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The Control of Thermal and Radiation Stability of Polypropylene Containing Calcium Carbonate Nanoparticles

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Summary: Thermal and γ radiation stability of iPP containing $CaCO_3$ nanoparticles were investigated by oxygen uptake procedure at 190 °C. The loading of iPP matrix was maximum 25% (w/w). The behavior on thermal oxidation was investigated for two formulations of iPP compounds differing by the surface characteristics of nanoparticles (i.e. uncoated and stearic acid-coated filler). Three irradiation doses (5, 15 and 25 kGy) were applied. The efficient protection of stabilizers that are present in the as-prepared formulations was emphasized by proper values of the kinetic parameters obtained for oxidation. The contribution of $CaCO_3$ nanoparticles to the oxidative process of iPP is discussed.

Keywords: carbonate nanoparticles; degradation; polypropylene; thermal stability

Introduction

A large number of studies on the preparation and characterization of polymer/nanoparticles matrix were reported,[1–10] because of their excellent functional properties. The presence of nanoscale inorganic fillers improves mechanical, thermal and gas barrier characteristics.[11–15] Several promising formulations of polymer hybrids were proposed for satisfying various requirements for a large number of applications. However, the problem of thermal stability of polymer composites is of a great interest being directly related to the material durability. The topic of thermal degradation has received a special attention due to the strong influence of the service conditions on the behavior of composites. The characterization of material depreciation by heat provides useful information for storage, processing and long-term use, namely the life of products. Ever using well-elaborated technologies of preparation, the stress factors act on any time. Recent papers[16,17] have emphasized the phenomenological analysis of degradation in connection with various testing methods. The most applied procedures for depicting the thermal behavior of polymer composites were DSC and TGA. [4,18–20] These papers have reported the difference between unloaded and polymer composites, which is caused by the modification in surface energy between the microphases, which would exist in the tested material.

For obtaining a high rate and advanced degradation, ionizing radiation may be used. Data obtained from accelerated ageing testing prove the capacity of material to resist for a certain period to the action of vigorous energetic agents. The durability of any material under high energy-radiation exposure depends on many features through which the chemical nature of basic material and the sample formulation determine the kinetic behavior during degradation.[21–23]

Effects of irradiation on polypropylene have been extensively studied. The most of

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them have emphasized the degradation of this polyolefin under radiochemical processing[21,24–30] or its crosslinking in the presence of suitable additional monomer.[23,31,32] Other assays on radiation resistance of polypropylene have investigated the effects of stabilization additives (antioxidants), which delay the start of oxidation and mitigate the rate of destruction.[33,34] The radiolysis of polymer substrate causes the free radical formation, which is followed by oxidation reactions.[35] The rate of oxygen consumption and the absorbent properties of calcium carbonate nanoparticles seem to influence the state of degradation of irradiated polypropylene.[36]

This paper describes the stability of irradiated polypropylene containing calcium carbonate nanoparticles. The main goal of this investigation is the characterization of additive effect on the polymer matrix, which is degraded in two different environments (air and water). The effect of environment determines the lifetime of products, and the warranty of equipments in which they are included.

Experimental

Isotactic polypropylene, a commercial grade material, was supplied by HMC Polymers Co., Ltd (Rayong, Thailand) as Moplen CS-42 HEXP type. Its initial characteristics were presented in a previous paper.[37] The compounding had concerned two types of $CaCO_3$ nanoparticles (average size: 40 nm). The samples containing uncoated filler received mark A, while i-PP samples having carbonate particles superficially modified with stearic acid were placed in category B. The process of sample preparation was described earlier.[37] The reference (pristine material) and five different iPP/carbonate filler formulations (5, 10, 15, 25 and 25% w/w) were prepared as thin sheets.

The exposure to γ-rays for control and modified i-PP sheets was performed in an irradiator GAMMATOR M-38-2 (USA) provided with a ^{137}Cs source. This step was carried out in air at room temperature. Two radiolysis surroundings (air and distilled water) were used in order to describe the oxidation resistance of material under these two common circumstances. For this investigation, a low value of dose rate (0.4 kGy/h) was used, which ensures an accelerated degradation. Three total doses, namely 5, 15 and 25 kGy were applied; higher irradiation doses were avoided due to the brittleness of polypropylene sheets accompanying high energy treatment in oxidizing medium.

