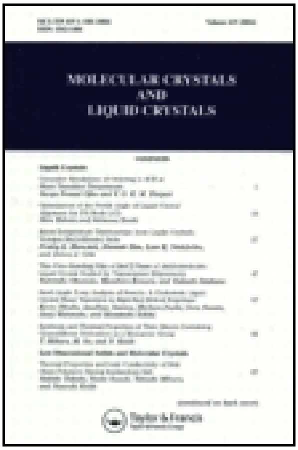
This article was downloaded by: [University of Haifa Library]
On: 09 August 2012, At: 14:14
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Influence of Modified Starch on Photostability and Adsorption Properties of Low Density Polyethylene Composite

M. Mucha [a] , S. Ludwiczak [a] & M. Kowalczyk [a]

[a] Faculty of Process and Environmental Engineering, Technical University of Lodz, Wolczanska Lodz, Poland

Version of record first published: 22 Sep 2010

To cite this article: M. Mucha, S. Ludwiczak & M. Kowalczyk (2008): Influence of Modified Starch on Photostability and Adsorption Properties of Low Density Polyethylene Composite, Molecular Crystals and Liquid Crystals, 484:1, 167/[533]-184/[550]

To link to this article: http://dx.doi.org/10.1080/15421400801904401

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

Mol. Cryst. Liq. Cryst., Vol. 484, pp. 167/[533]–184/[550], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801904401

Influence of Modified Starch on Photostability and Adsorption Properties of Low Density Polyethylene Composite

M. Mucha, S. Ludwiczak, and M. Kowalczyk
Faculty of Process and Environmental Engineering, Technical University of Lodz, Wolczanska Lodz, Poland

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

Materials used in the research are low density polyethylene (LDPE) pure and in the composites with glycerin-modified starch (S) of various content.

The aim of the present research was to specify the effect of UV radiation on a stability of the LDPE/S composite by analyzing FTIR spectra and discussing kinetics of photolysis.

It was found that the modified starch protected LDPE in the LDPE/S composites against UV radiation. A decrease of rate constant k of LDPE photodegradation was reported.

Results of water adsorption measurements of the composites are presented in the form of water adsorption kinetic curves and adsorption isotherms which were described well by the GAB model.

Keywords: kinetics of photolysis; LDPE/modified starch composites; photodegradation; water adsorption isotherms

INTRODUCTION

Polymer composites are an alternative to fully non-biodegradable plastics which constitute durable industrial wastes. Due to combining in one material the components that are resistant to biodegradation with easily biodegradable ones, e.g. natural polymers such as starch, cellulose or chitin or products of their modification, a material can be produced whose structure will be partly decomposed due to the action of biological agents and removed in the waste disposal environment,

---

Address correspondence to M. Mucha, Faculty of Process and Environmental Engineering, Technical University of Lodz, Wolczanska 213/215, 90-924 Lodz, Poland. E-mail: muchama@wipos.p.lodz.pl

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

while its external form will be destroyed permanently [1–3]. It is proposed [4] that the biodegradable component should be present in sufficient amount with exceeded percolation threshold, for starch equal to about 30% by volume [4]. It is needed for a microbial invasion or enzymatic diffusion.

The blending of biodegradable polymer such as starch with inert polymer as polyethylene has received a considerable attention for possible applications in waste disposal of polyethylene plastics. Over the last 30 years, starch-filled polyethylene plastics have been investigated mainly from the point of view of their morphological structure, mechanical properties and biodegradability by many researchers [5–12].

Although the incorporation of starch as an additive in synthetic plastic is highly attractive, the overall degradability of the final composite has been called into question. For example, outdoor weathering conditions are a multiaction mode of degradation where photooxidation due to the sun radiant energy in the presence of oxygen is very important. Irradiation treatment generates free radicals causing autooxidation. Some years ago Albertsson *et al.* [13,14] took into consideration thermo- and photodegradation of filled LDPE by measuring low molecular volatile products and change of molecular weight. They found, for example, that the presence of cornstarch in a LDPE/starch starch composite retarded the thermodegradation of PE.

Materials used in this research are low density polyethylene composites (LDPE) with glycerin-modified starch (S) of different composition.

The objective of this study was to compare the susceptibility of pure LDPE and LDPE mixed with modified starch to photodegradation. Characterization of the changes in the materials was carried out by changing of ATR-FTIR spectra.

Water sensitivity of the composites is another important criterion in many practical applications and biodegradability. The aim of our work was to get information on time dependence of the water uptake and to analyze isotherm curves of the water uptake.

EXPERIMENTAL

Materials

The composites in the form of films were obtained by melt extrusion and pressing of low density polyethylene (Malen E FABS, 23-D022) with a starch preparation (potato starch plastified with glycerin at

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

TABLE 1 Tested Samples with Various Weight Fractions of the Components w_f (no units)

Name	No.	LDPE	Starch	Glicerin
Polyethylene LDPE	1	1.00	–	–
	2	0.87	0.10	0.03
	3	0.73	0.20	0.07
Composite	4	0.60	0.30	0.10
LDPE/S	5	0.47	0.40	0.13
	6	0.40	0.45	0.15
	7	0.33	0.50	0.17
	8	0.27	0.55	0.18
	9	0.20	0.60	0.20
Modified starch	10	–	0.67	0.33

the weight ratio 3:1). After drying at $T = 100^\circ C$ the starch was plastified with glycerin at 120° for 2 h. Mixing LDPE with the modified S was performed in a laboratory extruder at $T = 160^\circ C$.

Films about 50 μm thick with different content of the starch preparation were obtained (Table 1). Figure 1 shows an example of the composite morphological structure.

