

HALINA KACZMAREK^{1), *)}, AGATA ZIELIŃSKA¹⁾, GRZEGORZ SIONKOWSKI¹⁾,
KRZYSZTOF BAJER²⁾, ANDRZEJ STASIEK²⁾, JANUSZ DZWONKOWSKI²⁾

The resistance of wood fibers-poly(vinyl chloride) composites to UV-irradiation

RAPID COMMUNICATION

Summary — Wood fibers-poly(vinyl chloride) (WF-PVC) composite and pure poly(vinyl chloride) samples, prepared by extrusion, were exposed to short wavelength UV-irradiation ($\lambda = 253.7$ nm). Scanning Electron Microscopy (SEM) micrographs shows heterogeneity of WF-PVC composite but the effect of UV-irradiation on surface morphology of sample is negligible. The course of photochemical reactions occurring in samples studied has been monitored by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The results obtained indicate the better photochemical stability of WF-PVC comparing to virgin PVC.

Key words: wood fibers-poly(vinyl chloride) composites, UV-irradiation, ATR-FTIR spectroscopy, surface morphology.

ODPORNOŚĆ KOMPOZYTÓW POLICHLORKU WINYLU Z WŁÓKNAMI DRZEWNymi NA DZIAŁANIE PROMIENIOWANIA UV

Streszczenie — Próbkki kompozytu poli(chlorku winylu) z włóknami drzewnymi (WF-PVC) i czystego poli(chlorku winylu), otrzymane metodą wytłaczania, poddano działaniu krótkofalowego promieniowania UV ($\lambda = 253,7$ nm). Metodą skaningowej mikroskopii elektronowej (SEM) wykazano heterogeniczność kompozytu WF-PVC (rys. 1), oraz stwierdzono, że wpływ promieniowania UV na morfologię powierzchni próbek jest nieznaczny. Przebieg reakcji fotochemicznych zachodzących w badanych próbkach monitorowano metodą odbiciowej spektroskopii w podczerwieni z transformacją fourierowską (ATR-FTIR) (rys. 2). Otrzymane wyniki wskazują na lepszą fotostabilność kompozytów WF-PVC w porównaniu z czystym PVC (tabela 1).

Słowa kluczowe: kompozyty poli(chlorku winylu) z włóknami drzewnymi, napromienianie UV, spektroskopia ATR-FTIR, morfologia powierzchni.

Increasing interest has focused on the study of wood-polymer composites (WPC) in recent decade. The filling of synthetic polymers with wood fibers (WF) is a simple method of preparation of inexpensive raw materials of valuable properties for building and furniture industries (e.g. siding, decking and other building profiles) [1–7]. The wood-polymer composites are characterized by enhanced mechanical properties, good weather resistance and reduced water uptake comparing to traditional wood products. Synthetic, hydrophobic polymers are generally immiscible with cellulose, which is the main wood component, fortunately, the compatibility can be modified by addition of proper compatibilizer or by grafting process [4]. The advantage of composite con-

taining dominant amount of wood component is its biodegradable nature. The final WPC properties depend not only on chemical structure of polymer matrix and origin of wood but also on internal morphology (average size and distribution of filler particles) as well as manufacturing conditions.

The modification of composite structure, leading to improvement of interfacial adhesion of components, is possible and necessary to obtain desired WPC properties. Recently it was found that reinforcement and flame retardation of poly(vinyl chloride)-wood fibers composite can be improved by its physical modification by inorganic filler such as montmorillonite [5].

However, there is a little information on photochemical stability of WPC composites, thus, the aim of this work was to study the effect of UV-irradiation on wood fibers-poly(vinyl chloride) (WF-PVC) specimens prepared by extrusion. The photochemical stability of WF-PVC composites is very important in case of various outdoor applications.

¹⁾ Nicolaus Copernicus University, Faculty of Chemistry, Gagarin 7, 87-100 Toruń, Poland.

²⁾ Institute for Plastic Processing "Metalchem", Maria Skłodowska Curie 55, Toruń, Poland.

^{*)} Corresponding author; e-mail: halina@chem.uni.torun.pl

EXPERIMENTAL

Materials

Composite PlastWood C (40 wt. % of PVC S-58 with additives + 60 wt. % of wood fibers Lignocel 120) in form of pellets supplied by AGAPLAST Olsztynek, Poland, was used in these studies. The composite was obtained using extrusion line, the main device of which was a counter-rotating, conical twin screw extruder with degassing (Metalchem, Poland).

A reference poly(vinyl chloride), not containing wood filler, was PVC S-58 produced by Anwil Włocławek (Poland). Wood fiber, which was a component of composite PlastWood C, was supplied by J. Rettenmaier & Sohne GmbH and CO Faserstoffwerke Holzmühle b. Ellwangen/J. (Germany).

Sample preparation

Using PlastWood C, samples in the form of slat (width of 50 mm, thickness of 3 mm) were extruded using extrusion line (single screw extruder from Barmag, Germany) with special die, which had two heating zones (168, 168 °C) and two cooling zones (132, 90 °C). Rotational speed of screw was 25 min⁻¹. The samples of 10 mm width were cut for UV exposure.

