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## THE PECULIARITIES OF FORMATION OF CROSS-LINKED POLY(2-ETHYL-2-OXAZOLINE) FILMS AND NANOCOMPOSITES ON THEIR BASE

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Cross-linked polymeric and nanocomposite films based on poly(2-ethyl-2-oxazoline) and modified mineral nanoparticles of hydroxyapatite and silica have been obtained via radical cross-linking initiated by peroxide containing reactive copolymers. The influence of temperature and additional cross-linking agents on the peculiarities of curing process has been studied. The obtained results reveal that at high temperatures the dependence of film gel-fraction values on time has the extremal character. Obtained cross-linked nanocomposite films are characterized by improved physico-mechanical properties that depend on the nature of mineral nanoparticles, content of peroxide containing copolymer and on the presence of additional cross-linking agent.

**Key words:** polyoxazoline, nanoparticles, cross-linking, nanocomposite, physico-mechanical properties.

### Introduction

The creation of filled organic-inorganic nanocomposites is one of the directions of obtaining biocompatible and biodegradable polymeric materials with high performance characteristics. Nanocomposites are the composites, in which at least one of the phases shows dimensions in the nanometer range (1–100 nm) [1]. These are materials that exhibit unusual property combinations and unique design possibilities and can be considered as the materials of the 21<sup>st</sup> century. A variety of nanofillers with different shapes can be used to produce polymer nanocomposites: mineral and polymer nanoparticles (NP), layered materials, nanofibers, nanotubes, etc [2]. It is known that at the nanoscale (below about 100 nm), a material's properties (conductivity, elasticity, strength, optical properties) change dramatically [3]. For example, for Au nanoparticles with diameter of 4 nm the melting point drops to 700 K from its value for bulk gold of 1337 K [4]. And white crystals of ZnO and TiO<sub>2</sub>, used as paint pigments or whitening agents become invisible to the human eye below about 15 nm [4]. At the same time, as particle dimensions reach the nanometer level, the interfacial surface and, in turn, surface energy increase sharply [5, 6]. Therefore, the modification of filler surface is

an important task to improve its compatibility with polymer matrix that causes the enhancement of nanocomposite physico-mechanical properties.

Nanostructured hybrid materials based on polymeric systems with 3D network structure and embedded mineral nanoparticles and especially composites based on biocompatible and biodegradable polymers have attracted increasing attention because of their unique and useful properties for obtaining materials and products for biotechnology, tissue engineering (implants for bone regeneration, model matrices for biomedical research), electronics (flexible film elements – screens, displays), optics, aerospace industry, catalysis, adsorbents, membranes, coatings etc. [7–9].

Depending on polymer matrix nature and field of composite application the diverse methods of polymer cross-linking and different cross-linking agents can be used: glutaraldehyde, trisodium trimetaphosphate, ions of polyvalent metals, epichlorohydrin, polycarboxylic acid, for example citric acid, peroxides [10–12]. It is known [13] that cross-linking of biodegradable polymers decreases the rate of their hydrolytic degradation. Hence, changing the cross-linking degree of polymers, one can control the processes of nanocomposite degradation and improve their physico-mechanical properties that is one of the key demands for materials applied in biomedicine.

Table 1

**Synthesis, composition and some characteristics of used peroxide-containing copolymers**

RC	Monomer mixture composition, %mol.				Copolymer composition, %mol.				Conversion, %	W <sub>pol</sub> ·10 <sup>3</sup> , %/c	Intrinsic viscos. in acetone, m <sup>3</sup> /kg	M <sub>w</sub> ·10 <sup>-3</sup> , g/mole
	AcAm	PM	BMA	MA	AcAm	PM	BMA	MA				
1	–	50	–	50	–	50.4	–	49.6	77.5	1.4	0.010	
2	30	30	–	40	37.9	24.5	–	37.6	77.8	6.5	0.006	7.0
3	20	20	20	40	25.6	19.5	14.8	40.1	82.1	4.9	0.007	10.6
4	–	20	40	40	–	17.7	40.0	42.3	76.1	4.7	0.008	28.9

In our previous works we have shown that the modification of disperse mineral fillers with functional peroxide-containing copolymers facilitates their disaggregation, decreases surface energy and, as a result, improves the compatibility with polymer matrix of different nature and on the other hand provides the formation of cross-linked 3D polymer networks due to the reactions of radical (non-specific) curing initiated by reactive groups present in the modifier structure [14, 15].