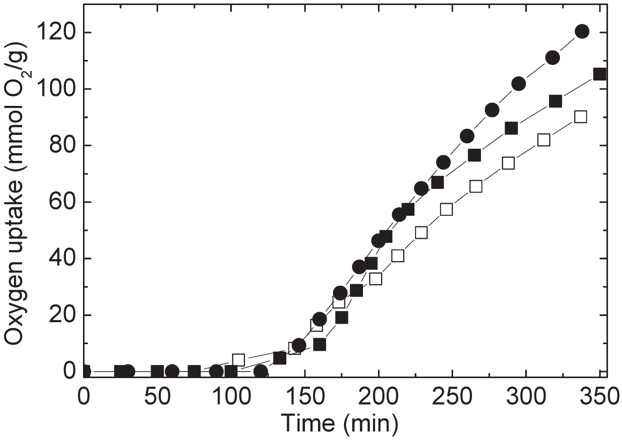

Figure 1.
The dependencies of oxygen uptake on degradation time for unirradiated samples consisting of i-PP and $CaCO_3$ nanoparticles coated with stearic acid. (□) control; (■) 5% loading; (●) 25% loading.

The oxygen uptake measurements were accomplish with a laboratory equipment, which was previously described.[38] The experimental conditions were chosen in order to obtain convenient values for kinetic parameters: 190 °C for thermal degradation, normal pressure of oxidation environment, air as testing medium. The selected temperature seems to be somewhat higher, but the supplied polypropylene (control and modified polymer) presented high thermal stability due to the presence of antioxidants. Thin films were cut in small pieces having around 20 mg each. They were placed in round aluminum trays to be thermally oxidized in an electrically heated oven at constant temperature. Irradiated specimens were investigated for their thermal oxidability soon as they were withdrawn from exposure room.

The main kinetic parameters of oxidation: oxidation induction time and oxidation rates were determined from the dependencies of consumed oxygen on thermal degradation time. From these curves (sigmoidal type) induction period was assessed by the crossing point of drawing the tangent from the propagation part with OX axis; the rate of oxidation was determined on the propagation step, where it attends the maximum value.

Results and Discussion

Radiation processing of polymers is a useful tool for the check of material resistance under hard service conditions and provides a conclusive picture on the manner through which the material follows standard recommendations. For composite, the accelerated tests offer suitable conclusions concerning the effects of additives and fillers on the long term usage. Ionizing radiation causes the split of weaker bonds. Polypropylene is subjected to radiation degradation due to the presence of tertiary carbons in macro-

Table 1.
The values of kinetic parameters of oxidation for radiolyzed nanostructured i-PP (environment: air).

Experimental conditions		i-PP/uncoated $CaCO_3$ particles		i-PP/stearic acid coated $CaCO_3$ particles	
$CaCO_3$ load (%)	Dose (kGy)	Induction period (min)	Oxidation rate.10^4 (mol $O_2 \cdot g^{-1} \cdot s^{-1}$)	Induction period (min)	Oxidation rate.10^4 (mol $O_2 \cdot g^{-1} s^{-1}$)
0	0	52	6.33	110	5.63
	5	60	7.06	118	5.84
	15	61	7.41	96	5.99
	25	48	8.77	78	6.53
5	0	62	6.53	168	5.46
	5	71	6.84	170	5.82
	15	75	7.11	154	6.61
	25	70	7.93	131	7.00
10	0	85	7.23	199	6.48
	5	96	7.58	161	6.82
	15	113	7.84	125	7.09
	25	148	8.03	112	7.22
15	0	172	7.22	160	6.61
	5	155	7.51	148	6.84
	15	149	7.85	133	7.27
	25	137	8.09	129	7.17
20	0	160	7.61	183	7.38
	5	145	7.90	146	7.55
	15	120	8.37	119	7.93
	25	90	8.72	89	8.14
25	0	163	8.47	153	8.43
	5	143	9.04	133	8.70
	15	117	10.06	106	9.55
	25	102	11.88	86	10.03

molecule backbone.[Y] Oxygen which preexists in virgin material or is diffused into polymer bulk during irradiation promotes oxidation by the reactions with free radicals. Final radiolysis products will be spread in the polymer mass in correlation with material crystallinity and the size of molecules. In the case of nanocomposites, the filler particles can influence the progress of oxidation.

Calcium carbonate nanoparticles modify the behavior of basic material because of their large specific surface and the homogenous dispersion in polymer. The decrease in mechanical properties was reported earlier,[36] but it would be accompanied by the change in thermal stability. In the case of coated particles, it would be expected that the covering film will influence the progress of oxidation.

Isotactic polypropylene filled with calcium carbonate nanoparticles presents slight differences in the values of oxidation induction time, while the propagation of oxidation looks somewhat unlike (Figure 1). The initial amount of dissolved oxygen is about the same for all samples, but, the O_2 diffusion into polymer during uptake measurements depends on the filler consistency. The higher the concentration of nanoparticles, the faster the oxidation degradation (Tables 1 and 2), namely, the thermal stability is determined by the homogeneity spreading of carbonate particle in polymer.

The exposure of i-PP samples to γ-radiation brings about the decrease in the both kinetic parameters: oxidation induction time and oxidation rate. The nature of degradation environment determines different values of kinetic parameters for the advance in oxidation. In Figure 2 the dependencies of consumed oxygen on time are presented for samples containing coated $CaCO_3$ nanoparticles, which were irradiated at 25 kGy in the both oxidative media.

