Effect of hindered amine light stabilizers on the resistance of polypropylene towards ionizing radiation

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Abstract The influence of hindered amine light stabilizers (HALSs) on physical and mechanical properties of irradiated and non-irradiated isotactic polypropylene (PP) was studied. The stabilizers under investigation were: Tinuvin 765 (T765) and Tinuvin 622 (T622) – derivatives of 1,2,2,6,6-pentamethyl piperidine and Chimassorb 944 (C944) – a derivative of 2,2,6,6-tetramethyl piperidine. It was found that the stabilizers reduce the amount of peroxyl radicals in the amorphous phase of PP. The irradiation with electron beam causes a drop of apparent viscosity both in the original and in the modified PP however the effect is smaller in the presence of HALSs. Admixture of T622 and T765 stabilizers increases the crystallization temperature of non-irradiated PP by about 8–10°C (measured by DSC) what results from the facilitated formation of a large number small microcrystals. It was concluded that HALSs initiate two opposite tendencies – chemical protection against damage initiated by free radicals and, simultaneously, physical enhancement of sensitivity towards irradiation by the increase of nucleation density. In the studied systems, the presence of maleic anhydride does not improve compatibility between the polymeric matrix and HALSs.

Key words polypropylene • stabilizers • HALS • electron beam • apparent viscosity • nucleation agent

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Introduction

HALSs are usually derivatives of 2,2,6,6-tetramethyl piperidine or 1,2,2,6,6-pentamethyl piperidine. In many resins they are used as both radical scavengers and antioxidants to protect the material against photo-degradation [2, 4]. It is generally accepted that the decomposition of polyolefines initiated by ionizing radiation proceeds comparably to UV-induced degradation, i.e. via free radical mechanism [9, 14], thus the application of amine stabilizer as a protecting agent against radio-degradation seems to be fully entitled.

The efficiency of light stabilizers depends on their molecular weight and structure. Conversion of amines into nitroxyl radicals following the reaction with peroxyl radical leads to relatively stable intermediate because unpaired electron is then localized predominantly at the low energy N-O bond. Other important factor determining such structure is the space screening of the electron by four methyl groups of piperidine ring. The nitroxyl radical is able to trap alkyl radicals effectively to form aminoethers that, in reaction with peroxyl radical, reproduce nitroxyl radical leaving alkyl peroxide as a stable product of radiolysis [3]. A series of the processes is known as the Denisov cycle and results in the regeneration of nitroxyl radical what limits the consumption of HALS during degradation. However, Gensler *et al.* [8] suggested that amine stabilizers effectively protect polypropylen only against oxidation products of polymer remaining inactive towards primary radicals; thus HALSs only delay the degradation processes.

Yield of the reactions depends not only on the substituents of piperidine ring but also on the molecular weight of amine molecules. Polymeric HALS shows a much higher thermal stability and better extraction resistance than that of low molecular weight. Therefore, recently the tendency for developing amine stabilizers in the form of oligomeric/polymeric macromolecules has been observed [13]. The low molecular weight stabilizers are usually liquid, volatile and easily decompose in thermal processing temperatures so the effective concentration of such admixture in the polymer is reduced. On the other hand, liquid additive has good mobility and usually it can be dispersed more homogeneously in polymeric materials than the solid one.

Wang *et al.* suggested that pentamethyl HALS has a higher stabilizing effectiveness than that of the corresponding tetramethyl substituents and that it is more effective in decomposing of hydroxyperoxide [15]. Another factor influencing efficiency of the additives is their compatibility and ability to create chemical bonds with the matrix.

Some methods were applied to characterise physical and mechanical properties of isotactic polypropylene modified by selected HALSs before and after irradiation. Three types of amine stabilizers were applied: two derivatives of 1,2,2,6,6-pentamethyl piperidine of low and high molecular weight (Tinuvin 765 and Tinuvin 622, respectively) and one polymeric derivative of 2,2,6,6-tetramethyl piperidine (Chimassorb 944). In order to increase the compatibility of HALS-polymer macromolecules, maleic anhydride was added to the composites [5] and the formation of linkage between the stabilizer and matrix was studied. Chemical stage of processes induced by ionizing radiation was investigated using EPR spectroscopy by the identification of free radicals generated in the polymer and by the determination of their relative concentration. Physical and mechanical alternations were estimated comparing the following properties of the material: apparent viscosity in melted state, changes in phase transitions, elongation at break and tensile strength, before and after electron beam exposure.