Polyoxazolines (PEOX) have drawn attention due to their good biological and chemical properties, such as high solubility, biocompatibility, low toxicity, and sensitivity in pH and temperature [16]. With these superior properties, PEOXs are investigated for various applications such as drug delivery, protein adsorption, and antibacterial materials.

This work is devoted to the study of the peculiarities of the processes of obtaining cross-linked nanocomposites based on poly(2-ethyl-2-oxazoline) and embedded mineral nanoparticles modified by peroxide-containing copolymers.

**Materials and methods of research**

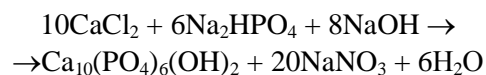
Synthesis of peroxide-containing reactive copolymers (RC) of butyl methacrylate (BMA), acryl amide (AcAm), maleic anhydride (MA) and peroxidic monomer 5-tert-butylperoxy-5-methyl-1-hexene-3-yne (PM) with different content of monomer links was carried out via radical copolymerization of the aforementioned monomers in 2-propanone at their diverse ratios (total monomer concentration was 3.5 mole/l) at 333 K in the presence of lauroyl peroxide as initiator ( $C_{PL}=0.03$  mole/l) as described elsewhere [17]. Composition and some chemical characteristics of synthesized RC are shown in Table 1.

The content of peroxide groups in RC was determined from the results of gas chromatographic analysis of the final decomposition products obtained at the RC thermolysis at 483K under argon with the use of gas-liquid chromatograph SELMICHROM-1 (Selmi, Ukraine) [18]. The content of MA subunits in RC was determined using a reverse potentiometric titration of carboxylic groups. The content of AcAm and DMAE subunits was estimated from the results of elemental [C, H, N] analysis. Intrinsic viscosity  $[\eta]$  of RC solutions was measured using Bishoff viscosimeter in acetone at 298 K [19]. Molecular weight of copolymers was determined by gel-permeation chromatography using Polymer Standard Service system (PSS, Mainz, Germany, MDS RI detector).

Poly(2-ethyl-2-oxazoline) (PEOX, trademark Aquazol-500) with molecular weight 500kDa was used as a matrix polymer.

Synthesis of SiO<sub>2</sub> NP was carried out in accordance with Stober method in the presence of reactive copolymers as described elsewhere [20].

NP of hydroxyapatite (HA) were synthesized via sol-gel method as described in [21] in accordance to the reaction:



To obtain cross-linked polymer films 20 % water solution of PEOX was prepared with 10–20 % of RC with respect to PEOX. The films were cast on a glass surface and after drying at ambient conditions were cured at 373–413 K for 1–3 hours. The films were formed with the thickness of 120–160 μm. Additionally, in order to study the influence of vinyl monomers onto curing process the small amounts (3–5 % with respect to polymer weight) of hydroxyethyl methacrylate (HEMA) or N,N'-methyl-

enebis(acryl amide) (MBA) were added to the polymer solution.

To obtain cross-linked composites based on PEOX the polymer solution (20 %) was prepared firstly. Suspension of mineral NP in water was prepared using UZDN-A ultrasonic disperser (SPE ACADEMPRYLAD Ltd, Sumy, Ukraine) and introduced into polymer. NP weight in suspension was calculated as 20 % with respect to polymer weight. The films were cast on a glass surface and after drying at ambient conditions were cured at 373–413 K for 1–3 hours.

The kinetics of film curing was investigated by gel fraction content. The soluble fractions were extracted from cured films in a Soxhlet apparatus by water during 12 hours. The gel fraction ( $H$ , %) was computed as:

$$H = (m_1/m_2) \cdot 100 \% \quad (1)$$

where  $m_1$  and  $m_2$  – the film weights after and before extraction, respectively.

