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Influence of environmental factors on functional properties of optical polymer films

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The paper is devoted to investigation of exploitation properties of optical film materials based on cross-linked polymers containing flavonoid fragments, namely 3,7,5,3',4'-pentahydroxyflavone (quercetin) and 3,7,5,3',4'-pentahydroxyflavone-8-sulphonic acid (sulfoquercetin) built into the polymer chains. The photoinduced destruction, fungal resistance and adhesion properties of these polymer materials were investigated. The photostability of polymer films was estimated using electronic absorption spectroscopy. Fungal resistance and fungistatic effect were tested using mold fungi species *Aspergillus niger* and *Penicillum chrysogenum* according to standard methods described in ISO 846-1997. Adhesion ability was determined according to ISO 2409. All the determined exploitation characteristics of the polymer films studied demonstrate the a very high functional level: a high photostability and fungal resistance, a substantial fungistatic effect and a high adhesion level, which confirms the prospects of using the flavonoid-containing polymers for preparation of optical films for applications in photonics purposes.

Keywords: cross-linked polymers, optical polymer films, exploitation properties, photostability, fungal stability, adhesion ability.

Вплив факторів оточуючого середовища на функціональні властивості оптичних полімерних плівок. *А.Дунаєва, Д.Мішуров, А.Воронкін, О.Неділько, О.Рошаль*

Досліджено експлуатаційні властивості матеріалів оптичних плівок на основі сітчастих полімерів, що містять вбудовані у полімерні ланцюги флавоноїдні фрагменти, а саме 3,7,5,3',4'-пентагідроксифлавон (кверцетин) та 3,7,5,3',4'-пентагідроксифлавон-8-сульфонова кислота (сульфокверцетин). Проаналізовано рівні фотоіндукованої деструкції, стійкість до дії пліснявих грибів та адгезивні властивості полімерів, що досліджувалися. Фотостійкість полімерних плівок охарактерізовано з використанням електронної абсорбційної спектроскопії. Фунгістатичний ефект та стійкість до пліснявих грибів оцінювали за допомогою штамів *Aspergillus niger* та *Penicillum chrysogenum* згідно зі стандартними методами, описаними в ISO 846-1997. Адгезивна здатність визначена згідно зі стандартом ISO 2409. Всі визначені експлуатаційні характеристики полімерних плівок демонструють дуже високий рівень: значну фотостабільність і стійкість до дії пліснявих грибів, значний фунгістатичний ефект та високий показник адгезії, що свідчить про перспективність використання флавоноїд-вміщуючих полімерів як матеріалів оптичних плівок у різних галузях фотоніки.

Исследованы эксплуатационные свойства оптических пленок на основе сетчатых полимеров, содержащих встроенные в полимерные цепи флавоноидные фрагменты, а именно 3,7,5,3',4'-пентагидроксифлавон (кверцетин) и 3,7,5,3',4'-пентагидроксифла-

вон-8-сульфоновая кислота (сульфокверцетин). Проанализированы степень фотоиндуцированной деструкции, устойчивость к действию плесневых грибов и адгезивные свойства исследуемых полимеров. Фотостойкость полимерных пленок исследована с использованием электронной абсорбционной спектроскопии. Фунгистатический эффект и устойчивость к плесневым грибам оценивали с помощью штаммов *Aspergillus niger* и *Penicillum chrysogenum* по стандартным методам, описанными в ISO 846-1997. Адгезивная способность определена в соответствии со стандартом ISO 2409. Все определенные эксплуатационные характеристики полимерных пленок демонстрируют очень высокие значения: значительную фотостабильность и устойчивость к воздействию плесневых грибов, существенный фунгистатический эффект и высокий показатель адгезии, что свидетельствует о перспективности использования флавоноид-содержащих полимеров как материалов оптических пленок в различных отраслях фотоники.

1. Introduction

Currently, optical films based on cross-linked polymers with chromophore or fluorophore fragments in polymer chains are widely used in various photonics applications. It is well known that they are a very good alternative to traditional crystal materials [1-9]. However, obtaining a high-quality level of exploitation properties of the polymer materials remains an urgent problem.

The quality of exploitation properties of optical polymer films is determined by such very important factors as their resistance to photoinduced destruction [10], the resistance to the action of some microorganisms (mold fungi) [11], as well as to the presence of some specific physico-mechanical properties (for example, adhesion of the polymer film to a substrate) [12].