Methods and materials

Isotactic polypropylene (Malen P J601) purchased from Basell Orlen Polyolefines was mixed with the following additives obtained from Ciba Specialty Chemicals: Tinuvin 622 (T622), Tinuvin 765 (T765) and Chimassorb 944 (C944), Scheme 1. Selected samples were mixed with maleic anhydride (MA) obtained from Fluka. Samples were prepared in a Brabender mixer at 180°C and subsequently compressed between two metal plates quenching with water. Concentration of additives was expressed as the parts per hundred resins (phr). Irradiation with a 10 MeV electron beam was performed using a linear electron accelerator LAE 13/9, in air at ambient temperature. All samples were irradiated to a dose of 25 kGy.

EPR signals were measured using a Bruker ESP 300 spectrometer with the rectangular cavity TE102. The number of accumulations was always adjusted according
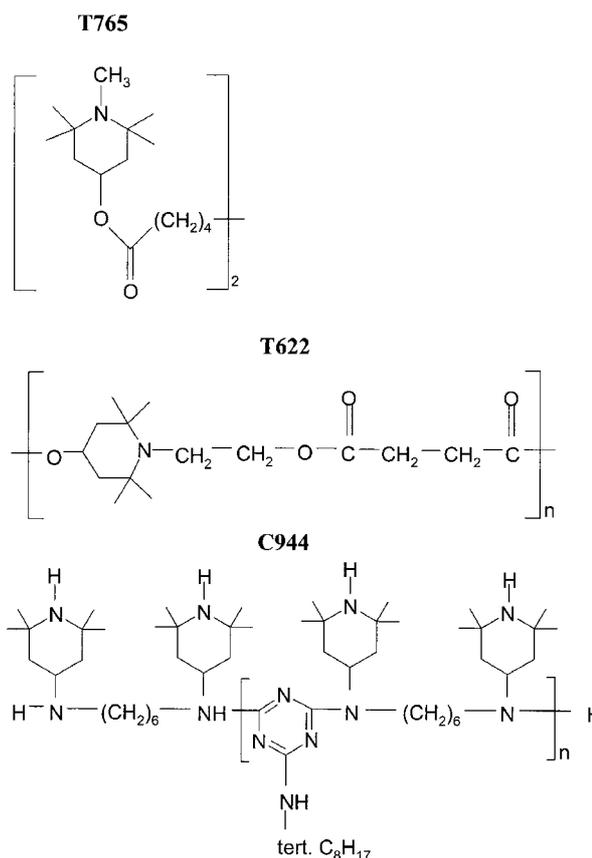
Scheme 1.

to the intensity of the signals. Relative radical concentration and analysis of the experimental spectra were performed by a comparison of the spectral areas measured by double integration using the Apollo program. Decay of radicals was monitored 3 and 6 days after irradiation.

Thermal analysis was carried out using a TA Instruments differential scanning calorimeter (MDSC 2920). The measurements were performed under nitrogen at a heating rate of 10°C/min. About 5 mg samples were placed in aluminum pans and inserted in the cell. During the first cycle, the cell was heated from the ambient temperature to 200°C, then kept for 5 min at this temperature and gradually cooled. Afterwards, the second run was performed applying the same conditions as for the first cycle.

Apparent viscosity was measured with a CAP 2000+H Brookfield viscometer at the temperature indicated in the figures. The process was computer controlled via Brookfield CALPCALC software.

Mechanical testing of the polymer samples was made using an Instron 5565 apparatus. All measurements were performed at ambient temperature.

