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RADIATION BEHAVIOUR OF NANOCOMPOSITE EPOXY MATERIAL

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Acoperirile epoxy modificate cu dioxid de titan (rutil) şi silice la diferite concentraţii până la 10%, au fost investigate pentru evaluarea rezistivităţii electrice şi modificarea calităţii suprafeţei după expunerea la îmbătrânire accelerată în câmp de radiaţii gamma. Au fost înregistrate schimbările de proprietăţi după iradieri la diferite doze de radiaţii gama (0, 10, 20, şi 50 kGy). Influenţa mediilor de degradare în care se face expunerea la radiaţii a fost realizată în două medii (aer şi apă distilată) la iradieri de energie ridicată, pentru a evalua comparativ, contribuţia produselor de radioliză a apei asupra materialului supus testării.

Epoxy resin sheets modified with titania (rutile) and silica on various concentrations up to 10 % were investigated relative to the evolution of electrical resistivity and the modification of surface quality, when they are subjected to accelerated ageing in γ-radiation field. The changes in foreseen properties were qualified after receiving different γ-irradiation doses (0, 10, 20 and 50 kGy). The influence of irradiation degradative environments (air and distilled water) in the exposure processs of the tested materials to high energy radiation was also studied and a comparative contribution of water radiolysis products on the materials was evaluated.

Keywords: nanocomposite, rutile, silica

1. Introduction

The synthesis of polymer composites corresponds to the necessity of new applications in various fields: dielectrics [1-5], coatings [6, 7], automotive manufacture [8, 9], radiation-cured products [10-12]. The functional properties of these epoxy composites can be defined in many respects by both behaviors of filler and host polymer, which interact on the interface region. Despite the good thermal properties of the crosslinked product and significant processing advantages, composites manufactured using radiation curing epoxy systems suffer

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from low compressive strength, poor interface between reinforcement and resin matrix, low interlaminar shear strength, and low fracture toughness. However, the addition of nanofillers brings about new features in the resistance of irradiation conditions [13] or during thermal oxidation [14].

The quality and performances of nanocomposites are related not only on the manufacturing parameters, but also on the action of external stressors during applications. The modification of termoset resins with various fillers induces new answer to the degrading factors which involves the scavenging of radicals appeared during material ageing.

The accelerated testing of polymers may be accomplished by thermal treatment or by the exposure to the action of ionizing radiation. The last procedure simulates the accident events, when the sudden energy transfer causes major changes in the structure of material. The environment where products are suppressed to mechanical and thermal charges may induce additional degradation effects. The main aspects that must be revealed are the implication of intermediates into the evolution of material as the result of bond scissions. The integrity of material depends on the substrate ability in the delaying of oxidation that occurs during the life of material with various rates in correlation with service environment. The selection of ageing conditions must be similar to the service parameters for drawing correct conclusions for structural characterization [15] durability investigations [16, 17].

In this paper, the influence of aging conditions on epoxy nanocomposites subjected to fast degradation under γ-radiation is analyzed based on electrical and surface modifications. The involvement of nanofiller particles is characterized by electrical measurements and imaging analysis of surface.

2. Experimental

A basic polymer material was obtained by curing of liquid epoxy resin, D. E. R.™ 353 (Dow, USA), which is a C_{12}-C_{14} aliphatic glycidyl ether modified bisphenol A/F based epoxy resin in the presence of hardener Epilox H 10-30, a modified cycloaliphstic polyamine epoxide adduct (LEUNA_Harze GmbH, Germany). The filler added in this curing systems was titania – rutile (ultrafine rutile – crystalline form, 17 nm) UV-TITAN L181 type (Kemira Pigments Oy, Finland), titania – anatase (TIOXIDE A-HR, crystal size, max. 100 nm) and silica (AEROSIL 200, Degussa, particle size between 7 and 40 nm, covered with siloxane). The selected concentrations of titanium dioxides were 1, 5 and 10 % (w/w). Samples with silica had filler concentration of 1, 5 and 7 % (w/w). The neat sample was also investigated.

Irradiation was performed in air at room temperature in GAMMATOR M-38-2 installation (USA), provided with ^{137}Cs source. Dose rate was 0.4 kGy/h.

Integrated doses were 10, 20 and 50 kGy, which ensure the primary degradation step. Exposure to the action of ionizing radiation was performed in air and distilled water at room temperature.

