

Charge Stabilization And Relaxation Processes In Polymer-Oxide Compositions Modified By Gamma-Irradiation

Durdana Rustamova Farkhad¹, Assistant Prof. Mehdiyeva Almaz Mobil², Assistant Prof. Rahim Rahimov Mahammad³, Elnara Firdus⁴

¹PhD in Physics. Head of department of Mechanics and Mathematics of the Western Caspian University, Azerbaijan durdana.rustamova@wcu.edu.az
<https://orcid.org/0000-0002-7752-7340>

²PhD in Technical sciences, Azerbaijan State Oil and Industry University, Azerbaijan
almazmehdiyeva@yahoo.com <https://orcid.org/0000-0002-3962-3980>

³Azerbaijan Technical University, Azerbaijan PhD in Technical sciences, rehim_muallim@mail.ru
<https://orcid.org/0000-0002-5312-5275>

⁴Assistant of department of Mechanics and Mathematics of the Western Caspian University, Azerbaijan elnare.firdus@wcu.edu.az
DOI: 10.47750/pnr.2023.14.502.114

Abstract

Nanotechnology, which is regarded as one of the major fields of global research, is currently generating more interest. We have worked in this direction for this aim. PP/ α -Al₂O₃ composite samples were exposed to various levels of radiation in the article. The kinetics of changes are shown to be non-linearly dependent on the strength and quantity of the dose according to the findings of research carried out by other researchers. As a result of the effect of gamma radiation, various α -, α' -, β -, δ -, etc. the change of molecular mobility of relaxation and structural elements. For the present period, it is very important to analyze the kinetics of the suggested processes of nanoscale fillers and the electret characteristics of polymer/nanocomposite systems following γ -irradiation. Considering the present importance of electret characteristics in practical applications for polymer/nanocomposite systems.

The paper also discusses the $\lg\rho_v = (T)$ dependences for PP/ α -Al₂O₃ composite samples exposed to various levels of radiation. The dependences showed that the most thermally stable samples are those that have not been exposed to radiation. The temperature dependency of ρ_v became more acute when the radiation dose was increased to $D = 80$ kQr. As a result, load carriers in samples with PP/ α -Al₂O₃ compositions are now more expensive.

Keywords: glass transition temperature, IYT, UMQ, YSPE, relaxation time, TSD, dielectric losses, surface charges, volume charges, dielectric, thermos activation current.

Introduction

In recent years, nanotechnology, which is considered one of the main directions of world science, is developing at a great speed. The advancement of nanotechnology is currently seen as the second technological and scientific revolution after that of information technology, and wealthy nations devote significant financial resources to these

sectors [1,2]. Nanotechnology studies particles with a size of 0.1 ÷ 100 nm and the physical, chemical and biological phenomena that occur in these structures. The acquisition, study, and application of new nanostructured materials serve as the foundation for this scientific and technological trend [3,4,5].

They divide the impact of radiation (α^{-2+} , e^- , γ^- , etc.) on the polymer (including in other aggregate states of matter) into two stages: physical (excitation, ionization, stabilization of the generated charges) and chemical (interchain construction, destruction, oxidation, etc.) [6, 7].

When ionizing radiation (fast electrons, γ -quanta, protons, fast and slow neutrons, etc.) interacts with polymers, it primarily causes physical-chemical changes in the form of charged particle formation, electrical conductivity changes, interchain building processes, destruction (disintegration), the structure of some of the charge carriers formed in polymers, stabilization in ion traps, etc.

