polymer report

Radiation stability of *in situ* stabilized polypropylene

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The radiation stability upon exposure to high-energy radiation of different bi- and terpolymers such as poly[propylene-*co*-4-(hept-6-enyl)-2,6-di-tert-butylphenol], poly(propylene-*co*-6-phenylhex-1-ene) and poly[propylene-*co*-4-(hept-6-enyl)-2,6-di-tert-butylphenol-*co*-4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine] was studied. The films were exposed to a radiation dose of 25 kGy. The extent of radiation-induced degradation of the samples was determined by size exclusion chromatography. The most stable polymers found were a copolymer containing 0.82 wt% of 4-(hept-6-enyl)-2,6-di-tert-butylphenol and a commercial radiation-resistant polypropylene. The copolymers containing chemically bound hindered phenol moieties exhibited better protective properties than polypropylene reference samples containing the same concentration of admixed 3-(3,5-di-tert-butyl-4-hydroxylphenyl)propionate (Irganox 1010). The copolymers containing 6-phenylhex-1-ene or admixed phenyl decane showed reasonably good stability against radiation, whereas the formulations containing hindered amine light stabilizers showed relatively poor radiation stability.

(Keywords: polypropylene; irradiation; stabilization)

INTRODUCTION

Plastics have many uses in medical applications. Polypropylene, for example, has good mechanical properties as well as high transparency, which make it one of the most popular polymers in the manufacture of medical disposables. Medical supplies require some form of sterilization before use, and this is widely carried out using electron beams or γ-rays. Irradiation of polymers, however, causes both crosslinking and chain scission, the dominant reaction being dependent on the structure of the polymer, i.e. polyethylene and rubbers[1] predominantly crosslink upon exposure to radiation while chain scission predominates in polypropylene[2]. The processes of main-chain scission and crosslinking lead to undesirable changes in the molecular weight and polydispersity, which are the main parameters determining polymer properties such as mechanical strength.

Many attempts to stabilize polypropylene against high-energy radiation have been reported, and the major conclusions from these studies are that homopolymers with narrow molecular weight distribution (MWD)[3] and the lowest possible crystallinity[4] should be chosen for radiation-sterilized medical devices. The inclusion of mobilizing additives is preferable[5], while the maximum oxidative inhibition and stability is achieved by adding radical scavengers to the polymer[6]. Sterically hindered phenols are well known antioxidants of the radical-chain-breaking type and hence effectively retard polymer degradation. The combination of these various alternatives will most likely result in successful stabilization of polypropylene against radiation degradation; however, during the past few years much attention has focused on the migration of polymer additives in medical devices as well as in food packaging[7]. The migration of stabilizers to drugs can have unpredictable toxic effects on consumers, and therefore several technical solutions to more permanent stabilizers have been presented[8,9]. Our previous work on copolymerization of propylene with 4-(hept-6-enyl)-2,6-di-tert-butylphenol[10] and 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine[11] led us to determine the radiation stability of these *in situ* stabilized polypropylenes. The migration of these stabilizers is prevented since the stabilizing moiety forms a permanent part of the polymer.

Although the deposition of radiation energy is considered to be spatially random, the radiation-induced chemical changes are not. Some chemical groups are more sensitive to radiation-induced reactions while others are particularly resistant to chemical change, and therefore the polymer chain can provide pathways for either energy transfer or energy trapping. Since aromatic groups have been recognized to give radiation resistance to organic molecules[12], we decided to include poly(propylene-*co*-6-phenylhex-1-ene)[13] with the polymers studied in this work.

EXPERIMENTAL

Materials

The polymers studied are listed in *Table 1*. The copolymers of propylene and 0.25 (**I**) or 0.82 wt% (**II**) 4-(hept-6-enyl)-2,6-di-tert-butylphenol, propylene and a combination of 0.3 wt% 4-(hept-6-enyl)-2,6-di-tert-butylphenol and 0.9 wt% 4-(hex-5-enyl)-2,2,6,6-tetra-

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Table 1 Sample identification

Sample	Material	Preparation
I	Poly[propylene-*co*-4(hept-6-enyl)-2,6-di-tert-butylphenol] (0.25 wt% 4(hept-6-enyl)-2,6-di-tert-butylphenol)	Copolymerization
II	Poly[propylene-*co*-4(hept-6-enyl)-2,6-di-tert-butylphenol] (0.82 wt% 4(hept-6-enyl)-2,6-di-tert-butylphenol)	Copolymerization
III	Poly[propylene-*co*-4(hept-6-enyl)-2,6-di-tert-butylphenol-*co*-4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine] (0.3 wt% 4(hept-6-enyl)-2,6-di-tert-butylphenol) (0.9 wt% 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine)	Copolymerization
IV	Poly(propylene-*co*-6-phenylhex-1-ene) (3.5 wt% 6-phenylhex-1-ene)	Copolymerization
V	Poly(propylene-*co*-6-phenylhex-1-ene) (9.8 wt% 6-phenylhex-1-ene)	Copolymerization
VI	Polypropylene + Irganox 1010 (0.25 wt% Irganox 1010)	Compounding
VII	Polypropylene + Irganox 1010 (0.82 wt% Irganox 1010)	Compounding
VIII	Polypropylene + Tinuvin 770 (1.9 wt% Tinuvin 770)	Compounding
IX	Polypropylene + (Irganox 1010 + Tinuvin 770) (0.3 wt% Irganox 1010 and 0.9 wt% Tinuvin 770)	Compounding
X	Polypropylene + phenyl decane (3.5 wt% phenyl decane)	Compounding
XI	Polypropylene + phenyl decane (9.8 wt% phenyl decane)	Compounding
XII	Polypropylene (Neste Chemicals V 64 19 K) (unknown method of stabilization)	Purchased
XIII	Polypropylene unstabilized	Polymerization