Results and discussion

Oxidative damage in polypropylene is the main reason for applying antioxidants as the radio-protective agents. HALSs are well known radical scavengers that inhibit the propagation of free radicals acting as their scavengers. Three days after irradiation, EPR spectra

Table 1. Relative concentration of radicals in neat and modified polypropylene irradiated with a dose of 25 kGy (normalised to the content in neat polypropylene)

Sample	Concentration of peroxyl radical [%]	
	3 days after irradiation	6 days after irradiation
PP	100	19
PP+0.30 phr MA	84	20
PP+0.50 phr T622	70	24
PP+0.50 phr C944	57	22

of original and modified by HALSs polypropylene revealed only the presence of peroxyl radicals. Table 1 shows the changes in relative contribution of the intermediate for the selected samples. Observed upon 3 days decrease in population of paramagnetic species in the presence of HALSs results from the reaction between peroxyl radicals and stabilizers leading to the formation of nitroxide compounds. The product subsequently scavenges the alkyl radical inhibiting chain processes. However, after 6 days, the decrease in peroxyl radical concentration was restrained as the level of these radicals was comparable in all samples (taking into account the error of the method). Two various phases occur in isotactic polypropylene – ordered domains of the crystalline phase and the variety of amorphous sites [9]. Thus, there are two types of peroxyl radicals situated in the totally different vicinity. Random orientation of macromolecules in the amorphous phase facilitates peroxyl radicals mobility and involves their faster decay. Therefore, initially the amount of the radicals considerably decreases in the presence of stabilizers. On the other hand, defined rigid structure of crystal delays the transfer of paramagnetic centers and the unpaired electrons induce post-irradiation damages for months. Assuming homogeneous distribution of the modifiers added to polypropylene in the melted state, we found unambiguously that the radicals are scavenged by HALSs predominantly in the amorphous phase as in the presence of hindered amines a significant decrease in the characteristic signal of peroxyl radical signal just in this phase was observed [12]. Influence of the additives on free radical processes in crystalline domains was not confirmed. Nevertheless, in the longer period of time, one cannot exclude analogous effect in crystals since the small intensity of EPR spectra measured several weeks after irradiation precludes quantitative determination of the component.
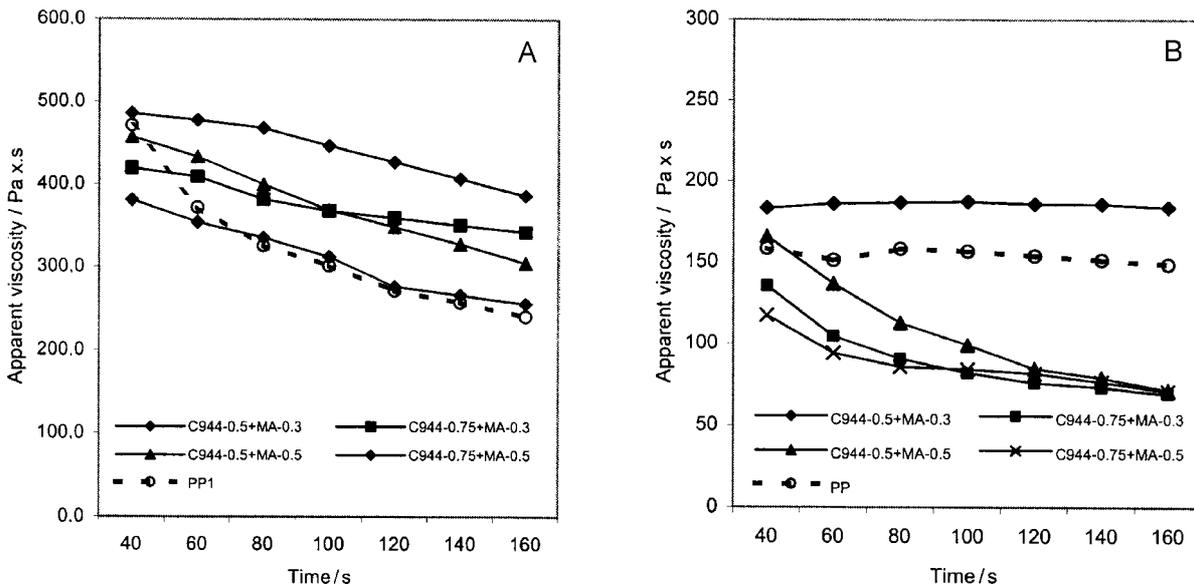
The apparent viscosity of polypropylene in the melted state is a sensitive indicator of modifications induced both by the admixture of stabilizers and by ionizing radiation, Fig. 1. Polypropylene in the presence of studied additives has a slightly higher viscosity than the initial material, however with elapse of time the thermal decomposition at 220°C and the shearing result in a gradual decrease of viscosity. Moreover, molecules of the stabilizer can act as a lubricant and may lead to the reduction of flow resistance.