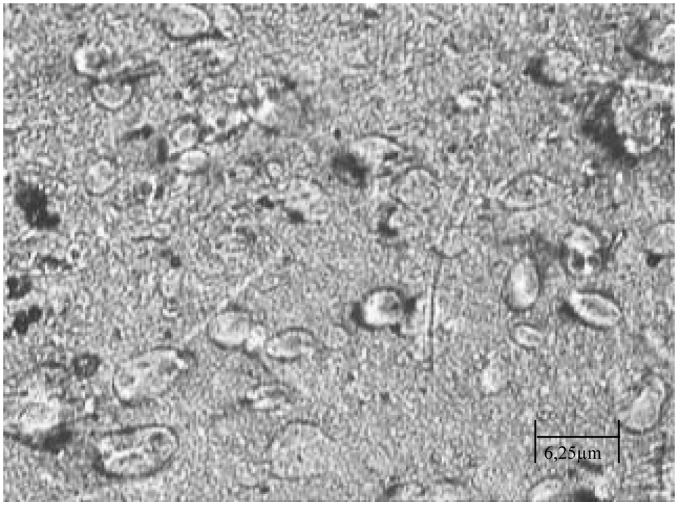


FIGURE 1 A microphotograph of sample No. 5.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

RESEARCH METHODS

Photodegradation

The samples were exposed to UV irradiation in the air, at room temperature at the distance of 4 cm from the radiator in time up to 440 h. For this purpose a LB-151.1 lamp emitting 90% UV radiation in the range $\lambda = 250–265\,\mathrm{nm}$ at radiation intensity $I_o = 700\mathrm{Lx}$ was used.

FTIR spectra at the 400–4000 cm^{-1} range were obtained using a Genesis II device (Mattson) by the reflection method (ATR).

Water Adsorption Study

Prior to adsorption measurement, the PE/modified starch composites were dried at the temperature 100°C for 60 minutes to constant mass. Next, they were placed in desiccators with saturated solutions of salts at different air relative humidity (water activity). From time to time the samples were withdrawn and their masses were determined on an analytical balance. The measurements were taken until constant equilibrium mass m_e was established. This time was about 4 hours. Moisture content in the sample X was calculated according to the formula: $X = (m_t - m_s)/m_s$, where: m_t – sample mass changing during the adsorption process; m_s – sample (dry) mass before adsorption.

Adsorption isotherms representing the dependence of equilibrium moisture content X_∞ on water activity a_w were obtained for composites with different content of PE.

RESULTS AND DISCUSSION

Photodegradation

Photolysis with UV light generate radicals that often lead to cleavage of polymer chain. Oxidation also occurs since exposure to light is in the presence of oxygen. The formation of carbonyl or ester groups is observed.

The changes in FTIR absorption spectra of LDPE/S films during photodegradation were observed. The FTIR band intensity represents the total concentration of various functional groups in a polymer (Table 2).

The following Figures 2 and 3 show chosen characteristic FTIR absorption bands in respect to $-CH_2$ groups vibrating at 2848 (symmetric stretching), 2915 (asymmetric stretching) and 719, 729 cm^{-1} (deformational swinging) changing with time of UV radiation due to destruction of the groups.

TABLE 2 Wave Numbers of Functional Groups for FTIR

No.	Wave number υ [cm^{-1}]	Group
1	2915	Asymetric stretching vibrations of $-CH_2-$ group
2	2848	Symetric stretching vibrations of $-CH_2-$ group
3	1471,1463	Deformational scission vibration of $-CH_2-$
4	1370	Deformational scission vibration of CH_3-(weak)
5	1350–1150	Fanning deformational vibration of $-CH_3-$ group (weak)
6	729,719	Swinging deformational vibration of $-CH_2-$ group

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

Figure 4 shows intensity of absorbance bands at various wave numbers $1/\lambda$ versus time of irradiation t. They are presented for three chosen samples. Due to polyethylene oxidation an increasing intensity of absorbance band at 1715 cm^{-1} and 908 cm^{-1} (carbonyl group formation) is observed in Figure 5.

Looking on the drawings in Figures 4 and 5 the induction period of the PE destruction is clearly seen close to 160 hours. Basing on the changes of absorbance bands of LDPE functional groups, rate constants of the characteristic processes, leading to a destruction of methylene groups were determined.

It was assumed that photodegradation of the tested films in respect to characteristic group destruction proceeded according to the 1st order reaction [15] according to the following equation.