An influence of the photoinduced oxidative destruction on the properties of polymers such as light transmittance in various ranges of the spectrum is due to peculiarities of the chemical structure of these polymers, particularly, to the nature of chromophore fragments. Depending on the presence of oxygen or nitrogen-containing groups in the chromophore fragment (as hydroxy group, amino group, ether bridge oxygen, etc.), and the operating temperature of the cross-linked polymer, light absorption can cause molecular rearrangements with or without a chain rupture. In this case, amorphous glassy polymers usually either do not exhibit significant color changes during oxidation or tend to be discolored. However, in the case of aromatic polymers, the oxidation leads to the hydroxylation of aromatic rings. This results in a bathochromic shift of polymers' absorption bands in electronic spectra, an appearance of a yellow or yellowish tint, and a decrease of the light transmittance in the short-wavelength range.

Another important factor is due to the fact that the air of enclosed spaces contains various microorganisms such as mold fungi of *Aspergillus niger* and *Pinicillum chrysogenum species*, whose influence on the polymer materials is unavoidable. The modification of the polymer films by mold fungi can lead to a loss of optical transparency that would limit use of the functional polymer materials in photonics and optoelectronics.

The third factor that substantially affects the exploitation properties of the polymer films is their adhesion to the substrate [13]. Low adhesion ability leads to the impossibility to use such materials in various optical applications.

The purpose of the present work was to investigate the exploitation properties such as photochemical stability, influence of mold fungi and adhesion to substrate of the thin polymer films based on cross-linked polymers with chromophore fragments of 3,7,5,3',4'-pentahydroxyflavone (quercetin), and 3,7,5,3',4'-pentahydroxyflavone-8-sulphonic acid in polymer chains. The latter substance was obtained by chemical modification of the initial quercetin [14].

2. Experimental

2.1. Materials

Di-, tri- and tetraglycidyl ethers of quercetin (2GEQ, 3GEQ, 4GEQ) used as monomers in the current study were synthesized by the method reported previously in [15]. Di-, tri- and tetraglycidyl ethers of 3,7,5,3',4'-pentahydroxyflavone-8-sulphonic acid (2GESQ, 3GESQ, 4GESQ) were synthesized according to the procedures described in [14, 15]. Structures of elementary flavonoid fragments embedded in the polymer chains are depicted in Fig. 1. Commercial diethylenetriamine (DETA) (Dow Chemical) was used as a hardener. Acetone used as a solvent for formation of the thin films was previously dried and distilled.

2.2. Polymer films preparation

Glycidyl ethers of quercetin (GEQ) were dissolved in acetone with a concentration of 0.1 g/ml. DETA was added to achieve a stoichiometric ratio DETA:GEQ close to 10:1 w/w. Glass microscope coverslips (used as a substrate for the polymer films) with a thickness of 170 μm were cleaned by sonication in detergent solution for about 10 min. After that, they were rinsed in deionized water, and then in boiling ethanol, and finally dried at 90°C for 10 min. Thereafter, thin films were spin-coated onto the precleaned coverslips at 1000 rpm for 0.5 min and cured at room temperature for 24 h in a vacuum. To remove the residual solvent, the polymer films were then annealed for 3h at 100°C. The presence of the residual solvent traces in the polymer films was monitored using FTIR-ATR spectroscopy. Quantification of the residual solvent was based on the values of optical density at 1720 cm^{-1} – in the absorption band maximum of acetone carbonyl group stretching.

2.3. Characterization

Photochemical stability of the polymer films was determined using irradiation of polymer specimens by intense ultraviolet light at wavelength $\lambda = 385$ nm. The light source contained a high-pressure mercury lamp DRS-250, and a monochromator MDR-12. The intensity of the light beam in front and behind polymer films was also checked.

The photochemical stability of the polymer thin films was investigated by measuring the ratio of optical density of the sample after (D_t) and before (D_0) irradiation (D_t/D_0) under room temperature [16]. The values of optical densities were measured with a spectrophotometer Hitachi-U3210 at the absorption band maximum of quercetin derivatives – 360 nm. Mathematical treatment of the absorption spectra was performed using Spectra Data Lab software package [17].

The films have been also examined to determine whether they are toxic, inert, or serve as a nutrient for mold fungi. For this aim, two main characteristics of polymers under investigation were examined – their fungistatic effect and fungal resistance. To occur such an examination the test specimens were contaminated by isolates of the mold fungi: *Aspergillus niger* (Tiegh) (thereinafter A.), *Penicillium chrysogenum* (Thom) (thereinafter P), which known as the most active polymer biodecomposers.

Isolates of these fungi species were obtained from local populations by soil cultivation and identified according to [18]. The cultures were grown on a medium Czapek Dox Agar (HiMedia Laboratories Pvt. Ltd., India) in test tubes. Aqueous spore suspensions of the isolates were prepared at a concentration of 1×10^6 spores/ml. The concentrations of spore suspensions were calculated using a Goryaev camera. The spore suspensions of each fungal isolate were mixed in equal proportions and then, used to contaminate the test specimens.

