RADIATION EFFECTS ON POLYPROPYLENE NANOCOMPOSITES CONTAINING TITANIA

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Abstract. *Nanocomposites containing polypropylene as host material and titania were studied over a large concentration range (up to 30 %). The contribution of inorganic phase was evaluated by nonisothermal chemiluminescence, when the difference between various formulation was pointed out. The electrical properties of these nanocompounds were investigated. The variation in the permittivity and dielectric loss are correlated with the sample compositions.*
Keywords: *titania, polypropylene, chemiluminescence, thermal degradation, electrical properties*

1. Introduction

Radiation processing of polymers has received an increasing interest from the academic and industrial specialists, which are looking for new materials and deep characterization of engineering products [1]. On this point of view, the applications of radiochemical investigations on nanostructured polymer materials cover a large area of interest because of the diversity of useful information on material stability [2 – 4] and on various modifications that can be induced in this sort of products [5 – 9] for enlarging performance spectra.

Nanocomposites are attracting materials for market requirements because of their potential of proving novel characteristics. It is expected that the tremendous interphase area, where interactions may promote favorable properties [10], brings about surprisingly results for large range of implementation. In these conditions, several researchers investigate polymer materials as nanostructured systems for different practices: high tonnage production of reinforced HDPE [11], electrical insulations [12 – 14], hydrophilic regenerated PVAc [15], dental restoration [16], heat resistant EPDM [17] and many others.

Because of the nanometer-size dispersed particles, the simple addition of small amounts of inorganic filler improves mechanical, thermal and physicochemical properties in comparison with pristine materials, which may be useful for certain special applications. Among various characteristics, the observed modifications in moduli and strength, heat resistance, gas diffusion and dielectric behavior represent the interesting advantages that recommend nanostructured polymers as advanced materials for certain fields of usage [18 – 20].

The European Union market of polymers is ensured by thermoplastic materials, polyethylene sans polypropylene cover about 70 % of sales [21]. The enormous attention that is focused on these materials opens new studies on advantageous features that may be exploited for commercial and economical purposes. The radiochemical investigations performed on these materials reveal the ability of compounds for the long term resistance, for significant modifications caused by the high rate energetic transfer, for involvement of fillers in the material durability and for deepening in material science knowledge.

This paper presents the behavior of iPP-TiO_2 systems subjected to the action of high energy exposure for their qualification for electrical applications. The correlation between composition and dielectric properties is also foreseen.

2. Experimental part

2.1. Materials

The samples consisting of isotactic polypropylene modified with different concentrations of titania (5, 10, 15, 20 and 30 % w/w) were prepared accordingly with the procedure reported earlier [22]. The average size of filler particles was 40 nm. The samples were pressed forming films with the thickness of about 150 □m. The uniform distribution of filler was obtained by the mixing of component in a plastograph unit.

2.2. Irradiation

The exposure of thin iPP/TiO_2 samples was carried out in an irradiator GAMMATOR M-38-2 (USA). The dose rate was 0.4 kGy/h. Air was the environment of irradiation at room temperature. The selected doses were 5 and 10 kGy for depicting slight action of ionizing radiation, which would be equivalent with sustained thermal exchange between environment and polymer material.

2.3. Measurements

Thermal stability of composed polypropylene samples was performed with LUMIPOL 3 (SAS, Slovakia) either by nonisothermal determinations of luminescence intensity as functions of temperature. The chemiluminescence investigations were done immediately after the end of irradiation, because of the presumable presence of short life intermediates formed during radiolysis. The chemiluminescence runs are detailed depicted in one of our previous paper [23].

Electrical investigations were performed with electrometer Keithley 6517A for the measurements of resistivity and with RLC bridge HIOKI 3532-50 (Japan) equiped with Angilent test fixture (USA) for dielectric loss and permittivity. The study of electrical properties of these materials serves for the usage of polypropylene for covering colored circuits and wires.

