Effect of Concentration of 3,5,7,3',4'-Pentahydroxyflavone on Nonlinear Properties of Doped Epoxy Polymers

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ABSTRACT

These Epoxy polymer doped with a natural chromophore 3,5,7,3',4'-pentagydroxyflavone (quercetin) at different concentrations of the dopant. Spectral characteristics and nonlinear optical properties of the polymer materials were studied by UV-vis and FTIR spectroscopy. Morphology of the doped polymer films was observed using scanning electronic microscopy. Quadratic second susceptibilities of the obtained polymer films were calculated according to one-dimensional, rigid oriented gas model. It is shown that the morphology and non-linear properties of the doped polymer films are directly dependent on the dopant concentration.

KEYWORDS: *Relaxation, Polymer films, Nonlinear polymers, Chromophores, Dyes/pigments.*

1. INTRODUCTION

Search of the new chromophores having high values of molecular quadratic polarizability (β) is one of the important modern trends in the development of materials with non-linear optical (NLO) properties[1-6]. Doping of polymer matrices by such chromophores results in the appearance of macroscopic NLO activity of the materials obtained.

To obtain the polymer NLO materials of "guest-host" type, low-molecular-weight synthetic and natural organic chromophores are usually used [7,8]. Previously, it was found that these chromophores must have some peculiarities

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of their chemical structure such as the presence of great π-system as well as electron-donating (D) and electron-withdrawing (A) substituents[9]. Such a structure is typical for natural pigments – flavonols [10] and, particularly, for 3,5,7,3',4'-pentahydroxyflavone (quercetin), whose chemical structure is shown in Fig. 1.
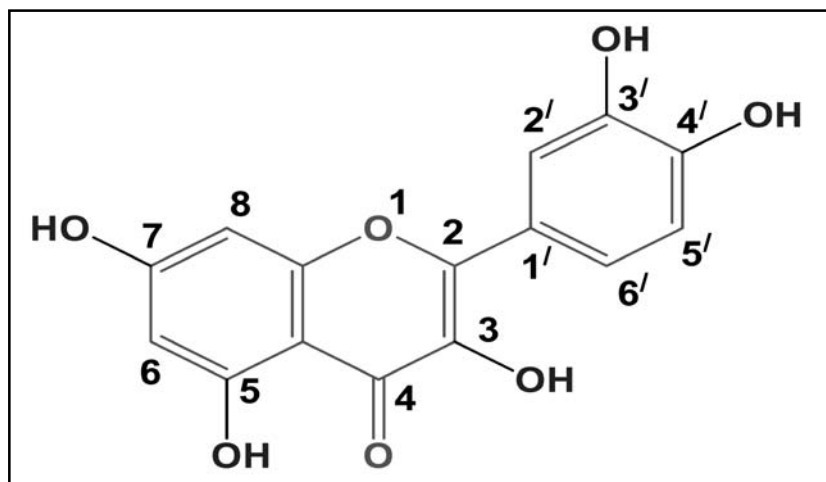

Fig. 1. Chemical structure of quercetin

Quercetin molecule consists of two conjugated mobile fragments – electron-withdrawing chromone moiety and side phenyl ring with two hydroxyl groups demonstrating electron-donating ability. The presence of these fragments explains a high dipole moment of the quercetin molecule in the ground and excited states and also interfragmental charge transfer occurring upon the excitation[11] . Therefore, it is supposed that quercetin could be appropriate dopant when developing the new polymeric NLO materials.

Moreover, the quercetin molecule has four hydroxyl groups that are able to form intermolecular hydrogen bonds and, thus, to form additional physical H-bond network, which can hinder re-orientation of the chromophore fragments over time.

It should be noted that the dopant addition to the polymer matrix has some concentration limitations due to influence of association of the chromophore molecules on optic properties of the polymers. It is known that dipole-dipole interaction between polar chromophore molecules leads to their anti-parallel orientation in the associates therefore total polarity of the associates is substantially weaker than that of the free molecules[8] . Because of increase of the dopant concentration in the polymer matrix leads to increase of the associate concentration that can result in decrease of the NLO properties of the doped polymer system [12, 13].

Thus, the present work is aimed to investigate optical, thermal, morphological and NLO properties of polymer films based on epoxy resin doped by 3,5,7,3',4'-pentahydroxyflavone

and to determine the optimum dopant concentration at which the NLO properties are not decreased and are maximal.

2. EXPERIMENTAL PART

2.1 Materials

Commercially available epoxy resin EPOXY 520 (EEW 184 g/eq., Spolchemie) based on diglycidyl ethers of Bisphenol A (DGEBA) was used for the current investigations. Diethylenetriamine (DETA, Dow Epoxy) and 3,5,7,3',4'-pentahydroxyflavone (Quercetin, Lachema) were used as a hardener and a dopant, correspondingly.

2.2 Doped polymer films preparation

Polymer films were obtained on glass substrates by spin-coating technique using different dopant concentrations.

Mixtures of DGEBA/DETA (with a stoichiometric ratio to 10:1 w/w) containing 5, 10, 15, 20, 30, 40, 50 wt.% of quercetin were dissolved in acetone. The concentration of the DGEBA/DETA/quercetin mixture in acetone solution was about 0.1 g/mL. Then, prepared solutions were spin-coated onto pre-cleaned glass microscope cover slides of 170 μm thickness at 1000 rpm during 30 s. Cover glasses were cleaned with detergent (aqueous solution of the tetrasodium salt of ethylenediaminetetraacetic acid) followed by washing thoroughly in water and finally isopropyl alcohol and then it were dried. To remove the residual solvent, obtained polymer films were treated at temperature of 50 °C for 8h in vacuum and further were dried at 100 °C for 3 h.

