

Surface Properties of Poly(vinyl alcohol) with Iron(III)chloride Before and After UV-Irradiation

Jolanta Kowalonek, Halina Kaczmarek,* Dagmara Bajer

Summary: Surface properties of poly(vinyl alcohol) (PVA) with low content of FeCl_3 (1, 5 wt.%) were studied by measurements of contact angles and atomic force microscopy. The results of contact angles and the surface free energy calculations revealed that the hydrophilicity of the surface of PVA films depended on the content of iron (III) chloride in these polymeric films. Introduced salt also affected photochemical reactions in poly(vinyl alcohol). Photooxidation of PVA was more effective in the presence of FeCl_3 because of formation of reactive chlorine atoms, which were capable of initiating new reactions. Also the morphology and roughness parameters of PVA film changed when iron (III) chloride was added.

Keywords: AFM; contact angle; iron(III)chloride; photochemistry; poly(vinyl alcohol)

Introduction

Surface structure of polymeric films and its properties differ from structure and properties in polymer bulk. Surface of the sample is the most outer layer which is exposed to treatment of various chemical and physical factors, like UV-light. Photochemical reactions caused by UV-irradiation begin on the surface at first. The course of photodegradation of pure polymers is known,^[1,2] but it is difficult to predict the course of photodegradation in polymers containing additives such as metal salts.

Films of poly(vinyl alcohol) (PVA) containing iron (III) chloride were studied by some scientists but not from photodegradative point of view.^[3–5] Structural, electrical, magnetic or optical properties of doped poly(vinyl alcohol) were investigated.^[3–5] PVA films containing Fe^{3+} ions showed higher electrical conductivity in comparison to pure PVA films.^[3] Moreover, γ -irradiation caused an increase in electrical conductivity of doped PVA films due to the release of ions, electrons and

free radicals, which were able to move in polymer matrix and enhance electrical conductivity. Addition of iron (III) chloride to poly(vinyl alcohol) changed the structure, electrical, magnetic and optical properties of PVA film significantly.^[3–5]

The purpose of the work was to study the influence of low content of iron (III) chloride on surface properties of poly(vinyl alcohol) films before and after UV-irradiation.

Materials and Methods

Poly(vinyl alcohol) (PVA) 87–90% hydrolyzed with mol. wt. 30,000–70,000 and iron (III) chloride reagent grade, 97%, were purchased from Sigma-Aldrich.

Thin polymeric films of poly(vinyl alcohol) with different content of FeCl_3 (1, 5 wt.%) were prepared by casting from water solutions onto levelled microscope slides and evaporation of solvent.

Samples were exposed to UV-irradiation with a low-pressure mercury vapour lamp (TUV 30W, Philips, Holland) in air atmosphere. The intensity of the incident light, measured by HD 9021 Radiometer (Delta OHM, Italy), was 19.5 W/m^2 . Different times of irradiation were applied.

Faculty of Chemistry, Nicolaus Copernicus University, Gagarin 7, 87-100 Toruń, Poland
E-mail: halina@chem.uni.torun.pl

The measurements of contact angle, by the sessile drop method, were carried out at room temperature using the DSA10 goniometer of Krüss GmbH (Germany). Glycerol (polar liquid) and diiodomethane (non-polar liquid) were used as the test liquids. The liquid drop was placed onto the polymer surface with a microsyringe. The drop image was recorded by a video camera and digitalized. The profile of a single drop was numerically solved and fitted by means of mathematical functions. Each contact angle is the average value of 6–8 measurements and the deviation from the average is within $\pm 2^\circ$. On the basis of measurements of contact angles the surface free energy and its components (polar and dispersive) were calculated by Owens-Wendt method.

AFM imaging in tapping mode and in ambient conditions was done using Multi-Mode NanoScope IIIa, Veeco Metrology Inc. (USA). Commercial silicon tips with spring constant 2–10 N/m were used. The roughness parameters such as arithmetic mean (R_a) and root mean square (R_q) were calculated for scanned area ($10\ \mu\text{m} \times 10\ \mu\text{m}$) using Nanoscope software. The AFM pictures and roughness calculations were obtained for different sample places and the most typical areas are presented.

