.1 M $NaNO_3$; flow rate: 0.8 ml/min; solution concentration: 1 mg/ml. Pullulans (SAC-10/7 Shodex) were standards for calibration.

X-ray analysis (XRD) was carried out on a Philips X'Pert PRO diffractometer using Cu Kα, Cu-filtered radiation in the diffraction angle range: 2–30°. Wavelength of emitted radiation is 1.54056 Å.

Transmission electron microscopy (TEM) was applied for observation of internal morphology of PVA modified by MMT. The microscope Joel Jem 1100, working at 100 kV voltage was used.

Insoluble gel formed during UV-irradiation was separated from sol and dried to a constant weight. Percentage amount of gel was calculated as an average from three values.

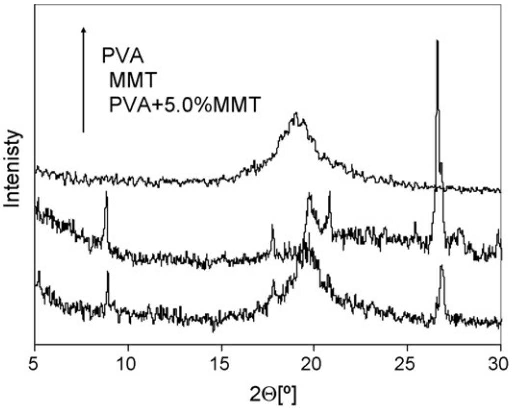


Fig. 1. XRD patterns of PVA, montmorillonite and PVA/MMT (5%) composite.

3. Results and discussion

3.1. Characterization of PVA/MMT composites

Because both polymer and filler used in this study have hydrophilic character, the modification of MMT for component mixing was not necessary. As was described in literature [16,17], the solution dispersion method of PVA/clay nanocomposite preparation is often used and successful. Such method combined with ultrasonic irradiation was also used in this work. The structure of obtained composites with different MMT amount was studied by x-ray diffraction. Fig. 1 shows the diffraction patterns of PVA, MMT and PVA composite with 5% MMT. The sharp signal for MMT appears at $2\theta = 8.95°$, thus, the calculated from Bragg's equation the interlamellar spacing, due to the (0 0 1) plane, is about 9.87 Å. The peak at higher angle (about 20°) corresponds to (1 1 0) and (0 2 0) crystallographic planes. As can be seen from Fig. 1, in PVA composite, these peaks are almost at the same position. In polymer patterns without MMT, the broad signal characteristic for amorphous phase occurs at about $2\theta = 19°$ and it also exists in patterns of composites. Similar XRD pattern was observed for PVA containing 1 or 3% MMT, only the signal intensity was proportionally lower. It means, that intercalation did not take place and structure of MMT is unchanged. Thus, obtained material can be classified as classic phase separated microcomposite, where the MMT agglomerates are enclosed (surrounded) by macromolecules, which do not penetrate the interlayer surfaces.

TEM photographs confirms above conclusion (Fig. 2). MMT aggregates, size of about 200 μm, are dispersed in PVA matrix (Fig. 2a). However, besides of separated domains of MMT in PVA matrix, the small regions of partially exfoliated structures exist. The higher magnification allows to perceive the details of this heterogeneous structure: partly separated layers of silicate (Fig. 2b), which indicates that some penetration of macromolecules to MMT at the phase boundary takes place. This process is not efficient enough to form fully exfoliated structure, which could be detected by XRD. The interactions can be explained by formation of hydrogen bonds between OH groups from PVA units and silanol (Si–O) groups from MMT sheets. Various specific interactions including hydrogen bonds