During radiochemical ageing of studied systems, the formed intermediates are

Table 2.
The values of kinetic parameters of oxidation for radiolyzed nanostructured i-PP (environment: water).

Experimental conditions		i-PP/uncoated $CaCO_3$ particles		i-PP/stearic acid coated $CaCO_3$ particles	
$CaCO_3$ load (%)	Dose (kGy)	Induction period (min)	Oxidation rate.10^4 ($mol\ O_2 \cdot g^{-1} \cdot s^{-1}$)	Induction period (min)	Oxidation rate.10^4 ($mol\ O_2 \cdot g^{-1} s^{-1}$)
0	0	52	6.33	110	5.63
	5	65	7.06	78	5.95
	15	70	7.72	70	6.41
	25	59	7.97	58	6.88
5	0	62	6.53	168	5.46
	5	86	7.24	157	6.34
	15	84	8.15	132	6.92
	25	80	8.43	109	7.70
10	0	85	7.23	122	6.48
	5	96	7.68	104	7.26
	15	101	8.44	90	7.65
	25	88	9.23	81	8.14
15	0	172	7.22	160	6.61
	5	148	7.91	140	7.43
	15	130	8.45	128	7.68
	25	120	9.49	119	8.93
20	0	160	7.61	183	7.38
	5	139	8.30	130	7.69
	15	132	8.96	109	8.34
	25	114	9.82	71	8.61
25	0	163	8.47	148	8.43
	5	121	9.14	103	9.86
	15	100	11.16	77	11.90
	25	87	12.73	63	13.29

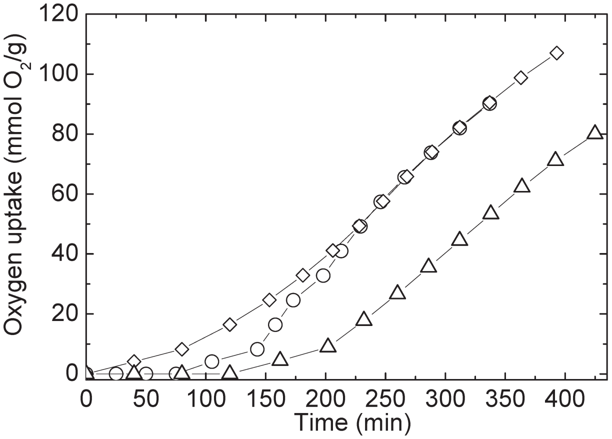

Figure 2.

Time dependencies of oxygen uptake for irradiated at 25 kGy i-PP samples/25% $CaCO_3$ coated nanoparticles. (○) control; (△) 10% loading; (◇) 25% loading.

spread in the bulk of polymer, closer of further from carbonate nanoparticles. The radiation energy that is transferred to samples increases the kinetic energy of intermediates. Consequently, the rate of diffusion of radicals through the polypropylene molecules is enhanced and the radiolysis products attend easily filler particles on which they would be adsorbed. On the first step of thermal oxidation (oxygen uptake measurements), the oxygen consumption decreases with carbonate loading. It means that the precursors of oxygenated final products are efficiently scavenged by particles. On the propagation step of oxidation, when the rate of oxidative degradation increases with carbonate concentration, the desorption of radiolysis products increases the oxygen uptake and the oxidation occurs fast.

The radiolysis of water generates various intermediated, especially radicals ($H^{\cdot}$, $HO^{\cdot}$, $HO^{\cdot}_2$), which initiate the superficial degradation of samples. The higher concentration of carbonate nanoparticles brings about an increase in oxidation induction time. The difference between the coated and pristine filler consists of the presumable penetration of organic shell by water intermediates, followed by their remove from stearic acid covering. This behavior was exhibited by all formulations of iPP/nanocarbonate specimens.

The advanced exposure of materials to the action of γ-rays promotes a larger degradation, due to the greater abundance of radical intermediates. Their depletion will require higher oxygen amount starting from the beginning of thermal measurements. However, the longer induction times are presented by the polymer samples containing carbonate loading higher than 15%.

The radiation ageing accelerates at higher rates the pristine polypropylene in comparison with the same material loaded with calcium carbonate nanoparticles; the coating shell ameliorates the thermal resistance of host material.

Conclusion

The polypropylene compounds with calcium carbonate nanoparticles exhibits favorable kinetic parameters (induction time and process rate) during accelerated oxidation. The presence of these small particles modifies the interphase diffusion of radiolysis intermediates, which would react with molecular oxygen. The thermal strength of polypropylene is improved.

The efficiency of carbonate nanoparticles in isotactic polypropylene on retardation of oxidation is a great advantage for prolongation of the product life, which are subjected to the action of various hazards.

The technological applications of iPP/carbonate nanoparticles requires the decision on the temperature regime in connection with filler loading to satisfy simultaneously the manufacture conditions and the improved life of products.

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