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Degradation of a model dye with zinc phthalocyanine sulphonamide embedded in polymer matrices

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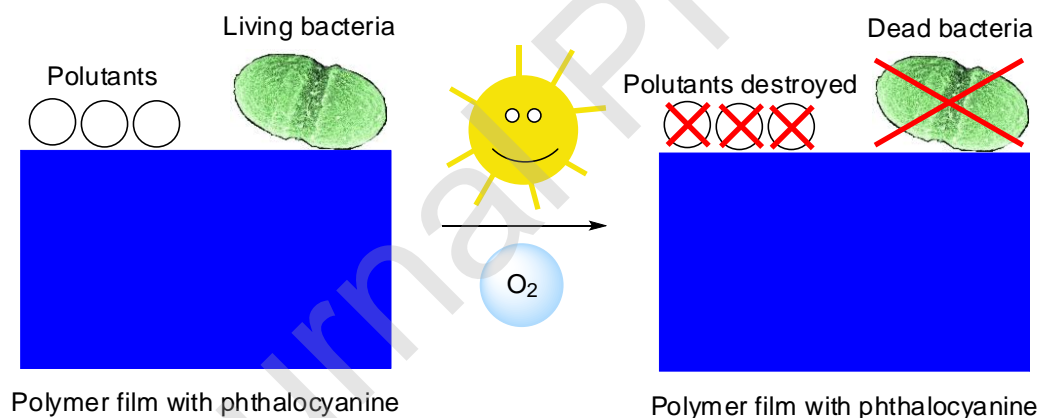
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Graphical abstract



Highlights

- Sulfamidic phthalocyanine was embedded in two polymer matrices
- Singlet oxygen production of the films was evaluated
- Clear effect of polymer film type on self-cleaning properties
- Polyethylene-vinyl acetate films have higher efficiency than polypropylene films
- Great potential for degradation of pollutants in the solid state

Abstract

Zinc phthalocyanine bearing aliphatic sulphonamide group was prepared and embedded in two polymer matrices (polypropylene, polyethylene-vinyl acetate), respectively. The composite films were evaluated for singlet oxygen production. Singlet oxygen production increased with increasing phthalocyanine concentration in both polymers. The degradation of a diketopyrrolopyrrole dye in thin layer doctor-bladed on the polymer films as well as antibacterial activity of the films were evaluated. It has been found that the polymer type had a crucial effect on the film properties. The degradation of the model dye in solid state was about four times faster with polyethylene-vinyl acetate film than polypropylene films. These films promise a broad potential for practical applications such as self-cleaning surfaces and antimicrobial protective films.

Keywords: Phthalocyanine; Dye degradation; Polypropylene; Polyethylene-vinyl acetate; Antibacterial activity.

1. Introduction

Phthalocyanines (Pcs) are aromatic compounds consisting of four isoindoline units connected with azomethine bridges, their structure was explained in 1934 [1]. Different metal ions can be easily incorporated into the central cavity of the phthalocyanine molecule. This modification has influence on their photoactivity. Some of the Pcs belong to the group of photosensitizers. Photosensitizers are compounds capable to generate singlet oxygen from air oxygen upon interaction with suitable light. The photosensitizing ability of Pcs depends mostly on the central ion and peripheral substitution. The most efficient photosensitizers are Zn, Si, Al, Ga, In and PbPcs. Singlet oxygen is a very reactive oxygen species which can primarily attack various chemical bonds, especially carbon-carbon double bonds, amino groups and sulphur atoms in

low oxidation states. Cycloaddition or oxidation reactions are typically observed [2]. This phenomenon has been used for study of degradation of various organic pollutants as described in a comprehensive review [3]. Among the tested pollutants and model compounds were phenols, thiols and various dyestuffs.

Initially, degradation studies were performed in solutions using soluble Pcs. The oxidative decomposition of chlorinated phenols and methyl orange was studied under basic conditions in water solutions containing sulfonated CoPc [4]. A similar ZnPc sulfonate was used for degradation of 4-chlorophenol by Kluson group [5-7]. Another studied group is represented by cationic ZnPc [8-11]. They are soluble in water and generally have high antimicrobial effect. However, for practical applications it is favourable to use a Pc bound to a suitable carrier, for instance to a polymer. The usage of polymer carrier has several advantages, e. g. simple manufacturing, effortless separation from solution, high surface area and prevention of leakage into the environment [3]. Polymer fibres of polyacrylic acid, polyurethane, polystyrene and polysulphone with incorporated Pcs of Zn and Lu were investigated for degradation of 4-chlorophenol, 4-nitrophenol and methyl orange [12-13]. Besides photosensitizers, also low photosensitizing FePc [14], CoPc and CuPc [15] were used. However, in this case, other source of reactive oxygen (most often H_2O_2) must be applied. The Pc serves here as a photocatalyst and the degradation mechanism is different [16]. Briefly, after excitation of Pc with light, an intramolecular electron transfer from the Pc ligand to central metal ion yields a Pc with reduced central ion. The reduced complex reacts with H_2O_2 and hydroxyl radicals are formed. Hydroxyl radicals then attack organic pollutant. Co and CuPcs bearing 2-decyn-1-oxy moieties were used for oxidation of substituted phenols in a mixture of hexane and acetonitrile (1:1) [15]. Similarly, rhodamine B was destroyed under influence of sulfonated FePc [16]. Nanofibers of poly-4-vinylpyridine/polyacrylonitrile modified with FePc were used for degradation of sulphonamide sulfaquinoxaline [17]. Immobilized CoPc on cellulose fibres was examined for degradation of

Acid Red 1 [18] or Green Acid 1 [19]. CoPc supported on melamine or Nafen [20] was used for oxidation of phenol. Polymeric Pcs of Cu, Co and Zn prepared by condensation of tetraamino Pcs with 1,4-benzenedialdehyde were evaluated in the case of degradation of organic pollutant rhodamine B [21]. Polymer-supported FePc with benzimidazolium was tested for degradation of methylene blue, methyl violet and Congo red [22].