Let's quickly examine the processes behind so many effective changes:

- they explain the change of electrical conductivity with the classic Rose-Fowler-Weisberg (RFV) model. According to this model, the radiation electrical conductivity (RE) is directly proportional to the power of the radiation dose

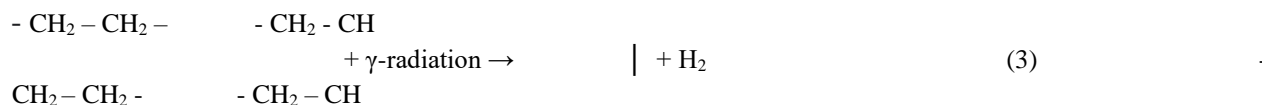
$$\gamma_{RE} = K_p \cdot R \quad (1)$$

For some polymers, $K_p = 0,6 \cdot 10^{-15} \text{ F/m} \cdot \text{Qr}$ in formula (1);

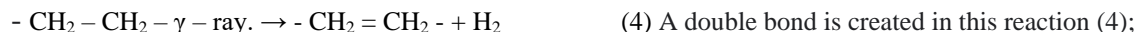
- the stable electrons' radiative chemical emission. The energy of the stabilized electrons per 100 eV is used to represent this chemical shift by the letter G. Following are the calculations for the radiative chemical emission of electrons.

$$G = 3/100 \text{ eV} \quad (2)$$

- Construction processes in polymers under the influence of γ or e^- radiation. Let's have a look at the scheme for this construction procedure (using PE as an example):



- Destructive processes caused by γ or e^- radiation in polymers. Let's consider the scheme of this destruction process (in PE-example):



- Recently, the dipole trap model and the radical trap model have also attempted to describe how polymers actually change under the action of γ or e^- radiation [8,9].

It takes a specific amount of time for a macromolecule (or one of its pieces) to become stable in polymers, polymer-based composites, and polymer nanocomposites. The relaxation time is the term used to describe the stabilizing period of polymer composite and nanocomposite systems [3]. During the classification of relaxation processes, both the structure (structure) and the stabilization of charge carriers (in suitable traps) for a certain period τ under the influence of one or another field occurs. These procedures play a crucial role in the compositions of radioactive polymers. As a result of the dynamics of the various kinetic structural units of the polymer changing as a result of radiation, radiation-destruction or radiation-construction activities have an impact on the relaxation processes (segments, lamellae, crystallites, etc.).

The number of electrons that might arise on the surface of nanoparticles and the radiation-chemical reactions that might take place in the matrix under the impact of α -quanta will both be proportional to the amount of N-atoms in the nanoparticles (5):

$$Q = 0,3 \cdot e^- \cdot N_0 \cdot N \quad (5)$$

In this formula, N_0 is the number of electrons in an atom, and e is the charge of an electron. Calculations show that 30% of atoms in 10 nm nanoparticles are on its surface. The work of the electron from the nanometal is $A_c = 4 \times 5$ eV.

As a result of the effect of gamma radiation, various α -, α' -, β -, δ -, etc. The kinetics of changes are nonlinearly dependent on the strength and amount of the dose and depend on the molecular mobility of relaxation and structural components. For example, in YSPE exposed to

$D=250$ kQr γ -irradiation, the relaxation and structural elements of α are maximally weakened, and such a process does not manifest itself in α' [10,11,12,13,14]. One of the issues of greater practical and theoretical importance is the study of the effect of γ -irradiation on the glass transition temperature T_g and the flow temperature T_α of the polymer composite (relevant processes) [15,16,17]. Additionally, it involves the investigation of how supramolecular structures affect the rate at which various radiation-chemical processes occur [16,18,19,20]. The electret characteristics of polymer/nanocomposite systems following γ -irradiation are of particular interest for the present period, as is researching the impact of nano-sized fillers and magnetic fields on the kinetics of the aforementioned processes [21, 22, 23, 24]. Considering the present importance of electret characteristics in practical applications for polymer/nanocomposite systems.

It appears that the production of non-equilibrium charge carriers (e- and ions) and their relaxation as a result of external forces are among the primary radiation changes in polymer dielectrics and polymer-based composite materials caused by the effect of γ -radiation.