The irradiation with a dose of 25 kGy induces a drastic drop of viscosity, both in original PP and in its
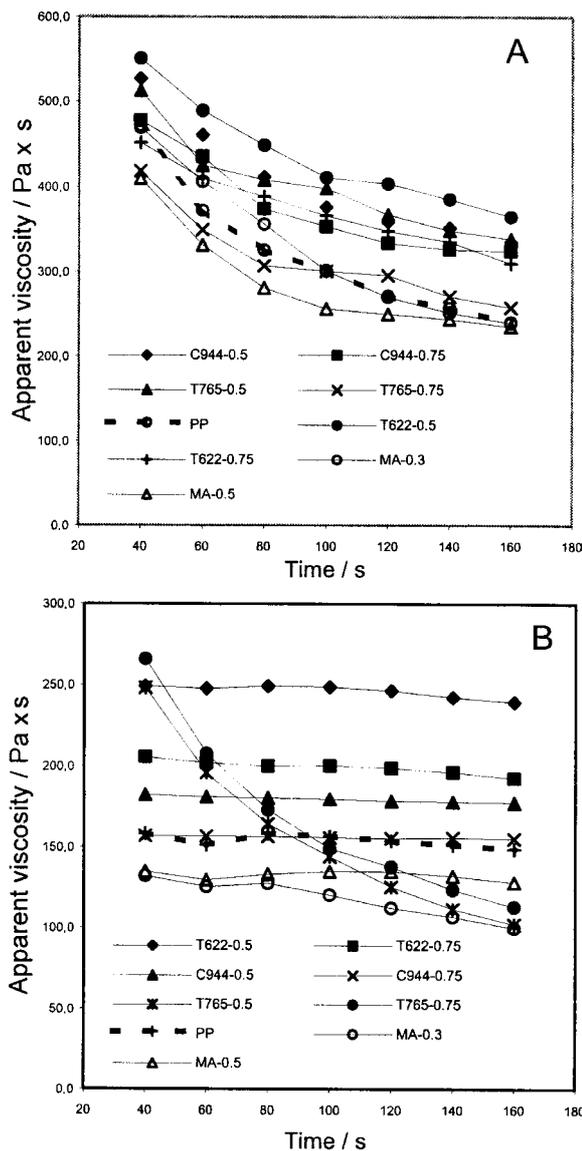
Fig. 1. Relationship between time of shearing and apparent viscosity for original polypropylene and modified by HALS or MA; (A) before irradiation, (B) 72 days after irradiation with a dose of 25 kGy; t = 200°C, shear rate 33 s^{-1}.

composites, due to main chain scissions resulting in a significant decrease in molecular weight. Viscosity of the virgin material decreases 3 times, whereas in the presence of T622 only twice. Viscosity of PP+T622 does not vary with time of shearing, contrary to the viscosity of PP+T765 that, at the beginning of the measurement, is relatively high but after 160 s decreases twice. Tinuvin 765 is a liquid dimer of low molecular weight and high volatility and can be used as an efficient stabilizer unless material needs long processing at elevated temperature. C922 increases PP viscosity by 15% only at low concentration. The character of the relationships shown in Fig. 1 indicates that the content of stabilizers should not be excessive otherwise the effect is opposite to the intended one.

The composite containing both the stabilizer and the MA usually exhibits poor properties in the melted state after irradiation. Examples of such a dependence are shown in Fig. 2. Only in the presence of C944 and

Fig. 2. Relationship between time of shearing and apparent viscosity for original polypropylene and modified by HALS and MA; (A) before irradiation, (B) 72 days after irradiation with a dose of 25 kGy; $t = 200°C$, shear rate 33 s^{-1}.

MA at low concentrations the viscosity of PP slightly increases, however even then the results are worse than that obtained for samples without the admixture of MA. We concluded that the compatibility between HALS and PP cannot be enhanced by maleic anhydride that interacts with the matrix independently lowering its melt viscosity, as seen from Fig. 1.