2.3 Doped polymer films poling

The polymer films were poled by corona poling technique at the elevated temperature. A thin tungsten needle placed 10 mm above the polymer films and oriented perpendicularly to their surface was used as a positive corona electrode. Corona current was 2.5 μA with the electrode potential of 7 kV. Electrical field of the corona discharge was imposed for 1h to the films preheated at 130°C (higher than T_g). Then, in the presence of the corona discharge, the films were cooled to the room temperature.

2.4 Characterization

UV–Visible spectra of the polymer films were recorded using UV-VIS Spectrophotometer Hitachi-U3210 in the range of 250 – 800 nm. Mathematical treatment of the spectra was performed using the Spectra Data Lab software package[14]. FTIR spectra were obtained by Spectrum One spectrophotometer (Perkin Elmer) in KBr in the range of 400-4000 cm^{-1}. Detection of the residual solvent was based on the absorption analysis at 1720 cm^{-1} where strong band of acetone C=O group stretching is centered. Photomicrographs of the polymer film surfaces were obtained using scanning electronic microscopy (JSM JEOL Model 840) with operating voltage of 20kV. Since the polymer films under investigations are dielectrics, the preliminary vacuum deposition of electrically conducting chrome layer of 100 nm thickness on the films surfaces was made. DSC analysis was carried out by Q 2000 thermal analyzer with specimens' weights of 9-6 mg in nitrogen atmosphere. The glass transition temperature of each doped polymer was obtained from the second scan between 0 and 180 °C with the heating rate of 10°C/min. T_g values were determined as the temperatures corresponding to maxima on DSC first derivative curves. Densities of the doped polymer films (ρ) were determined using the Archimedes principle in the RADWAG analytical balance, model AS 110/C. The specimens and the glass substrates were weighted in air and water at the temperature-controlled environment. Then substrates weights were deducted from the specimens weights. Obtained φ values were averaged resulting from at least five replications. Thickness of the polymer films was measured using Linnik-type interference microscope MII-4. The Linnik interferometer configuration (a kind of the Michelson configuration) was described previously[15].

3. RESULTS AND DISCUSSION

3.1. Optical properties of doped polymer films.

FTIR spectra of the polymer films doped by quercetin are presented in Fig. 2. It can be seen that these spectra contain bands that are typical for both the dopant and the polymer matrix based on bisphenol A.
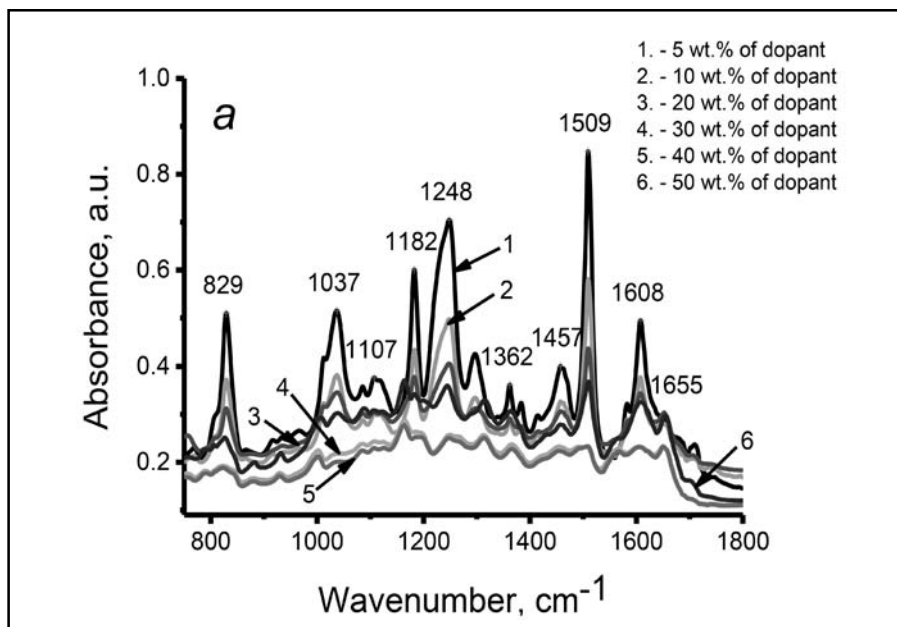
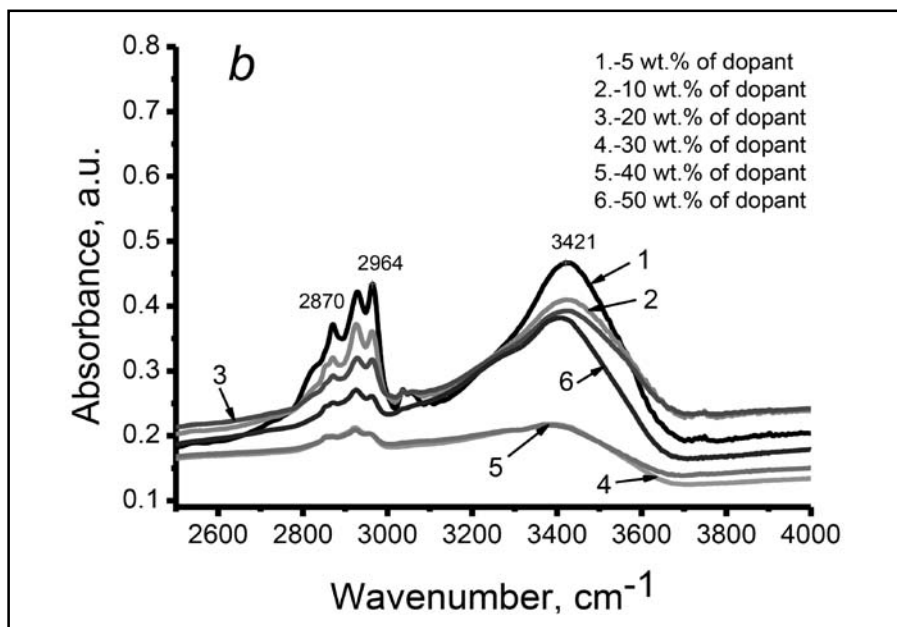Fig. 2a. FTIR spectra of doped films in low-wavenumber range