$$\ln\left(\frac{A_i}{A_0}\right) = -k \cdot t \qquad (1)$$

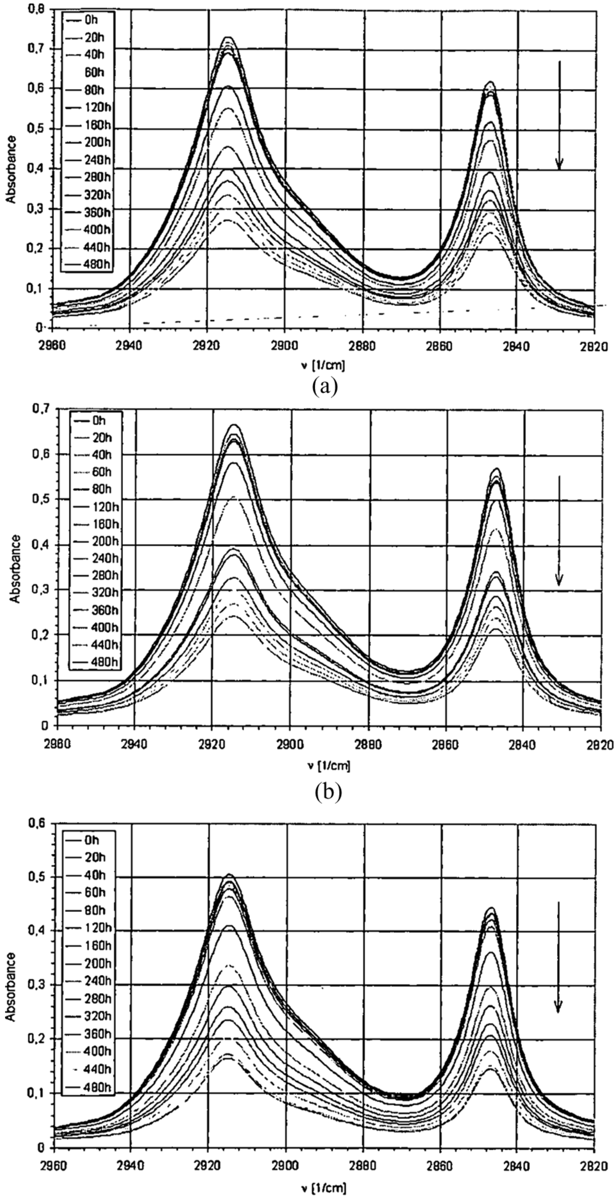
where A_i/A_o – relative change of intensity of absorbance band, k – rate constant. The value of k was determined by the approximation of experimental points in the system $\ln(A_i/A_o) = f(t)$, straight line – by the least squares method.

An example of the dependence of the logarithm of relative intensity of absorbance bands at 729 and 1471 cm^{-1} on photodegradation time taken for samples 1–4 is presented in Figure 6. Calculated rate constants of the first-order reaction are presented in Figure 7 for 3 chosen bands of the methylene group destruction.

Basing on the results it was found that addition of the modified starch protects LDPE against UV. With an increase of weight fraction of the modified starch in the LDPE/S composites, a decrease of rate constants k of LDPE photolysis (CH_2 destruction) is recognized.

Perhaps hydrogen bonded aromatic molecules of the modified starch can absorb UV photons and convert the photon energy into

Downloaded by [University of Haifa Library] at 14:14 09 August 2012



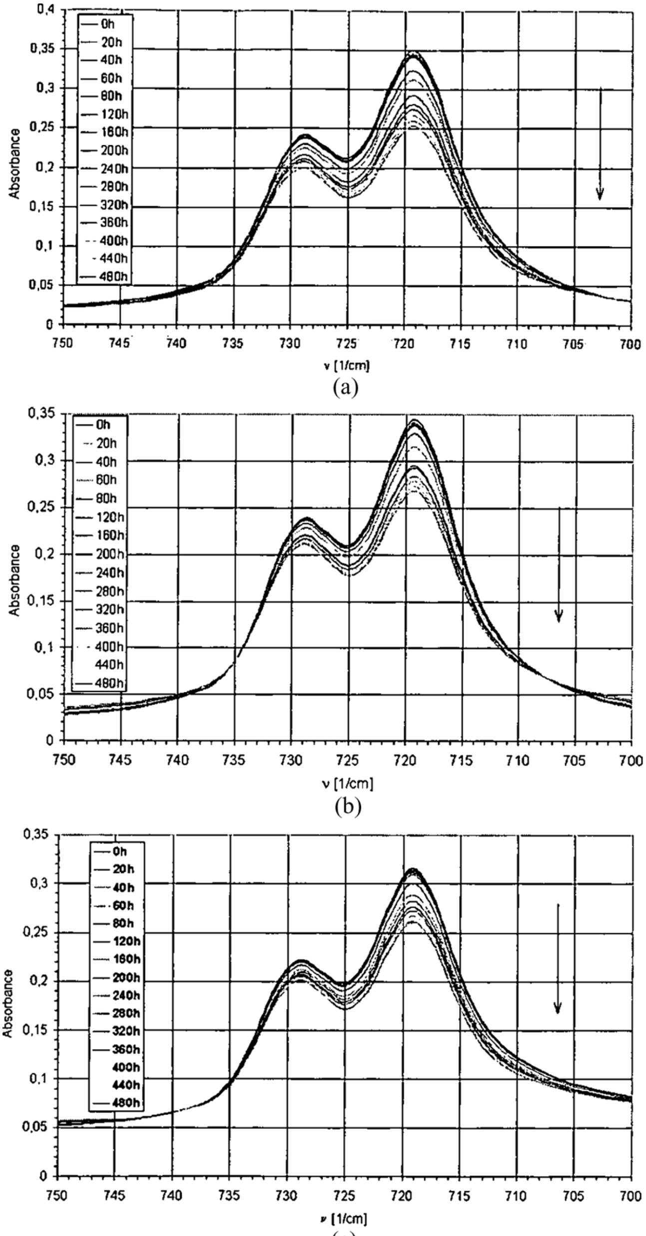
(a)

(b)

(c)

FIGURE 2 FTIR absorbance band at 2848 cm^{-1} and 2915 cm^{-1} changing with time of photodegradation: a) sample No. 1, b) sample No. 2, c) sample No 5.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012



(a)

(b)

(c)

FIGURE 3 FTIR absorbance band at 719 cm^{-1} and 729 cm^{-1} changing with time of photodegradation: a) sample No. 1, b) sample No. 2, c) sample No. 5.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