FTIR spectra were recorded on JASCO 4200A spectrophotometer at 50 scans and 4 cm^{-1} resolution. The 1609 - 1762 cm^{-1} region was found to be characteristic for spectral modification under γ-exposure.

Electrical measurements were performed by laboratory equipment megohmmeter METREL under the tension of 1000 V. The presented values mean the average of ten measurements on different points placed inside a square of 1 cm^2.

The investigations on surface quality was accomplished by VEECCO Wyko NT1100 microscope using interferometry with white light for high resolution scanning of subnanometric to micrometric 3D roughness. The surface states are characterized by several parameters:

- R_t- the height difference between the highest point and the lowest point in the region,
- R_p- the highest point in the region relative to the zero level,
- R_v-the lowest point in the region relative to the zero level,
- R_a- the average roughness as calculated over the entire region,
- R_q- the root mean squared roughness calculated over the entire region.

3. Results and Discussion

Characterization of oxidative stability

The degradation of studied epoxy resin systems starts after samples receive medium irradiation doses according to the preliminary investigations [6]. The modifications in IR spectra appear later, when exposure dose exceeds 50 kGy. The changes in IR spectra on the region of 1600 – 1730 cm^{-1} were noticed, where unsaturation appears. It can be noticed that initial unsaturation is decayed, these absorption bands being replaced by the bands of oxidation products.

The oxidative resistances of unirradiated samples containing added oxide fillers are depicted in figure 1. The deep difference between pristine and modified epoxy resin is revealed. The ascendant values of chemiluminescence intensity denote a continuous oxidation as a result of oxygen diffusion which feeds the polymer matrix when oxygen content is partially consumed. On the other side, the initial values of I_{CL} demonstrate the increasing content of oxygen adsorbed on filler nanoparticles because of their enormous interphase surfaces. However, the presence of nanoparticles is a barrier against the diffusion of oxygen, which would feed the oxidation process.

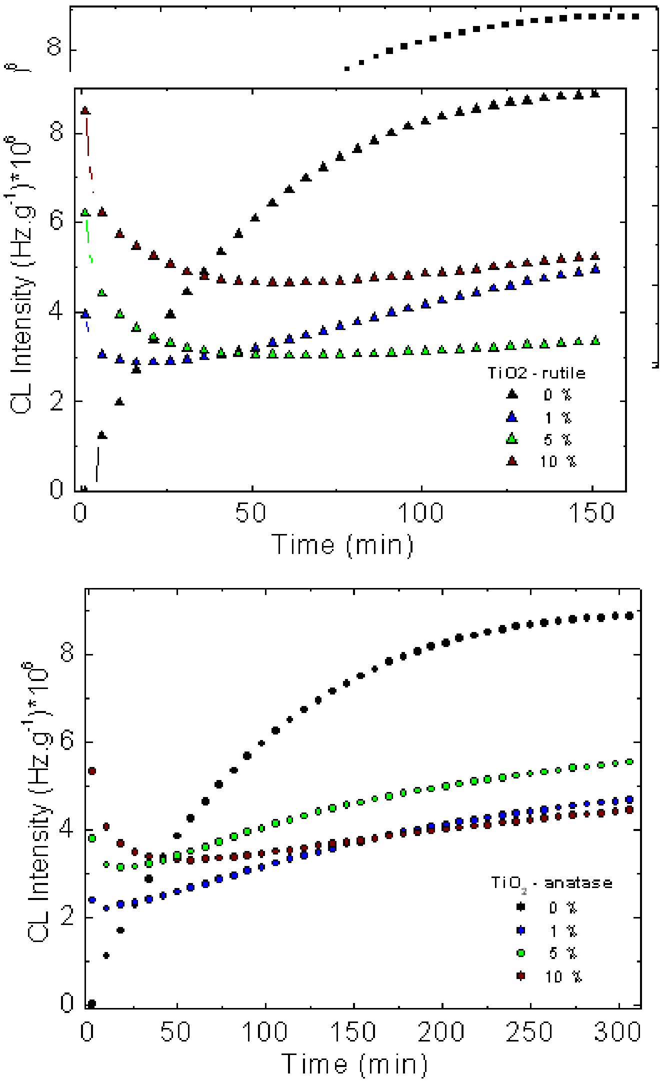


Fig. 1. CL curves depicting the progress of oxidation on epoxy resin nanocomposites

γ-Irradiation brings about an improvement in the material stability (figure 2). It can be assumed that the large surface of nanoparticles of oxide filler may adsorb the intermediates formed during oxidative radiolysis of these epoxy resin nanocomposites. The contribution of fillers to the thermal stability of basis polymer consists of the scavenging of radicals, which sharply diminishes the oxidation rate.