Apparent viscosity of the irradiated resins changes considerably with time thus the parameter reflects also post-irradiation degradation proceeded in the modified material, Fig. 3. The fast decrease of flow resistance directly upon irradiation is followed by a small increase during the first several days. Such effect might be a consequence of the alkyl radical combinations, as was found by EPR spectroscopy. Carbon centered radicals either

convert to diamagnetic stable products or undergo oxidation to peroxyl radicals. The first pathway leads to partial reconstruction of the damaged macromolecules and, as can be observed in Fig. 3, such processes are facilitated by the amine stabilizers. In the next several days the viscosity decreases due to long-term degradation resulting from chain scissions, thus the subsequent measurements had to be carried out at 200°C instead of at 220°C (i.e. temperature that was set up at the beginning of experiment). For a short time of shearing (30 s) and a shear rate equal to 33 s^{-1} both Tinuvins seem to be the most efficient radioprotectors.

Phase transitions of polypropylene are also influenced by electron beam irradiation. The melting behavior of PP, shown in Fig. 4, indicates that the
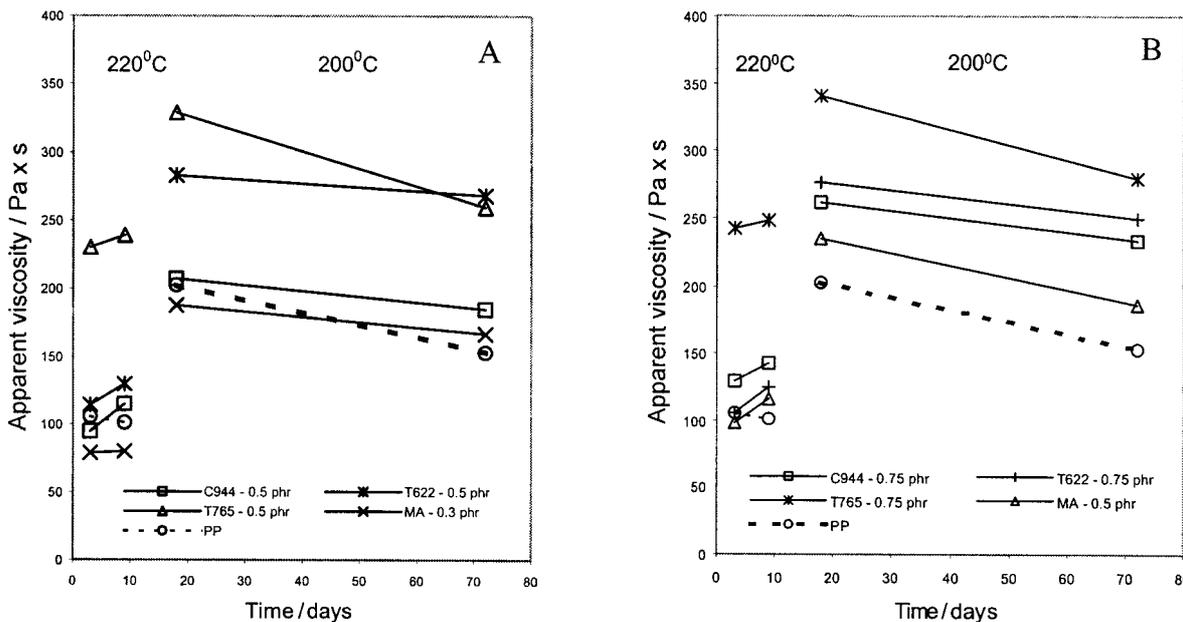
Fig. 3. Apparent viscosity of original and modified polypropylene following irradiation with a dose of 25 kGy in function of time, shear rate 33 s^{-1}. (A) smaller and (B) greater concentration of additives.
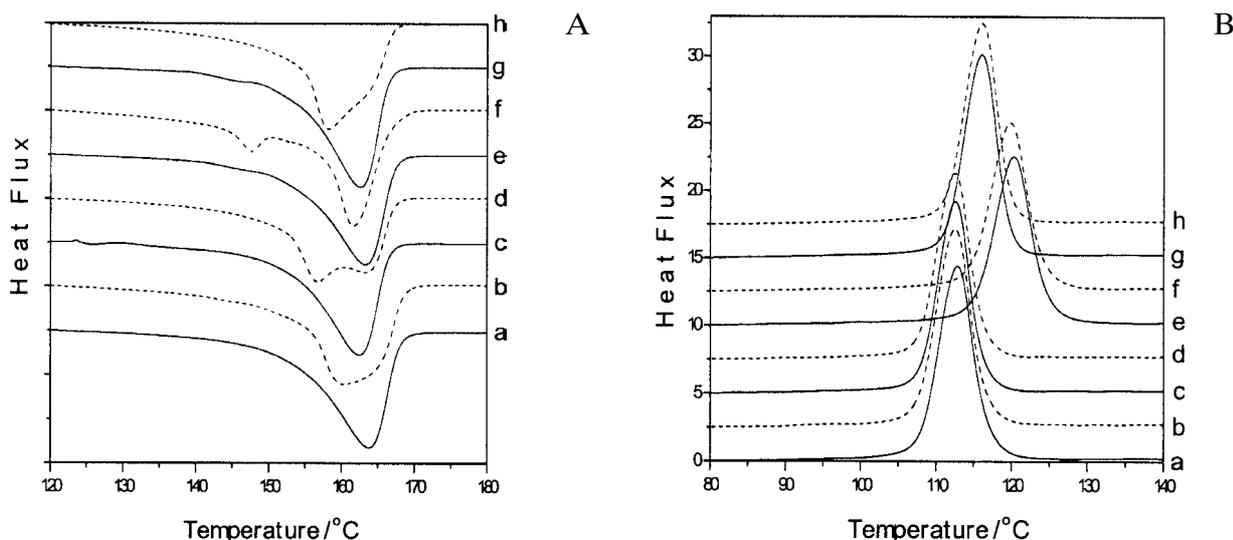
Fig. 4. Phase transitions of PP (a, b, c, d) and PP+0.5 phr T622 (e, f, g, h). Lines marked with a, b, e, f represents signals before irradiation and with c, d, g, h after irradiation with a dose of 25 kGy. Solid line – first cycle; doted lines – second cycle. (A) melting endotherms, (B) crystallization exotherms.