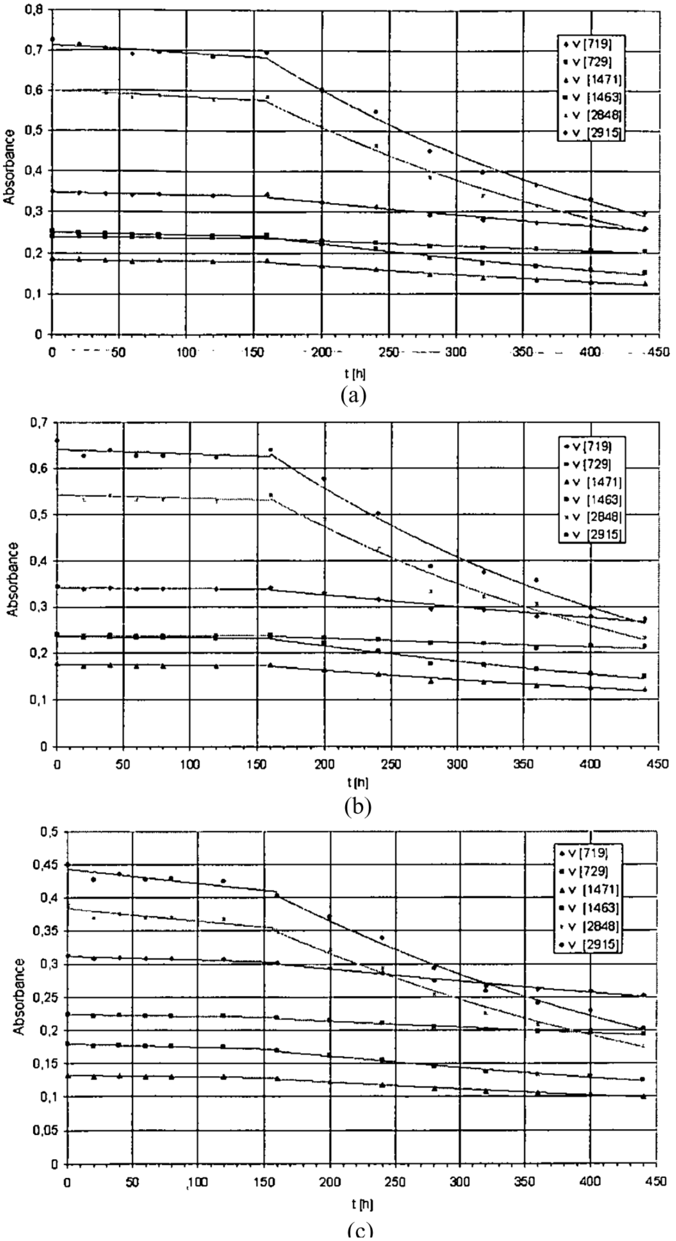
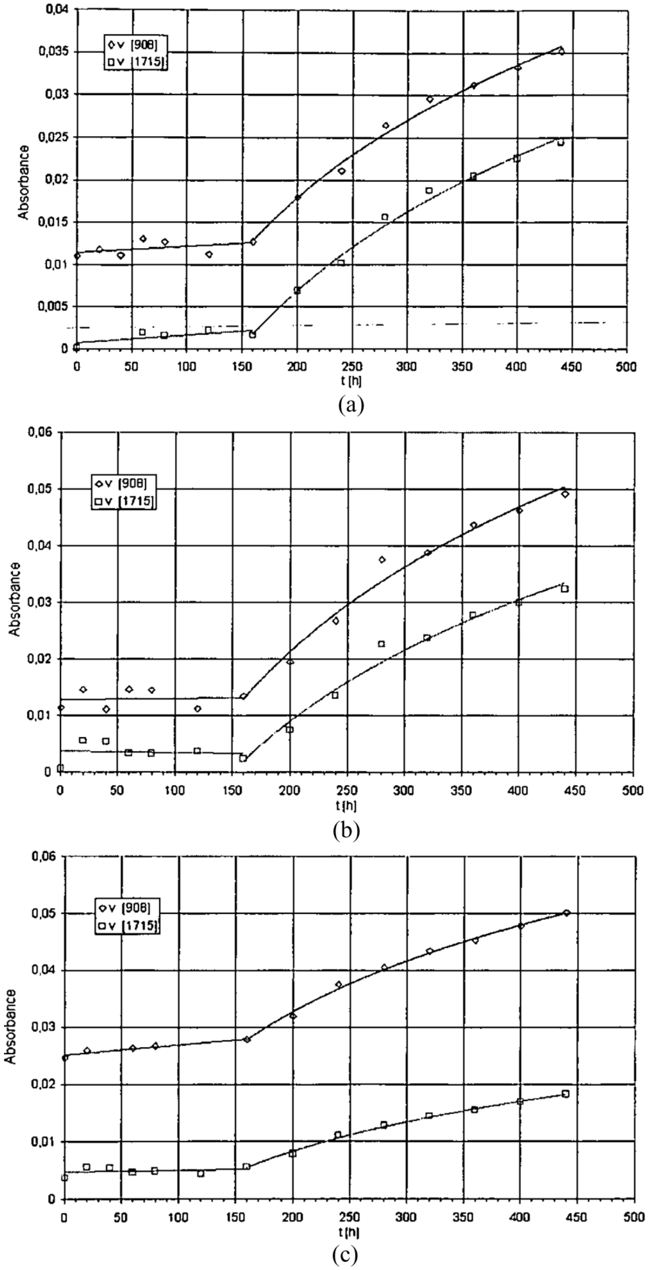


FIGURE 4 Intensity of the characteristic absorbance bands changing with time of photodegradation: a) sample No. 1, b) sample No. 2, c) sample No. 5.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012