The dependences of $\lg\rho_v = (T)$ for PP/ α -Al₂O₃ composite samples exposed to various levels of radiation are shown in Figure 1. The samples that were not exposed to radiation (curve 1) had the highest thermal stability, as can be observed from the dependency. When a result, the temperature dependence of ρ_v becomes sharper as the radiation dose is increased up to $D = 80$ kQr, which raises the price of charge carriers.

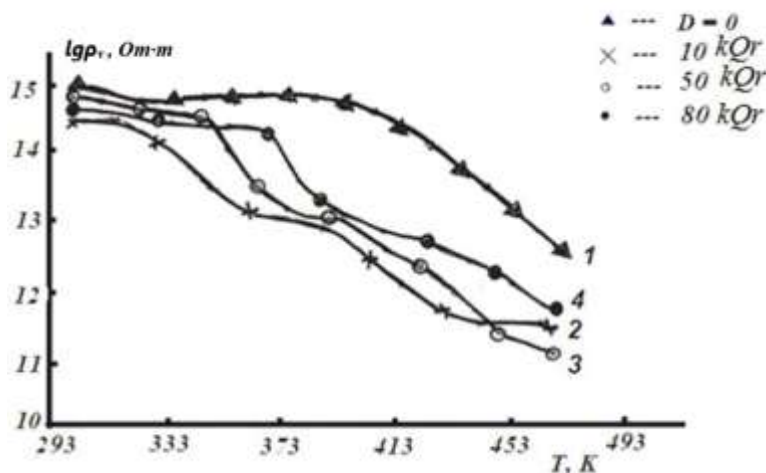


Figure 1. Temperature dependences of specific resistance ($\lg\rho_v=f(T)$) of PP + 10% α Al₂O₃ (90:10% by volume) composite samples irradiated at different doses.

Dependence of dielectric characteristics of PP/ α -Al₂O₃ composite samples (by changing the amount of filler) at different frequencies is given in table 1.

Table 1. Dielectric characteristics of PP/ α -Al₂O₃ type composite samples at different frequencies ($\rho_v, \epsilon \nu \text{ tg}\delta \cdot 10^4$)

Of the filler composition % by volume	$\rho_v \cdot 10^{16}$ Om·m	Frequency, Hs.								
			103		106		$5 \cdot 10^8$		1010	
		ϵ	tg ϵ	ϵ	tg ϵ	ϵ	tg ϵ	ϵ	tg ϵ	
0	1,2	2,2	2,5	2,3	2,5	2,3	2,6	2,2	2,6	
15	16,1	2,5	4,0	2,5	4,0	2,5	4,0	2,4	4,0	
30	10,7	2,8	3,9	2,6	4,6	2,6	5,6	2,6	3,8	
40	8,2	2,9	3,9	2,8	4,2	2,9	5,5	2,8	3,9	

As can be seen from this table, at high frequencies ($(10^8 \div 10^{10})$ Hs) the value of dielectric losses (tg ϵ) changes little. For specific resistance, an extremum is observed. Thus, the maximum value of ρ_v ($(10 \div 20) \cdot 10^{16}$ Om·m) is observed when the amount of filler in the composition is (10÷15)% by volume. In addition, the dielectric losses do not undergo noticeable changes, as can be seen from the frequency dependence of tg δ .

Parameters of tg δ , ρ_v , ρ_s in polymer nanocomposite samples by determining thermodepolarization currents and their temperature dependence, it is possible to study the effect of γ -irradiation on the amount of stable or unstable charge carriers. Figure 2. TSD of samples exposed to PP (1) and D = 5 Mrad radiation (3) The study of the electrical and optical properties of active defects, particularly the mechanism of the relaxation process of unstable charges, is made possible by the measurement of the thermos activation current spectrum of dielectrics. Here, the temperature dependence of TSD current is also shown for composite samples based on α -Al₂O₃ nanofiller.