The swelling kinetics of cured polymer films was determined as follows: the weighed sample of the dry film was covered with water and kept in water for the certain time. Thereafter the unabsorbed water was decanted, the swelled hydrogel was unloaded on a filter paper to remove the remaining unabsorbed water. The swelling degree ( $W$ , %) was calculated as:

$$W = ((m_s - m_f)/m_f) \cdot 100 \% \quad (2)$$

where  $m_s$  – the weight of the swelled film and  $m_f$  – the weight of the film sample.

The film hardness ( $T$ ) was determined using M-3 pendulum apparatus:

$$T = \tau_p/\tau_g \quad (3)$$

where  $\tau_p$  – time of M-3 pendulum swings on polymer film cured on glass plate (s),  $\tau_g$  – time of M-3 pendulum swings on glass plate (s).

Tensile strength ( $P$ , kPa) and relative elongation at break ( $\epsilon$ , %) of cross-linked films were determined using TIRA test 2200 testing machine.

## Results and Discussion

Previously we have studied the processes of cross-linking biocompatible polymers such as polyvinyl alcohol (PVA) and poly acrylamide (PAA) and have shown that cross-linking degree increases with the increase in temperature, cross-linking time and peroxide-containing RC concentration [16].

In the case of polymer films based on PEOX the gel-fraction dependence on cross-linking time and temperature changes significantly. At  $T=413$  K

this dependence has extremal character (Fig. 1). Gel-fraction value reaches its maximum after 1-hour heating and then decreases drastically. It should be noted that in the case of the film containing 20 % RC the value of maximum gel-fraction is higher than for film with 10 % RC. But with the increase of heating time up to 3 hours the gel-fraction value drops down to 0 % in both cases.

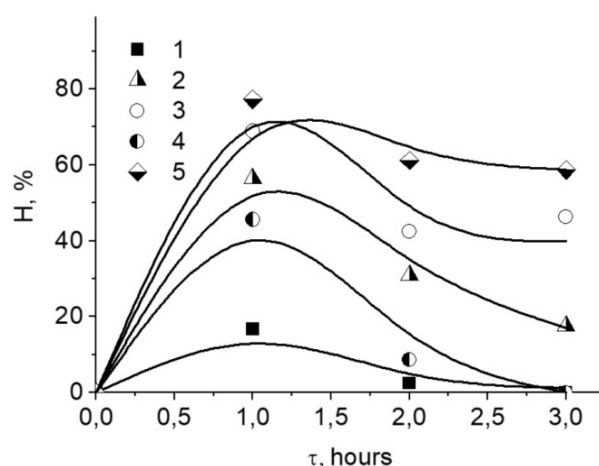


Fig. 1. Dependence of gel-fraction of PEOX polymer films cross-linked by RC-2 and vinyl monomers on time: 10% RC (1); 10 % RC+3%HEMA (2); 10 % RC+5 % MBA (3); 20 % RC (4); 20 % RC+5 %MBA ( $T=413$ K)

Colombo et al. [22] described oxidative degradation of poly(2-ethyl-2-oxazoline) in the nanocomposite filled with  $\text{TiO}_2$  NP under UV-irradiation ( $\lambda < 400$  nm) at the presence of oxygen as a result of the hydroperoxide formation on the carbon atom in  $\alpha$  position to the nitrogen with further chain decomposition and generating secondary amide and carboxylic acid. Evidently, in our case thermooxidative destruction of PEOX carbon chain occurs under the influence of high temperature and oxygen and is promoted by free radicals formed at decomposition of RC peroxide fragments.

To prove this assumption, we have studied the influence of the temperature of PEOX film cross-linking on the viscosity of their water solution. As it is known, the solution viscosity is proportional to polymer molecular weight that allows estimating molecular weights of polymers with the same composition. The intrinsic viscosity of polymer film solutions of and their kinematic viscosity at certain concentration have been determined (Table 2).