As shown above, organic pollutants were decomposed in aqueous or organic solutions. However, no report dealing with degradation in the solid state has been found. For some applications such as self-cleaning surfaces, it would be necessary to confirm that the degradation occurs directly in the solid state. For this purpose, we prepared ZnPc bearing a long-chain sulphonamide group (ZnPc-OA). We selected a Zn phthalocyanine which is not soluble in water and should be easily incorporated in the polymer matrices. Moreover, this compound is easy to prepare in large scale. ZnPc-OA was embedded it in two widely commercially used polymers – polypropylene (PP) and polyethylene-vinyl acetate (EVA). PP and EVA belongs to the group of semi-crystalline thermoplastics and amorphous elastomer, respectively [23]. PP range in group of polyolefins and is one of the most widely used polymers in plastic industry because of its good comprehensive mechanical properties, outstanding temperature and chemical resistances, its low density and easy processing, as well as its low cost [24]. PP is used in a variety of applications including packaging for consumer products, plastic parts for various industries (e.g. automotive industry), textiles, etc. [25]. EVA polymer is produced in large quantity for use in emulsion paints, adhesive and textile finishing operations because of its good adhesion to a number of substrates [26]. Both PP and EVA are often coloured with different types of pigments during thermoplastic processing. From this reason, Pcs seems to be good alternative to get coloured products with added value. The films were prepared from ZnPc-OA modified polymers and were used for our study. Among the investigated properties were singlet oxygen production and degradation of a model colorant – a diketopyrrolopyrrole derivative

using fluorescence measurements. The antibacterial activity against Gram-positive and Gram-negative bacteria was also explored.

2. Experimental

2.1 Chemicals and equipment

1,3-diphenylisobenzofurane and oleylamine (technical grade) was purchased from Aldrich, USA. Solvents (methanol, ethanol, hexane) were supplied by Penta Chemicals (Czech Republic) and used as received. ZnPc was manufactured in our laboratory. Chlorosulphonic acid was provided by Merck, Czech Republic. Polypropylene (PP, Braskem C706) was provided by Resinex Czech Republic, ethylene-vinyl acetate copolymer (EVA, Greenflex FC45) by Fatra a.s. Microorganisms *Enterococcus faecalis* CCM 3956 (Gram-positive) and *Escherichia coli* CCM 4517 (Gram-negative) were obtained from Czech Collection of Microorganisms, Masaryk University, Czech Republic.

UV-VIS spectra were measured on a spectrophotometer SPECORD 200 PLUS. The spectra of Pcs in polymers were measured using reflective spectra with a solid sample holder. Fluorescence spectra were measured on a FluoroMate FS-2 (Scinco) fluorescence spectrometer with FluoromasterPlus software.

2.1.1 Preparation of ZnPc-OA

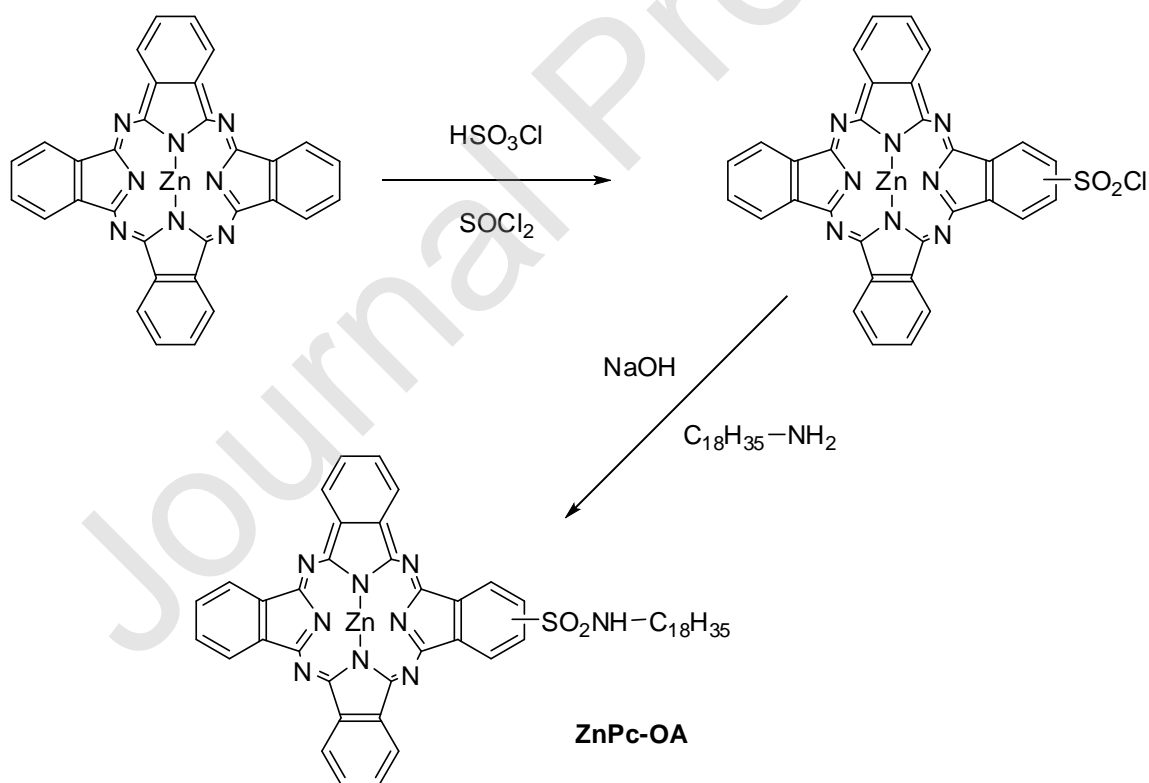
ZnPc-OA was prepared by a two-step process (Scheme 1).

280 ml of chlorosulphonic acid was placed in a 1.5L flask and cooled to 0-5 °C in an ice bath. 92 g (159 mmol) ZnPc was then added in several portions up to 20 °C and stirred for 1 h at 20 °C. Reaction mixture was then heated to 110 °C for 1 h, cooled to 100 °C, 58 ml SOCl₂ added dropwise and maintained at 100 °C for another hour. After cooling to 20 °C, it was dropped onto a mixture of water and ice. The precipitate was collected by filtration and the filter cake

washed several times with cold water until negative reaction to sulphates and chlorides. The resulting paste of Pc sulphochloride (Pc-SO₂Cl, 458 g) was put in a refrigerator. The paste was analysed for hydrolysable chlorine and dry mass at 80 °C.

Dry mass: 23.5 %, hydrolysable Cl (calculated to dry mass): 5.4 % (theoretical value for monoderivative 5.24 %).