Studies of both fungistatic effect and fungal resistance were carried out according to the existing guidelines ISO 846:1997 [18]. Before the experiments, all the polymer specimens were purified from external contaminants by dipping them in ethanol for 1 minute and the following drying.

The specimens were placed separately in sterilized Petri dishes with a mineral salt medium (MSM) without carbon source. Then, they were sprayed by mixed spore suspension. MSM solution contained 2.0 g $NaNO_3$; 1 g K_2HPO_4; 0.5 g $MgSO_4{\cdot}7H_2O$; 0.5 g KCl; 0.01 g $FeSO_4 7{\cdot}H_2O$ per 1l of distilled water. Final pH (at 25°C) was 6±0.2. The specimens were incubated at 24±1°C and at a relative humidity of > 95% for four weeks.

After four weeks, the surfaces of the specimens were examined visually by stereoscopic microscope Micromed-1 with a photo camera of SciencaLab DCM 130 (at a magnification of ×200), and the fungistatic effect was estimated by absolute values of areas of fungal mycelium relative to the whole area of a cover slip.

The fungal resistance was estimated by losses of specimen weight determined as the difference in the specimen weights before contamination and after fungal colonies removing.

The fungistatic effect and fungal resistance of the polymer films were compared with control specimens (EP), which were epoxide polymer films of similar structure, but none-containing quercetin and sulfoquercetin fragments.

All the specimens were in tenfold replication.

The adhesion of the polymer films to a glass substrate was determined by a cross-cut method according to ISO 2409 [19]. On the polymer coatings, a grid of parallel and perpendicular cuts through the coating was made by hand cutting tool (sharp razor blade). The space between the cuts was equaled to 1 mm apart. Then an adhesive tape was placed firmly onto the grid by a soft brush for 90 sec. After this time the