UV exposure

PVC and WF-PVC samples were exposed to UV radiation of wavelength 253.7 nm emitted by low-pressure mercury vapor lamp (TUV-30W, Philips, Holland) in the presence of air. The intensity of incident radiation was equal to 37.425 W/m²; time of irradiation was in the range of 1–12 h.

Methods of testing

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy using Genesis II Spectrophotometer (Mattson, USA) was applied. ATR device contained zinc selenide crystal.

Surface morphology was studied by scanning electron microscopy (SEM) using microscope of type LEO 1430 VP (England).

RESULTS AND DISCUSSION

Sample morphology

The samples of WF-PVC were completely non-transparent, slightly brown, contrary to virgin PVC. The composite inhomogeneity was seen with the naked eyes. More details of internal structure can be observed in SEM micrographs presented in Figure 1. The WF microphotograph (Fig. 1a) shows that the microfibers of diffe-

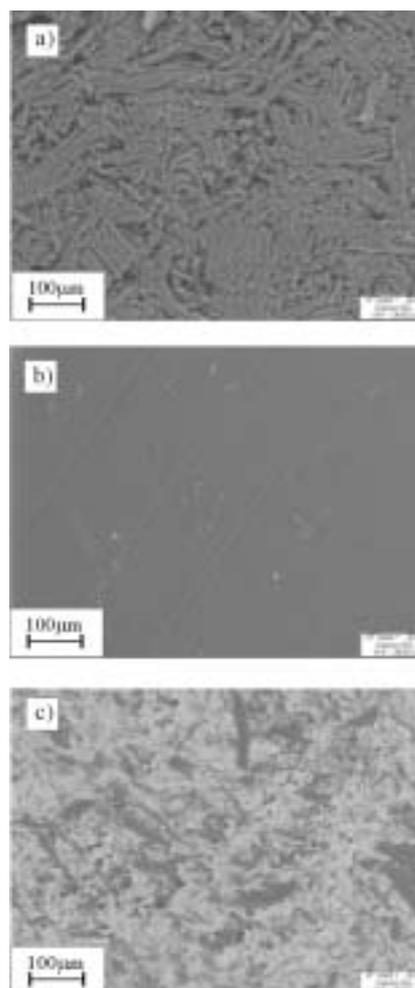


Fig. 1. SEM micrographs of unexposed samples of: a) WF, b) PVC, c) WF-PVC composite

rent size are present in wood fibers. Some of them are parallel oriented, others are more or less entangled. Sample of PVC (Fig. 1b) is relatively homogenous without any special features. In WF-PVC composite (Fig 1c) few fibers of different size are embedded in PVC matrix. Although WF component is dominant (60 wt. %), PVC still forms a continuous phase. The volume of empty space is insignificant (no voids and cavities), what allows to predict the good usefull properties of the composite (for example, good water resistance or mechanical properties).

The UV-irradiation does not cause any significant changes in observed surface morphology of WF-PVC composite.

ATR-FTIR spectroscopy

The changes in chemical structure of PVC, WF and WF-PVC composite induced by UV-irradiation were monitored by ATR-FTIR spectroscopy. Systematic developments of hydroxyl and carbonyl bands were observed in PVC and WF-PVC spectra during irradiation. It is connected with photooxidation progress of macro-