Results and Discussion

Table 1 shows the values of glycerol and diiodomethane contact angles of poly(vinyl alcohol) and of this polymer with 1% of FeCl_3 or 5% of FeCl_3 . Before UV-irradiation the surfaces of studied polymeric films were rather hydrophobic as the values of glycerol contact angles were higher than the values of diiodomethane contact angles. Glycerol interacts with surface by polar forces, i.e. dipole – dipole, dipole – induced dipole, hydrogen bonding interactions, but diiodomethane interacts with surface by dispersion forces.^[6–9] The lowest value of glycerol contact angle is found for PVA + 1% FeCl_3 , which suggests that this surface is the most hydrophilic. The highest value of glycerol contact angle is for PVA + 5% FeCl_3 and it is the most hydrophobic surface. As it can be seen, the addition of 1% of FeCl_3 into PVA makes the surface of this polymer more hydrophilic, but addition of 5% of FeCl_3 makes this polymeric surface hydrophobic. Probably hydrophilic groups of PVA such as hydroxyl groups come out on the surface when 1% of FeCl_3 is added. When the content of iron (III) chloride is higher the hydrophilic groups are below the surface. Possible interactions between OH groups of PVA and iron (III) chloride

Table 1.

The values of glycerol and diiodomethane contact angles of PVA, PVA + 1% FeCl_3 and PVA + 5% FeCl_3 before and after UV-irradiation.

Sample	Time of UV-irradiation (h)	Contact angle (deg)	
		Glycerol	Diiodomethane
PVA	0	68.4	54.3
	5	61.0	53.7
	10	70.2	45.7
	15	68.3	48.4
	20	61.7	51.0
PVA + 1% FeCl_3	0	62.7	57.5
	5	64.1	44.9
	10	59.3	47.6
	15	61.5	51.6
	20	51.5	50.4
PVA + 5% FeCl_3	0	86.5	56.5
	5	54.5	46.8
	10	55.1	48.4
	15	54.3	50.1
	20	44.4	43.8

as well as the distribution of FeCl_3 in poly(vinyl alcohol) film depend on the content of this salt.^[3,4]

After UV-irradiation glycerol contact angles decrease (Table 1), especially in the case of PVA + 5% FeCl_3 , which indicates the formation of new products containing hydrophilic groups. Iron (III) chloride facilitates the photooxidation of PVA, especially higher content of FeCl_3 favours the formation of oxidized groups on the sample surface.

More detailed information can be obtained by analysing the surface free energy and its components (Table 2). Before UV-irradiation the differences in values of surface free energy are not large for all studied samples. The values of dispersive component are much higher than these of polar component, which indicates predominantly hydrophobic properties of the surfaces. The value of polar component is the lowest for PVA with 5% of FeCl_3 , which indicates rather hydrophobic character of this surface. The highest value of polar component is characteristic of PVA with 1% of FeCl_3 , which means that this surface possesses some polarity.

After UV-irradiation surface free energy and its polar component increase in all samples, the most in PVA with 5% of FeCl_3 , the least in pure PVA, which

indicates that the new polar groups appear on the surfaces of studied samples. Thus, the presence of iron (III) chloride makes the photooxidation process easier. The dispersive component of surface free energy does not change significantly, especially in the case of PVA with 5% of FeCl_3 , which suggests that the dispersion interactions do not change substantially after irradiation.

Figure 1 shows AFM images of studied sample surfaces. Before UV-irradiation all surfaces were very flat, especially these with iron (III) chloride. In this figure it is seen that the surface of pure PVA is slightly more folded than the surfaces of PVA with iron (III) chloride, which indicates that added salt caused smoothing the sample surfaces. The values of roughness parameters of these samples (Table 3) were very low before irradiation. Slightly higher values of these parameters are characteristic of pure poly(vinyl alcohol).

After U-irradiation surfaces of studied samples changed significantly - holes and hills appeared, which is seen in AFM images in the Fig. 1. However, roughness parameters (R_a , R_q) increased insignificantly (Table 3). Such changes in sample surfaces may result from various photo-oxidation, photodegradation and photocrosslinking reactions occurring in poly(vinyl alcohol).

Table 2.

The values of surface free energy and its polar and dispersive components of PVA, PVA + 1% FeCl_3 and PVA + 5% FeCl_3 before and after UV-irradiation.