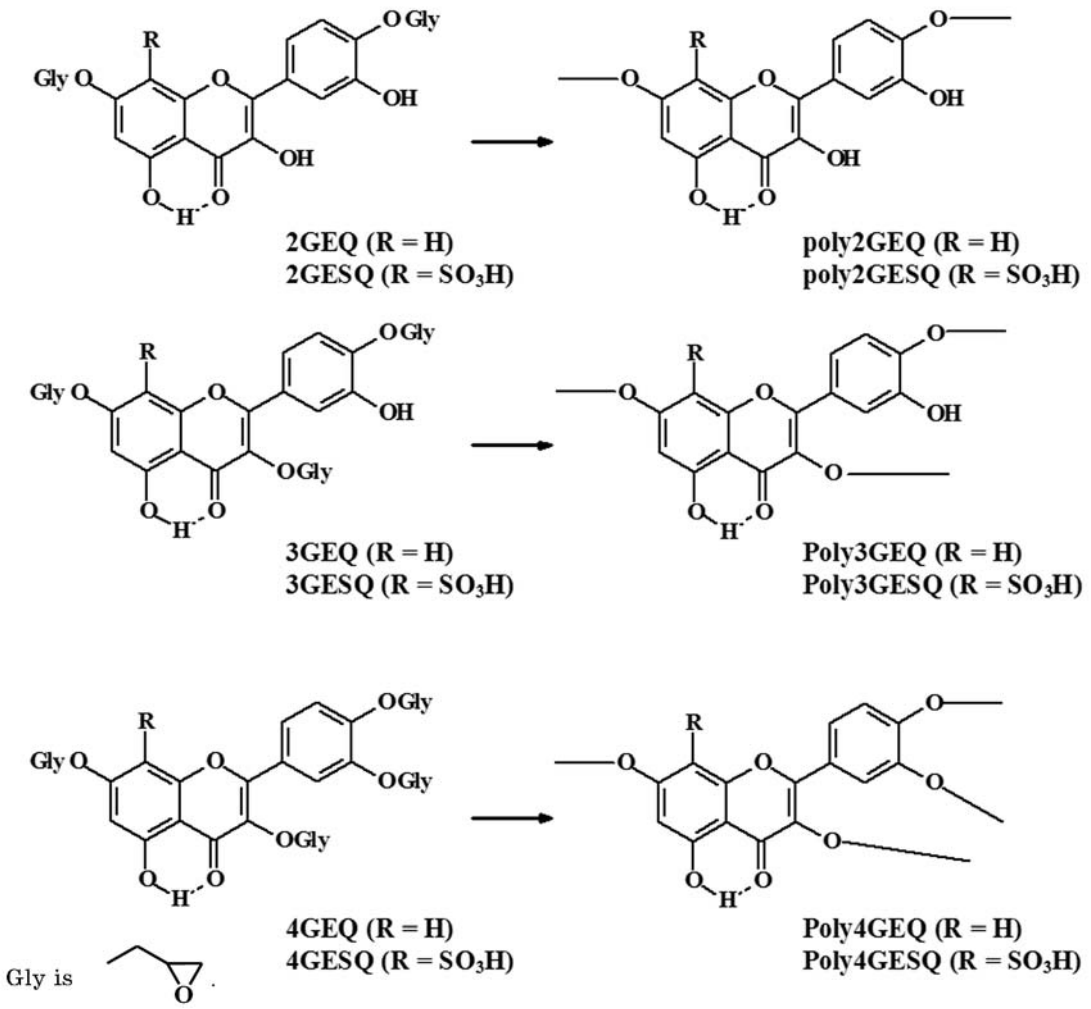

Fig. 1. Chemical structures of glycydyl ethers of quercetin (2GEQ, 3GEQ, and 4GEQ) and 8-sulfoquercetin (2GESQ, 3GESQ, and 4GESQ), as well as corresponding quercetin and 8-sulfoquercetin fragments of chains in cross-linked polymers – poly2GEQ, poly3GEQ, poly4GEQ, and poly2GESQ, poly3GESQ, poly4GESQ.

adhesive tape has been torn off. The adhesion was rated in accordance with a scale which is listed in ISO 2409 [19].

The thickness of the polymer films was measured using Linnik-type interference microscope MII-4, which was 1 μm. The Linnik interferometer configuration (a kind of the Michelson configuration) was described previously in [20].

3.Results and discussion

3.1. Photostability of polymer films

Photochemical stability of the thin polymer films was estimated using the ratio of optical density values at 360 nm after and before UV light irradiation – D_t/D_0. To compare photostability of the films based on different quercetin derivatives, we also used a relative value – PS=$(D_t$-$D_0)/D_0$.

The exposition of all the specimens under summary irradiation dose – 144 kJ/cm^2, showed a negligible decrease in D_t/D_0 ratios (Fig. 2). In all the cases, the obtained PS values did not exceed 3-4% that evidenced a high photostability of the films studied.

Since the photostability level is directly connected with the concentration of free radicals in the sample [21] it must depend on the presence of residual quantities of an initiator and non-linked active groups in the polymer chains. Small PS values indicate a low concentration of the active groups and evidence complete chain cross-linking in the polymers.

3.2. Fungistatic ability and fungal resistance of polymer films

Fungistatic properties and fungal resistance of polymer films based on di-, tri-,

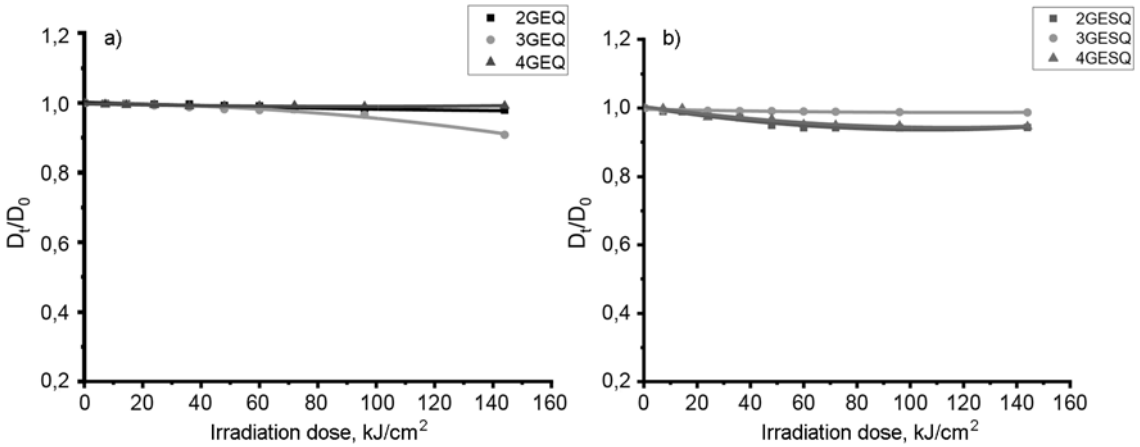

Fig. 2. Photostability of polymer films based on glycidyl ethers of: a) quercetin, b) sulfoquercetin.

and tetraglycidyl ethers of quercetin and sulfoquercetin against mold fungi *Aspergillus niger* and *Penicillium Chrysogenum* were determined according to procedure described in ISO 846-1997. Photographs of the specimens under investigations after the influence of A and P during 28 days are presented in Fig. 3.

This Figure shows the results of the influence of fungi A effect on the polymer films. It can be seen that specimens poly(3GEQ), poly(4GEQ), and poly(2GESQ) demonstrate the growth of mycelium at the edges of the samples. However, in the case of poly(2GEQ), poly(4GESQ) та poly(3GESQ), the mycelium growth takes place on the whole surface of specimens.

