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Invited Paper

Nanostructured isotactic polypropylene-TiO_2 systems

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In this paper the thermal and radiochemical behavior of nanocomposite materials consisting of isotactic polypropylene and various content of TiO_2 (5, 10, 20 and 30 % w/w) are characterised. The contribution of nanofiller component is pointed out by the increase in oxidation induction time for the enhancing nanoparticles of titania. Although the radiation exposure decreases the thermal resistance of this kind of samples, the modification in activation energy corresponds to the ability of filler for the scavenging of radiolysis intermediates.

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1. Introduction

The use of plastics materials has substantially increased over the last decade for various industrial and commodity applications. In the same time, the manufacture of nanocomposites must satisfy the market requirements related to the improved properties during long term service [1-3].

The modification of material consistency by the addition of nanofiller brings about important changed in physical and chemical behaviour due to the large interface area between polymer matrix and inorganic compound. The nanoparticle concentration is also a main technological parameter, which characterises the thermal strength of material. On the last period, there were reported several studies on the composites based on polypropylene matrix [4-9], but few of them are concerned on the thermal stability. Previous our research on iPP/carbonate nanoparticle systems has proved the correlation between the alteration of thermal strength due to the strong attack of intermediates that are formed in and outside material subjected to degradation. However, on the nanoscale the carbonate particles may interfere with polymer substrate during its oxidation [10]. The nature of covering layer on nanoparticles determines the thermal resistance of products.

TiO_2 is largely used as pigment in the manufacture of various products. A study on the radiation stability of elastomers was already reported [11].

The filler nanoparticles play the role of structure modifier, but they are directly involved in the adsorption of degradation oxygenated products generated according to the Bolland oxidation mechanism [12] (figure 1).

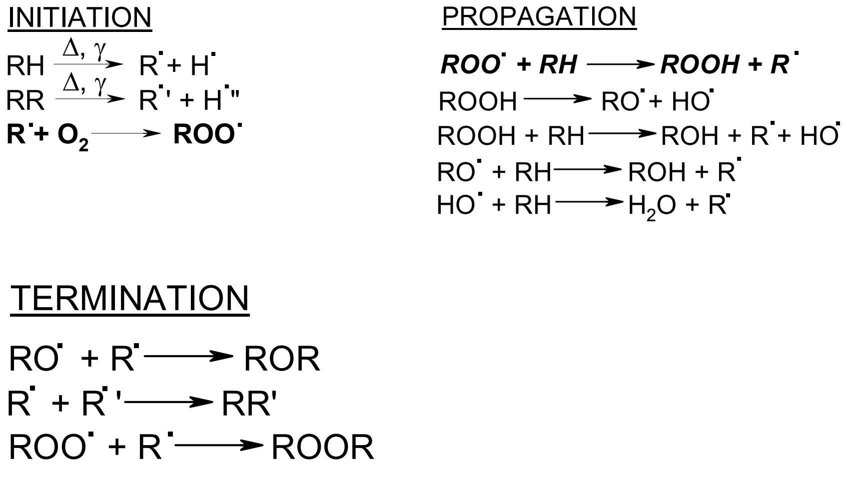

Fig. 1. The mechanism of thermal and radiation degradation of polyolefins.

The thermal and radiation oxidative degradation is a chain process, which is delayed by the depletion of radical intermediates by adsorption and reactions. The presence of increasing amount of hydroperoxides accelerates the progress in the polymer alteration, due to the high rate of generation. The determinative step of degradation is the reaction of radical oxidation and the depletion of peroxyl radicals on different ways.

Thermal stability of some polymers [13,14] and the structural modifications, induced by high energy irradiation [15,16] were studied in our previous papers.

This paper discusses the contribution of titania nanoparticles to the stabilization of isotactic polypropylene.

2. Experimental

The present investigation was carried our on isotactic polypropylene (HP 400K, HMC Polymer, Rayong, Thailand) filled with TiO_2 nanophase. A large range of filler concentration (0, 5, 10, 20 and 30 % w/w) was selected. Titania nanoparticles had average diameter 50 nm being coated with stearic acid (hydrophilic surface) [17]. Each type of samples was subjected to the action of high energy radiation (^{137}Cs) at an irradiation dose of 5 kGy (in air) to investigate the effect of degradation effect. A low dose rate of 0.4 kGy/h was applied.