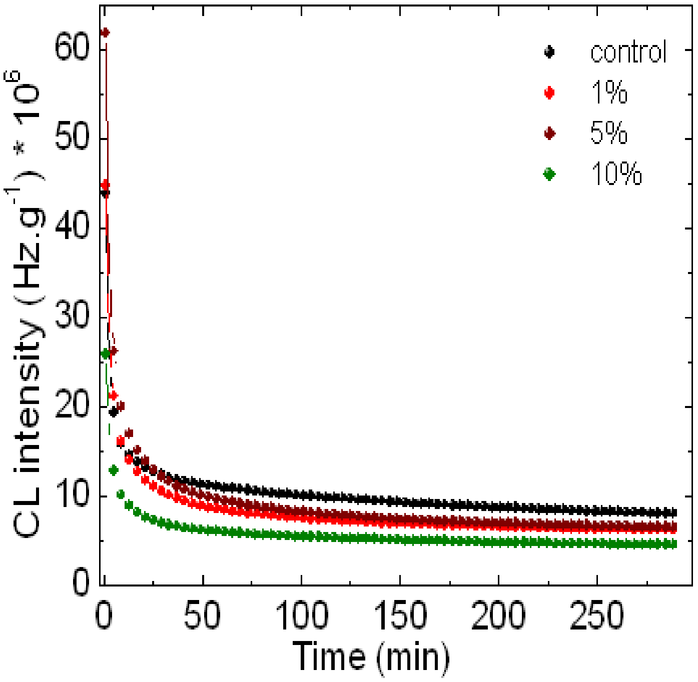


Fig. 2. CL curves for oxidation of γ-irradiated epoxy resin/TiO_2 (rutil) nanocomposite; received dose: 50 kGy

The polarity of filler influences the availability for catching radicals . The consequence of this feature is the material stability on the steady state. Rutile and anatase, which have titanium as metallic element of oxide, exhibit stronger attraction relative to uncoupled electron of radical than silicon, which has a neutral behavior. There is not any difference between the contributions in the oxidation activity during thermal ageing.

γ-Irradiation causes molecular modifications, but the presence of oxygen in the initial structure of polymer, the mechanism of degradation runs by the scission of C – O bond. The two types of radicals react differently in respect with further oxidation. The first type, which presents terminal oxygen atom may be easier bonded that the other type characterized by carbon atom end. The self-catalyzed degradation which involves the second category of radicals progresses through the reaction of substituted carbon, which presents the lowest activation energy requires for bond scission.

The sharp decrease in the chemiluminescence emission intensity on the first 10 minutes highlights the filler capacity for the inhibition of oxidation. The highest amount of radicals, which are formed during γ-exposure is consumed very fast by the coupling with titanium or silicon atoms. The existence of Si(Ti) – OR bridge can be revealed by spectroscopic and dielectric investigations [18].

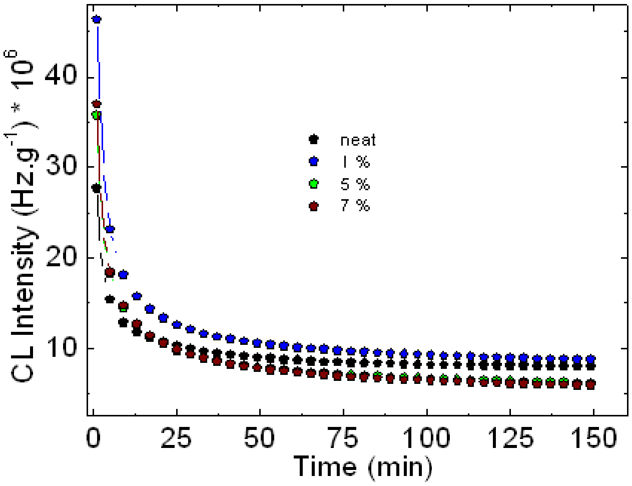


Fig. 3. CL curves for oxidation of γ-irradiated epoxy resin/SiO_2 nanocomposite; received dose: 50 kGy

The similitude in the development of oxidation in irradiated nanocomposites of epoxy resin with TiO_2 and SiO_2 fillers for a large range of oxide concentrations may be considered as a favorable feature for high resistance of this kind of materials in ionizing radiation field (figure 2 and 3).