The ratios of areas of mycelium grown to areas of the whole film surfaces for different studied samples are listed in Table 1. For quercetin-containing polymer films– poly(2GEQ), poly(3GEQ), and poly(4GEQ) the mycelium areas are 4.8 %, 2.7 %, and 3.3 %, correspondingly. Polymer films with sulfoquercetin fragments have the mycelium areas 4.1 %, 6.7 %, and 4.6 %.

The growth of P occurs on the whole surface of the polymer films, regardless of the polymer nature. The mycelium area does not exceed 9% of the film in the case of quercetin-containing polymers (Figure 2d-f) and 11% for sulfoquercetin-containing polymers (Fig. 4d-f). Thus, the values listed in Table 1 show that in the case of P the polymer films demonstrate lower fungistatic activity than in the case of A. Besides, it would be fair to note that the chemical modification of quercetin fragment by its sulfonation in C8 position does not result in any drastic effects.

When comparing average mycelium areas for all the quercetin-containing and all the

Table 1. Mycelium area of mold fungi relatively area of the whole film surface (%)

Polymer films	Mold fungi	
	Aspergillus niger	*Penicillium chrysogenum*
EP	18.7	14.0
poly(2GEQ)	4.8	5.2
poly(3GEQ)	2.7	7.2
poly(4GEQ)	3.3	8.8
poly(2GESQ)	4.1	10.8
poly(3GESQ)	6.7	9.0
poly(4GESQ)	4.6	8.8

sulfoquercetin-containing polymers, it is obvious that the area values are 1.3-1.4 times higher for sulfoquercetin-containing polymers regardless of the mold fungi species. Thus, the fungistatic effect of the latter polymers is noticeably lower.

Comparison of quercetin and sulfoquercetin-containing polymers with the unmodified one shows that mycelium areas of A and P on EP films were correspondingly about 4 – 5 times and 1.5 – 2 times greater (Figures 5a and 5b). This shows that the presence of sulfoquercetin and particularly quercetin fragments in the studied polymers increases their fungistatic action.

According to ISO 846-1997, the values obtained for polymer films containing quercetin and sulfoquercetin fragments can be assigned to level 1, that is, to objects showing significant fungistatic ability. An interesting fact is that in uncontaminated samples, which were under mentioned above experimental conditions and periodically contacted with the environment, the pres-

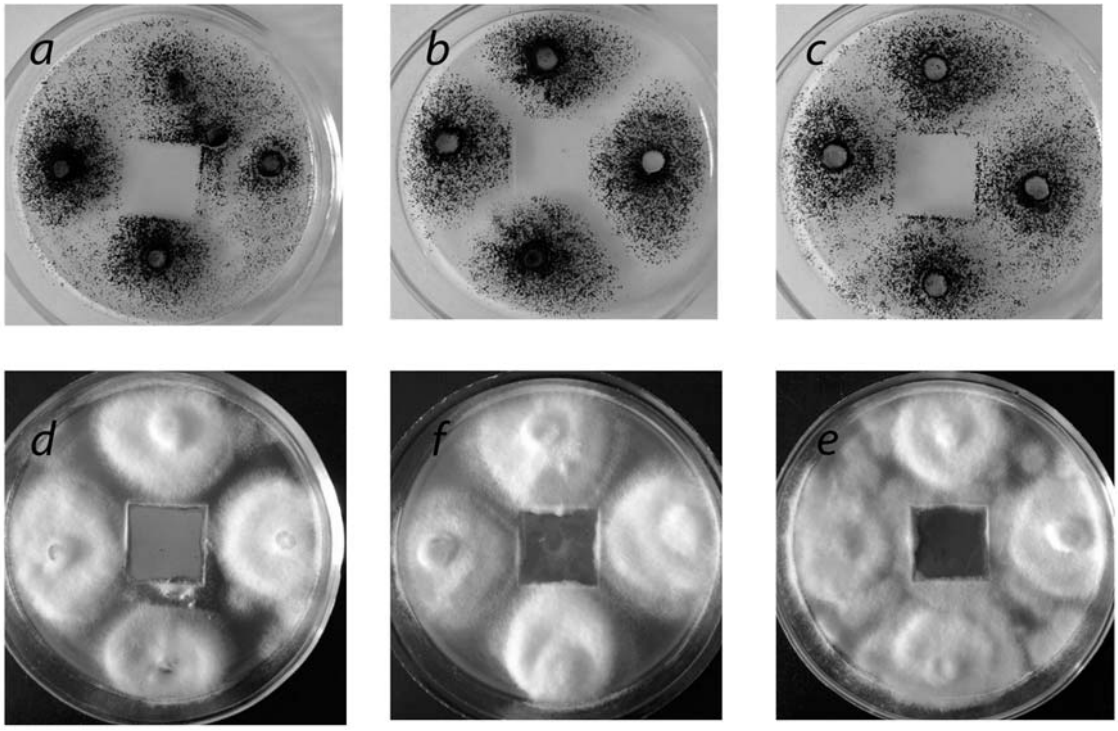

Fig. 3. Photographs of specimens of quercetin-containing polymer films after the influence of mold fungi during 28 days: a) poly(2GEQ) + A; b) poly(3GEQ) + A; c) poly(4GEQ) + A; d) poly(2GEQ) + P; e) poly(3GEQ) + P; f) poly(4GEQ) + P.

ence of mycelium of any mold fungi was detected. The weight losses of polymer films in determining the fungal resistance are listed in Table 2.