Table 2

**Dependence of intrinsic and kinematic viscosity of water solution of PEOX/RC films on cross-linking temperature**

Film composition	Intrinsic viscosity in water, m <sup>3</sup> /kg		Viscosity of 2 % solution in water, cSt	
	293 K	413 K	293 K	413 K
PEOX	0.78	0.55	3.68	2.3
PEOX+10 % RC2	0.82	0.57	3.84	2.39
PEOX+20 % RC2	0.75	0.41	3.35	2.14
PEOX+10 % RC4	0.69	0.46	3.36	2.31
PEOX+20 % RC4	0.52	0.35	3.21	2.01

One can see that as a result of film heating at 413 K the intrinsic viscosity of their water solution and kinematic viscosity of 2 % solution decreases symbatically. Worthy to note, that these values decrease for film without RC as well. On the other hand, the increase in RC content in the film causes the sharper decrease in solution viscosity. It should be noted also that obtained films dissolve in water almost completely that indicates the absence of cross-linked polymer in them. Hence, obtained data witness in favor of our assumption about thermooxidative destruction of PEOX polymer films at elevated temperature and the acceleration of this process in the presence of peroxide-containing RC.

The study of PEOX film cross-linking at lower temperatures have demonstrated that at  $T=373$  K gel-fraction value grows monotonously with the time (Fig. 2a). So, the influence of thermooxidative destruction process onto cross-linking degree is negligible. However, at  $T=393$  K the maximum on the curves of gel-fraction dependence on time is observed similarly to the plots obtained at  $T=413$  K (Fig. 2b).

In this case, unlike films cross-linked at  $T=413$  K, the maximum is observed after 2 hours curing (with increasing curing time), that is explained by diminishing rate of destruction process at lower temperature. Thus, obtained results witness that curing at 373 K during 3 hours or at 413 K during one hour are the optimal conditions for obtaining PEOX cross-linked films.

The investigation of the influence of small (3–5 %) of additional vinyl monomers onto cross-linking process reveal that the introduction of acrylic acid does not affect cross-linking degree of polymer films – gel-fraction values change by 2–5 % only, that is, within the experiment error. But addition into the system of HEMA and, especially, of bifunctional

MBA provides essential increase in gel-fraction value – 25–180 % gel fraction increase when HEMA is used and 30–320 % for MBA (Fig. 1, 2).

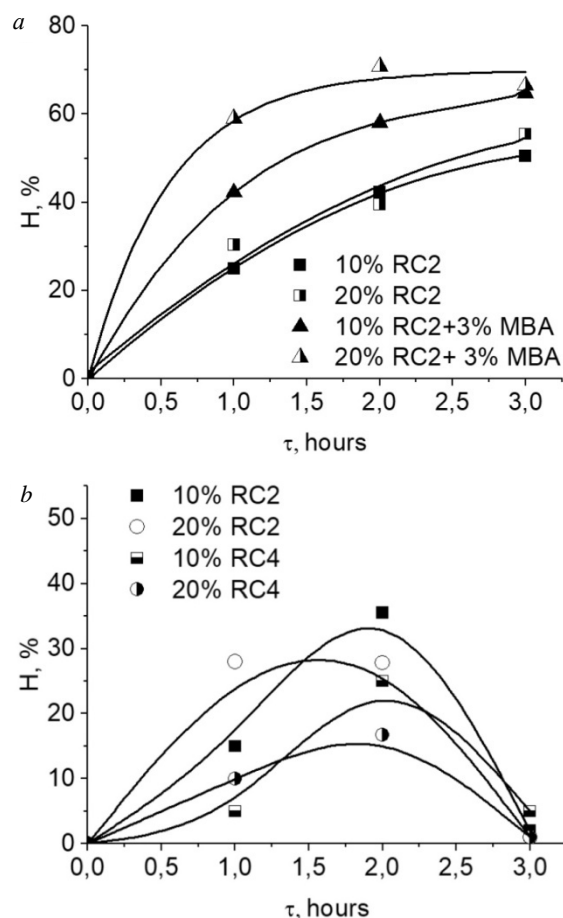


Fig. 2. Dependence of gel-fraction of PEOX films cross-linked by RC at 373K (a) and 393K (b) on time

The same character of the dependence of gel-fraction value on temperature is observed for nanocomposite PEOX films filled by mineral NP with peroxide-containing shell (Table 3). One can see that after curing for 1–2 hours at 413 K gel-fraction of nanocomposite films based on PEOX at the absence of additional cross-linking agent reaches 50% when peroxidized HAP nanoparticles are used as film filler. This witness about higher ability of such peroxidized filler to participate in chain transfer reactions.