Fig. 2b. FTIR spectra of doped films in high-wavenumber range

Analysis of the low-frequency range of the FTIR spectra (Fig. 2b) showed the presence of group stretchings of aromatic rings at 1580-1620 cm^{-1}. Intensive band at 1509 cm^{-1} may be assigned to aromatic ring stretch vibrations, also. The increase of the dopant concentration results in appearance and further intensity growth of band at 1650-1655 cm^{-1}, as well as in broadening the "aromatic" band at 1602 cm^{-1} due to appearances of band at 1612-1615 cm^{-1}. The bands centered at 1650-1655 cm^{-1} and 1612-1615 cm^{-1} were earlier assigned to group stretching of carbonyl fragment and double bond of pyrone cycle of 5-hydroxyflavones[16].

It is worth to note that the band assigned to bending vibrations of oxyrane cycle at 910-920 cm^{-1} was not detected in any of FTIR spectra investigated. This indicates the absence of free epoxy groups and proves the completion of DGEBA crosslinking reaction.

A broad band in the range of 3175–3500 cm^{-1} is due to O-H stretching vibrations of hydroxyl groups of the matrix and the dopant. Bands at 2964 and 2870 cm^{-1} can be assigned correspondingly to C-H stretching of CH and CH$_2$ fragments of the polymer chains. Also, bending vibration bands of these fragments were found at 1300-1380 and 1429-1457 cm^{-1}. It can be seen in Fig. 2a that decrease of intensity of these bands occurs with increase of the quercetin concentration and, correspondingly, with decrease of the polymer fraction. This evidences a fact that "hydroxyl" absorption is mainly due to hydroxyl groups of the polymer matrix, quantity which quantity is substantially greater than of included hydroxyl groups into the quercetin molecules.

A band near 1700-1720 cm^{-1} assigned to acetone carbonyl group was neither found. This evidences the absence of residual solvent –
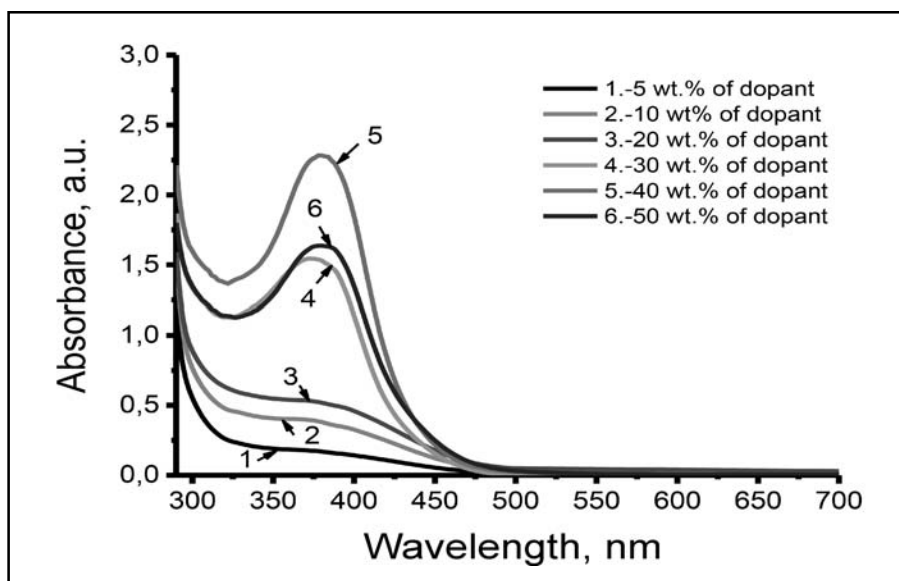

Fig. 3. Absorption spectra of doped polymer films

acetone, from which the polymer composite films were obtained[17].