Characterization of electrical resistivity

The high rate transmission of energy that occurs during γ-irradiation induces a modification in the dipole distribution. The generation of oxygen-containing structures leads to the accumulation of polar functions, which increases the electrical conductivity of samples. This turning onto lower resistivity is accelerated by the action of products of water radiolysis that influence the movement of charge carriers through the macromolecular chains (figure 4).

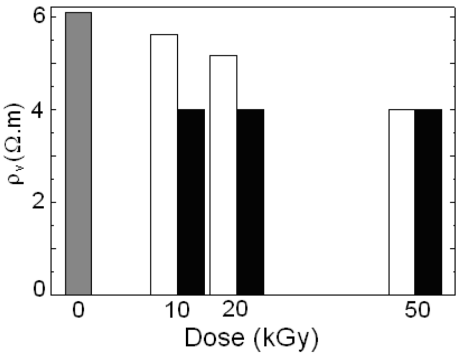
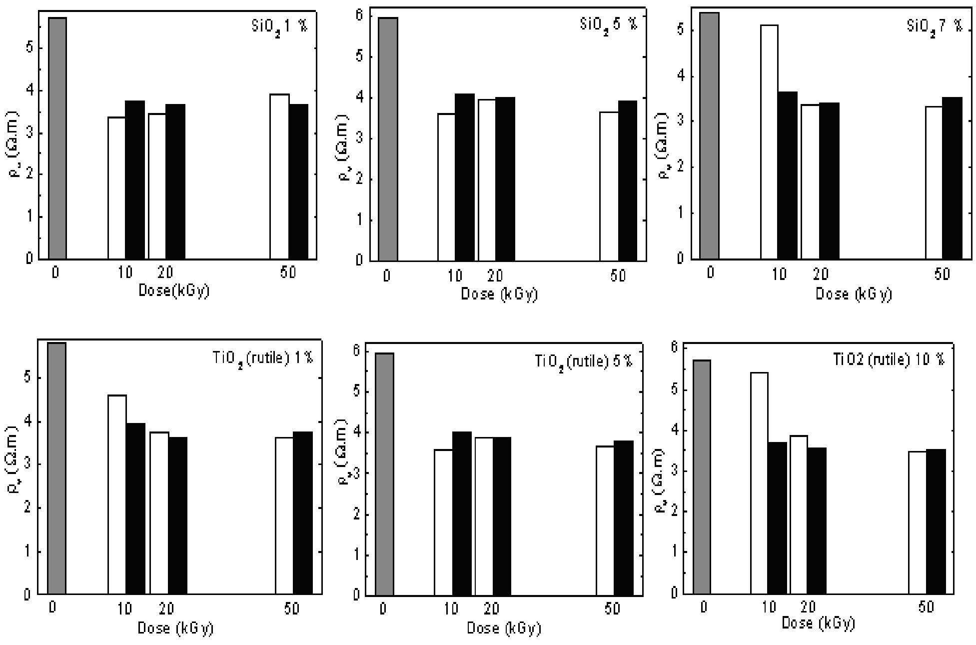


Fig. 4. Resistivity of unmodified epoxy resin subjected to γ-irradiation.
(grey) pristine material; (white) irradiation in air; (black)irradiation in water

The presence of filler can modify the response of material to oxidation evaluated by electrical conductivity (figure 5). The decrease in ρ_v values is closely related to the penetration of oxygen into polymer matrix, this feature being controlled by the amount of filler and the receive dose.