It can be seen that the weight losses for control and studied specimens do not excide 1% that corresponds to levels 0 – 1 of the fungal stability standard. The results also show that the growth of the mold fungi substantially occurs on the polymer film surfaces and does not in the film layer. Since, according to ISO 846-1997 standard, the polymer has positive fungal resistance if the weight losses are less than 3 points, all the studied quercetin and sulfoquercetin-containing polymer films can be considered as fungal resistive.

Thus, based on the above results, it can be concluded that quercetin and sulfoquercetin-containing polymer films are resistant to fungi [22] and even have some fungistatic action, which makes it possible to ignore such an environmental factor as the mold impact on the mentioned polymer films when using for optical purposes.

3.3. Adhesion of polymer films to glass substrate

Since polymer optical materials are usually used as thin films applied on the glass substrate, the important physico-chemical characteristic is the polymer adhesion. As mentioned above, the adhesion of quercetin and 8-sulfoquercetin containing was estimated by a cross-cut method according to ISO 2409 standard. Photomicrographs of

Table 2. Weight losses of polymers when the fungal resistance determining

Specimen	Weight before the experiment, g	Weight after the experiment, g	Weight losses, %
EP+ A	0.2359	0.2354	0.20
EP+ P	0.2425	0.2419	0.27
2GEQ+A	0.2430	0.2420	0.41
2GEQ+P	0.2405	0.2400	0.21
2GESQ+A	0.2480	0.2470	0.41
2GESQ+P	0.2475	0.2470	0.21
3GEQ+A	0.257	0.2560	0.39
3GEQ+P	0.2525	0.2515	0.39
3GESQ+A	0.2375	0.2365	0.43
3GESQ+P	0.2515	0.2535	0.80
4GEQ+A	0.2485	0.2485	0.41
4GEQ+P	0.2470	0.2460	0.41
4GESQ+A	0.2590	0.2580	0.39
4GESQ+P	0.2480	0.2475	0.20