Fig. 3 shows electronic absorption spectra of the films containing different concentrations of

the dopant. It can be seen that the increase of quercetin concentration results not only in the absorption bands intensity growth but also in changing the spectral curves shape.
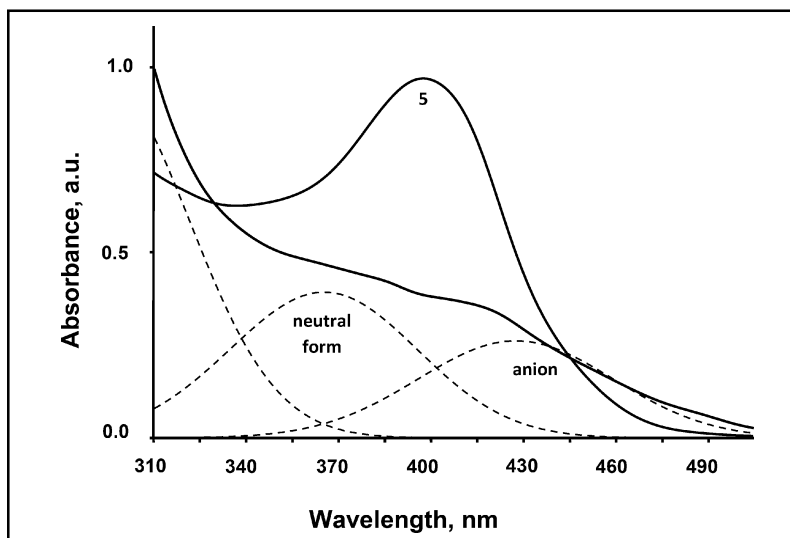

Fig. 4. Normalized absorption spectra of 5% (1) and 40% (5) quercetin containing films
Bands of neutral and anionic forms of quercetin indeconvoluted spectrum of (1)

Deconvolution of the composite films spectra having low quantities of quercetin (Fig. 4) showed that the long-wavelength absorption is due to the presence of two bands in the ranges of 310-390 nm and 400-470 nm.

The band from the first range can be assigned to absorption of neutral quercetin, and the long-wavelength band can be due to quercetin anion. The presence of the anion, in our opinion, can be explained by the fact that polymerization of the polymer matrix was occurred in presence of hardener DETA, whose pH is close to 12.5. Although DGEBA and DETA are taken in stoichiometric ratio the hardener residual quantities can be responsible for some basicity of the polymer medium, which is sufficient for

quercetin ionization (quercetin's $pK_{a'1}$ is 7.2). When increasing the dopant concentration, the quercetin-anion absorption band becomes negligible.

In polymer composites containing high concentrations of the dopant, the absorption band of the later bathochromically shifts up to 380 nm. This spectral phenomenon could be explained by self-association of quercetin molecules that is a new crystalline phase in the polymer matrix. The absorption band maximum in the spectra of neat quercetin at 395-400 nm is centered.

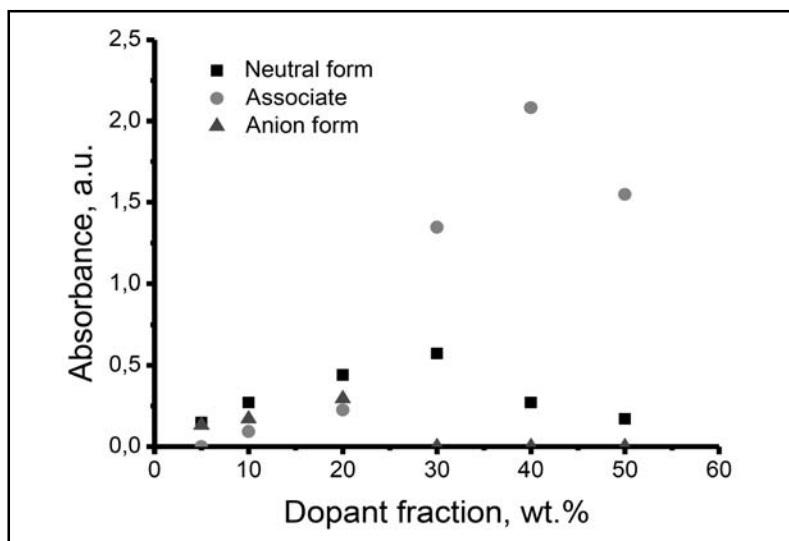The absorption spectra deconvolution on bands of the neutral quercetin, its anion and its

Fig. 5. Dependence of optical density of neutral, anionic and associated forms of quercetine on general concentration of the dopant in polymer matrix

associate allowed to estimate the dependence of quantity of each form on the dopant concentration in the films. Fig. 5 shows that some quantity of associated quercetine appears even at 10 wt.% of the dopant in the polymer matrix. When the concentration of the dopant exceeds 30 wt.%, the associate becomes predominating form, and absorption of the anion is not detected, most likely, because of overlapping of its band with much more intense neighbor band of the associate.

3.2. Thermal analysis of doped polymer films

Some relationship between the dopant concentration and thermal properties of the polymer composite films can also be seen. Fig. 6 shows thermograms obtained for the studied polymer composite films by DSC method. The thermograms of polymer composites with

5-20 wt.% of quercetin are identical. The glass-transition temperatures (T_g) obtained by differentiation of the DSC curves are 49.3°, approximately. In the case of films containing 30 wt.%, 40 wt.% and 50 wt.% of quercetin T_g increases upto 53.2 °C, 55°C and 54.2 °C, correspondingly.