But with increasing curing time up to 3 hours the gel-fraction value diminishes. This can be explained (as in the case of unfilled PEOX films) by the occurring competitive reaction of polymer macromolecules destruction under the action of free radicals generated by peroxide fragments of NP

polymer shell. It should be noted that in the case of SiO<sub>2</sub> nanoparticles modified with RC6 gel-fraction value begins to decline after 2 hour heating but when the same SiO<sub>2</sub> NP with grafted poly(N-vinylpyrrolidone) are used as a filler gel-fraction decreases only after 3 hour heating. Evidently it can be explained by better compatibility of modified in such a way NP with matrix polymer and as a result by better uniformity of NP dispersion in polymer that causes higher efficiency of initiation of chain transfer radical reactions by peroxide groups immobilized at NP surface.

The use of the additional cross-linking agent provides the increase in gel-fraction of nanocomposite film. Evidently, in this case the cross-linking process is offset by a competing process of destruction of main polymer chain and a small amount of cross-linking agent is not sufficient to form a continuous three-dimensional network. There-

fore, the study of nanocomposite films cross-linking at T=373 K has been carried out (Table 4).

One can see that for nanocomposite films cured at T=373 K the gel fraction values rise with the increasing curing time that witness in favor of cross-linked 3D films. The highest degree of cross-linking is observed for the films with embedded HAP nanoparticles modified with RC1 that contain the largest amount of peroxide fragments in their shell. The addition of small amount of MBA additional cross-linking agent increases gel-fraction value significantly. The study of physico-mechanical properties of obtained films reveals that they are characterized by high enough tensile strength (Table 4). Besides, when MBA cross-linking agent is added the strength of nanocomposite films increases 2–3 times and relative elongation at break decreases. This proves the formation of denser three-dimensional network as well.

Table 3

**Composition and some characteristics of nanocomposite films based on PEOX and mineral NP modified by peroxide-containing RC (NP content – 20 % with respect to polymer, T<sub>cur</sub>=413 K)**

NP nature	Nature of immobilized RC	A <sub>RC</sub> , mg/g	C <sub>O-O</sub> , %	Polymer of grafted to NP surface shell	Hardness, a.u.			Gel-fraction, %		
					293K	1 hour	3 hours	1 hour	2 hours	3 hours
SiO <sub>2</sub>	RC6	34.1	0.072	–	0.62	0.62	0.57	43.8	39.7	10.9
SiO <sub>2</sub>	RC6	34.1	0.072	poly (N-VP)	0.60	0.55	0.70	18.0	43.5	8.7
SiO <sub>2</sub>	RC2	39.9	0.070	–	0.61	0.67	0.67	3.6	36.7	10.8
HAP	RC1	19.3	0.11	–	0.60	0.53	0.53	50.8	59.8	38.2
Films with additional cross-linking agent (3 % MBA)										
SiO <sub>2</sub>	RC6	34.1	0.072	–	0.44	0.48	0.57	63.5	52.6	47.3
SiO <sub>2</sub>	RC6	34.1	0.072	poly (N-VP)	0.47	0.48	0.58	44.6	37.1	29.9
SiO <sub>2</sub>	RC2	39.9	0.070	–	0.58	0.54	0.58	62.2	33.8	25.8
HAP	RC1	19.3	0.11	–	0.37	0.45	0.67	56.3	65.0	64.2
Films with additional cross-linking agent (5 % HEMA)										
HAP	RC-1	19.3	0.11	–	0.16	0.45	0.52	57.6	59.7	47.6

Table 4

**Composition and some characteristics of nanocomposite films based on PEOX and mineral NP modified by peroxide-containing RC (NP content – 20 % with respect to polymer, T<sub>cur</sub>=373 K)**