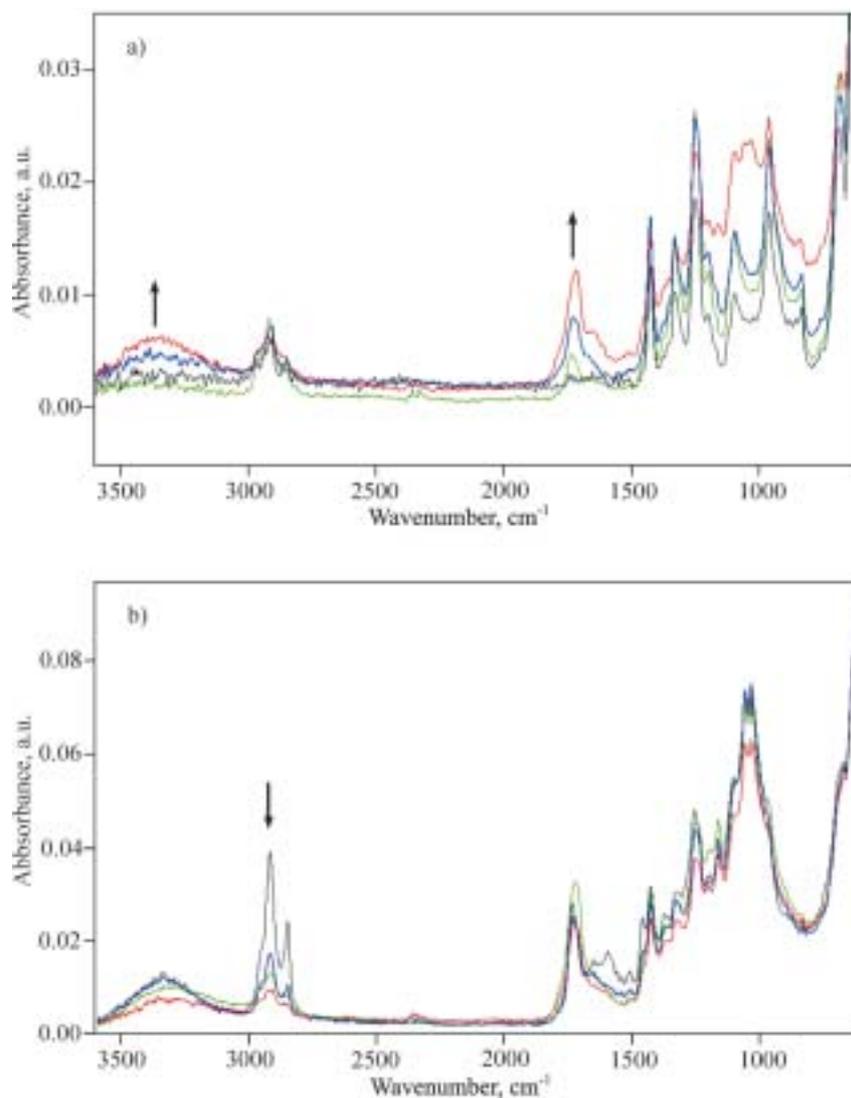


Fig. 2. Effect of UV-irradiation time (0—8 h, arrows indicate the change direction) on ATR-FTIR spectra of: a) PVC, b) WF-PVC composite

molecules. Photooxidation seems to be accompanied with main chain scission because a drop of the height of the band assigned to C-H stretching vibration was found. However, other chemical transformations are also responsible for changes in stretching vibration region. For example, well known and important photochemical reaction in PVC, besides of oxidation and chain breaking, is dehydrochlorination. The band at about 1640 cm^{-1} due to vinyl groups is also observed in recorded spectra and is an evidence of the presence of double bonds. This band partially overlaps a carbonyl band. Example spectra of PVC and WF-PVC composite are shown in Figure 2.

The WF spectrum exhibits the bands typical for cellulose, what is the main component of wood fibers. On the base of ATR-FTIR spectra of UV-irradiated samples we can notice that photooxidation of wood fibers leads mainly to formation of carbonyl groups (significant increase in C=O band absorbance), while the changes in the amount of hydroxyl groups are negligible.

In WF-PVC composite spectrum, the absorbance changes were very irregular, which indicates that the competitive reactions occurred in this case. Generally, the decrease in total amount of OH and C=O has been observed and the fastest changes in this sample were found during first hour of exposure to UV.

Prolongation of irradiation leads to very small changes in both carbonyl and hydroxyl bands in spectrum of WF-PVC blend comparing to origin PVC exposed at the same conditions.

The integral intensities (I) of hydroxyl/hydroperoxide ($3040\text{--}3710\text{ cm}^{-1}$) and complex carbonyl/vinyl ($1520\text{--}1840\text{ cm}^{-1}$) bands were calculated from the spectra of the composite (as the surface area of absorption band) and compared to suitable values obtained for PVC and WF themselves. For comparison of the irradiation effect on PVC, WF and WF-PVC samples, the relative changes of ΔI were obtained according to the formula:

$$\Delta I = \frac{I_t - I_0}{I_0} \quad (1)$$

where: I_0 — integral intensity of the band of unexposed sample, I_t — integral intensity after irradiation time t .

Table 1. Relative changes of OH and C=O groups' amount (ΔI) in WF, PVC and WF-PVC composite calculated on the base of ATR-FTIR spectra according to eq. (1)

Irradiation time, h	ΔI (OH)			ΔI (C=O)		
	WF	PVC	WF-PVC	WF	PVC	WF-PVC
1	0.02	19.8	-0.76	0.67	6.22	-0.49
2	-0.17	22.9	-0.12	0.94	7.44	-0.06
4	0.16	69.8	-0.06	1.54	15.02	0.18
6	0.25	57.4	-0.67	2.02	14.75	-0.45
8	0.17	74.4	-0.22	2.23	19.89	0.31
10	0.51	70.0	-0.07	3.01	18.64	0.40
12	0.41	104.9	-0.84	2.17	22.33	-0.41

The results are listed in Table 1. Observed changes clearly indicate that pure PVC is very sensitive to photo-oxidative degradation, whereas pure WF and WF-PVC composite are much more resistant to UV-irradiation — the changes of total amount of oxidized groups (OH/OOH, C=O/C=C) are very low in these samples.

CONCLUSIONS

Melt blending and extrusion of wood fibers with PVC (60/40) leads to formation of thermoplastic com-

posite characterizing by good dispersion of a filler in PVC matrix, what was studied by SEM. The dense, compact structure of WF-PVC composite allows to predict good mechanical properties and good water resistance of this material.

ATR-FTIR spectroscopy was very useful for monitoring the course of photochemical reactions in samples studied. It was found that the obtained composites were more resistant to UV-irradiation comparing to origin PVC, which was an advantage in case of exterior applications.

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