In our opinion, this fact can be explained by the percolation theory, which allows us to describe the thermal properties of filled amorphous polymers[18, 19]. According to this theory, with a slow change in the dopant concentration, the thermal properties of the amorphous filled system must change sharply near the percolation threshold. Up to the critical concentration, the dispersed particles of the dopant are arranged discretely in the polymer matrix. After passing this threshold, formation of a continuous cluster from the dopant dispersed particles occurs and the thermal
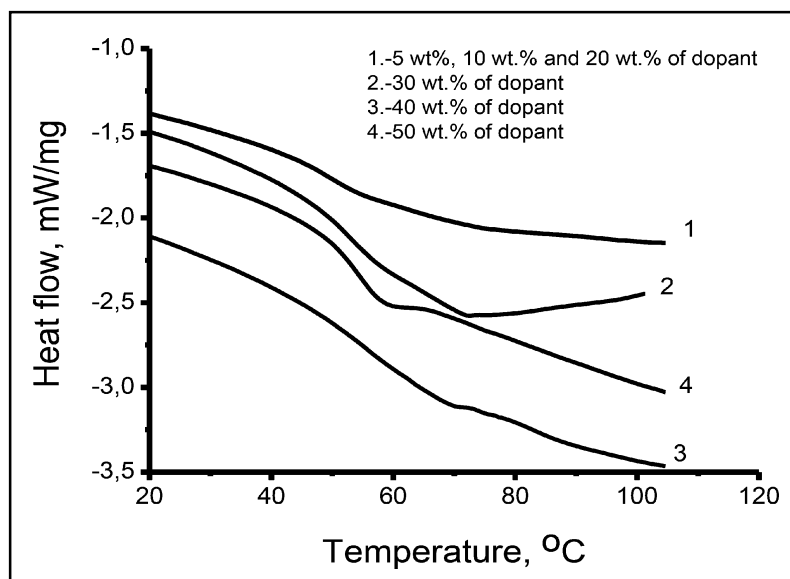
Fig. 6. Thermograms of polymer films with different concentrations of dopant

properties are changed dramatically. Thereby, there is the percolation threshold near the dopant concentration of 20 wt.%.

It should be noted that the thermal data considerably correlate with experimental data of the optical studies of the doped polymer composites.

3.3. Morphological characteristics of doped polymer films

Surface photomicrographs of the obtained polymer films are presented in Fig. 7. Figs 7a-c show that at the concentration of quercetin to 20 wt.% the polymer-rich structures are very similar to the so-called Turing's patterns.

When increasing the dopant concentration, the "pattern" size also increases that demonstrates the influence of dopant molecules on the polymer matrix morphology. According to the spectrophotometric data, the specimens with

5-20 wt.% of the dopant (Figs 7a-c) contain predominant quantities of monomolecular – neutral and anionic forms of quercetin. The composite film with 30 wt.% of the dopant, which contains substantial quantities of associated quercetin, has another type of the surface morphology. In this case (Fig. 7d), the surface heterogeneity increases, and two species of phases can be seen. It can be assumed that these two phases are quercetin-rich structure and polymer-rich structure.

Photomicrography of the polymer composite with 40 wt.% of the dopant (Fig. 7e) shows the polymer-rich structure destruction: quantity of the "patterns" becomes negligible, sizes of spherical micro-objects increase and their edges are more diffuse.

In the polymer film with 50 wt.% of the dopant (Fig. 7f), the surface morphology changes once
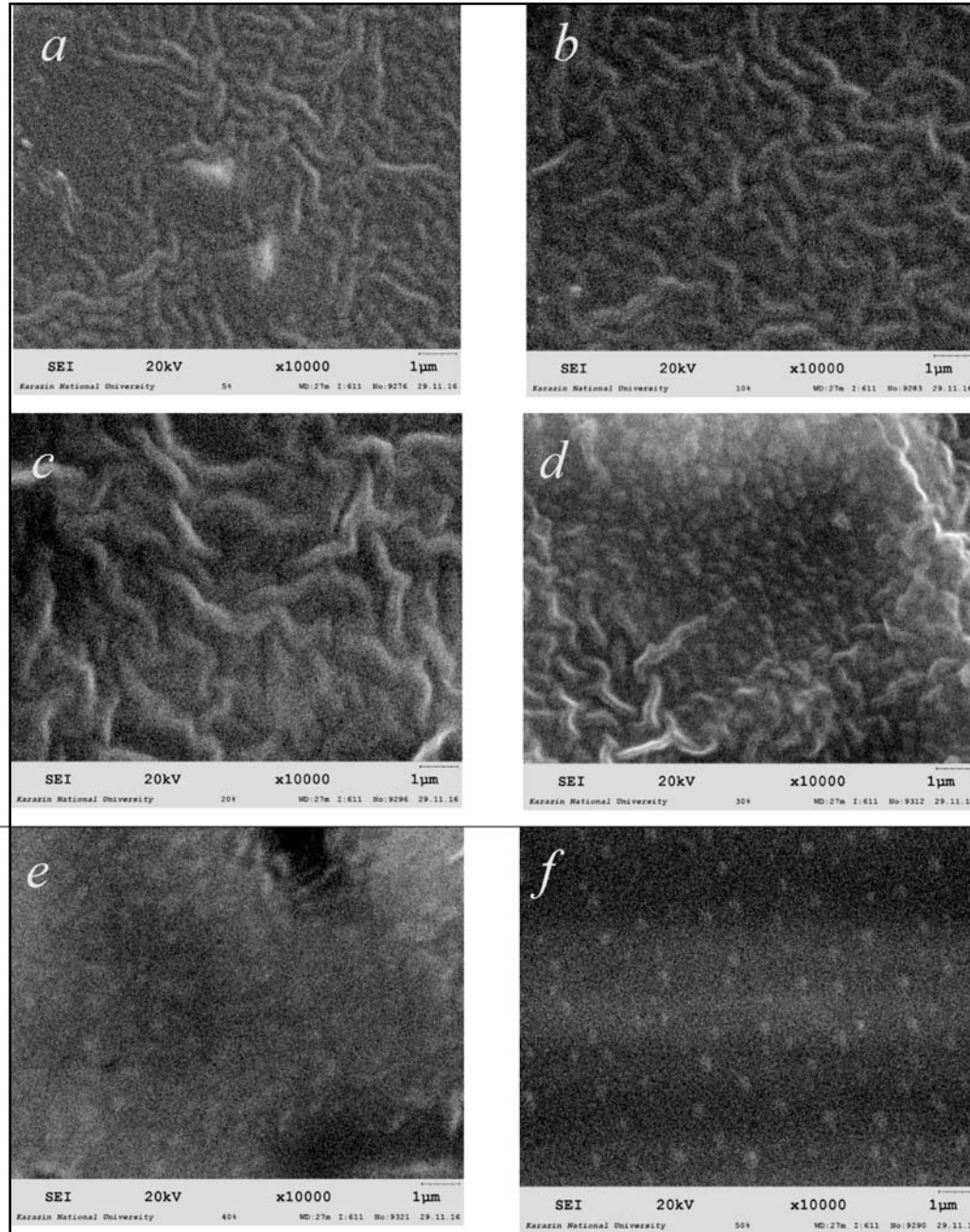
Fig. 7. Photomicrographs of polymer films containing 5% (a), 10% (b), 20% (c), 30% (d), 40% (e), 50% (f)