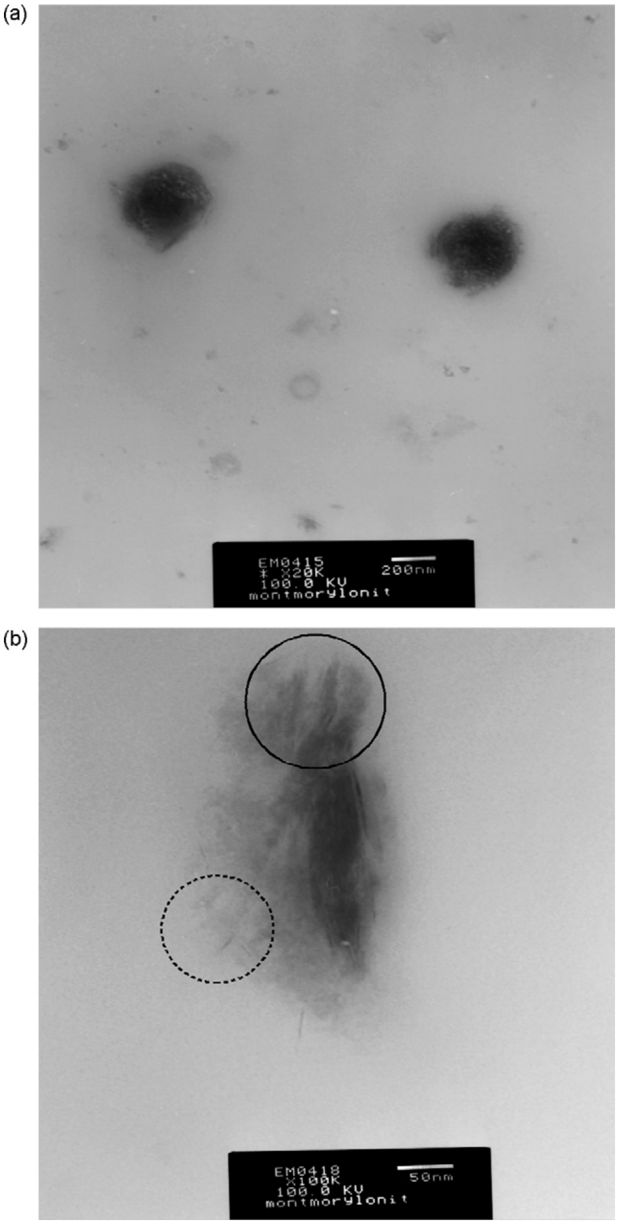


Fig. 2. TEM microphotographs of PVA/MMT (5%) composite at magnification 20,000× (a) and 100,000× (b); circled area at 2b shows the exfoliated and intercalated fragments of MMT aggregate.

strongly influencing the molecule order and adhesion in such system were described in literature [24,31–34].

FTIR spectra give additional information about the structure of composites studied. In Fig. 3, examples of spectra of PVA, MMT and PVA/MMT (5%) at 600–3600 cm^{-1} range are shown. MMT spectrum is composed of broad hydroxyl and silanol bands at 3000–3600 and 1000–1200 cm^{-1}, respectively [4]. Pure PVA exhibits typical bands for vinyl polymers. Bands at 2800–3000 cm^{-1} are due to stretching vibrations of CH and CH_2 groups and bands attributed to CH/CH_2 deformation vibrations are present at 1300–1500 cm^{-1} range. Also very intensive, broad hydroxyl band occurs at 3000–3600 cm^{-1} and accompanying C–O stretching exists at 1000–1260 cm^{-1}. Low intensive carbonyl band, resulting of residual acetate groups, is detected at 1735 cm^{-1} in PVA spectrum. All these bands are also present in composites with MMT.

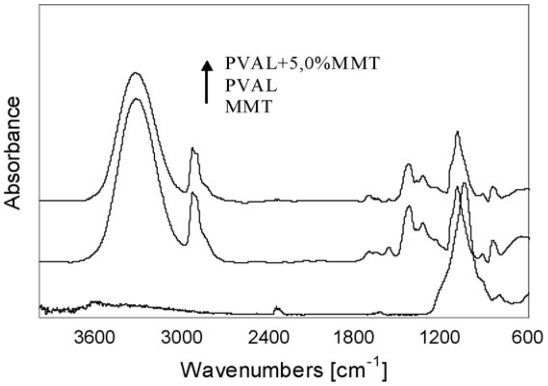


Fig. 3. FTIR spectra of MMT, PVA and PVA/MMT (5%) composite.

The presence of carbonyl groups in PVA arises from production of polymer. PVA is obtained from poly(vinyl acetate) by hydrolysis, thus, it is always polluted by residual acetate groups resulting of not complete process (Scheme 1). Although the C=O contamination in PVA used is low (about 2% units) but its effect on photochemical processes in polymer can be decisive.