6.4 g (23.9 mmol) oleylamine was dispersed in 80 ml water and acetic acid (33.5 ml) was added until dissolution. 57 g of frozen Pc-SO₂Cl paste well dispersed in 160 ml cold water was added, the reaction mixture (pH ~ 3) alkalized with 2.5M NaOH until pH reached 9 and stirred overnight. Then, it was heated at 60 °C for 2 h, cooled to about 25 °C and filtered. The filter cake was washed well with water to remove salts and dried at 60 °C. The yield was 17.2 g (95 %) of blue ZnPc-OA. ¹H NMR (CDCl₃, 500 MHz) δ: 7.8-10.3 m (Ar-H), 5.0-5.6 (3H, NH-CH₂), 1.1-3.3 (CH₂), 0.8-0.9 (CH₃).



Scheme 1: Synthetic route yielding ZnPc-OA

2,5-bis(2-ethylhexyl)-3,6-diphenyl-1*H*, 2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP) was prepared by a modification of the process published recently [27], using K₂CO₃/DMF instead of Cs₂CO₃/CH₃CN.

2.1.2 Preparation of polymer films

Polymer (PP Braskem C706 or EVA Greenflex FC45) was mixed with an appropriate amount of ZnPc-OA in a twin-screw compounder DSM Xplore with volume of grinding chamber of 15 mL. The mixture was blended at 100 rpm for 5 minutes at 190 °C for PP and 160 °C for EVA, respectively. Thin films of 0.5 mm were then press moulded from prepared mixtures using a manual vulcanizing press for 5 minutes at temperatures mentioned above. Films were prepared with the Pc content of 0, 0.1, 0.2, 0.5, 0.75 and 1.0 weight per cent. Photographs of the films with Pc are enclosed in the supplementary file (Fig. S1).

2.2 Singlet oxygen measurements

The singlet oxygen determination used the method published previously [28]. DMF was used as the solvent for ZnPc-OA and hexane for polymer films. The photobleaching of the indicator was monitored spectrometrically at a wavelength of 411 nm. Red laser light (MAESTRO CCM, 40 mW, $\lambda = 661$ nm) was used as the light source. Polymer films were cut to squares of 7 x 7 mm, one square put into a quartz cuvette and 2 mL of hexane were added. After stirring with a magnetic stirrer bar, 20 μ L of indicator 1,3-diphenylisobenzofurane (DPIBF) in hexane (concentrated fresh solution) was added and stirred for about 1 minute. The cuvette was then irradiated with laser light, doses used were 1-10 J/cm⁻². For every measurement, about 10 light doses were used, until the absorbance of the indicator decreased to approximately 0.2–0.3. Observed rate constants (k_{obs}) were estimated. The final rate constant k was calculated from equation $k = k_{obs} - k_{blank}$, where k_{blank} is a rate constant of the pure polymer in the presence of indicator.

2.3. Degradation of DPP

Solution of DPP in methanol (0.5 mL, 0.4 mg/mL) was applied by a doctor blade on the studied film (2 x 4 cm) and dried at 45 °C. The films were then irradiated by a Narva Red light tube (spectrum is shown in Fig. S2) with irradiance intensity in the range of 620-750 nm of 7 W/m². The samples were taken at regular intervals and decrease of fluorescence was measured by solid state fluorescence spectrophotometry (excitation: 440 nm, emission: 524 nm).

The degradation products were determined by high performance liquid chromatography (HPLC) measured using a Shimadzu model LC-20AD/T LPGE KIT on a LiChroCAR 250-4 LiChrospher 100 RP-18 (5µm) column and LiChroCART 4-4 Lichrospher 60 RP-select B (5µm) as a pre-column. The mobile phase contained 95 % A (methanol) and 5 % B (distilled water with few drops of concentrated ammonia). The determination was isocratic with 0.5 mL/min at 40 °C and the detection wavelength was 254 nm.

2.4 Antibacterial activity

The antibacterial activity of the films with Pc was evaluated according to the standard ISO 22196:2011 [29] with some modifications. The films were cut to squares of 2.5 x 2.5 cm and the cover polypropylene foil to 2 x 2 cm squares; both were disinfected by 70% ethanol before testing. Bacterial suspension (*E. faecalis* or *E. coli*) for testing of antimicrobial activity was prepared at concentration of 10⁵-10⁶ CFU/mL. After inoculation of bacterial suspension on polymer foils, the samples were covered with PP foil and half of the samples was incubated at 35 °C, 95 % RH for 18 h under illumination with a Narva D-65 (artificial daylight, 36W, Czech Republic) tube at 30 cm distance from samples. The second half of the samples was incubated under the same conditions in the dark, as specified by the standard. Then, the number of viable bacteria was determined by the dilution and spread plate technique.

2.5 Microscopic measurements

Microscopic photographs were taken using a Nikon Eclipse LV100D industrial microscope. Scanning electron microscopy (SEM) was performed on the Phenom Pro (Phenom-World BV, Netherlands) at an electron accelerating voltage of 5 kV. SEM examination was performed on cryo-fractured surfaces of neat PP and EVA films as well as films with 0.5 and 1.0 % of ZnPc-OA in order to evaluate the degree of homogeneity.

2.6 Contact angle measurements

Water contact angle (WCA) measurements were performed on an optical video contact angle instrument (Model OCA 40, Dataphysics, Germany) at room temperature. A 3 μ L droplet of water or diiodomethane (DIM) was utilized by the aforementioned sessile drop method. The evaluation of surface energy (σ) was done by See Software according to Owens – Wendt method [30]. The measurements were triplicated using different positions on the film. The deviation was calculated on basis of Dean-Dixon method [31].

3. Results and discussion

3.1 Characterization of Pc and Pc films

The Pc was prepared by a two-step process (chlorosulphonation and amidation) commonly adopted for sulphamidic Pcs which are employed in large scale in industry, for example as dyestuffs. These dyestuffs often represent complex mixtures of several isomers which are difficult to analyse properly. However, the number of isomers may be much reduced by optimization of reaction conditions. The chlorosulphonation was guided to yield Pc with prevalent one $-\text{SO}_2\text{Cl}$ group. The intermediate was characterized by dry mass and hydrolysable Cl content. The theoretical amount for Cl in $\text{ZnPc-SO}_2\text{Cl}$ is 5.24 %. The analysis showed the content as 5.4 % Cl which corresponds to ZnPc with 1.04 sulphonyl chloride groups. Subsequent reaction with an excess of oleylamine was started at acidic pH where possible

hydrolysis of Cl was fully suppressed. Under such conditions all sulphonyl chloride groups were converted to the corresponding sulphonamides. Thin layer chromatography of the ZnPc-OA in a mixture of propan-1-ol and ammonia (2:1, v/v) on silica gel (Merck, 40 mesh) shows <5 % of more polar disulphonamide. ^1H NMR in $\text{DMSO-}d_6$ provided a series of signals typical for a mixture of two monosulphonamides with the substituent in positions 1 or 2 at the Pc ring, respectively. Further purification of ZnPc-OA was not performed because it is not necessary for considered applications. The blue resulting ZnPc-OA is soluble in DMF, DMSO, THF, toluene, chloroform and insoluble in water or hexane.