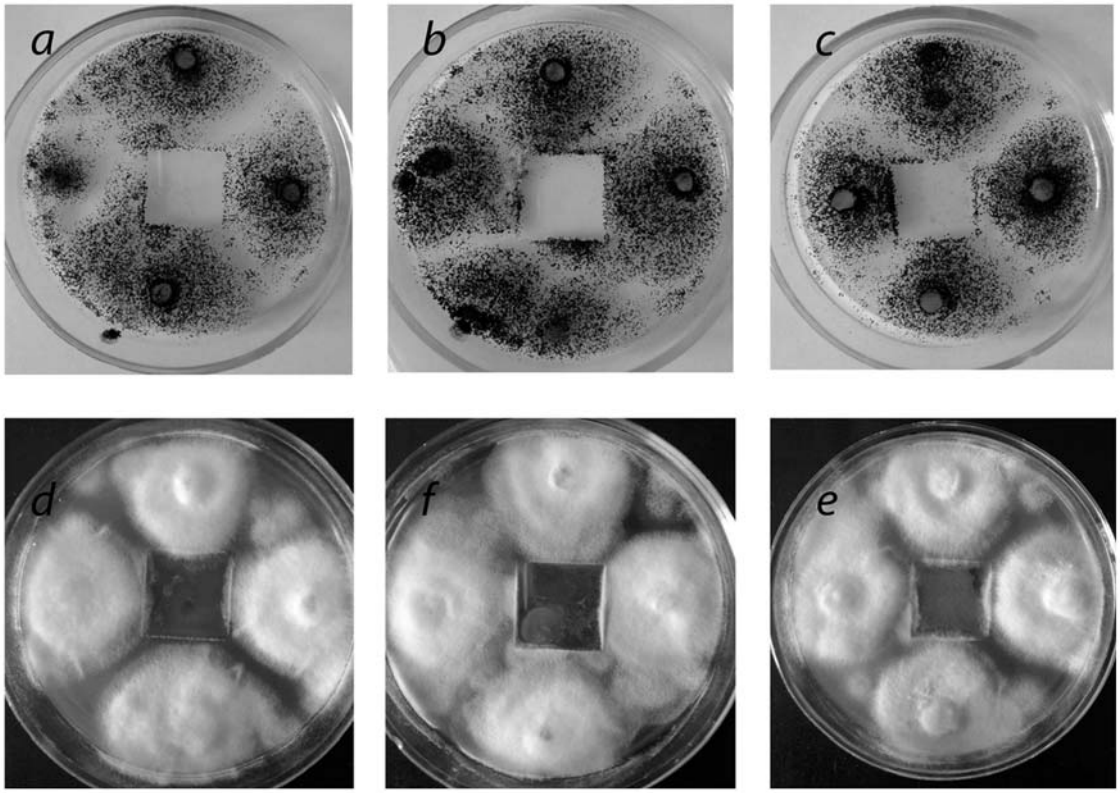

Fig. 4. Photographs of specimens of sulfoquercetin-containing polymer films after the influence of mold fungi during 28 days: a) poly(2GESQ)+ A; b) poly(3GESQ) + A; c) poly(4GESQ) + A; d) poly(2GESQ) + P; e) poly(3GESQ) + P; f) poly(4GESQ) + P.

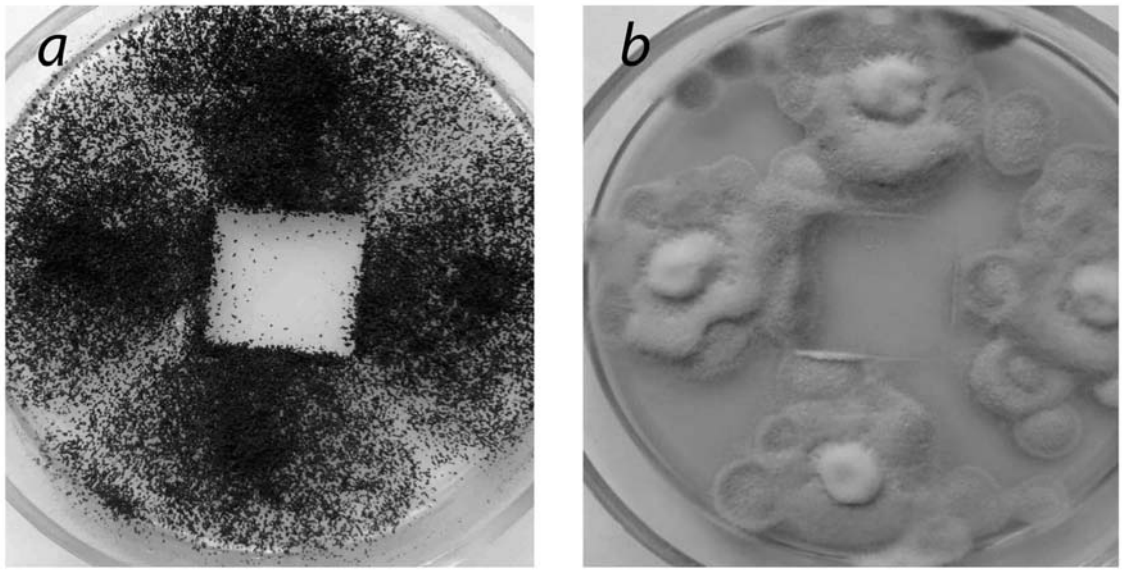

Fig. 5. Photographs of control specimens of polymer films after the influence of mold fungi during 28 days: a) EP + A; b) EP + P.

the cross-cut polymer films are presented in Figures 6 and 7.

The studies showed maximal adhesion level (level 0 according to ISO 2409 [18]) that is typical for various unmodified epoxide polymers, whose interaction with the substrate has chemical and mechanical character. In the first case, the adhesion is due to formation intramolecular hydrogen bonds between hydroxy and oxy groups on the