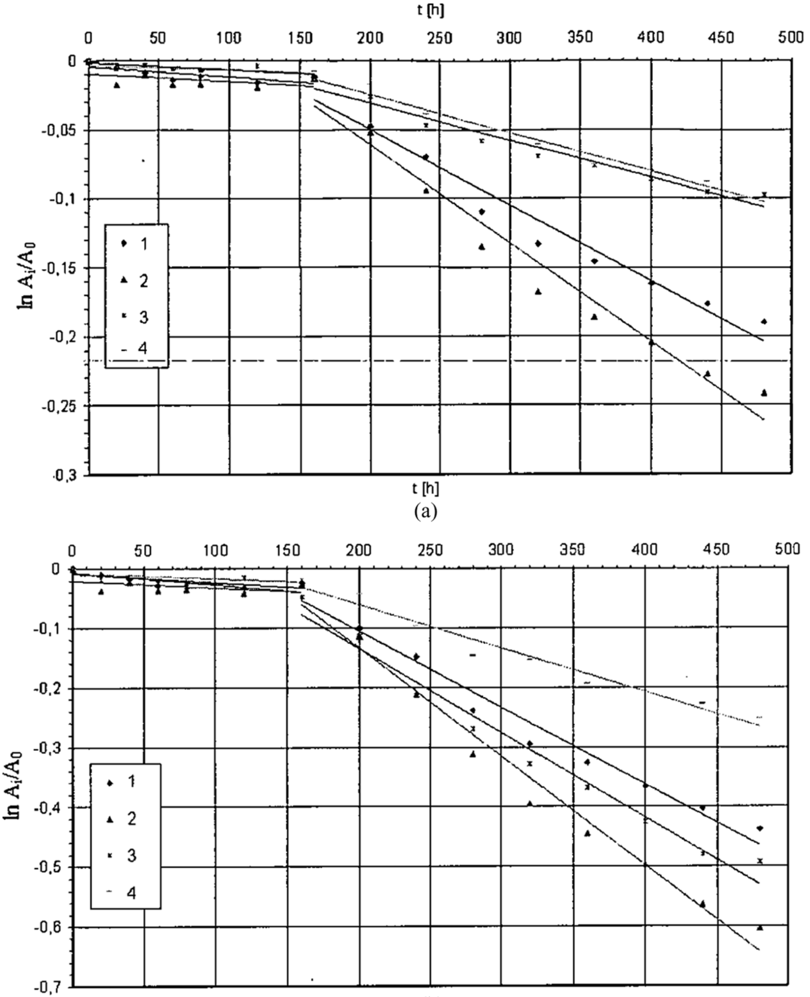
(a)

(b)

(c)

FIGURE 5 Intensity of absorbance bands of carbonyl at 1715 cm^{-1} and vinyl at 908 cm^{-1} groups versus time of photodegradation: a) sample No. 1, b) sample No. 2, c) sample No. 5.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012



(a)

(b)

FIGURE 6 Dependence of the logarithm of relative absorbance intensity of samples No. 1–4 on photodegradation time: a) at 729 cm^{-1} b) at 1471 cm^{-1} (CH_2 scissoring peak).

vibrational energy without undergoing destructive photochemical reactions in starch and polyethylene. The interesting concept of hydrogen band protection of living matter against UV irradiation was presented elsewhere [16].

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

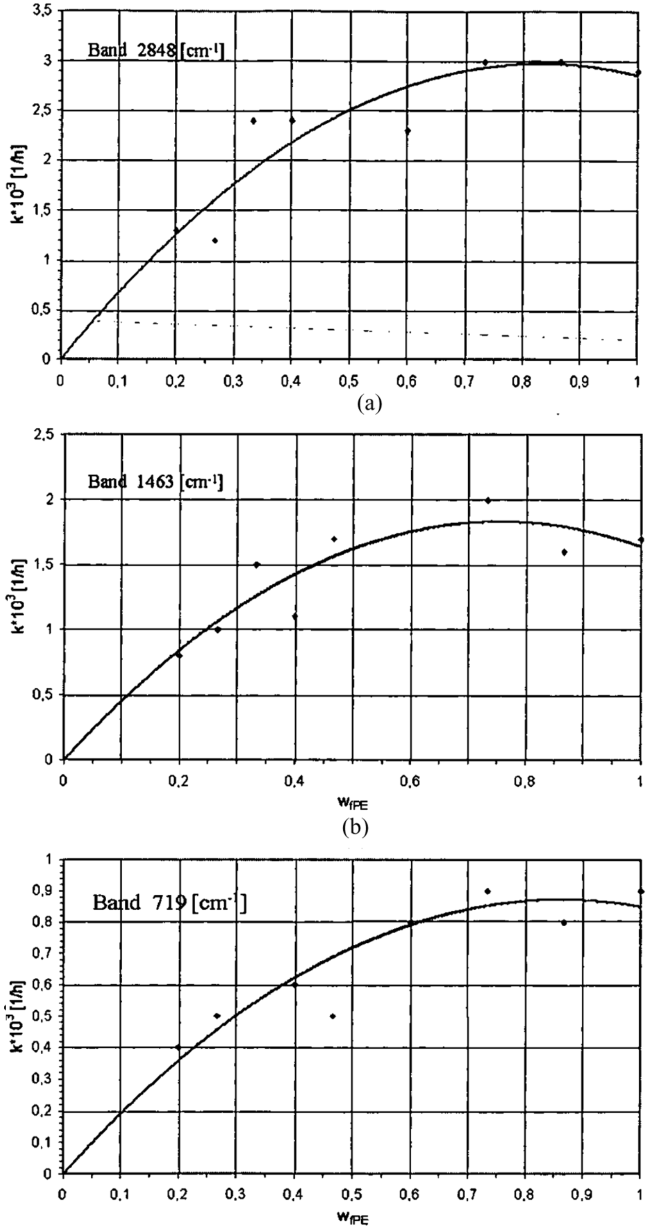


FIGURE 7 Rate constants k[1/h] of LDPE photodegradation vs. polyethylene weight fraction w_{fPE} in the composites: a) at $2848\,cm^{-1}$, b) at $1463\,cm^{-1}$, c) at $719\,cm^{-1}$.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

Water Adsorption

Starch-based materials are hydrophilic and they tend to absorb water molecules because the hydroxyl group in starch can form a hydrogen bond with water. Influence of the PE type on water absorption of PE/starch was shown in paper [17]. It was stated that the water absorption rate was lower in LDPE/starch blends than in HDPE/starch blends.