Sample	Time of UV-irradiation (h)	Surface free energy γ_s (mJ/m ²)	Polar component γ_s^p (mJ/m ²)	Dispersive component γ_s^d (mJ/m ²)
PVA	0	35.98	8.46	27.52
	5	39.23	12.43	26.79
	10	38.77	5.82	32.96
	15	38.25	7.20	31.05
	20	39.72	11.29	28.49
PVA + 1% FeCl_3	0	37.31	12.55	24.76
	5	40.96	8.54	32.42
	10	41.88	11.75	30.13
	15	39.66	11.55	28.11
	20	44.68	17.24	27.44
PVA + 5% FeCl_3	0	30.77	1.72	29.06
	5	44.22	14.32	29.90
	10	43.49	14.42	29.07
	15	43.39	15.41	27.98
	20	48.72	19.46	30.26

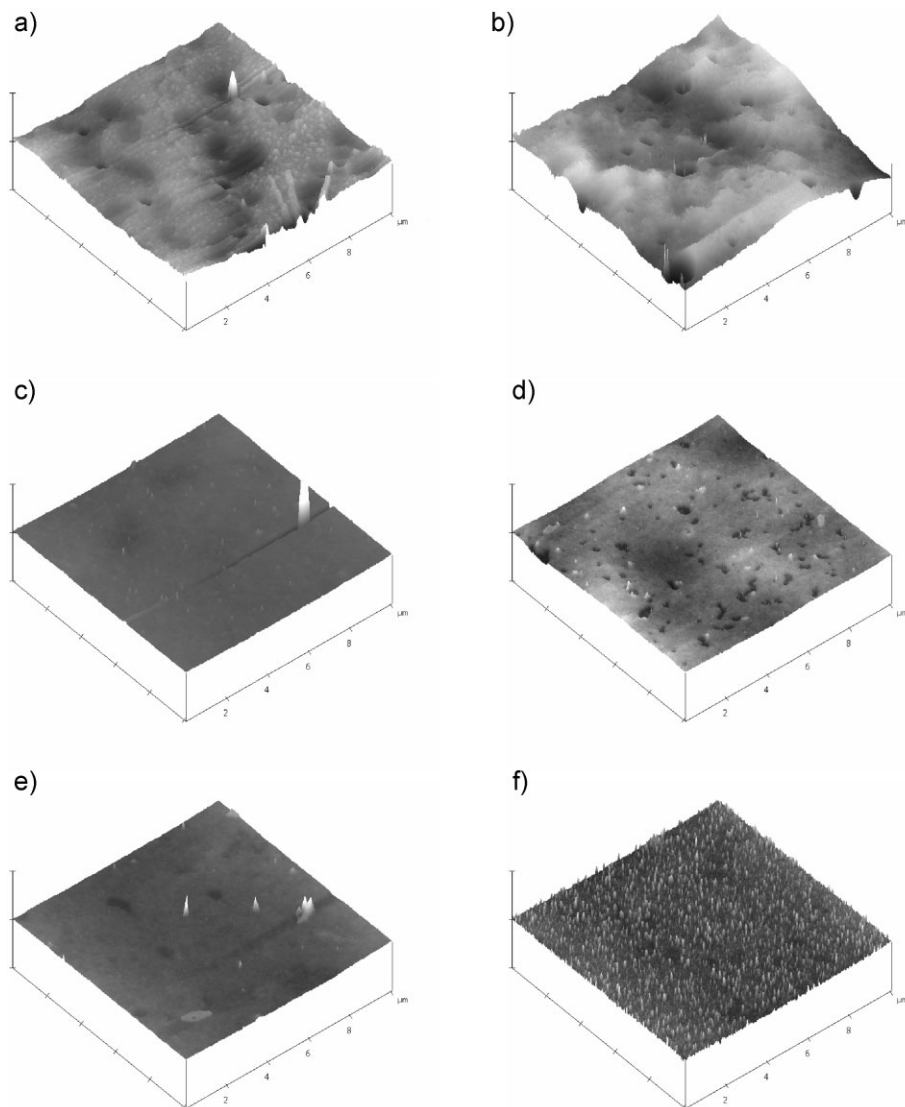


Figure 1.

The AFM images: (a) PVA before UV-irradiation, (b) PVA after 15h irradiation, (c) PVA + 1% FeCl_3 before UV-irradiation, (d) PVA + 1% FeCl_3 after 15h irradiation, (e) PVA + 5% FeCl_3 before UV-irradiation, (f) PVA + 5% FeCl_3 after 15h irradiation. Scan area $10\ \mu\text{m} \times 10\ \mu\text{m}$, z-scale 60 nm.