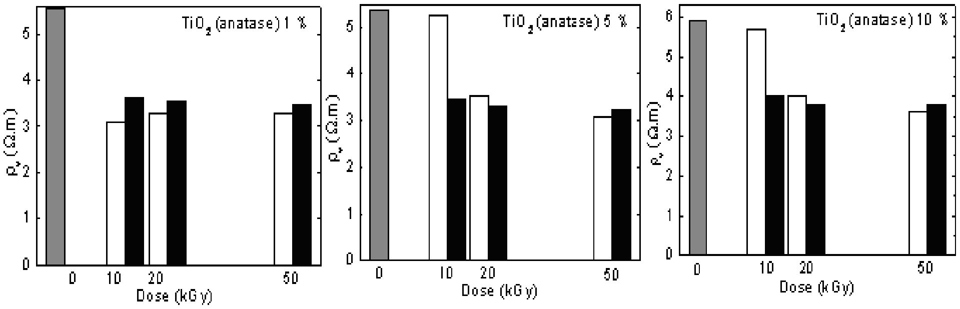


Fig. 5. Volume resistivity of radiation processed epoxy resin nanocomposites

The most evident changes occurred in the resistivity of these nanocomposites can be noticed in the case of TiO_2 1%. The measurement error placed at ± 5 % allows us to evaluate the high resistance of epoxy resin to the advance in oxidation process caused by high energy irradiation. By comparing these results with the information obtained by thermal investigation a satisfactory agreement can be remarked. For the most of γ-exposures there are not significant differences between the irradiation results in air and water. It can be explained by the remarkable stability of polymer substrate to which the presence of filler increases the chemical resistance. On the other hand, the majority of irradiation at the lowest applied dose (10 kGy) exhibits a sharp lowering in the resistivity of nanocomposites. It means that the further action of nanofiller can be considered as a passivation of several outer molecular layers of polymer.

Characterization of surface modification

The surface state is always the result of the action of outer degrading agents: mechanical charge, chemical attack, radiation action. The first molecular layers are predominantly changed and the material displacement is happened. The most evident changes were observed after the γ-irradiation in water [19, 20].

$$H_2O \overset{e^-,\gamma}{\rightsquigarrow} H, HO^{\bullet}, HO^-, e^-_{aq}, H_2O_2$$

These reactive entities attack polymer surface causing a removing of material as the result of the scission of several bonds.

Two illustrative examples are presented (figure 6 and figure 7). The largest surface modification occurred in accordance with the propagation of oxidation chain. The evolution of roughness depends strongly on the initial state of surface, but the depth of hollows is in connection with the evolution of degradation.

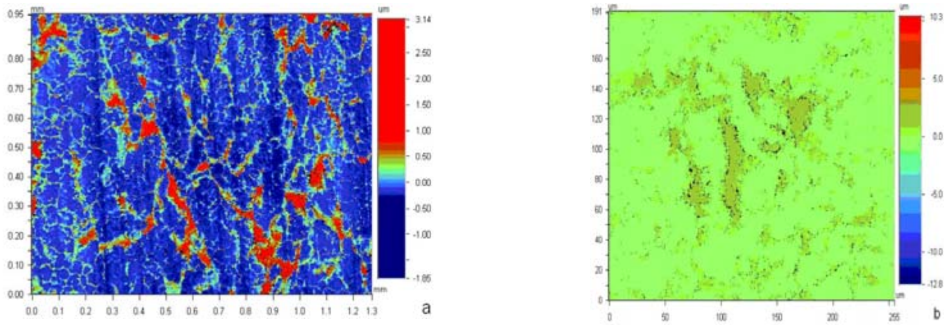


Fig. 6. Modification in the roughness of epoxy resin/TiO_2 (anatase) 1 % composite caused by γ-irradiation in water: (a) nonirradiated sample; (b) 20 kGy

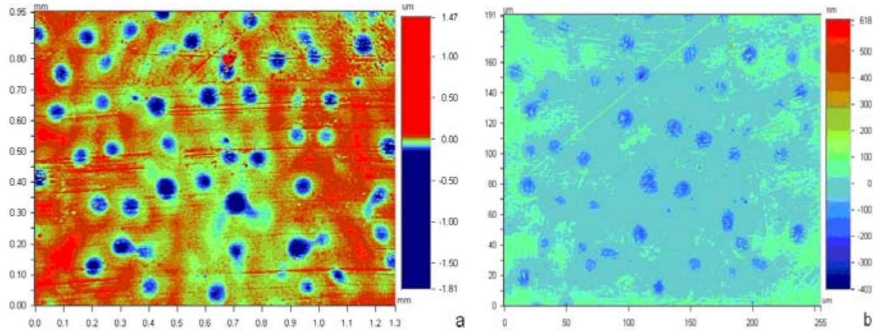


Fig. 7. Modification in the roughness of epoxy resin/SiO_2 5 % composite caused by γ-irradiation in water: (a) nonirradiated sample; (b) 20 kGy in water

The overall effect of γ-irradiation on studied nanocomposites can be analyzed from table 1.