In the presented study the influence of polyethylene content on adsorption properties of the LDPE/S composite is determined. Our results on water uptake are presented in the form of water adsorption kinetic curves and adsorption isotherms.

Kinetic curves of water adsorption at $a_w = 0.765$ obtained for LDPE/S composites with various PE contents are shown in Figure 8a. Figure 8b shows the curves obtained for sample 4 at different water activities a_w.

The analysis of water adsorption results shows that the amount of water adsorbed by the composites depends on water activity and is directly proportional to the weight fraction of hydrophilic modified starch.

Based on the analysis of experimental curves of adsorption kinetics, effective diffusion coefficient D was determined using the second Fick's law for unidirectional diffusion (2):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{2}$$

where C – concentration, D – effective diffusion coefficient, t – time, x – distance

In the case of the initial stage of water diffusion, a simplified formula (3) can be assumed:

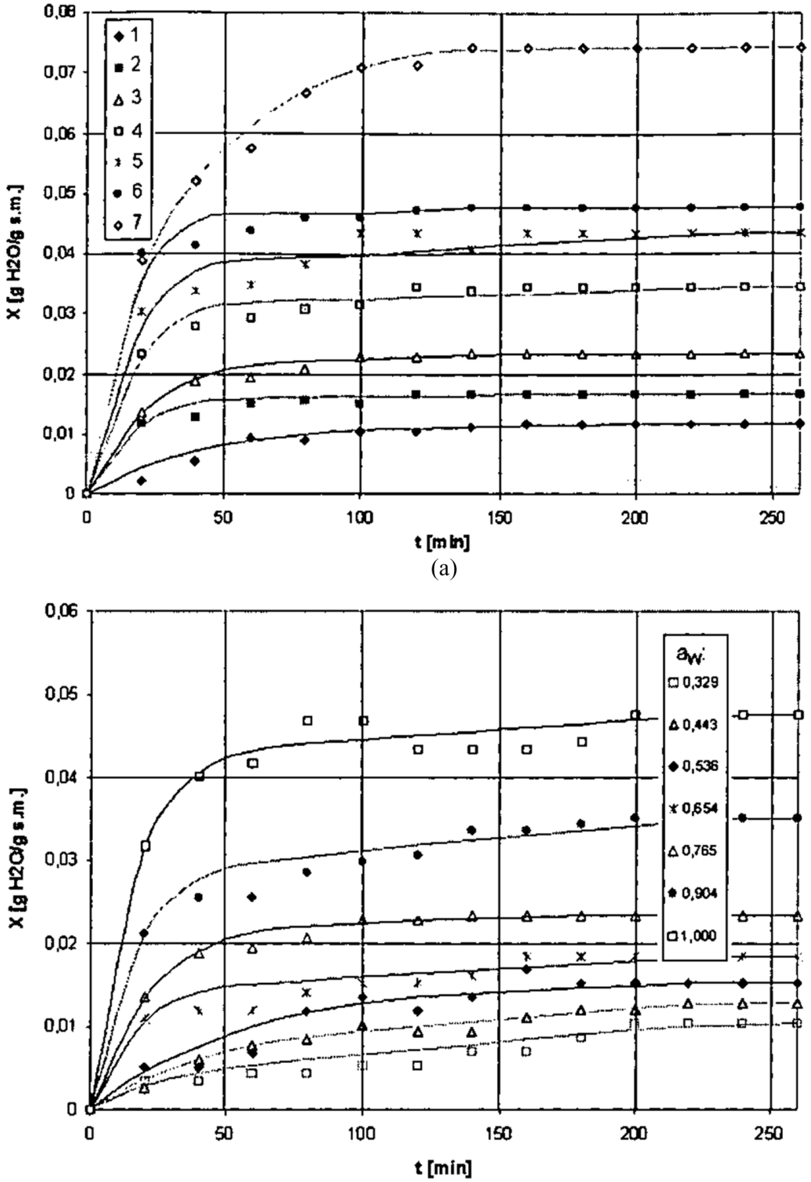
$$\frac{X}{X_\infty} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{3}$$

where L – sample thickness, t – time, X – moisture concentration in the sample in time t, X_∞ – maximum moisture content absorbed by the sample.

Basing on the relation: $X/X_\infty = f(t)^{1/2}$, effective diffusion coefficients were determined for the composites and their values were drawn as a function of polyethylene weight fraction w_{fPE} and water activity a_w (Fig. 9).

In the literature [18–20] there are many relations for a mathematical description of water adsorption isotherms by biological materials.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012



(a)

(b)

FIGURE 8 Kinetic curves of water adsorption (moisture content X versus time t) for LDPE/S composites: a) of various polyethylene contents (sample 1–7), b) of sample 4 at various water activities a_w.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