3. Results and discussion

The interest in the material characterization by high energy exposure is stimulated by the realization of simulation conditions for the applications under hard condition of operation. The production of nanoscale composites involves about 10 to 50 % for the original manufacture of special products [24]. The nanostructured polymer products must reflect some essential requirements:

(a) the new structures must exhibit improved properties for the functional features for which they are produced;
(b) the long term resistance during the action of environmental stressors would be attended;
(c) their production on each industrial scale may be managed;
(d) the production cost has to be convenient simultaneously with the low consumption of raw materials.

The long secure period for the studied systems depends in a large extend on the interaction between component on the boundary zone and on the ability of filler to scavenge or blocking significant amount of intermediates that would result by the oxidation reactions occurring in polymer phase [25]. Unfortunately, environmental pollutants, heat, light etc. bring about more or less fast alteration of physical and chemical peculiarities strongly related

to their service life. The detailed knowledge on the durability of materials is required for the planning of maintenance operation and for the warranty of systems where they are incorporated.

The thermal stability of isotactic polypropylene modified with titania at various concentrations is presented in fig.1 by means of nonisothermal dependencies of CL intensity on temperature. It can be easy noticed that the intercept of the tangent drawn from the ascendant part of the curves gets increasing values. It means that the start of oxidation is delayed by the nanophase, which would adsorb the early intermediates formed during thermal treatment. It may be supposed that the scission rate keeps constant values for low and medium temperature values (up to 80^0C), but the oxidation rate (the rate of the reaction between free radicals and molecular oxygen) increases due to the diffusion rate of oxygen. At superior temperatures the oxidation rate attends higher values caused by the accelerated oxidation. However, it can be remarked that the higher content of titania confers increased thermal stability of host polymer matrix as it has been also reported for the iPP/$CaCO_3$ nanoparticle mixtures [26].

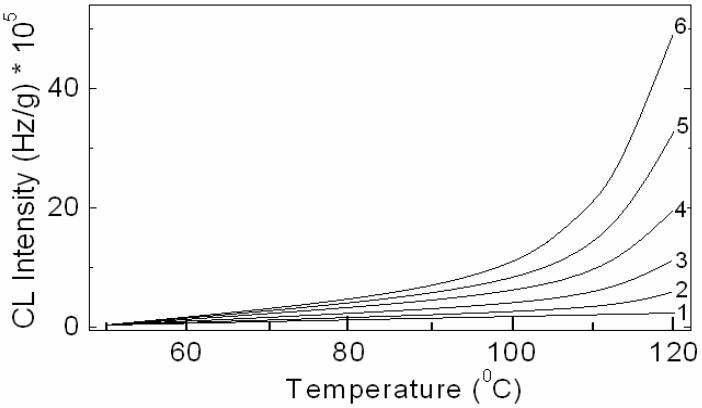

Fig. 1. Nonisothermal curves for degradation of unirradiated iPP/TiO_2 samples (1) neat polymer; (2) TiO_2 5 %; (3) TiO_2 10 %; (4) TiO_2 15 %; (5) TiO_2 20 %; (6) TiO_2 30 %.

The exposure of iPP/TiO_2 samples brings about a modification in the thermal resistance of materials. If pristine polypropylene is oxidized by monotone manner, the compounded polymer specimens present an initial high CL emission suggesting that the nanofiller catalyses the oxidative degradation (fig. 2). The interaction between titanium dioxide and free radicals promotes oxidation with an increasing rate as the filler concentration is enhanced. This aspect is a critical behavior for the plastics containing titania as pigment. It may be assumed that the service conditions are smoother than the γ-irradiation offers. The presence of one efficient antioxidant would repairs this disadvantage that would shorten the life time of product. On the low temperature range, the oxidation is accelerated for the point characterized by 75^0C. Along the higher temperature region, the sample containing 5 % TiO2 is closed to the pristine material. It means that the higher amount of received energy increases the absorption probability of peroxyl radicals on the surface of oxide nanoparticles.