TSD curves of irradiated samples can be distinguished by the following distinguishing characteristics:

1. At T = 350 K, inversion is seen. The TSD current shifts from a positive to a negative direction. If the first peak is connected to surface charges (in the positive section, it is connected to surface charges, surface charges trapped in low-energy traps), this can be explained. Surface charges are released more quickly, and in the temperature range T>350 K, volume-polarization charges are responsible for the negative value of the current (and in the negative part, the volume is related to loads).

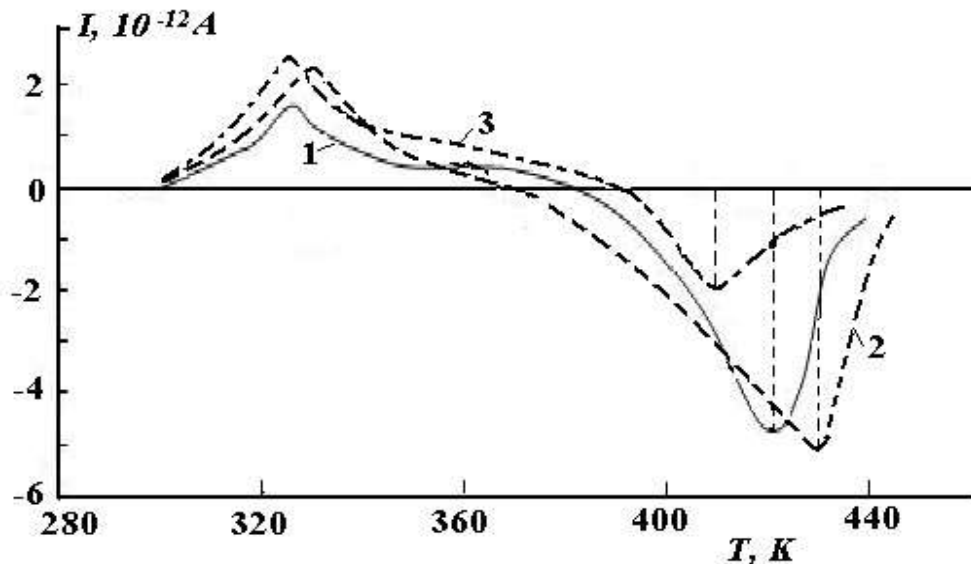


Figure 2. Temperature dependence of thermos depolarization (TSD) current of virgin polypropylene (1), PP+5 % α - Al_2O_3 nanocomposite (2) and PP+5 % α - Al_2O_3 samples (3) irradiated with γ -rays at a dose of $D = 50$ kQr.

Other electret materials have also shown the TSD current's inversion, as seen in Figure 2. The second peak, known as the inversion peak, is thought to be connected to interphase localized electric charges, while the first peak, as we previously said, is connected to the orientation of dipoles [25].

2. According to the Maxwell-Wagner process, the relaxation of volume charges is what causes high-temperature TSD peaks. We take into account the dynamics of both dipoles and volume charges when calculating the charge of the electret. Therefore, the time dependences of TSD currents of PP/ Al_2O_3 nanocomposite samples in Fig. 2 are proportional to the dielectric doublelayer and electret charge densities $\sigma(t)$ and the difference of polarization $p(t)$, i.e. $\sigma(t)-p(t)$ happens.

$$U(t) = \frac{\sigma(t)-p(t)}{\epsilon_0 \cdot \epsilon} \quad (6)$$

$\epsilon_0 \cdot \epsilon$

In expression (6), h is the thickness of the sample, ϵ is the dielectric permittivity, ϵ_0 is the electric constant. In such models, electret is assumed to consist of two layers with dielectric permittivity ϵ_1 and ϵ_2 . It should be noted that these models cannot fully explain the experimental dependence of $\sigma(t) = f(t)$.