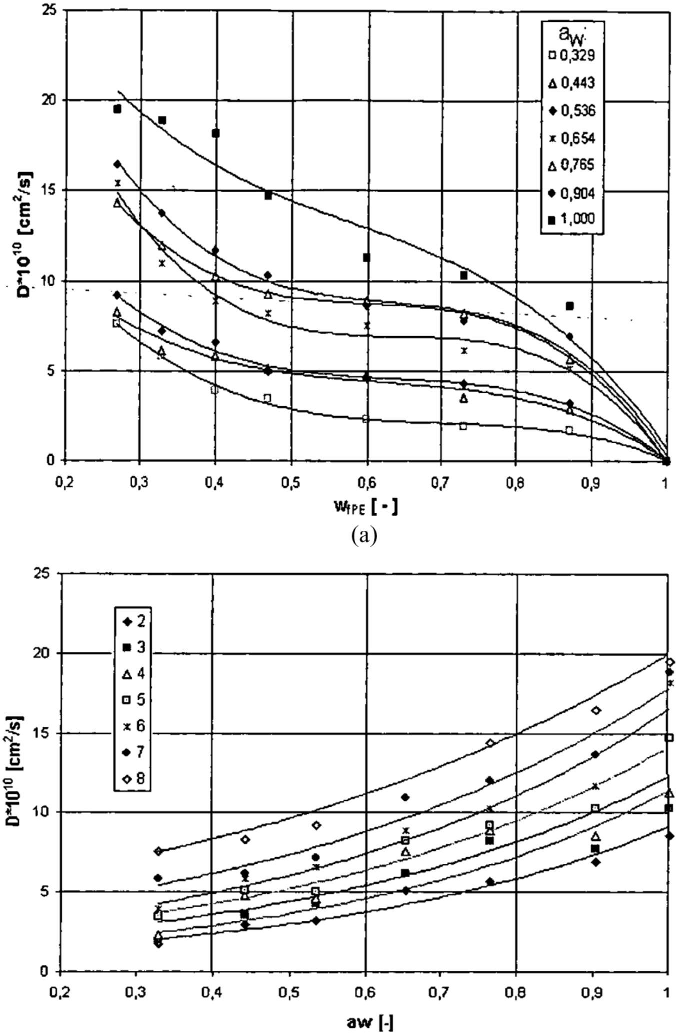


FIGURE 9 Dependence of effective diffusion coefficient D on: a) weight fraction w_{fPE} of polyethylene b) water activity a_w (samples No. 2–8).

The GAB model presented in Eq. (4) is used most often:

$$\frac{X}{X_m} = \frac{C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot [1 + (C - 1) \cdot K \cdot a_w]} \tag{4}$$

where X – moisture content in the sample; X_m – moisture content in the monomolecular layer; $a_w = p/p_s$ – water activity defined as the ratio of water pressure (p) to pressure over the tested sample (p_s) (relative humidity); $K = e^{d/RT}$ – parameter in the equation; d – energy needed to transport water to the inside of a multiparticle absorbent layer; C – parameter in the GAB equation related to the heat of adsorption; T – process temperature; R – gas constant.

The GAB equation is well applicable in the water activity range from 0.1 to 0.9. In the tested case the values of parameters K, X_m and C were determined.

Figure 10 shows water adsorption isotherms of the composites (points) along with isotherms describing them according to the GAB model (solid lines – Eq. (4)).

Parameters of the GAB equation (X_m, C, K) were determined by the iteration method in the Origin 7.0 program and presented in Figure 11 depending on the weight fraction of polyethylene-w_{fPE}.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

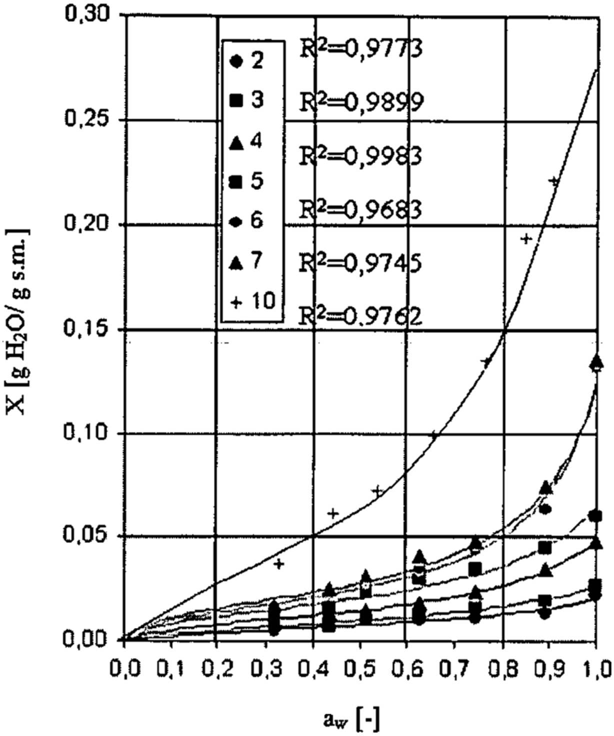


FIGURE 10 Water adsorption isotherms for LDPE/S composite (samples No. 2–7 and 10); points – experimental data, lines – GAB equation.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