The Pc was then incorporated into two polymers (EVA and PP) and films produced. The film colour is blue-green and the intensity increased with increasing Pc concentration (Fig. S1). EVA films have generally darker and uniform appearance on the contrary to PP films.

The UV-VIS spectrum of ZnPc-OA in THF (Fig. 1) shows three major peaks located at 348, 608 and 670 nm, respectively. The observed peaks are characteristic for the monomeric form of Pc. The molar absorption coefficients ϵ were calculated from the absorbance at 670 nm using Lambert-Beer law. Thickness of the film (0.05 cm) was used for solid state samples. Molar absorption coefficient ϵ of ZnPc-OA in THF at 670 nm is $116,670 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. A similar spectrum was found for EVA film with 0.1 % Pc with ϵ of $508,170 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The higher value of ϵ in EVA is caused by high absorbance of the thin film (0.5 mm versus 1 cm in cuvette). The spectrum of PP film with 0.1 % Pc changed significantly, the Q-band is shifted by 8 nm to 678 nm and is strongly reduced in intensity ($\epsilon = 82,470 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). This decrease of ϵ in PP is typical for aggregated form of Pc. It is apparent that Pc is well dispersed in EVA forming a solid solution. In PP, the Pc is present in larger particles.

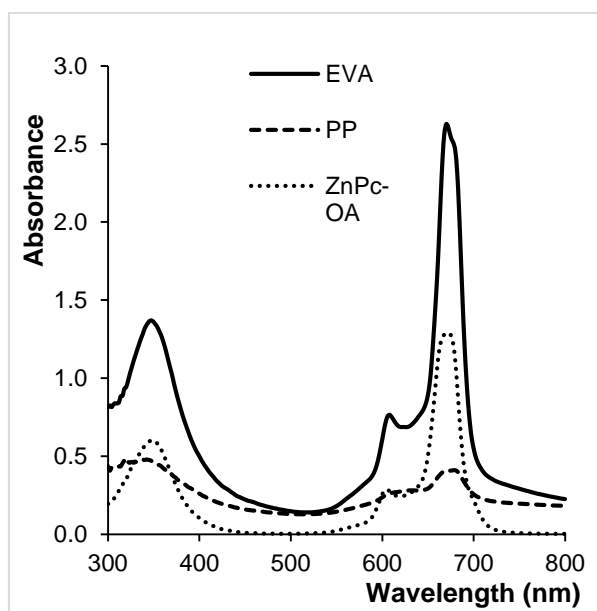


Fig. 1: Spectra of ZnPc-OA in THF (10 mg/L) and ZnPc-OA embedded in polymer films (PP or EVA) at 0.1 % concentration.

Additionally, microscopic photographs of films containing 1.0 % ZnPc-OA were taken (Fig. 2). In EVA polymer, no Pc aggregates with size in micrometres were detected. On the contrary, many Pc aggregates with size of 1-3 μm were found in PP. This is in accordance with UV-VIS spectra.

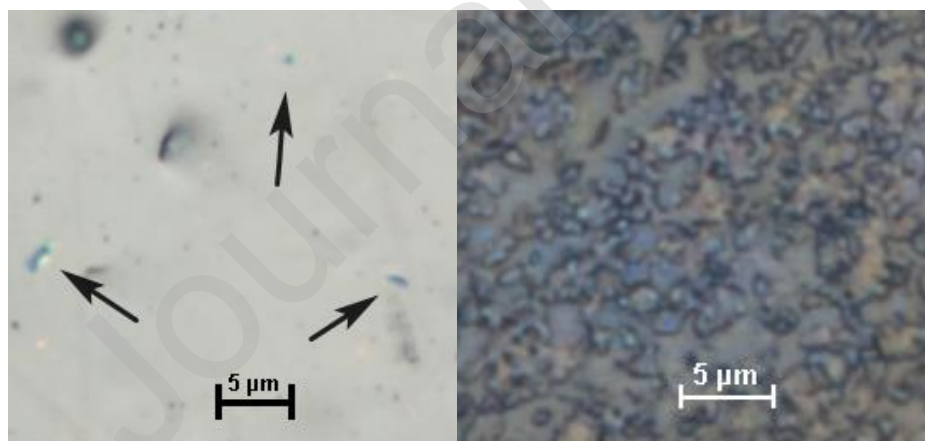


Fig. 2: Microphotography of films with 1.0 % ZnPc-OA (left – PP, right – EVA), the Pc aggregates are marked with arrows.

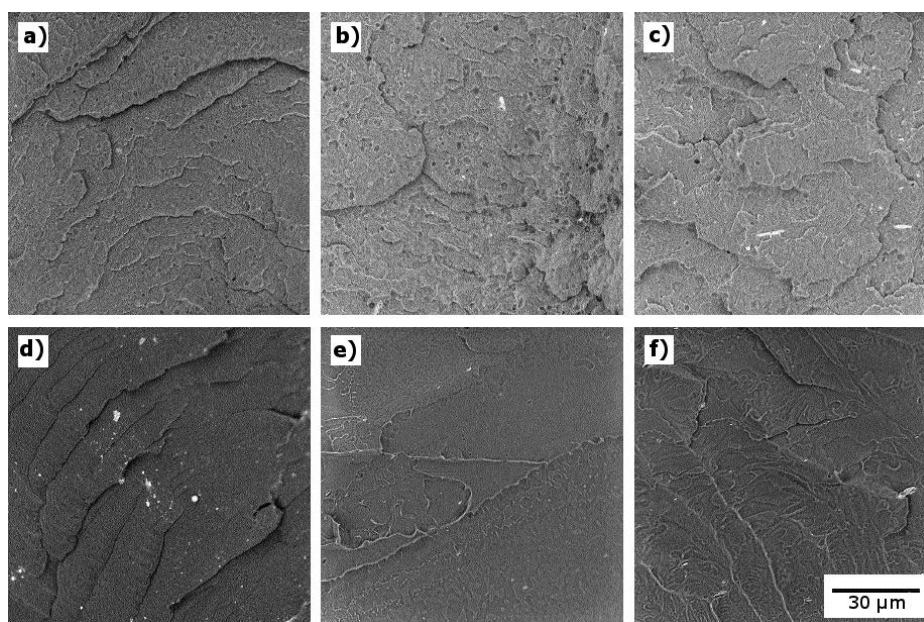


Fig. 3: SEM micrographs of a) neat PP, b) PP + 0.5 % ZnPc-OA, c) PP + 1.0 % ZnPc-OA, d) neat EVA, e) EVA + 0.5 % ZnPc-OA and f) EVA + 1.0 % ZnPc-OA