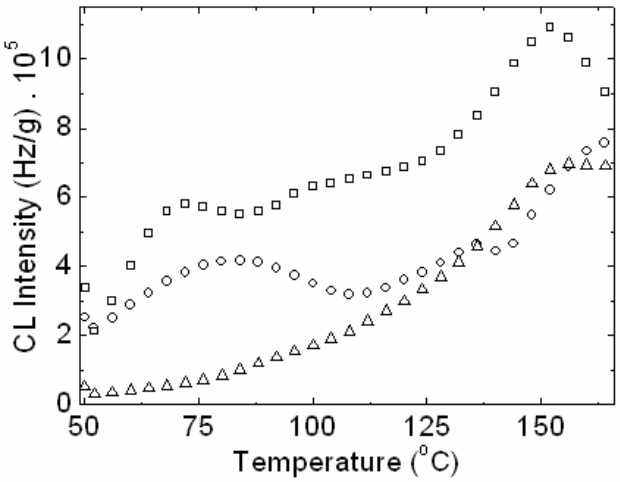

Fig. 2. Nonisothermal curves obtained for some iPP/TiO_2 samples irradiated at 10 kGy (□) pristine iPP; (○) iPP + 5 % TiO_2; (Δ) iPP + 20 % TiO_2.

The dielectric properties of polypropylene and its compounds with TiO_2 nanoparticles are presented in figs. 3 and 4. The decrease either in ε_r, or in tg δ for the frequencies less 1 kHz for neat polypropylene emphasizes the light joint of polar units onto the surface of filler particle. Their movement of dipoles at these low frequencies denotes a low involved energy. By contrary, on the higher frequency range, the increased probability for the detachment of dipoles from the particle surface causes a significant increase in permittivity and loss factor of polypylene.

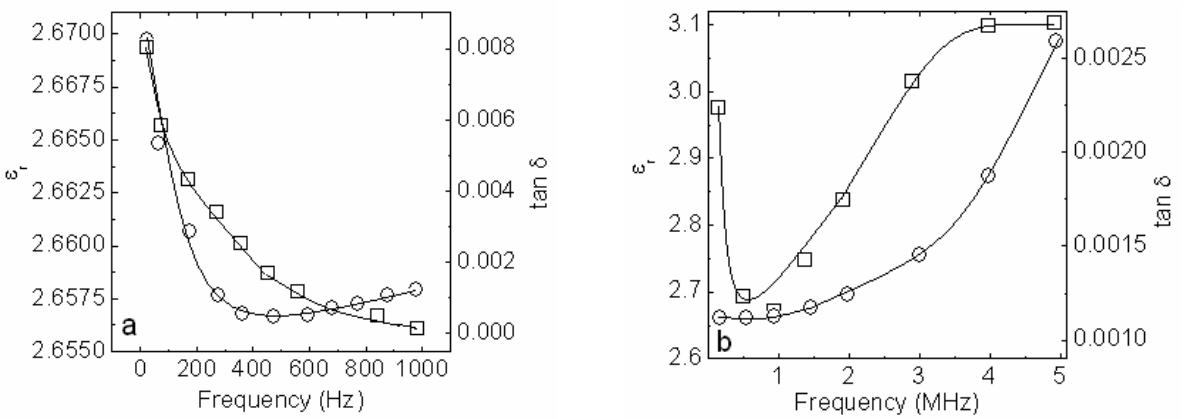

Fig. 3. Variation in the permittivity and dielectric loss for unirradiated pristine iPP with measuring frequency. (○) permittivity; (□) dielectric loss.