more: it can be seen the spherical objects of approximately similar size – 0.2-0.3 μm with clearly visible boundaries on the more-less homogeneous background. At the same time, the optical density of this film is lower than that of the film containing 40 wt.% of the dopant. Thus, the transition from one type of the phase structure to another type passes through the region of interpenetrating continuous phases, which there is at the percolation threshold, and determines the phase's inversion region[20].

As the presence of micro-objects it can be caused the light dispersion, while changes in the polymer matrix morphology with increasing the dopant concentration can influence on the level of optical losses in the range of 500-700 nm (where is no own electronic absorption of quercetin or the polymer matrix). The values of optical losses (in three replications) at different dopant concentrations are depicted in Fig. 8.
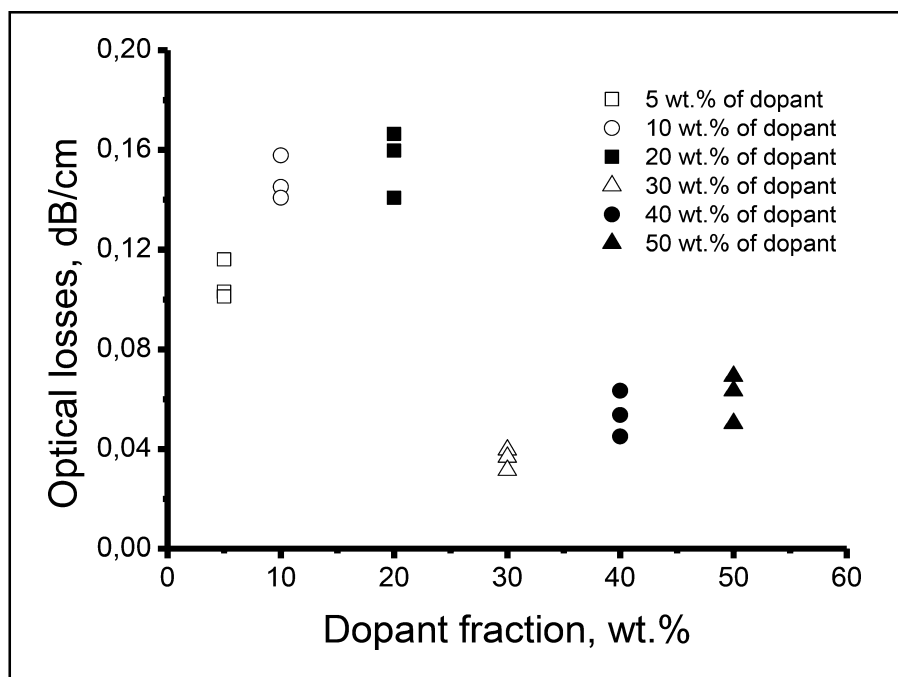

Fig. 8. Optical losses of doped polymer films

This Figure shows that the presence of mentioned "patterns" in the doped polymer films with 5-20 wt.% of quercetin provides optical losses in the range of 0.106 – 0.155 dB/cm. Changing the polymer composites morphology when increasing the dopant quantity, namely decrease of the micro-objects sides results in decrease 2-3 times of the optical losses values down to values 0.035 – 0.060 dB/cm.

It should be noted that the morphological investigation confirmed the previous results, which were obtained based on the optical and thermal studies.

3.4. Dependence of enhancement of macroscopic second-order NLO polarizability on dopant concentration

To determine the effect of chromophore concentration on NLO properties of the doped epoxy networks, their macroscopic second-order NLO polarizability values ($\chi^{(2)}$) were calculated. The calculation was made according to the one-dimensional, rigid oriented gas model as follows[21]:

$$\chi^{(2)}(-2\omega, \omega, \omega) = N\beta(-2\omega, \omega, \omega)\, F\, \langle \cos^3 \theta \rangle \quad (1)$$

where N is molecular number density; β is molecular first hyperpolarizability of chromophore; F is the local field correction factor; $\langle \cos^3 \theta \rangle$ is the average alignment factor:

$$\langle \cos^3 \theta \rangle = (0.6\Phi)^{1/2} \quad (2)$$

where Φ is the order parameter characterizing the poling-induced dipole re-orientation of the chromophore moieties.