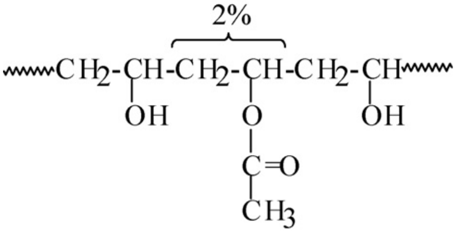
UV–vis spectroscopy confirms the presence of residual carbonyl groups in PVA and its composites. The low intensive band due to $n \rightarrow \pi^*$ transition appears 278 nm.

IR spectroscopy supplies also evidences of interactions between macromolecules and filler particles, which was suggested above. The small shifts of absorption maximum and alteration of band shape are results of changes in the nearest surrounding of functional groups. These observations are illustrated in Fig. 4 for bands in region 1000–1700 cm^{-1}. For example, band at 1425.7 cm^{-1} in spectrum of pure PVA occurs at 1429.3 cm^{-1} for PVA + 1% MMT and at 1430.1 cm^{-1} for PVA + 5% MMT. Neigbouring band situated at 1333 cm^{-1} in PVA spectrum is shifted to 1329.8 and 1329.7 cm^{-1} in PVA + 1 and PVA + 5% MMT, respectively.

3.2. *The effect of UV-irradiation on PVA/MMT composites*

3.2.1. *Main chain scission*

First expected photoreaction in PVA and its composite is main chain scission. Our aim was to check if the addition of MMT to polymer matrix have an influence on the efficiency of this reaction. For this purpose, gel permeation chromatography was applied.



$$\sim\!CH_2-\underset{OH}{\underset{|}{CH}}-\overbrace{CH_2-\underset{\begin{array}{c}|\\O\\|\\C{=}O\\|\\CH_3\end{array}}{CH}}^{2\%}-CH_2-\underset{OH}{\underset{|}{CH}}\!\sim$$

Scheme 1. Chemical structure of PVA containing residual acetic groups.

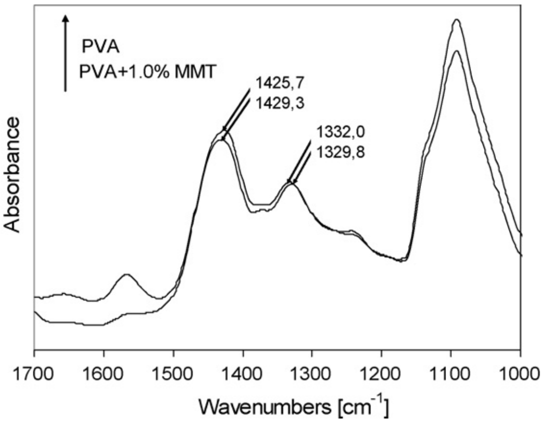


Fig. 4. FTIR of PVA and PVA/MMT (1%) composite in 1000–1700 cm^{-1} region.

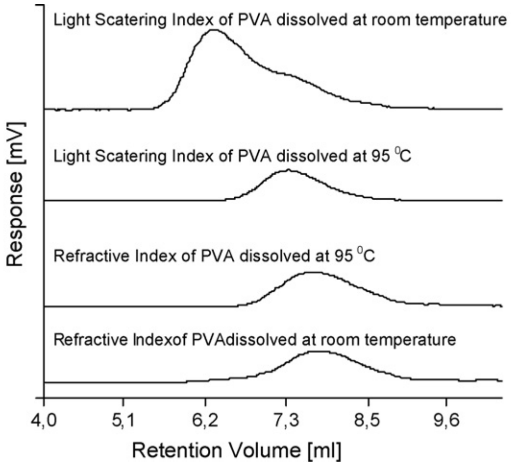


Fig. 5. GPC curves of PVA dissolved at room temperature (20 °C) and at 95 °C from refractometer and light scattering detector (analysis temperature = 40 °C).