The Figure 3 shows cryo-fractured surfaces of prepared films with 0, 0.5 and 1.0 % ZnPc-OA, respectively. It can be seen that neat polymers (Fig. 3 a) and d)) contain small particles (showing as dark in PP and pale in EVA films, respectively). They are probably admixtures supplied by the plastic granulate manufacturer to improve thermoplastic processability. EVA matrices with incorporated ZnPc-OA report good homogeneity with no additional aggregates. In PP matrices, some pale particles appeared whose amount increases with increasing ZnPc-OA content. It is very likely that they represent phthalocyanine aggregates. Their size corresponds quite well with those observed on microphotography.

Contact angle is an important parameter showing how is the surface wetted. The results of measured contact angles as well as surface energy of the films are summarized in the Table 1. Contact angle for both polymers with water is about 85° which indicates good wettability and hydrophilicity of the films. The impact of ZnPc-OA on the surface properties of prepared films is minimal, the differences are within the error of determination by the chosen methods.

Table 1: WCA and surface energy of films

Film	DIM (°)	Water (°)	σ (mN/m)
PP	55.46 \pm 3.01	78.50 \pm 0.96	37.24
PP + 0.1 % ZnPc-OA	56.83 \pm 2.33	86.52 \pm 0.69	33.64
PP + 0.2 % ZnPc-OA	52.48 \pm 1.49	82.63 \pm 2.27	36.89
PP + 0.5 % ZnPc-OA	54.83 \pm 0.67	85.00 \pm 1.09	35.04
PP + 0.75 % ZnPc-OA	55.27 \pm 1.83	87.21 \pm 4.61	34.12
PP + 1.0 % ZnPc-OA	49.34 \pm 1.92	85.65 \pm 2.67	37.29
EVA	41.67 \pm 2.50	85.52 \pm 1.85	40.79
EVA + 0.1 % ZnPc-OA	41.30 \pm 1.79	77.43 \pm 2.31	43.26
EVA + 0.2 % ZnPc-OA	38.14 \pm 0.53	84.91 \pm 3.33	42.46
EVA + 0.5 % ZnPc-OA	40.76 \pm 2.43	85.99 \pm 2.43	41.04
EVA + 0.75 % ZnPc-OA	36.19 \pm 1.10	82.95 \pm 2.39	43.76
EVA + 1.0 % ZnPc-OA	42.12 \pm 4.25	76.59 \pm 1.67	43.46

3.2 Singlet oxygen measurement

Singlet oxygen ($^1\text{O}_2$) is generated only under illumination with light. The mechanism of its production is well described [32-33]. Briefly, after excitation of Pc with light of suitable wavelength, an intersystem crossing leading to triplet state of Pc occurs. Then, the triplet state of Pc transfers energy to every-present diatomic oxygen resulting in formation of $^1\text{O}_2$. In the case of Pc embedded in polymer it is likely that only Pc located on the surface is activated by light. The $^1\text{O}_2$ production of the polymer films with embedded Pc was determined in solution with DPIBF as the indicator. The polymer films are insoluble in hexane and hence the indication

reaction was adopted for this solvent. The results are summarized in the Table 2. For comparison, $^1\text{O}_2$ production was also measured for ZnPc-OA in DMF at 1 mg/L ($\Phi = 0.66$), unsubstituted ZnPc was used as internal standard with $\Phi = 0.56$ [34].

Table 2: Singlet oxygen production of the polymer films with Pc in hexane

Pc concentration (%)	EVA k (J^{-1})	PP* k (J^{-1})
0.10	0.0925	0.007
0.20	0.1350	0.023
0.50	0.1566	0.036
0.75	0.1731	0.081
1.00	0.2049	0.097

* Large standard deviations (± 0.01) due to inhomogeneity of PP films

The rate constants k increase with increasing amount of Pc in both films. In the case of film, the $^1\text{O}_2$ can be generated by Pc only at film surface. Both Pc monomers (k_M) and aggregates (k_A) are tributes to the total rate constant k , $k = k_M \cdot [M] + k_A \cdot [A]$, where $[M]$ and $[A]$ are concentrations of monomers and aggregates in percentage of weight, respectively. For Pcs, it is reported [35] that $k_M \gg k_A$ and monomers generate more than 90 % of $^1\text{O}_2$. The dependences of k in EVA on Pc concentration is not linear and the observed effect can be explained by two properties: i) higher degree of aggregation of Pc with increasing Pc amount and ii) saturation of the polymer film surface at high Pc amount. The effect fits well to the above-mentioned equation with values of $k_M = 0.925 \text{ J}^{-1}$ and $k_A = 0.085 \text{ J}^{-1}$. The maximum monomer concentration was 0.137 weight %. In PP, the $^1\text{O}_2$ production is proportional to the Pc content. Dispersibility of Pc in PP is worse than in EVA (paler shades and aggregates) and therefore the value of k here conforms to be $k_A = 0.097 \text{ J}^{-1}$. It is apparent that the values of k_A in both polymers are almost identical and about ten times smaller than k_M . This is in good agreement with

reference [35]. Based on these results, EVA polymers should exhibit higher effectivity in degradation of organic compounds.

3.3 Degradation of DPP

The degradation of compounds in the solid state represents real conditions where pollutants are stuck to various surfaces, for example on the factory floors. We have found that fluorescence in the solid state is susceptible to small concentration changes of various fluorescent compounds. However, it was difficult to find a suitable model compound for the corresponding study. After several preliminary trials, we selected the DPP derivative for several reasons: i) high photo-stability, ii) solubility and processability in organic solvents (simple preparation of thin layers) and iii) high fluorescence in the solid state in the range 450-600 nm not overlapping main Pc spectral region. This DPP also represents a resistant compound, which is difficult to destroy by conventional methods. Fluorescence spectra during irradiation with light are shown in Fig. 4.