The order parameter Φ was calculated from absorbance values of the films after (A_1) and before (A_0) the corona poling according to the following equation[22]:

$$\Phi = 1 - \frac{A_1}{A_0}. \quad (3)$$

The molecular quadratic polarizability of quercetin (β) was defined previously and it was equal to $108{,}2 \times 10^{-40}$ m⁴/V $= 25.6 \times 10^{-30}$ esu[23].

TABLE 1. Physical and non-linear parameters of doped polymer films

Weight fraction of quercetin, wt.%	*N, molecules/cm³	**F	***<cos³θ>	$\chi^{(2)}$, pm/V
5	0.55×10^{20}	30.4	0.01	0.18
10	1.13×10^{20}	30.9	0.02	0.75
20	2.29×10^{20}	31.8	0.17	13.28
30	3.55×10^{20}	32.7	0.35	43.58
40	4.85×10^{20}	33.7	0.19	33.31
50	6.24×10^{20}	34.7	0.17	39.48

*Number density of chromophore; ** Local field correction factor; *** average alignment factor.

Also, the important factors, which determine the polymer materials NLO properties, are packing density of chromophore molecules per unit volume (N) and the order parameter (Φ). These parameters are listed in Table 1.

Fig. 9 shows the dependence of $\chi^{(2)}$ values on the chromophore concentration. The curve of this dependence has extreme character. The weight fraction of the dopant at which the macroscopic quadratic polarizability is maximal
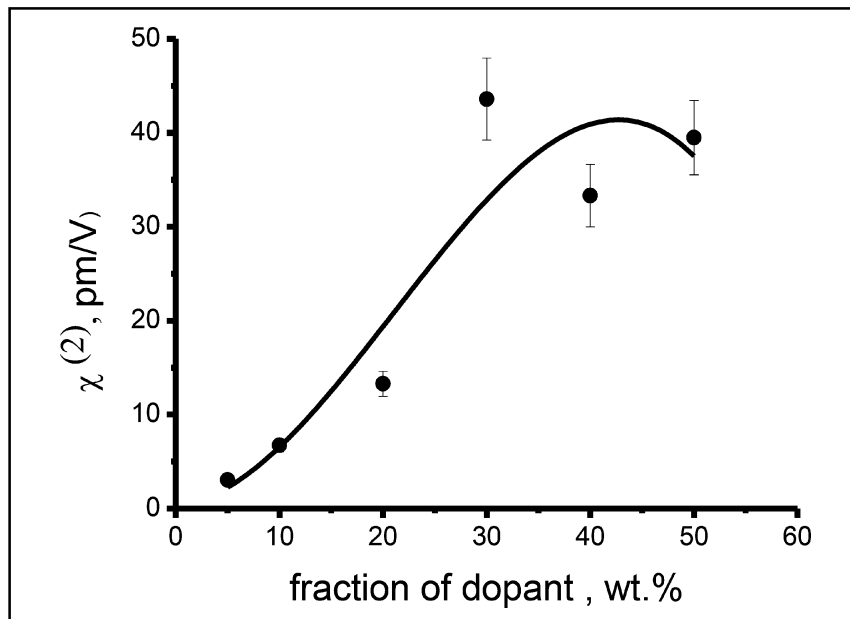
Fig. 9. Dependence of nonlinear quadratic polarizability values of polymer films on dopant concentration
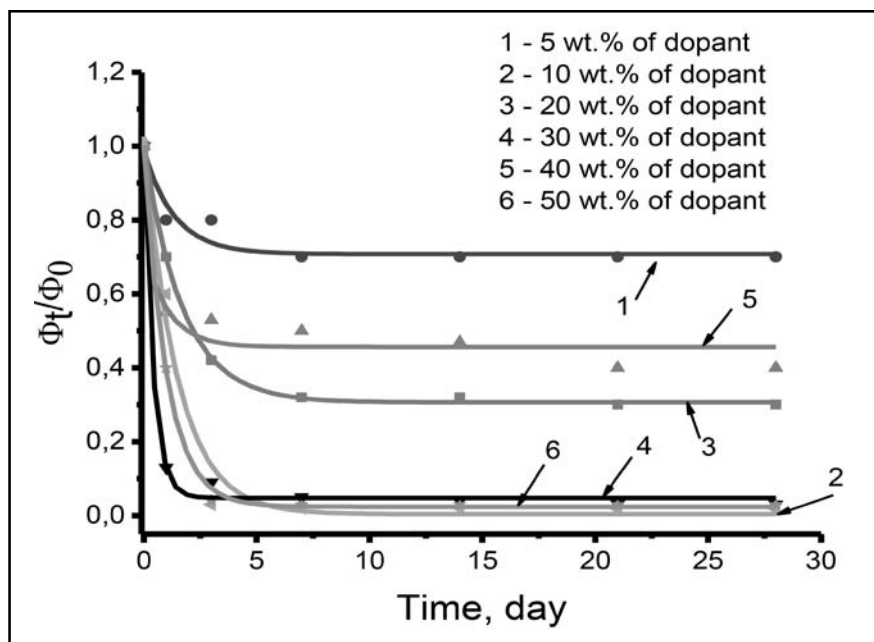

Fig. 10. Temporal stability of doped epoxy films

equal 30 wt.%. This fact is explained by the fact that at larger dopant concentrations its associates hinder with dopant molecules orientation at the corona discharge electric field [24].