Table 2
Gel amount (%) formed during UV-irradiation in PVA composites

Sample	Irradiation dose (kJ/m^2)						
	0	115	230	465	700	925	1150
PVA	–	–	–	–	–	–	–
PVA + 0.1%MMT	2	2	2	2	2	2	2
PVA + 0.5%MMT	3	4	2	4	2	2	2
PVA + 1.0%MMT	4	3	4	4	4	3	3
PVA + 3.0%MMT	6	9	8	8	5	4	4
PVA + 5.0%MMT	6	7	10	14	8	9	12

Although PVA is a water-soluble polymer, GPC analysis showed the formation of polymer aggregates in aqueous solution, where sample was dissolved at room temperature. After preliminary heating of solution to 95 °C and applying elevated temperature (40 °C) during GPC analysis, the aggregates disappear (Fig. 5). Thus, for correct estimation of molecular weight, 40 °C was applied for analysis of all samples.

Table 1 shows the number and weight average molecular weights ($\overline{M_n}$, $\overline{M_w}$) and polydispersity values, calculated as $P = \overline{M_w}/\overline{M_n}$ ratio for PVA and its composite containing 5% MMT. It should be noted, that the molecular parameters of unirradiated PVA were measured before and after sonication because ultrasounds were used for PVA/MMT composite preparation. As can be seen from Table 1, the ultrasonication leads to slight decrease of both molecular weights and polydispersity. It is a known fact; ultrasonic degradation was observed in case of other polymers and was described in literature [35–37].

Ten hours of UV-irradiation caused above 25% drop of $\overline{M_n}$ of PVA but after sonification the changes exceeded 30%. The percentage changes of $\overline{M_w}$ are somewhat lower. Simultaneosuly, the polydispersity increases in PVA after UV and ultrasonic degradation.

Photodegradation of composite with 5% MMT is slightly more efficient $-\overline{M_n}$ decreased about 36% at the same time of UV exposure. The changes of polydispersity (P) are also higher than that in PVA alone. The rise of *P* value indicates that besides of chain breaking, the processes of macroradical recombination take place.

3.2.2. Photocrosslinking

Estimation of insoluble gel supplies an information on photocrosslinking in PVA and its composites. The efficiency of this process is inconsiderable (Table 2). Pure PVA does not undergo crosslinking even after 10 h UV-irradiation (i.e. under maximal applied dose = 1150 kJ/m^2). Interestingly, that prepared composites were not completely soluble: 2–6% gel (after subtraction of MMT mass) was found, dependently on initial composition. The reason is probably formation of numerous hydrogen bonds between polymer and clay molecules with or without water participation (Scheme 2).

Gel amount formed after UV-irradiation in composites varies from 2 to 14%. As can be seen, photocrosslinking is most efficient in PVA with 5% MMT among the samples studied. However, the changes are irregular with prolongation of irradiation time, which again indicates that competitive processes (crosslinking and bond breaking) occur simultaneously. The reason of alteration of gel amount can be also the reversible reaction

Table 1
Average molecular weights and polydispersity of PVA and PVA/MMT (5%) composite before and after UV-irradiation (+ means, that ultrasounds were applied).

Sample	Dose (kJ/m^2)	Ultra- sounds	$\bar{M}_n$	$\Delta \bar{M}_n$ (%)	$\bar{M}_w$	$\Delta \bar{M}_w$ (%)	P	ΔP (%)
PVA	0	–	41000		100500		2.45	
PVA	1150	–	30500	25.6	77500	22.9	2.54	3.6
PVA	0	+	39000		92000		2.36	
PVA	1150	+	27000	30.8	69500	24.5	2.57	8.9
PVA + 5%MMT	0	+	41500		98500		2.37	
PVA + 5%MMT	1150	+	26500	36.1	72000	26.9	2.72	14.8

Table 3
Percentage changes of total carbonyl ($I_{C=O}$) and vinyl ($I_{C=C}$) index calculated from FTIR spectra of PVA and its composites with MMT after UV-irradiation

Dose (kJ/m^2)	$I_{C=O}$ for following content of MMT in PVA					$I_{C=C}$, for following content of MMT in PVA				
	0	0.1 (%)	0.5 (%)	3.0 (%)	5.0 (%)	0	0.1 (%)	0.5 (%)	3.0 (%)	5.0 (%)
0	31	19	16	21	26	5	3	1	2	2
115	30	20	23	22	30	7	3	1	3	4
230	31	19	17	22	28	7	3	1	4	5
465	26	17	21	22	31	4	2	2	3	5
700	26	17	21	22	32	4	2	1	3	4
925	30	17	24	22	33	7	3	2	5	5
1150	28	18	22	23	32	4	2	2	5	7

of hydrogen bonding (some hydrogen bonds split upon UV but they can be reproduced during secondary processes).