3. For the composite samples made with nanoparticles that are being taken into consideration, the maximum value of the TSD current is seen at $T = 440$ K (curve 2). As a result, the favorable effects' additivity, as seen in lower doses of nanoparticles ($D < (50 \div 100)$ kQr), is not seen. Small-sized nanoparticles can create new crystallization centers within the polymer [26,19,27], and at the same time filler Al_2O_3 particles can prevent the formation of large-diameter spherulites in PP.

4. It has been demonstrated that γ -quanta in low dosages alter the rates of radiation building (between chains) and degradation processes [28,17, 29].

Conclusion

The study of the relationship between the dielectric parameters ϵ , $\text{tg}\epsilon$, ϵ_v , and percolation limit and the size and concentration of γ -irradiated nanocomposites produced composite samples that have significant theoretical and practical implications.

High radiation resistance was also noticed, and composite polymer dielectrics for ultrahigh frequency (IHF) technology are stable with regard to dielectric characteristics (ϵ and $\text{tg}\epsilon$). The acquisition of new nanostructured materials and polymer composites with high filler content (%) was found to be practically crucial.

α - Al_2O_3 , Fe_3O_4 , ZnO_2 , TiO_2 , MgO -oxide fillers, white soot, powdered shungites, talc, etc., which give polymer composites various physical-mechanical, luminescent, electroactive, magnetic properties. nanocomposites are of special importance. α - Al_2O_3 alumina annealed at a temperature of 800°C (A800) is an active sorbent for fluorine and has a high radiation resistance (the width of the forbidden zone is 7.6 eV).

In the work done, the α -radiation resistance limit D of the composite consisting of nanosized α - Al_2O_3 oxide fillers was determined.

From the research conducted in different directions, it became known that such Al_2O_3 samples have high sensitivity when irradiated with ultraviolet and X-ray radiation.

The results of the experiment enable for the creation of new kinds of polymer composite samples that are more α -irradiation resistant. Electroactive converters can be made using composite samples that have acquired these properties.

The obtained new nanostructured materials were proposed as dosimetric materials. Studying interphase interactions, impacts, and frost resistance during the operation of such nanostructured materials is crucial for future research.