Fig. 10. shows the temporal stability of quercetin-doped epoxy films. As can be-seen from Fig. 10 there is no direct relationship between the content of the dopant and the temporal stability of NLO properties of the doped polymer films.

After poling, in the polymer composites with 5 wt.% of the dopant, the parameter Φ_t/Φ_0 is reduced by 26 % after 3 day. The decrease of the same parameter at the dopant content of 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.% and 50 wt.% is 86%, 41%, 95%, 53% and 91%, respectively, during the same period. In our opinion, a varying of the chromophore molecules relaxation intensity in the polymer matrix and the availability associate molecules quercetin causes such a different temporal behavior of the NLO properties of the polymer composites. Obviously, the relaxation rate of associate molecules chromophore "frozen" in the cross-linked polymer matrix depends on their local environment. Therefore, the relaxation process can run faster in areas that contain topological defects caused by the polycondensation process of the epoxy oligomer *in situ*. Thus, in the polymer matrix that has more number of topological defects, the influence of steric difficulties on the polymer matrix is weaker.

4. CONCLUSIONS

Thus, based on the studies of the epoxy cross-linked polymer doped with quercetin, it is found that under conditions of synthesis of the polymer composite materials the dopant molecules exist in neutral, anionic forms and associates. Influenced by the corona discharge electric field at the low concentrations of quercetin, the anion form of the dopant in polymer matrix is oriented, generally. In the same time, the molecules in the neutral form are nonoriented, practically. This phenomenon is because of the dopant anions are polar and more easily oriented along the applied electric field. With increase in the concentration of quercetin from 30 to 50 wt.%, the molecules of the dopant are predominantly in neutral form and in the associates. The formation of associates leads to difficulties in orientation of the dopant molecules at the poling procedure and it causes reduction in the nonlinear optical properties of the doped polymer materials. These conclusions are in a good correlation with the morphological, thermal and optical investigations.

REFERENCES

1. W. Lin, Y.Cui, J. Yu, Y. Yang, G. Qian, *Dyes and Pigments* **136** (2017) 791.

2. L.R. Dalton, S. Benight, *Polymers* **3** (2011), 1325.

3. S.R. Marder, B. Kippelen, A.K.-Y. Jen, N. Peyghambarian, *Nature* **388** (1997) 845.

4. J. Wu, W. Wang, L. Wang, J. Liu, K. Chen, S. Bo, *Mater. Lett.* **164** (2016) 636.

5. J.M. Hales, S. Barlow, H. Kim, S. Mukhopadhyay, J.-L. Bredas, J.W. Perry, S.R, *Chem. Mater.* **26** (2014) 549.

6. A.N. Alias, Z.M. Zabidi, A.M.M. Ali, M.K. Harun, *Int. J. Appl. Sci. Eng. Tech.* **3** (2013) 11.

7. Y. Wang, W. Mahler, *Opt. Commun.* **61** (1987) 233.

8. O. Güllü, A. Türüt, *Sol. Energ. Mater. Sol. Cell* **92** (2008) 1205.

9. W. Liu, R. Guo, *J. Colloid Interface Sci.* **302** (2006) 625.

10. A. Bora, S. Avram, L. Crisan, L. Halip, R. Curpãn, L. Pacureanu, I. Ciucanu, *Rev. Roum. Chem.* **60** (2015) 175.

11. F.C. Spano, *Phys. Rev. Lett.* **66** (1991) 1197.

12. T. Hanemann, J. Bohm, K. Honnef, E. Ritzhaupt-Kleissl, J. Hauelt, *Macromol. Mater. Eng.* **292** (2007) 285.

13. I. Rau, P. Armatys, P.-A. Chollet, F. Kajzar, Y. Bretonniere and C. Andraud, *Chem. Phys. Lett.* **442** (2007) 329**.**

14. A.O. Doroshenko (1999) Spectral Data Lab software, Kharkiv.

15. D. Mishurov, A. Voronkin, A. Roshal and S. Bogatyrenko, *Opt. Mater.* **64** (2017) 166.

16. M. Heneczkowski, M. Copacz, D. Nowak and A. KuŸniar*, Acta Pol. Pharm. Drug Research* **58** (2001) 415.

17. A. Mezzetti, S. Protti, C. Lapouge and J.-P. Cornard, *Phys. Chem. Chem. Phys.* **13** (2011) 6858.

18. J.E.G. Lipson, S.T. Milner, *Eur. Phys. J. B Condens. Matter.* **72** (2009) 133.

19. Y. Ylmaz, D. Kaya, A O. Pekcan, *Eur. Phys. J. E* **15** (2004) 19.

20. J. Rotrekl, L. Mat!jka, L. Kaprálková, A. Zhigunov, J. Hromádková, I. Kelnar, *Express Polymer Lett.* **6** (2012) 975.

21. H.-Q. Xie, Z.-H. Liu, H. Liu, J.-S. Guo, *Polymer* **39** (1998) 2393.

22. H.-Q. Xie, X.-D. Huang, J.-S. Guo, *J. Appl. Polym. Sci.* **60** (1996) 537.

23. D. Mishurov, A. Voronkin, A. Roshal, *Struct. Chem.* **27** (2016) 285.

24. V.V. Shevchenko, À.V. Sidorenko, V.N. Bliznyuk, I.M. Tkachenko, O.V. Shekera*, Polymer Sci. Part A* **55 (**2013) 1.