3.2.3. Photooxidation and chromophore formation

Polymer oxidation accompanied the main chain scission reaction because the irradiation was conducted at air atmosphere. FTIR spectroscopy is very useful tool for monitoring the formation of oxidized products during polymer irradiation. Usually the hydroxyl and carbonyl absorption band are used for process evaluation. However, in case of PVA, only the carbonyl band was chosen for this purpose because of strong hydroxyl band present in origin PVA. Moreover, PVA strongly absorbs water, even from air, thus hydroxyl or hydroperoxide groups covalently bonded to polymeric chains can be screened by absorbed water, which would give wrong information on photooxidation. It should be added that side groups (OH) can be abstracted during photodestruction and the water is evolved as a low molecular degradation product during secondary process [38].

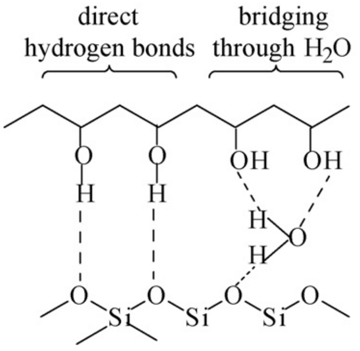
For quantitative evaluation of photoproducts containing C=O groups, the integration of carbonyl band at 1600–1800 cm^{-1} range was done and carbonyl index, expressed as $I_{C=O}$ (formula 1), was calculated. The complex carbonyl band was decomposed mathematically onto three constituents with maximum at 1736, 1710 and 1674 cm^{-1}, corresponding esters, ketones and double bonds conjugated with ketones (–CH=CH–CO–), respectively.

Other type of photoproducts found in PVA were unsaturated units with characteristic absorption at 1648 cm^{-1}. For this photoproduct, also vinyl index, $I_{C=C}$, was calculated according to Eq. (2):

$$(I_{C=O}) = \frac{S_{1736} + S_{1710} + S_{1674}}{S_{1420}} 100\% \quad (1)$$

$$(I_{C=C}) = \frac{S_{1648}}{S_{1420}} 100\% \quad (2)$$

where S_x is the integral intensity that is, the surface area of peak with maximum at x cm^{-1}; band with maximum at 1420 cm^{-1} is a standard peak.



Scheme 2. Different types of hydrogen bonds between PVA and MMT.

The values of both indexes and their changes during UV-irradiation for PVA and its composites with MMT are listed in Table 3. Slight increase of total carbonyl group amount was observed during UV-irradiation of composites containing ≥0.5% MMT contrary to pure PVA and PVA + 0.1% MMT. In most PVA/MMT composites, the carbonyl index is lower than that in PVA alone after the same irradiation time.

Table 4 presents the values of integral intensities of carbonyl band components. Two peaks were chosen for discussion of photooxidation process in PVA: at 1710 and 1736 cm^{-1} assigned to ketones and ester groups. At first sight, the results do not allow for conclusion generalization. One can only notice that photooxidation leads mainly to ketone formation because positive changes of A_{1710} were observed, whereas the changes of ester groups are rather negative, especially after higher doses. We can conclude that photooxidation of PVA/MMT is somewhat less efficient than that in PVA.

Only very small changes of vinyl index were noted in samples investigated (Table 3). It means that reactions leading to unsaturation are not efficient. Similar observation was found during thermal degradation of PVA, where the amount of conjugated or isolated double bounds was negligible, contrary to other vinyl polymers [35]. It indicates that elimination of side groups in PVA is random process in both photochemical and thermal degradation.

Electronic spectra confirm the above conclusion. Although in initial spectra of PVA and its composites with MMT, the low intensive band at 278 nm was observed due to absorbing impurities (mainly carbonyl residue), there are no significant changes during UV-irradiation of samples (Table 4). After low dose (corresponding 1-h exposure), the small drop of intensity at 278 nm was observed in all samples, which is followed by further slight increase of absorbance. This small increase of absorbance during prolonged UV-irradiation is caused by for-

Table 4
Percentage changes of component of carbonyl band at 1710 cm^{-1} and 1736 cm^{-1} in FTIR spectra of PVA and its composites with MMT after UV-irradiation