melting peak revealed during the first cycle at 163°C becomes wider in the second cycle due to increase of low temperature endotherm. For irradiated PP, a single peak detected during the first heating in the second cycle splits and two distinct minima are observed. High temperature melting peak is less intensive, whereas the intensity of low temperature peak significantly increases indicating that ionizing radiation induces changes in morphology of the polymeric material. Multiple-peak endotherms reveal separation of different crystals that occurs during slow recrystallization in the first cycle [10]. The samples contain only α phase and two purely resolved melting endotherms correspond probably to the crystals of different orders [6].

In the presence of T622 single peak endotherm obtained in the first run splits after slow heating/cooling procedure in the second cycle, but then the low temperature peak has a minimum at 147°C. The trace of peak at this temperature is detectable also in the irradiated sample. Character of the main asymmetric peaks for both cycles is similar to that obtained for undoped samples and all these endotherms represent probably the same polymorph. It seems that the low-temperature peak at 147°C represents β crystalline form [12]. Morphology of the sample is complex; the small area under the β peak shows that the content of this form is much lower than the α form. The coexistence of various crystalline structures must be initiated by the T622 stabilizer and results from the composite polymorph transitions. The character of changes in PP doped with other HALSs is similar.

The structure of crystals influences considerably crystallization transition [11]. The position of peaks during the first and second cycles for all samples is the same within the limits of experimental error ± 0.5°C. A representative example of calorimetric measurement for T622 is plotted in Fig. 4. Although the enthalpy of transition for all samples, both unirradiated and upon exposure to a dose of 25 kGy, varies in a narrow range from 87 to 89 J/g, the shape of curves changes –

following the exposure to ionizing radiation. The growth of peaks is observed simultaneously with reduction of their width. The crystallization temperature (T_c) recorded for PP doped with stabilizers increases considerably. The T_c values determined from DSC curves for original and modified PP, both before and after irradiation, are collected in Table 2. For the system PP+Tinuvins, the exothermic transitions are shifted even by about 10°C and crystallization is finished at the temperature corresponding to T_c of pure polypropylene. The observed changes clearly indicate that initially the stabilizers promote the conversion of melt to crystals and facilitate the formation of crystal nuclei what consequently determines the amount and distribution of

Table 2. Crystallization temperatures of neat and modified polypropylene, before irradiation and 72 days after irradiation