Varied radicals produced in poly(vinyl alcohol) because of UV-irradiation can react with oxygen from air forming alkoxy radicals and in consequence of this reaction new oxidized groups are formed.

More effective photooxidation reactions of PVA in the presence of FeCl_3 may be caused by reactive chlorine atoms which are formed as a result of photoreduction of iron (III) complexes according to the reaction:^[10,11]

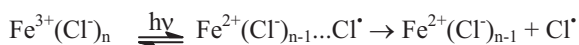
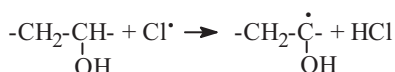


Table 3.

The values of roughness parameters (R_q , R_a) (nm) of PVA, PVA + 1% FeCl_3 and PVA + 5% FeCl_3 before and after UV-irradiation (R_q - root mean square R_a - arithmetic mean).

Sample	Time of UV-irradiation (h)	Roughness parameters (nm)	
		R_q	R_a
PVA	0	3.05	2.36
	15	4.28	3.34
PVA + 1% FeCl_3	0	1.60	0.94
	15	4.17	2.02
PVA + 5% FeCl_3	0	1.08	0.77
	15	2.01	1.43

These reactive chlorine atoms can react with polymer and produce new radicals:



The new polymeric radicals may take part in many various secondary reactions. Free radicals combine to form inactive compounds, including crosslinking structures, and to finish the photodegradation processes in polymer.

Conclusion

PVA with 5% of FeCl_3 has the most hydrophobic surface while PVA with 1% of FeCl_3 has the least hydrophobic surface among the studied samples, which means that the hydrophobicity of PVA surface depends on the quantity and the distribution of added FeCl_3 .

After UV-irradiation glycerol contact angles decrease and the surface free energy and its polar component increase, which indicates that new oxidized groups appear on the surfaces of the samples. The most significant rise in these values is in the case of PVA with 5% of FeCl_3 , the smallest changes of these values are found for pure PVA.

The surfaces of PVA and PVA with FeCl_3 are flat, they have very low values of roughness parameters. The surface of pure

PVA has slightly higher values of roughness parameters than surfaces of PVA with iron (III) chloride.

After UV-irradiation roughness parameters increases insignificantly in all samples as a result of photooxidative degradation of PVA.

Probably chlorine atoms which originated from iron (III) chloride are responsible for more effective photooxidation reactions in PVA containing iron (III) chloride.

- [1] J. F. Rabek, "Polymer Photodegradation, Mechanisms and Experimental Methods", Chapman & Hall, London 1995.
- [2] J. F. Rabek, "Mechanisms of Photophysical Processes and Photochemical reactions in Polymers", John Wiley & Sons, Chichester 1987.
- [3] G. V. Kumar, R. Chandramani, *Appl. Surf. Sci.* **2009**, 255, 7047.
- [4] A. Tawansi, A. El-Khodary, M. M. Abdelnaby, *Curr. Appl. Phys.* **2005**, 5, 572.
- [5] P. Obreja, D. Cristea, E. Budianu, R. Rebigan, V. Kuncser, M. Bulinski, G. Filoti, *Progress in Solid State Chemistry* **2006**, 34, 103.
- [6] A. Rudawska, E. Jacniacka, *International Journal of Adhesion and Adhesives* **2009**, 29, 451.
- [7] Ch.-S. Liao, Ch.-F. Wang, H.-Ch. Lin, H.-Y. Chou, F.-Ch. Chang, *J. Phys. Chem. C* **2008**, 112, 16189.
- [8] F. Chai, N. Mathis, N. Blanchemain, C. Meunier, H. F. Hildebrand, *Acta Biomaterialia* **2008**, 4, 1369.
- [9] E. Chibowski, K. Terpilowski, *J. Colloid Interface Sci.* **2008**, 319, 505.
- [10] J. F. Rabek, L. Å. Linden, H. Kaczmarek, B. J. Qu, W. F. Shi, *Polym. Degrad. Stab.* **1992**, 37, 33.
- [11] J. F. Rabek, J. Lucki, B. J. Qu, W. F. Shi, *Macromolecules* **1991**, 24, 836.