Dose, (kJ/m^2)	A_{1710} for following content of MMT in PVA					A_{1736} for following content of MMT in PVA				
	0	0.5 (%)	1.0 (%)	3.0 (%)	5.0 (%)	0	0.5 (%)	1.0 (%)	3.0 (%)	5.0 (%)
115	+26	+25	+5	+5	+5	−21	+28	−14	−14	−6
230	+55	−2	0	−23	−23	−30	−1	0	+6	+4
465	−25	+16	+32	−20	−20	+25	0	−21	+3	+1
700	−20	+27	+31	+8	+83	+20	+11	−14	−25	−14
925	+41	+27	+46	+10	+108	−41	−11	−14	−27	−17
1150	−8	+19	+25	+10	+13	+5	−1	−7	−30	−77

Table 5
Changes of absorbance at 278 nm in electronic spectra of UV-irradiated PVA and its composites with MMT

Dose (kJ/m^2)	MMT content in PVA					
	0	0.1 (%)	0.5 (%)	1.0 (%)	3.0 (%)	5.0 (%)
0	0.014	0.015	0.028	0.026	0.039	0.075
115	0.010	0.012	0.026	0.024	0.031	0.065
230	0.012	0.017	0.026	0.024	0.033	0.063
465	0.010	0.018	0.028	0.026	0.036	0.068
1150	0.012	0.019	0.031	0.029	0.044	0.080

mation of oxidized absorbing products in polymer but, as can be seen from Table 4, no clear MMT effect on this process. The analogical trend of changes was observed in whole absorption region (200–800 nm)(Table 5).

3.3. Brief discussion of photooxidative degradation mechanism

The mechanisms of PVA photodegradation has been described previously [38,39–45]. The observed photoxidative degradation in PVA and its composites can be considered as process initiated by chromophore impurities always present in polymer. Neither pure PVA, nor MMT does not absorb 254 nm radiation. As was mentioned before, the residue of acetic side groups can influence the course of PVA photodegradation because carbonyls strongly absorb UV-radiation and undergo excitation. Besides of non-hydrolyzed acetate groups also other structural defects can be present in PVA: branching points, tail-to-tail structures, aldehyde-end groups.

Excited unit can transfer energy to other part of polymeric chain or directly decompose into free radicals. Thus, C=O groups initiate degradation or sensitize this process in PVA. The formed once radicals or macroradicals can propagate chain degradation processes until to their termination by recombination or disproportionation.

The filler impurities (e.g. various metal cations) can also act as catalyst during PVA exposure, however, their effect in our case was negligible.

Resulting of PVA photodegradation, the complex mixture of products are formed. As detected by FTIR and UV–vis spectroscopy, degraded macromolecules contained various carbonyl and unsaturated (C=C) groups.

The effect of MMT on photochemical reactions observed in PVA can be explained by heterogeneity of samples and specific interactions between components partially reinforcing the structure of composites. The different MMT content in polymeric matrix leads to different size of agglomerates and various dispersion degree. The developed surface area of clay facilitates contacts with macromolecules and numerous interactions occur. They prevent harmful, destructive action of UV-radiation. However, in our case two opposite effects were found—slight acceleration of main chain scission and retardation of oxidation in exposed PVA/MMT comparing to unmodified, origin PVA.

The formed hydrogen bonds between composite constituents can be destroyed upon UV and reversibility of this reaction is probably the reason of irregular changes in physical and chemical properties of composite studied.

4. Conclusions

The ultrasonication of PVA and MMT aqueous mixture at elevated temperature led to formation of heterogeneous composites with small nanocomposite (exfoliated) domains.

On the base of conducted experiments one can conclude that UV-irradiation leads to relatively efficient photodegradation of PVA. The presence of MMT in PVA somewhat accelerates the main chain scission, which was proved by GPC.

However, the photocrosslinking does not occur in PVA alone in studied conditions. MMT leads to formation of low amount of stable insoluble aggregates just before UV action. Gel amount increases somewhat upon UV but the observed changes are irregular, which confirms that competitive and reversible processes take place simultaneously.

PVA photooxidation leads mainly to formation of ketonic groups in macrochains but the presence of MMT slightly hampers this process.

Irregular changes and variation in efficiency of photochemical processes are caused by sample inhomogeneity, which is dependent on the amount and dispersion degree of added filler.

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