NP nature	Nature of immobilized RC	A <sub>RC</sub> , mg/g	C <sub>O-O</sub> , %	Polymer of grafted to NP surface shell	Gel-fraction, %			Tensile strength, MPa*	Relative elongation, %*
					1 hour	2 hours	3 hours		
SiO <sub>2</sub>	RC6	34.1	0.072	–	20.2	37.3	41.7	8.1	19.9
SiO <sub>2</sub>	RC6	34.1	0.072	nN-BII	15.5	35.5	39.9	7.1	92.7
HAP	RC1	19.3	0.11	–	18.2	38.2	54.4	5.4	5.6
Films with additional cross-linking agent (3 % MBA)									
SiO <sub>2</sub>	RC6	34.1	0.072	–	41.8	47.1	52.2	13.1	2.7
SiO <sub>2</sub>	RC6	34.1	0.072	nN-BII	21.4	36.5	55.1	14.7	11.2
HAP	RC1	19.3	0.11	–	43.1	51.1	68.8	16.7	1.9

\* Tensile strength and relative elongation has been determined for films cured for 3 hours.

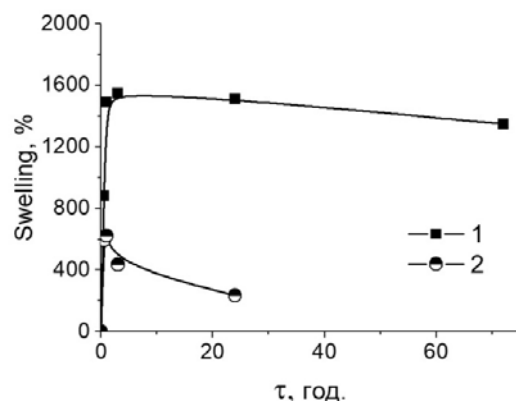


Fig. 3. Swelling kinetics of polymer nanocomposite films based on PEOX with embedded 20 % HAP nanoparticles with 3 % MBA (1) and without MBA (2)

Obtained cross-linked polymer nanocomposite films are able to swelling in water. But as our investigation proves, in order to reach high swelling level and stability of formed hydrogels the additional cross-linking agent is necessary for increasing film cross-linking level (Fig. 3).

### Conclusions

The processes of cross-linking polymer films based on PEOX by peroxide containing curing agents have been studied and it has been shown that this process has some peculiarities compared to cross-linking polyvinyl alcohol or polyacrylamide. Obtained results witness that the dependence of gel-fraction value on time at elevated temperatures (393–413 K) has the extremal character while at 373 K this value increases monotonously with time. Curing at 373 K during 3 hours or at 413 K during one hour are the optimal conditions for obtaining PEOX cross-linked films. That is caused by thermooxidative destruction of PEOX carbon chain under the influence of high temperature and oxygen and can be promoted by free radicals formed at decomposition of RC peroxide fragments. The introduction into polymer films of additional vinyl monomers such as HEMA and bifunctional MBA provides the gel-fraction enhancement by 25–320 % depending on concentration of RC and process parameters. The peculiarities of nanocomposite film crosslinking initiated by RC peroxidic fragments immobilized onto the surface of mineral NP embedded are similar to those for PEOX polymer films. Obtained nanocomposite films are characterized by high enough physico-mechanical properties (tensile strength, relative elongation at break), which depends on the nature of RC and mineral NP.

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## **ОСОБЛИВОСТІ ФОРМУВАННЯ СТРУКТУРОВАНИХ ПЛІВОК ПОЛІ(2-ЕТИЛ-2-ОКСАЗОЛІНУ) ТА НАНОКОМПЗИТІВ НА ЇХ ОСНОВІ**

Шляхом радикального структурування, ініційованого пероксидовмісними реакційноздатними кополімерами, отримано структуровані полімерні та наноккомпозитні плівки на основі полі(2-етил-2-оксазоліну) і модифікованих мінеральних наночастинок гідроксиапатиту та діоксиду силіцію. Досліджено вплив температури і додаткового зшиваючого агента на особливості процесу отвердження. Отримані результати свідчать, що при підвищених температурах залежність гель-фракції від часу має екстремальний характер. Отримані структуровані наноккомпозитні плівки характеризуються покращеними фізико-механічними властивостями, що залежать від природи мінеральних наночастинок, вмісту пероксидвмісного кополімеру та присутності додаткового зшиваючого агента.

**Ключові слова:** поліоксазолін, наночастинок, структурування, наноккомпозит, фізико-механічні властивості