Table 1

Roughness parameters of radiation processed epoxy resin (ER) nanocomposites irradiated in water

Sample type	Dose (kGy)		R_q (mm)	R_a (mm)	R_t (mm)	R_p (mm)	R_v (mm)
Pristine ER (resin in pure state)	0		0.34	0.18	3.94	3.33	-0.61
	10		0.34	0.24	4.09	1.25	-1.11
	20		0.29	0.21	3.49	2.15	-0.83
	50		0.85	0.66	4.11	2.33	-1.83
SiO2 1%	0		1.33	0.91	6.23	5.55	-0.68
	10		0.82	0.58	4.79	3.64	-1.45
	20		0.62	0.47	8.90	3.80	-1.24
	50		0.41	0.33	2.32	1.47	-0.95

SiO2 5%	0		0.07	0.05	0.75	0.49	-0.26
	10		0.06	0.05	0.43	0.19	-0.24
	20		0.07	0.07	0.25	0.05	-0.22
	50		0.05	0.04	0.20	0.06	-0.16
SiO2 7%	0		0.47	0.41	2.10	1.58	-0.53
	10		0.37	0.29	2.02	1.72	-0.36
	20		0.47	0.38	2.87	2.38	-1.55
	50		0.34	0.26	3.29	1.44	-1.85
TiO2 1 % (rutile)	0		1.13	0.46	11.23	7.84	-3.39
	10		0.38	0.27	4.37	2.23	-2.65
	20		0.95	0.48	5.24	4.56	-0.74
	50		0.49	0.40	2.48	1.98	-0.60
TiO2 5 % (rutile)	0		0.89	0.74	3.45	3.15	-0.30
	10		0.40	0.27	2.58	2.18	-0.61
	20		0.51	0.36	5.83	4.56	-2.58
	50		0.39	0.29	2.21	1.69	-0.53
TiO2 10 % (rutile)	0		0.37	0.20	2.33	1.94	-0.39
	10		0.41	0.32	4.65	3.03	-1.62
	20		0.40	0.30	3.13	1.82	-1.31
	50		0.30	0.23	1.79	1.34	-0.44
TiO2 1 % (anatase)	0		0.32	0.23	1.79	1.43	-0.35
	10		0.38	0.31	1.38	2.44	-0.76
	20		0.57	0.43	8.11	4.56	-3.55
	50		0.35	0.28	3.17	1.75	-1.42
TiO2 5 % (anatase)	0		0.42	0.26	3.15	2.28	-0.87
	10		0.46	0.36	4.97	2.13	-2.84
	20		0.33	0.22	2.60	1.53	-1.07
	50		0.52	0.28	7.49	5.93	-1.96
TiO2 10 % (anatase)	0		0.45	0.28	4.89	2.25	-2.64
	10		0.45	0.34	4.27	3.26	-2.48
	20		0.42	0.27	6.13	4.70	-1.44
	50		0.57	0.40	6.30	4.87	-1.44

The peculiarity of each sample demonstrates the involvement of several factors in the evolution of surface state. γ-Exposure brings about the weakness of material that is the first step in the deterioration of outer layers. The propagation of degradation illustrated by the changes in material roughness is characteristic for compositions and irradiation environment, which conduct the magnitude of penetration in direct connection with the chemical stability of material. The alteration of surface determines the lifetime of products and the interaction between the outer thresholds with other contact surfaces keeps different levels. According with the history of material its roughness may determine the operation conditions of equipments in which it is operating.

4. Conclusion

The epoxy resin modified with oxide (TiO_2 or SiO_2) nanoparticles is a proper material that can be used for various purposes in high energy radiation fields. The thermal resistance of the nanocomposites with different filler concentrations up to 10 % is closed to the similar characteristic of pristine material. It means that the improved oxidation strength attained after γ-irradiation is based on the filler capacity of radical scavenging, which blocks the propagation of oxidation degradation for sufficient long time (more than 150 min).

The electrical behavior is controlled by the irradiation dose received by material, which determines the dimension of degradation. The accumulation of dipoles occurs faster for the first ten minutes, when the concentration of radicals attends a certain upper limit. After the accumulation of oxygenated radiolysis products, they are efficiently gathered around nanoparticles. The irradiation environment plays a certain role in the progress of oxidative ageing in epoxy resin nanocomposites.

The long term usage of these kinds of materials assumes the inhibition of degradation, which leads to a preservation of molecular structure with direct consequences on functional characteristics. The increasing concentration in nanofiller brings about a hindering of oxygen diffusion inside of polymer that enhances the probability in the preservation of initial material features.

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