Literature

1. Lushcheykin G.A., Ivanova L.A. Polymer piezoelectric materials. M., NIITEKHIM, 1988. 79 p.
2. Morgunov R.B., Golovin Yu.I., Yakunin D.V., Trofimova I.N. Electromagnetoplastic effect in amorphous polymethyl methacrylate //Vysokomolekul. soed.ser.B, 2002, t.44, №1, p.129-131
3. Aliguliev R.M. Relaxation spectroscopy of polymer dielectrics. Izd. "Elm", 1997, 328 p.
4. Arzhakova O.V., Ermusheva S.Yu., Yarysheva L.M. и др. General patterns of formation and structure of metal-filled polymer nanocomposites based on cross-linked polymer matrices //Vysokomol.soed. 2003, ser. A, p. 45, No. 6, p. 955-962
5. Vannikov A.V., Matveev V.K., Sichkar V.P., Tyutnev A.P. Radiation effects in polymers. Electrical properties. M., Nauka, 1982, p. -271
6. Pleskachevskiy Yu.M., Smirnov V.V., Makarenko Yu.M. Introduction to radiation material science of polymer composites. г. Минск, Science and technology, 1991, 190 p.
7. Trushin O.V. Physical foundations of radiation material, Saint Petersburg. 1996
8. Kuleshov I.V., Nikolsky V.G. Rhodothermoluminescence of polymers. M; Chemistry, 1991, 128 p.
9. Trusin O.B. Fizicheskie osnovy radiatsionnoy materialovedeniya, s-p, 1996
10. Mikitaev A.K., Kozlov G.V., Zaikov G.E., Polymer nanocomposites: many types of structural forms and applications. M., Nauka, 2009
11. Selikova V.I., Tikhomirov V.S. Influence of ionizing radiation on the structure and properties of polyethylene of different mass and on the supramolecular structure. //Vysokomolekul. soed.ser.A, 2001, t.43, №3, c. 434-440
12. Serenko O.A., Lushcheykin G.A. и др. Electrical properties of composites based on polystyrene and hybrid nanosized particles of silicon dioxide //ZhTF, 2011, t.81, v.9, p. 63-66 13. Tyutnev A.P., Saenko V.S., Pozhidaev E.D., Kostyukov N.S. Dielectric properties of polymers in the fields of ionizing radiation. Book 5, M. "Science" 2005, p.-453 14. Maharramov A.M., Ramazanov M.A., Alizade R.A., Asilbeyli P.B. properties of nanocomposites on the basis of polyethylene with Fe₃O₄ nanocomposites //Digest Journal of Nanomaterials and Biostructures, 2013, v.8, №4, p.1447-1454
15. Magerramov A.M., Rustamova D.F., Bagirbekov Kh.V., Nuriev M.A. Dielectric Properties and Radiothermoluminescent Features of Polypropylene/ α -Al₂O₃. //Surface Engineering and Applied Electrochemistry, 2013, Vol.49, No.2, p.176-179.
16. Magharramov A.M., Structural and radiation modification of electret and piezoelectric properties of polymer composites. Baku, Elm, 2001, 327 p.
17. Tarasevich B.N., Moscow State University named after M.V. Lomonosov, Faculty of Chemistry, Department of Organic Chemistry. IR spectra of the main classes of organic compounds. Reference materials. Moscow, 2012, 57 p.
18. Temnov D.E., Famicheva E.E., Stability of electret state of polypropylene films depending on the content of dispersed filler (aerosil) //Izv. Rossiysk. gosud pedagogical. University of A. Hertsena, 2010, No. 135, p. 92-100
19. Magerramov A.M., Rustamova D.F. Effects of γ -irradiation on the electroactive properties of vinylidene fluoride copolymer with tetrafluoroethylene. / "Prospects of peaceful use of nuclear energy" dedicated to the 100th anniversary of Malikzade, Mr. conference, 2010, Baku, p.63-73
20. Ashis Dey, Amitabha De, De S.K. Electrical transport and dielectric relaxation in Fe₃O₄-polypyrrole hybrid nanocomposites //J.Phys.Condens. Mater, 2005, v.17, p.5895-5910 21. Weisberg C.Э. Reversible radiation effects in polymers. B kn. Radiation chemistry of polymers. M. Nauka, 1973, c. 376-443
22. Golovin Yu.I., Morgunov R.B., Liksutin S.Yu. Influence of pulsed magnetic field on mechanical properties of polymethyl methacrylate // Vysokomol. soed ser.B, t.40, №2, c. 373-376
23. Pomogailo A.Д. Hybrid polymer-inorganic nanocomposites //Uspekhi khim. 2000, 69, no. 1, p. 60-89
24. Starostin V.V. Materials and methods of nanotechnology. M. Binom, pod.ed. prof. L.I. Patrikeeva, 2010, 2-oe. izd. 431 p.
25. Electrets. Under the editorship. G. Sessler. M, Mir, 1983, p. 342-356
26. Magerramov A.M., Nuriev M.A., Shukyurova A.A. Influence of γ -radiation on the charge state of polytetrafluoroethylene /CdS nanocomposites. //Journal of Radiation Research (ANAS), 2015, v.2, No.1, p.18-25
27. Tyutnev A.P., Abramov V.N., Saenko V.S. и др. Radiation conductivity of polymers // Chemical physics, 1994, vol. 13, No. 3, p. 10
28. Maharramov A.M., Rustamova D.F. Effect of magnetic field on the structure and electrical strength of polystyrene //Azerb. Journal of Physics. 2012, v. XVIII, No. 2, Sec. Az, p. 32-35 29. Magerramov A.M. Effect of UV radiation on electret properties of polymers Chemical physics 2001, p. 20, No. 9, p. 34-38