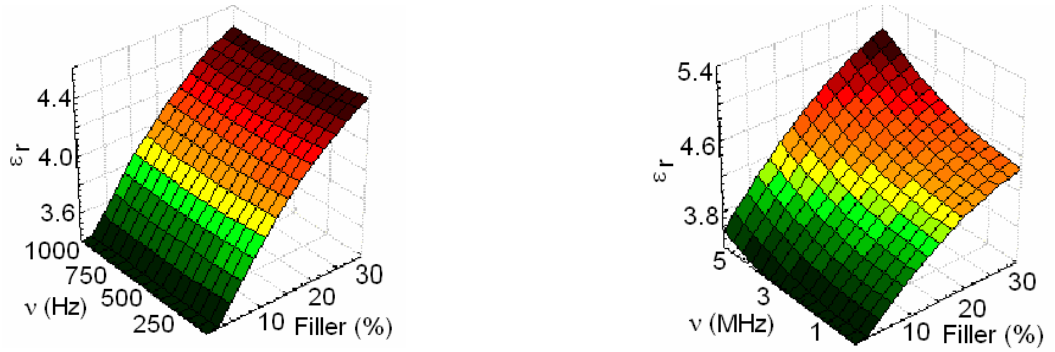

Fig. 4. Changes in permittivity for all investigated iPP/TiO_2 samples at .various filler concentrations and frequency

The variation in the permittivity of TiO_2 – modified iPP takes place in the same sense for all titania contents. If on the low frequency range (fig. 4a) the increase in ε_r values occurs similarly for all concentrations of filler, on the high frequencies, the variation in the permittivity of iPP/TiO_2 samples is lower for the highest content of nanophase. The increase in the interphase surface hinders the movement of dipoles with the direct consequence on the material polarization.

The content of nanofiller influences the electrical conductivity of iPP/TiO_2 samples (figures 5a and 5b). The decrease in the volume resistivity values is directly connected by the charge distribution in the bulk of polymer samples. Various kinds of charge traps act and they are emptied in the relation with their depth or energy. The accumulation of oxygenated products during radiolysis (or oxidative degradation) decreases the material resistivity, which tends to enlarge the distances between the curves for low applied voltage. It seems to be due to the strong trapping action of oxygen that is included in the molecular structures of oxidation products.

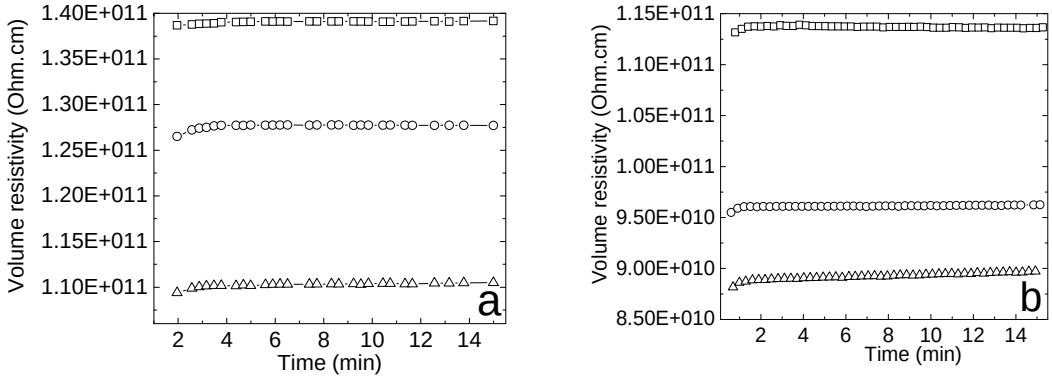

Fig. 5. Volume resistivity for unirradiated (a) and 10 kGy irradiated (b) iPP/TiO_2 5 % measured at (□) 25 V; (○) 100 V (Δ) 500 V.

The enhance in the TiO_2 nanofiller content creates barriers in the movement of electrical charges and it determines a decrease in the material conductivity. The presence of oxygen atoms in titania molecules brings about additional modification in the electrical conductivity of studied nanocomposite systems based on iPP due its electronegativity.

4. Conclusions

The nanosystems produced by the intimate mixing of isotactic polypropylene and titania particles reveal satisfactory endurance features for their application in electrical engineering. The thermal stability is improved by the increasing in the concentration of nanofiller phase, bringing about a longer durability of products that are manufactured on their basis. The pigmentation of polypropylene, like other polyolefins, does not cause a significant alteration of material stability for low concentrations less 5 % in the filler content, because it acts as an adsorber of early formed degradation intermediates.

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