Sample	Radiation dose [kGy]	T_c [°C]
PP	0	116.8
	25	116.4
PP+0.50 phr T622	0	125.0
	25	119.7
PP+0.75 phr T622	0	124.5
	25	119.8
PP+0.50 phr T765	0	126.9
	25	115.1
PP+0.75 phr T765	0	125.2
	25	115.6
PP+0.50 phr C944	0	121.4
	25	115.5
PP+0.75 phr C944	0	117.1
	25	114.6
PP+0.30 phr MA	0	117.6
	25	115.3
PP+0.50 phr MA	0	121.0
	25	114.9

Table 3. Mechanical properties of neat and modified polypropylene before and 18 days after irradiation

Sample	0 kGy		25 kGy	
	Tensile strength [MPa]	Elongation at break [%]	Tensile strength [MPa]	Elongation at break [%]
PP	47	955	42	784
PP+0.3 phr MA	47	922	41	811
PP+0.5 phr MA	46	927	37	766
PP+0.5 phr T622	44	914	38	737
PP+0.5 phr C944	43	912	41	827
PP+0.75 phr C944	47	955	38	822
PP+0.5 phr T765	48	939	38	778
PP+0.75 phr T765	49	955	38	747
PP+0.3 phr MA+0.75 phr T622	47	873	34	736
PP+0.03 phr MA+0.75 phr C944	43	859	30	594
PP+0.3 phr MA+0.75 phr T765	46	906	42	805

microcrystals in the matrix [7]. The increase of T_c results from the creation of a large number of small nuclei leading to shortening of the crystallization time. From the industrial processing point of view such effect is desired.

The results obtained for PP modified by amines show that T_c decreases by about 6–10°C upon exposure to ionizing radiation. Thus, upon irradiation the additives loss partly the nucleating properties, probably due to chemical changes of HALS stabilizers during the Denisov cycle that leads to the decrease in crystallization temperature. It was found by Ahmed and Basfar that polypropylene in the presence of nucleating agent is less resistant towards irradiation than without such admixture [1]. Therefore, considering the interaction of HALS with PP one has to take into account that amines, prompting formation of nuclei, increase imperfection of crystals what results in easier and stronger stabilization of unpaired electrons in the crystal defects. In this way amines strongly influence the radiosensitivity of crystalline phase, whereas their role as radical terminators in this phase is limited, contrary to the amorphous one (as was confirmed by EPR study).

Tensile strength and elongation at break characterize the changes in mechanical properties resulting from the interaction between the matrix and additive. The tensile strength of PP varies slightly if the stabilizers are added to the material, Table 3, while elongation at break of PP+HALS is usually lower than for the original PP. The tendency is stronger in the presence of both the additives, stabilizer and MA. The most significant decrease of elongation at break was confirmed for the PP+MA+C944 sample.

Upon irradiation, reduction of the elongation at break and tensile strength are attributed to the degradation of polymer. For polypropylene with stabilizers, the value of elongation is usually lower than for the pure material. Nevertheless, the hindered amines protect PP against radiation, as was confirmed by EPR and the apparent viscosity results, thus the improvement of mechanical properties of PP should be expected. The reverse trend must be attributed to the changes in the morphology of PP. The stabilizers acting as a nucleating agent involve the reduction of stability towards ionizing radiation. On the other hand, they protect polypropylene from degradation by scavenging radicals and decomposing hydroperoxides (at least in amorphous phase). Thus macroscopic (mechanical) properties reflect both the effects and the influence of HALSs on the resistance of PP towards radiation must be attributed both to their chemical activity and to the physical preferences to the formation of many small crystals.

Conclusion

In the electron beam irradiated polypropylene, the three studied HALS stabilizers (Tinuvin 622, Tinuvin 765 and Chimassorb 944) induce a faster decay of radicals in amorphous phase what can result in the inhibition of free radical damage (the most significant effect was observed for C944).

The experimental results also demonstrate that the apparent viscosity is a very sensitive parameter that enables determination of the degradation degree. Relationship between the time of shearing and viscosity at the established temperature reveals indirectly the thermal stability of material during processing. From that point of view, the application of a low molecular weight volatile stabilizer, e.g. Tinuvin 765, is not recommended. The amine stabilizers, protecting PP against radiation during chemical processes via free radical scavenging in the amorphous phase, simultaneously modify crystallization transitions facilitating the formation of a large number of small microcrystals. The later effect induces worsening of the resistance towards ionizing radiation, therefore, the protection of PP against radio-degradation by HALSs is ambiguous, contrary to their role in photo-degradation.

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