Isothermal CL measurements at 165^0C (if other temperature is not specially mentioned) were carried out in LUMIPOL 3 (SAS, Slovakia). Specimens of about 4 mg were placed in aluminium tray for chemiluminescence investigation.

3. Results and discussion

Organically modified titania nanoparticles that were incorporated in isotactic polypropylene influence the thermal behavior of polymer substrate. The filler phase presents a large boundary area in relation with polymer that determines a broad interaction between the two composite components. In Fig. 2 the chemiluminescence curves, which depict the progress in the degradation of iPP substrate, are presented.

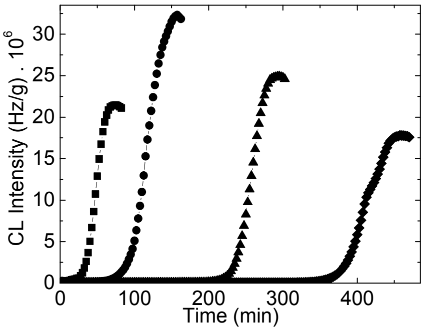

Fig. 2. Isothermal chemiluminescence curves for the thermal oxidation of iPP/nanoTiO_2 systems @ 165 ^{0}C Content of filler: (■) 5 %; (●) 10 %; (▲) 20 %; (♦) 30 %.

The delay of degradation is evident by the increase in the titania content. It means that the enlargement of interphase area promotes an advanced adsorption level. From Fig. 3 the variation of oxidation induction time in the function of increasing titania concentration may be noticed that the linear dependence confirms the involvement of filler nanoparticles in the process of thermal degradation of polymer substrate.

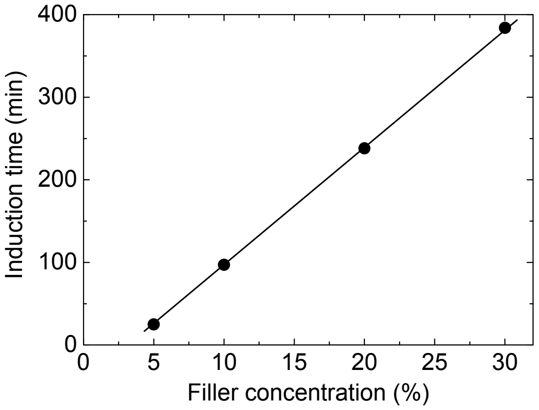

Fig. 3. Dependence of oxidation induction time on nano-TiO_2 concentration obtained for the measurements performed at 165 ^{0}C (correlation coefficient is 0.9997).

The extrapolation of the results shown in the Fig. 3 would get a negative intercept that is physically unexplainable. However, if it is considered the iPP/TiO_2 composites as other type of material, which is differently penetrated by the diffusion of environmental molecular oxygen, the neat material represents the phase through which the supply with oxygen takes place. The filler consistency diminishes the possibility of oxygen spreading onto polymer component and its increase restrains the reaction between free radicals and O_2 on the first stage of degradation (initiation, Fig. 1).

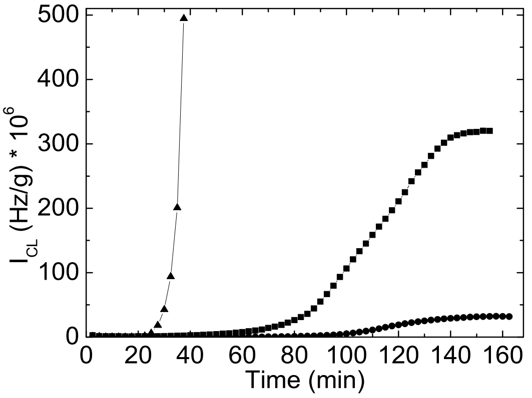

Fig. 4. Isothermal chemiluminescence curves drown for the iPP/nano TiO_2 samples (10 % filler) @ (●)155 ^{0}C, (■) 165 ^{0}C and (▲) 172 ^{0}C.