methylpiperidine (**III**) and propylene and 3.5 (**IV**) or 9.8 wt% (**V**) 6-phenylhex-1-ene have been reported elsewhere[10,13,14]. The radiation stability of these *in situ* stabilized polymers was compared with polypropylene[15] samples mixed with 0.25 (**VI**) or 0.82 wt% (**VII**) Irganox 1010 (Ciba-Geigy), 1.9 wt% Tinuvin 770 (**VIII**) (Ciba-Geigy), 0.3 wt% Irganox 1010 and 0.9 wt% Tinuvin 770 (**IX**) or 3.5 (**X**) or 9.8 wt% (**XI**) phenyl decane. Mixing of polypropylene and the additives was conducted in a Haake Buchler 50 cm^3 mixer at 190°C for 7 min. A commercially available radiation-resistant polypropylene (**XII**) (Neste Chemicals, V 64 19 K) and unstabilized polypropylene (**XIII**) were included in this study. Films of the polymer samples were prepared by compression moulding at 190°C.

Irradiation

The film samples were irradiated using an Electrocurtain® electron accelerator operating at 175 kV. The samples received a radiation dose of 25 kGy.

Analysis

The radiation degradation of the polymer samples was assessed by determining the change in molecular weight M_w upon exposure to radiation. The size exclusion chromatograms were recorded using a Waters 150C ALC/GPC equipped with a refractive index detector. The operating temperature was 139°C and unstabilized 1,2,4-trichlorobenzene was used as eluent. The column system consisted of a precolumn containing glass beads and three commercial analytical columns in the following series: Shoedex 806/S, Shoedex AC-80M/S and Shoedex AC-803/S. The samples were dissolved at 140°C for 3 h in concentrations of about 1 mg ml^{-1}. Small amounts of Topanol CA (ICI) were added during the dissolution step. The injection volume was 0.5 ml and the elution rate was 0.6 ml min^{-1}. Narrow MWD high density polyethylene (HDPE) (NBS 1475) and a broad MWD HDPE (Marlex 6009) with known cumulative weight distributions were used for calibration. The universal calibration principle[16] was applied. For Mark–Houwink equation, values of $K = 1.76 \times 10^{-4}$ and $a = 0.73$ were used for polypropylene.

The radiation stability of the polymer samples was determined by calculating the percentage change in M_w upon exposure to radiation. Hence the smallest change indicates better stability against radiation.

RESULTS AND DISCUSSION

The results from the size exclusion measurements are arranged in order of increasing radiation stability in *Table 2*. A comparison of the M_w values of the unirradiated samples **VI** to **XI** shows that only Irganox 1010 prevents thermal degradation of polypropylene during admixing of the additives. Partial degradation of polypropylene already takes place during admixing polypropylene with additives such as Tinuvin 770 and phenyl decane. The most radiation-resistant polymer found was the poly[propylene-*co*-4-(hept-6-enyl)-2,6-di-tert-butylphenol] (**II**) containing 0.82 wt% stabilizer. The commercially available radiation-resistant polypropylene (**XII**) showed the second best stability upon exposure to radiation. The addition of phenyl decane (**XI**) or copolymerizing propylene with 6-phenylhex-1-ene (**V**, **IV**) resulted in reasonably good stability to radiation. The propylene copolymer containing both 4-(hept-6-enyl)-2,6-di-tert-butylphenol and 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine (**III**) showed no remarkable difference in radiation stability in comparison to the polymer sample containing admixed Irganox 1010 and Tinuvin 770 (**IX**). The polymers prepared by admixing stabilizers (**VI**, **VII** and **VIII**) showed only a small stabilizing effect upon exposure to radiation.

CONCLUSIONS

Polypropylene stabilized *in situ* with 4-(hept-6-enyl)-2,6-di-tert-butylphenol has good stability upon exposure to high-energy radiation. Propylene copolymerized with 6-phenylhex-1-ene has reasonably good radiation resistance which may be attributed to the energy trapping ability of the aromatic functionality. Formulations using hindered amine light stabilizers showed poor radiation stability. Since the phenolic stabilizer in poly[propylene-*co*-4-(hept-6-enyl)-2,6-di-tert-butylphenol] forms a permanent part of the copolymer and cannot be lost by extraction, volatilization or leaching from the polymer even under extremely aggressive environments, it is suggested that this copolymer is well suited for use in medical applications.

Table 2 Change in M_w and M_n values upon exposure to a radiation dose of 25 kGy, arranged in order of decreasing decomposition

	Dose						
	0 kGy			25 kGy			
Sample	$M_w \times 10^3$ (g mol^{-1})	$M_n \times 10^3$ (g mol^{-1})	M_w/M_n	$M_w \times 10^3$ (g mol^{-1})	$M_n \times 10^3$ (g mol^{-1})	M_w/M_n	Change (%)
XIII	394	77	5.1	41	11	3.7	90
VI	752	82	9.2	120	36	3.8	84
VII	726	81	9.0	187	48	3.9	74
VIII	513	68	7.6	137	40	3.4	73
IX	556	68	8.2	156	43	3.6	72
III	436	53	8.2	121	30	4.1	72
X	420	66	6.3	121	35	3.4	71
I	319	52	6.2	91	28	3.2	71
IV	324	56	5.8	107	27	4.0	67
V	181	39	4.7	66	18	3.6	64
XI	415	67	6.2	156	42	3.7	62
XII	263	38	6.9	141	27	5.2	46
II	220	49	4.5	139	36	3.9	37

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