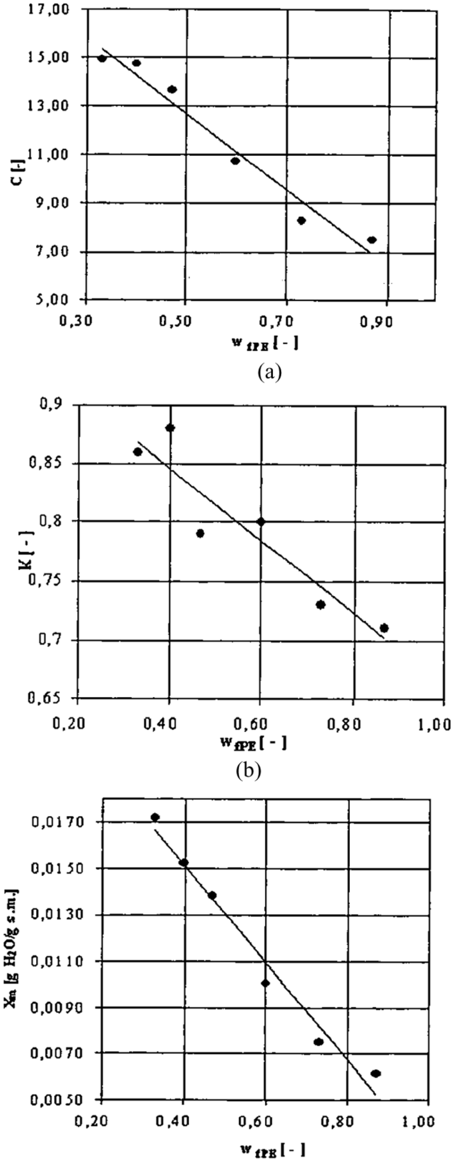


FIGURE 11 Dependence of C (a), K (b) and X_m (c) parameters (in the GAB equation) on polyethylene content in the composite w_{fPE}.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012

The analysis of the determined parameters in the GAB equation shows that parameter K changes a little and it ranges from 0.71 to 0.88. Both parameter C responsible for the heat of adsorption and parameter X_m which determined moisture content in the monomolecular layer, increase with the fraction of modified starch in the composite (a decrease of w_{fPE}).

The experimental data are well described by fitted curves obtained from GAB equation (4). The GAB equation can be easily applied in other polymeric systems [21].

CONCLUSIONS

- Pure starch is reported [22] to be sensitive to UV-light. However, no morphological change in the starch was noticed for LDPE/glycerin-modified starch samples up to 480 h of irradiation.
- Pure LDPE is less resistant to UV irradiation with the wavelength λ close to 257 nm than the polymer in the LDPE/s composites. The induction time of photolysis of LDPE and composites was observed as $t = 160\,h$.
- With an increase of modified starch content in the LDPE/S composite, a decrease of the analyzed kinetic constants k of LDPE photodegradation was observed. Addition of modified starch seems to have a protective action to LDPE in the LDPE/S composite.
- LDPE in the composite is also oxidized during photolysis in air. The band absorbance of carbonyl group >C=O appears and its intensity increases with time of photolysis.
- The LDPE/S composites have shown a controlled water uptake dependent on the starch content.
- Effective coefficients of water diffusion D decrease non-linearly with an increase of PE content.
- Water adsorption isotherms are well described by the GAB equation. Parameters of the equation C and X_m decrease linearly in the tested range of w_{fPE} growth.

REFERENCES

[1] Reis, R. L., Mendes, S. C., Cunha, A. M., & Bevis, M. J. (1997). *Polymer International*, *43*, 347.

[2] Żuchowska, D., Steller, R., & Meissner, W. (1998). *Polymer Degradation and Stability*, *60*, 471.

[3] Raghavan, D. (1995). *Polymer Technol. Eng.*, *34*, 41.

[4] Peanasky, J. S., Long, J. M., & Wool, R. P. (1991). *J. Polymer Sci. Polymer Phys. Ed.*, *29*, 565.

[5] Rodriguez-Gonzalez, F. J., Ramsay, B. A., & Favis, B. D. (2003). *Polymer*, *44*, 1517.

[6] Shujun, W., Jiugao, Y., & Jinglin, Y. (2006). *Journal of Polymers and the Environment*, *14*, 65.

[7] Matzions, P., Bikiaris, D., Kokkou, S., & Panayiotou, C. (2001). *J. Appl. Polym. Sci.*, *79*, 2548.

[8] Bikiaris, D., Prinos, J., Koutsopoulos, K., Vouroutzis, N., Pavlidou, E., Frangins, N., & Panayiotou, C. (1998). *Polym. Degrad. Stab.*, *59*, 287.

[9] Wang, S. J., Yu, J. G., & Yu, J. L. (2005). *Polym. Degrad. Stab.*, *87*, 395.

[10] Wool, R. P., Raghavan, D., Wagner, B. C., & Billieux, S. (2000). *J. Appl. Polymer Sci.*, *77*, 1643.

[11] Rodrigues-Gouxalez, F. J., Ramsay, B. A., & Favis, B. D. (2003). *Polymer*, *44*, 1517.

[12] Chandra, R. & Rustgi Renu. (1998). *Progress in Polymer Sci.*, *23*, 1273.

[13] Albertsson, A. C., Barenstedt, C., Karlsson, S., & Lindberg, T. (1998). *Polymer Degr. and Stabil.*, *61*, 329.

[14] Erlandsson, B., Karlsson, S., & Albertsson A. C. (1997). *Polymer Degr. and Stabil.*, *55*, 237.

[15] Rabek, J. F. (1996). *Photodegradation of Polymers*, Springer Verlag: Berlin Heidelberg.

[16] Sobolewski, A. L. & Domcke, W. (2006). *Europhysics News*, *37*, 20.

[17] Mani, R. & Bhattacharya, M. (1998). *Eur. Polym. J.*, *34*, 1467.

[18] Brunauer, S., Emmett, P. H., & Teller, E. (1938). *J. Amer. Chem. Sci.*, *60*, 309.

[19] Van der Berg, C. (1984). Engineering and foods. In: *Description of Water Activity of Foods for Engineering Purposes by Means of the GAB Model of Sorption*, McKenna, B. M. (Eds.), Elsevier: New York, Vol. 1, 311.

[20] Lewicki, P. P. (1997). *Int. Journal of Food Science and Technology*, *32*, 553.

[21] Mucha, M. & Ludwiczak, S. (2005). *Mol. Cryst. Liq. Cryst.*, *448*, 133.

[22] Tomasik, P. & Zaranyika, M. F. (1995). *Advances in Carbohydrate Chemistry and Biochemistry*, *51*, 243.

Downloaded by [University of Haifa Library] at 14:14 09 August 2012