The influence of temperature on the thermal resistance for iPP/TiO$_2$ nanocomposites can be assessed by the modification in the viscosity of samples. The temperature of 165 ^{o}C is placed in the vicinity of melting point of polymer. This temperature value may be found in the first part of softening range. On the other hand, the addition of filler causes an important decreasing in the melting point of heated material. Thus, the degradation can occur with higher rate at higher temperature. The accumulation of primary intermediates (peroxyl radicals) yields a great amount of hydroperoxides as the precursors of final and stable products (Fig. 1).

The difference between the thermal resistances of isotactic polypropylene containing various filler amount can be noticed from Figs. 4 and 5. The availability of polymer component to oxidation is depicted by the increasing of chemiluminescence intensities from one temperature to the higher ones.

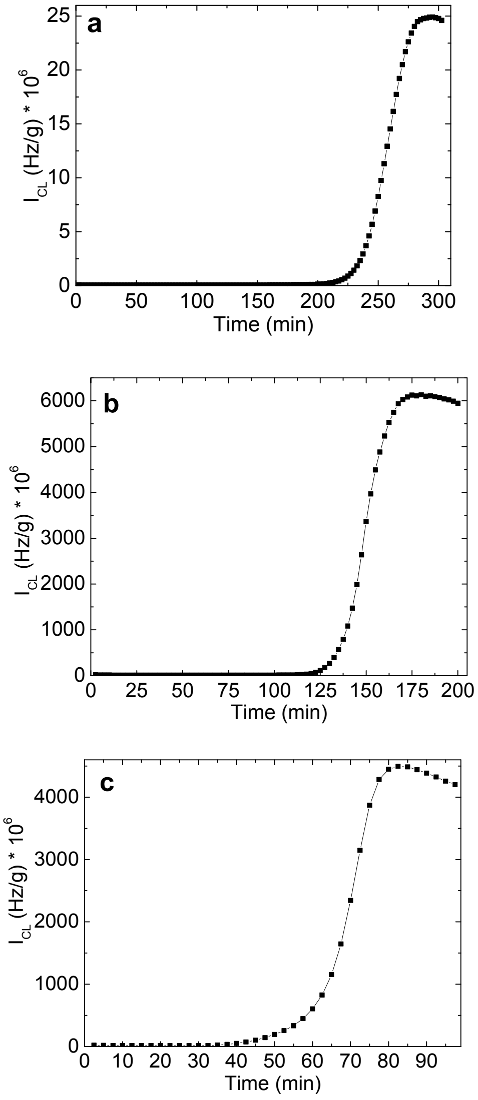

Fig. 5. Isothermal chemiluminescence curves drown for the iP P/nanoTiO$_2$ samples (20 % filler) (a) 155 ^{0}C, (b) 165^{0}C and (c) 172^{0}C.

The calculation of activation energies (table) required for the thermal degradation of iPP/nano-TiO$_2$ points out that in this kind of composites there are two.

The activation energy required for oxidation of isotactic polypropylene decreases with the advance in the degradation level. It means that the reaction between oxygenated intermediates (RO$_2^{\cdot}$, ROOH, RO$^{\cdot}$ and HO$^{\cdot}$) during the propagation step (Fig. 1) contributes in a larger extend to the modification of oxidation state of polypropylene macromolecule (RH) [18].

The listed values (see table) for the activation energy of oxidation in neat polypropylene is in agreement with other previously reported figures, though the state of stabilization and the applied technology influence strongly the energetic duty [19-21].

Table 1. Activation energies calculated from Arrhenius diagrams.

Input kinetic parameter	TiO$_2$ amount (%)	Temperature range (^{0}C)	Activation energy (kJ/mol)	Correlation factor
Oxidation induction time	0	160 – 180	176.33	0.9928
	5	155 – 172	121.22	0.9955
	10	165 – 180	67.88	0.9961
	20	165 – 180	80.39	0.9975
	30	165 – 180	167.41	0.9835
Demioxidation time	5	155 – 172	97.63	0.9994
	10	165 – 180	64.56	0.9833
	20	165 – 180	86.84	0.9979
	30	165 – 180	151.91	0.9870
Maximum oxidation time	5	155 – 172	76.54	0.9984
	10	165 – 180	55.94	0.9825
	20	165 – 180	84.12	0.9958
	30	165 – 180	130.49	0.9966

The content of titania modifies the activation energy for the oxidation of organic substrate.