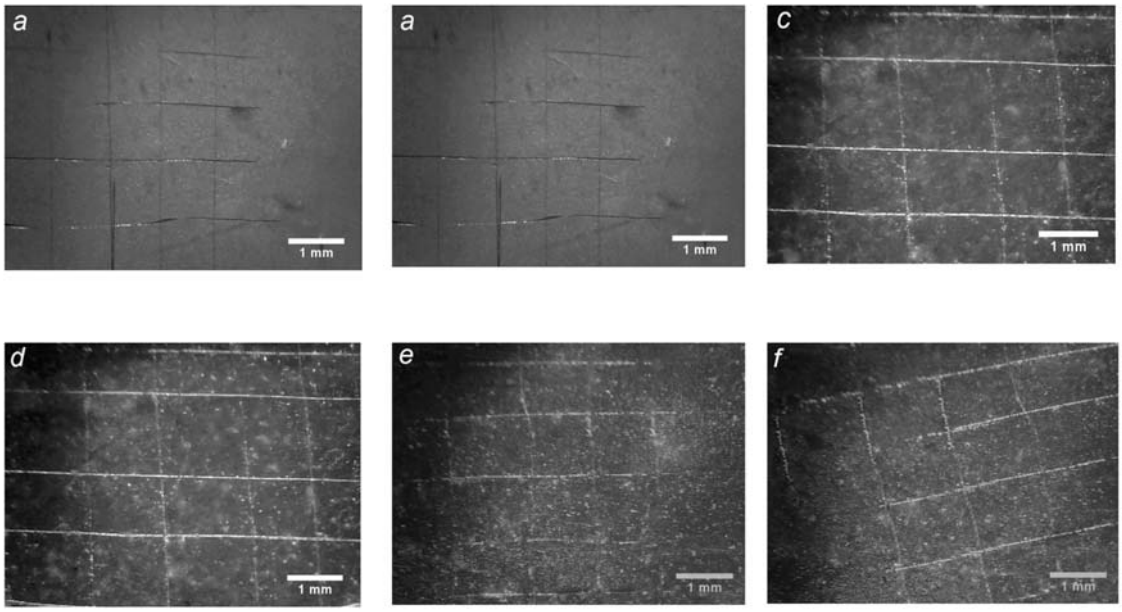

Fig. 6. Microphotographs of the polymer films poly(2GEQ): a) before testing; b) after testing; poly(3GEQ): c) before testing; d) after testing; poly(4GEQ): f) before testing; e) after testing.

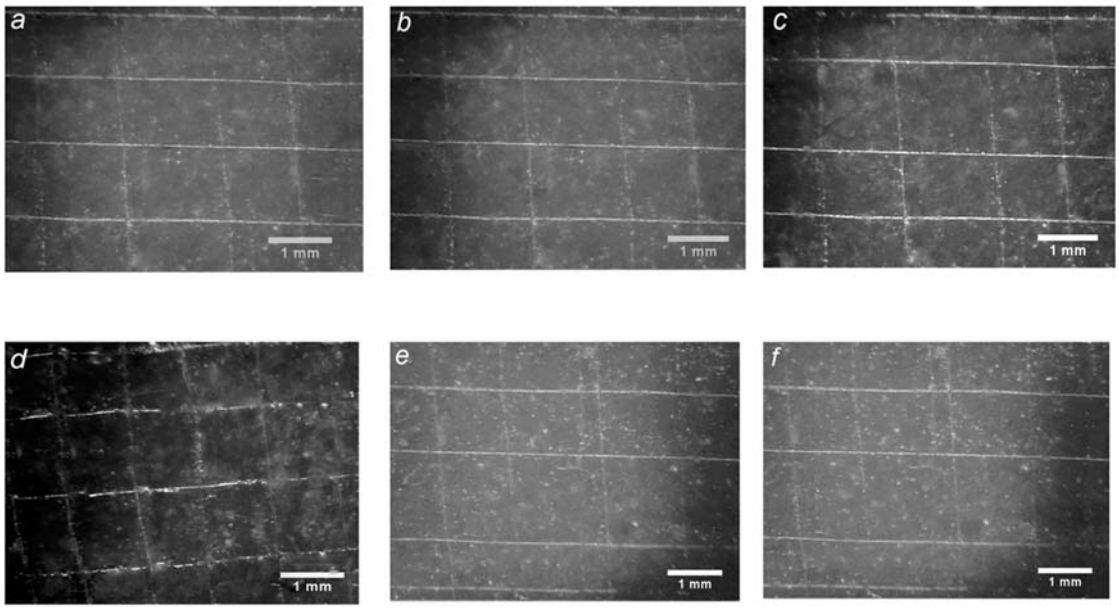

Fig. 7. Microphotographs of the polymer films poly(2GESQ): a) before testing; b) after testing; poly(3GESQ): c) before testing; d) after testing; poly(4GESQ): f) before testing; e) after testing.

glass surface and hydroxy groups of the polymer chains, quercetin fragments, as well as oxygen atoms of sulfo groups. The mechanical component of the adhesion is due to the formation of the mechanical interlocking between polymer layer and substrate surface defects.

Other physico-chemical characteristics of the polymer films were not studied, because the substrate width is 170 times greater than that of the polymer films. In this case, measured parameters of specimens under investigations are determined by the substrate properties.

4. Conclusions

Summarizing the results obtained, it can be concluded that all the determined exploitation characteristics of polymer films based on quercetin and sulfoquercetin-containing cross-linked polymers are at a very high level. Not depending on a network

structure, which is due to number of glycidyl groups, all the polymer films demonstrate a high photostability, fungal resistance, a substantial fungistatic effect and a high adhesion level. Consequently, such films are not sensitive to damaging effects of the environment and must keep their good performance properties during a long time. This allows using flavonoid-containing polymers for preparation of optical films for various applications in photonics and optoelectronics.

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