The degradation of DPP doctor-bladed on polymers are summarized on Figs. 5 and 6. During irradiation a decrease of fluorescence was observed, with no other fluorescent compound detected. It is apparent that the degradation rates increase with increasing Pc concentration for both films. However, the rates are much higher for EVA films, with the half-times of DPP degradation of 4-16 hours compared to 2-6 days for PP film. This is in good agreement with production of $^1\text{O}_2$.

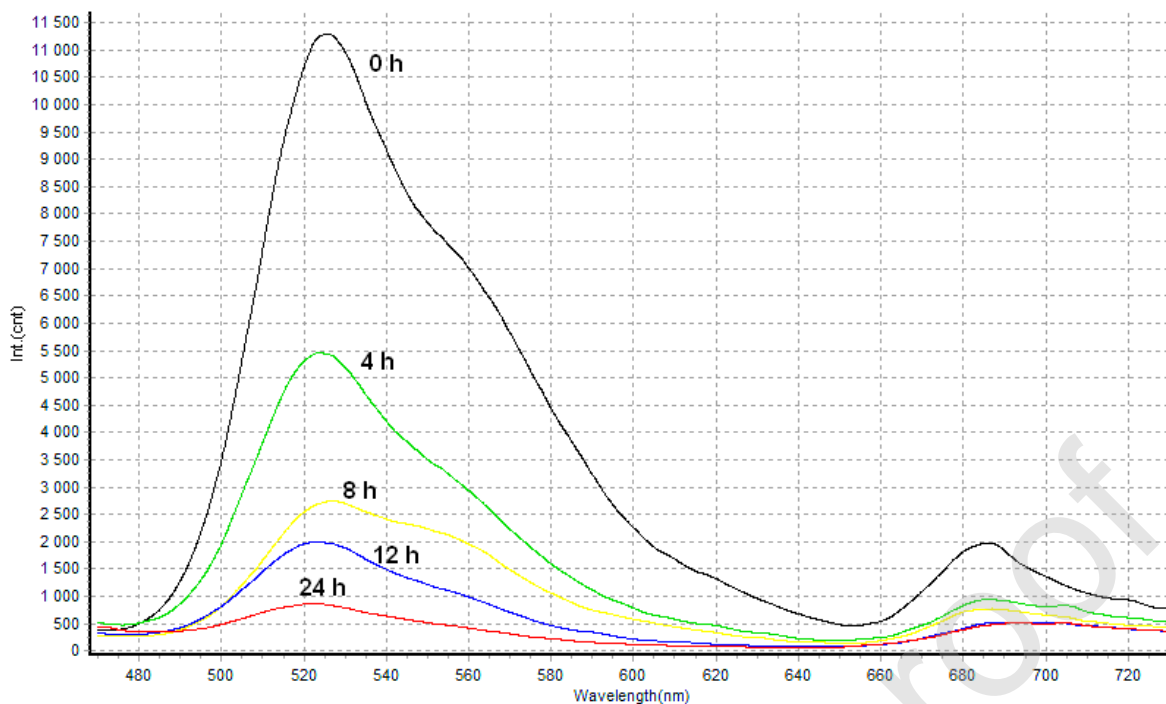


Fig. 4: Fluorescence spectra of irradiated DPP on EVA films with embedded Pc

Films with 0.5 % and 1.0 % Pc were also recycled by washing the DPP residual from first measurement with hexane, dried and fresh layer doctor-bladed as previously. During the recycling no visual or microscopic changes of film colour or its surface were observed. It has been found that the degradation rate of recycled films remained unchanged for 0.5 % Pc and was only negligibly reduced for 1 % Pc film.

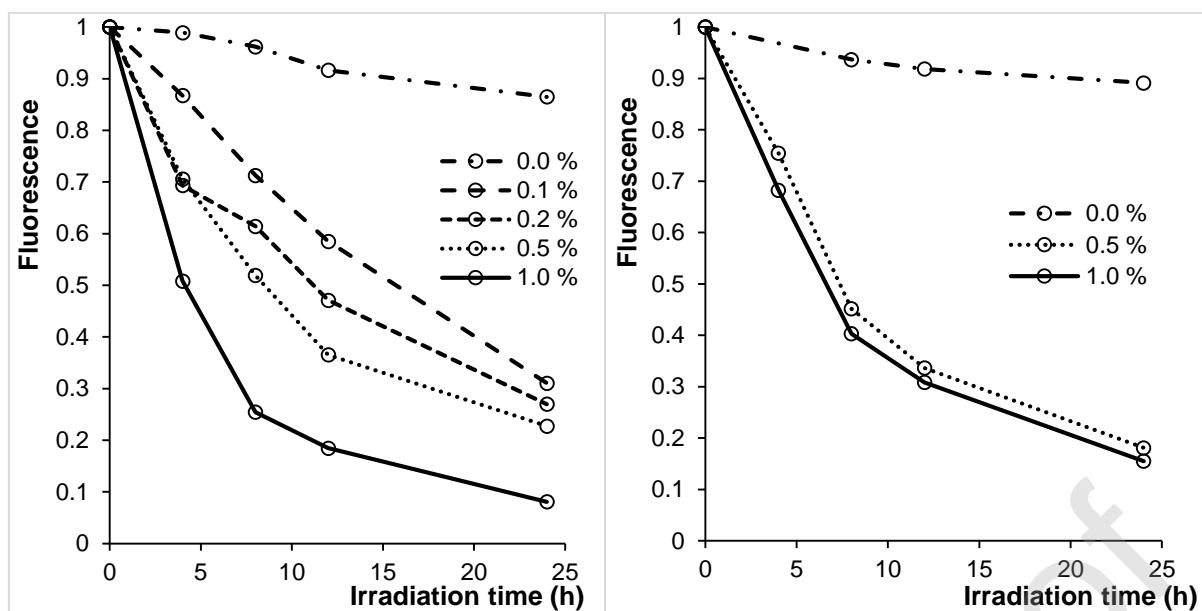


Fig. 5: Fluorescence decrease of DPP in solid state upon irradiation by EVA film with embedded ZnPc-OA, left – fresh film, right – after recycling