This behavior may be explained by the possibility of adsorption/desorption equilibrium. In the case of lowest studied concentration, the oxidative degradation of polypropylene occurs with light influence of the filler, because the temperature range is lower one and the diffusion of oxygen takes place in solid state samples. The concentration of 10 % nano-TiO$_2$ decreases dramatically the thermal resistance of studied specimens, which are in the soft solid state.

The lowest values of activation energies would be explained taking into account the prevailing of oxygen diffusion rate relative to the superficial scavenging of thermolysis intermediates. For the samples containing 20 % or 30 %, the average distances that separate nanoparticles become shorter and shorter.

The probability of adsorption of primary and derived intermediates increases as the TiO$_2$ concentration is higher.

The exposure to the action of ionizing radiation (γ-rays) causes a decrease in the thermal stability of polypropylene nanocomposites (figure 6).

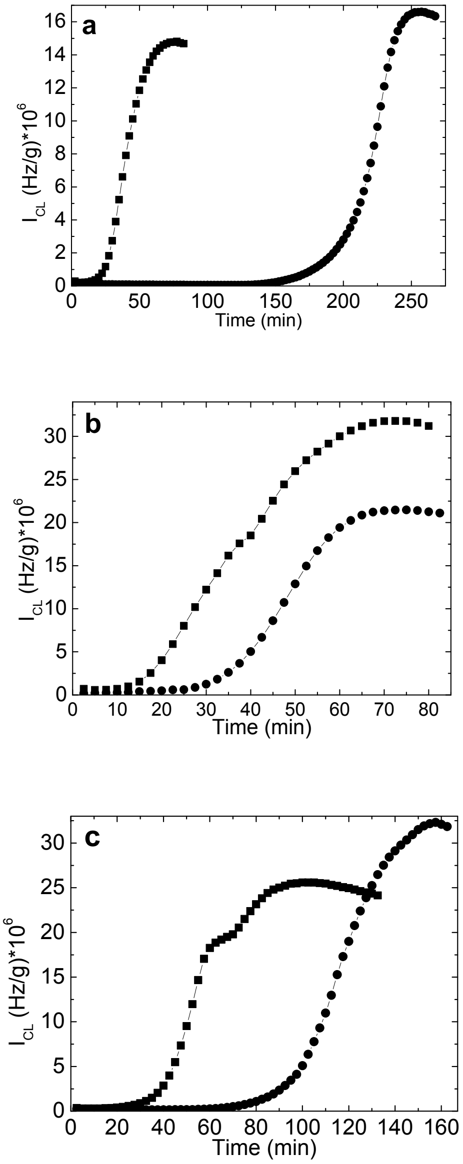

Fig. 6. Isothermal chemiluminescence curves for (a) iPP (neet), (b) iPP with 5 % nano TiO_2 and (c) iPP with 10 % nano TiO_2 measured @ 165 ^{0}C. (●) nonirardiated samples; (■) dose 5 kGy.

The absence of nanofiller brings about a very fast degradation in the neat isotactic polypropylene. The increase in the nano-TiO_2 content enlarges the differences between the curves of nonirradiated and 5 kGy exposed composites. The induction time of irradiated samples becomes longer as the content of TiO_2 is enhanced. However, the instability of polypropylene under the irradiation in air is maintained, though a light positive adjustment was observed. The contribution of nanofiller in the protection of polypropylene is diminished because the concentration of oxidation intermediates during radiolysis of polypropylene is quite high and their adsorption does not efficiently happened.

4. Conclusion

The thermal resistance of isotactic polypropylene is increased by the presence of nanoparticles of titania. The content of 20-30 % in TiO_2, as it would be happened in the painting materials brings about a longer durability demonstrated by the high activation energy required for thermal degradation. The contribution of TiO_2 nanofiller to the delay of degradation consists of the equilibrium between adsorption/desorption simultaneously occurred on the polymer boundary layers that surround nanoparticles.

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