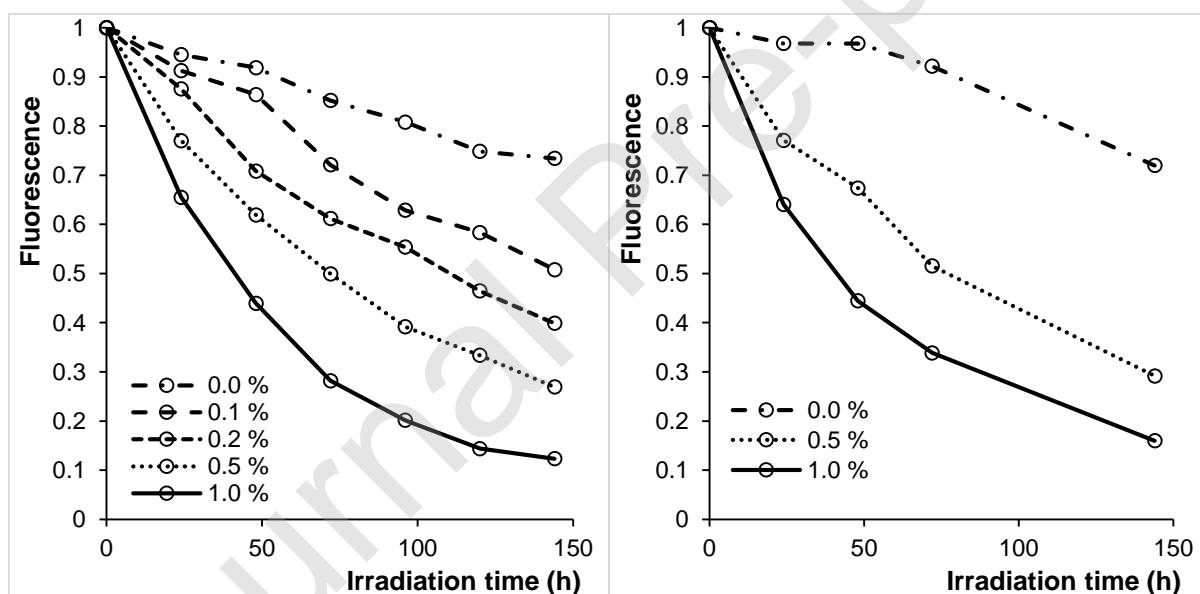


Fig. 6: Fluorescence decrease of DPP in solid state upon irradiation by PP film with embedded ZnPc-OA, left – fresh film, right – after recycling.

The DPP layer during irradiation changed colour from yellow to almost colourless which indicated efficient DPP degradation. The degradation products at the end were washed out with hexane and checked using HPLC. Only traces of *N*-(2-ethylhexyl)benzamide were detected.

The structure of this intermediate was confirmed by mass spectroscopy using the same compound prepared by the literature process [36]. The degradation of DPP by the action of $^1\text{O}_2$ is not reported in the literature and the reaction mechanism was suggested based on published principles for heterocycles [37] (Fig. 7).

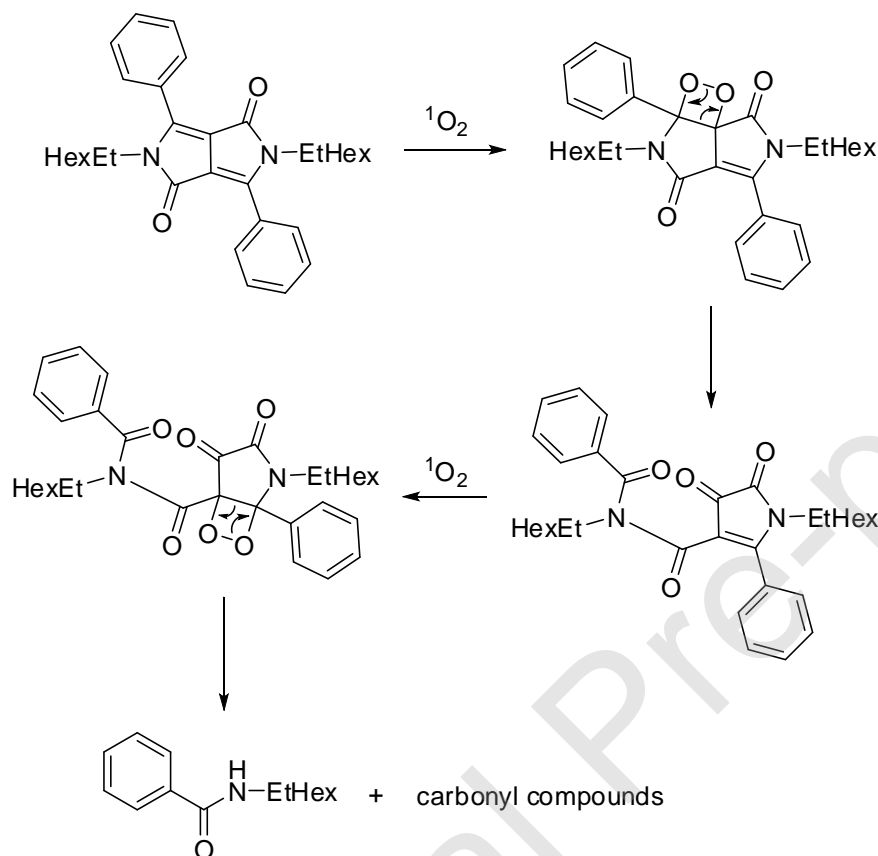


Fig. 7: Possible degradation pathway for DPP

The degradation of DPP is a multi-step process which likely starts with a [2+2] cycloaddition of generated $^1\text{O}_2$ to the pyrrole ring. This reaction is favoured in the case of *N*-alkylindoles. The resulting dioxetane is not stable and decomposes to a urea derivative. Then, the pyrrole substituent is attacked again by $^1\text{O}_2$ yielding another dioxetane which decomposes to *N*-(2-ethylhexyl)benzamide and some undetected carbonyl compounds. However, in final reaction steps an abstraction of H from surroundings (water in air or polymer matrix) needs to take place. Due to a very low concentration of *N*-(2-ethylhexyl)benzamide it is also possible that this

compound is further decomposed. However, we have not studied the degradation reaction in detail and more experiments will be required to fully explain the degradation mechanism.

3.4 Antibacterial activity

The results of antibacterial activity against Gram-positive *E. faecalis* are summarized on Fig. 8. It is apparent that EVA films has a strong antibacterial effect under irradiation. The effect is increasing considerably with increasing Pc concentration. The inhibition is more than 99 % for EVA films with Pc concentration of ≥ 0.2 %, where lower concentrations exhibit bacteriostatic activity (logarithmic decrease < 2). No effect of Pc in EVA polymer on the bacteria growth was confirmed in the dark.

PP films with any Pc concentrations showed only bacteriostatic properties. Inhibition of Gram-negative *E. coli* did not exceed 80 %.

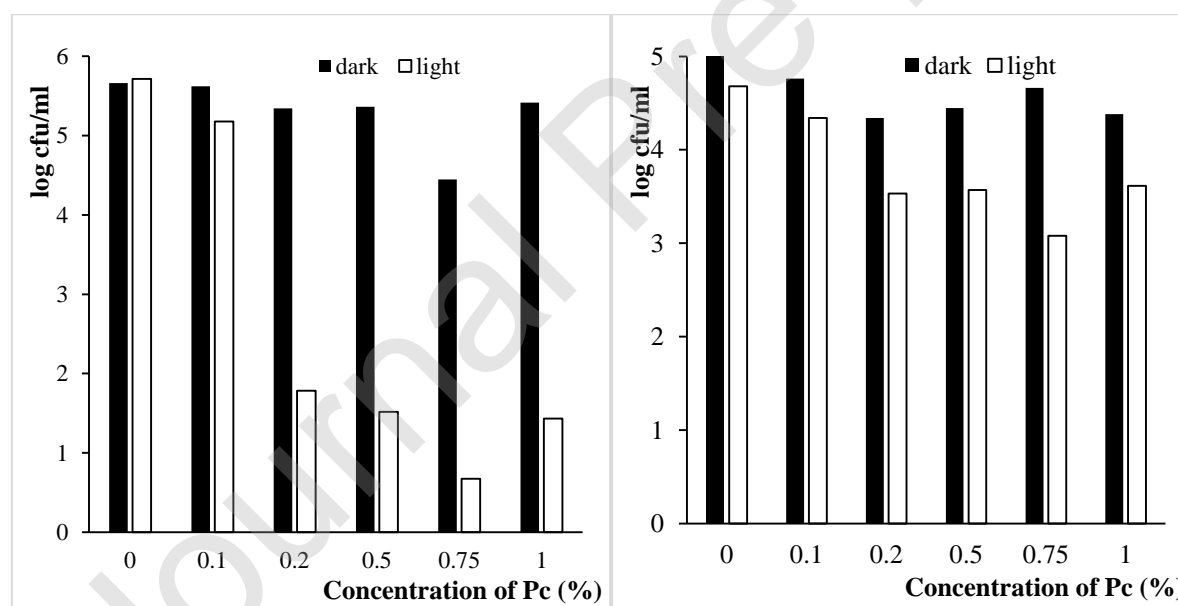


Fig. 8: Inactivation of *E. faecalis* by Pc incorporated in EVA polymer (left) and PP (right).

The antibacterial activity cannot be simply related to the $^1\text{O}_2$ production only. The mechanism of the inactivation of microorganisms is a multi-step complex process. Initially, $^1\text{O}_2$ has to be generated at the film surface during irradiation with light. Then, $^1\text{O}_2$ is transported by diffusion

to the surroundings. Singlet oxygen in solution has only a very limited lifetime of about 4 microseconds [38]. During that time $^1\text{O}_2$ can reach only a very short radius from the surface (tens of nanometres). Therefore, the type of contact of microorganisms with the polymer surface plays a key role. Provided that the bacteria are in close contact with the surface (within the area containing $^1\text{O}_2$), they can be inactivated effectively. Insufficient contact causes only minimal effects on microorganisms, because $^1\text{O}_2$ is fast deactivated by physical quenching.

Gram-positive bacteria, in general, are more sensitive to the action of $^1\text{O}_2$. The contact of *E. faecalis* as Gram-positive bacteria with the polymer surface is tight in the case of EVA polymer and the inhibition is fast and effective. PP films are less hydrophilic and the inhibition is much less efficient. Gram-negative bacteria have thicker and more structured cell wall in comparison with Gram-positive bacteria strains and an effective inactivation of photosensitizers is usually observed in the case of cationic photosensitizers [39] which can bind directly to the cell wall. Previous experiments have shown that Pcs are less effective against *E. coli*. This is consistent with the results of Bozja [40] who investigated modified nylon fibres using protoporphyrins. This trend may be also related to the total charge of the Pc, which increases its ability to bind to Gram-negative bacteria [41]. According to Ruiz-Gonzalez [42], mainly the central metal in the structure of Pc has a pivotal effect on the Pc properties, and Zn compounds are more effective against bacteria growth than Pcs with other metals.

4. Conclusions

Pc bearing a long-chain sulphamidic group (ZnPc-OA) was prepared and embedded successfully in polymers EVA and PP. The resulting films were characterized by UV-VIS spectroscopy and $^1\text{O}_2$ production in solution. The type of polymer has a crucial impact on the film properties. The varying properties can be explained by the state of Pc in the polymer matrix. While in EVA is Pc well dispersed forming a solid solution, in PP it appears as 1-3 μm

particles. The most efficient degradation of DPP in the solid state has been confirmed for all modified EVA films. The highest concentration of Pc was capable to degrade 80-90 % DPP within 24 hours. The same extent of degradation with PP films was completed in about a week. The degradation seems to be proportional to singlet oxygen production of the films. EVA films with Pc showed also increasing antibacterial activity against *E. faecalis* (Gram-positive bacteria strain) with increasing Pc concentration. The growth reduction of more than 99 % occurred with Pc concentration of ≥ 0.2 %. Inactivation of Gram-negative *E. coli* did not exceed 80 %. These results indicate very promising properties of polymer films with embedded Pc, especially EVA films. The combination ability to degrade difficult organic pollutants and antibacterial activity has a great potential for many important applications. A possible application is for self-cleaning surfaces and protective coatings, for example for sewage plants, clean rooms and floor coverings for stock raising or medical environment.

Author statement:

Vojtěch Trousil – Investigation, visualization, Jiří Černý – Investigation, writing – original draft and review, Radka Kořínková – investigation, supervision, Martina Pummerová – investigation, writing – original draft, Veronika Mikulcová – investigation, Marie Herynková - investigation

Conflict of interest

The authors declare that they don't have any conflicts of interests.

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